Chemistry at interfaces: Electropositive metals on polymer surfaces

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This paper presents a study of chemical interactions between polymer surfaces and metal atoms deposited from the vapor phase. Such interactions may play an important role in interfacial metal–polymer adhesion. The chemical nature of the interface formed when an electropositive metal (chromium or cesium) is deposited onto the surface of PMDA–ODA polyimide has been investigated using chemical model studies coupled with photoelectron spectroscopic techniques. X-ray photoelectron spectroscopy, synchrotron-radiation-excited core-level photoemission, and near-edge X-ray absorption spectroscopy were used to analyze changes in polymer surfaces during deposition of chromium and cesium. Chemical model studies using cyclic voltammetry and UV-visible spectroscopy were performed using several simpler polymers or monomeric model compounds which contained structural subunits of the polyimide. Results of these experiments show that chromium (and other electropositive metals studied so far) initially reacts rapidly with the carbonyl groups of polyimide, causing reduction of the dianhydride portion of the polymer, with concomitant chromium oxidation. Continued deposition of chromium onto the reacted polymer surface results in the formation of chromium carbide, oxide, and nitride species, indicating a disruption of the polymer chemical structure.

Introduction

The deposition of thin metal films onto polymer surfaces by evaporation or sputtering is finding increasing use in the manufacturing of integrated circuit chips and packages [1]. The ability to produce adherent thin metal films on polymers is critical to these applications. For the case of polyimide films, which are commonly used in these applications, it is well known that evaporation of copper metal directly onto the polymer surface results in films with relatively poor adhesion. However, if a thin film of chromium is deposited first, adhesion is dramatically increased [2(b)]. The mechanism by which chromium causes this improved adhesion has been extensively studied by surface techniques such as X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), and electron energy loss spectroscopy (EELS), as well as by

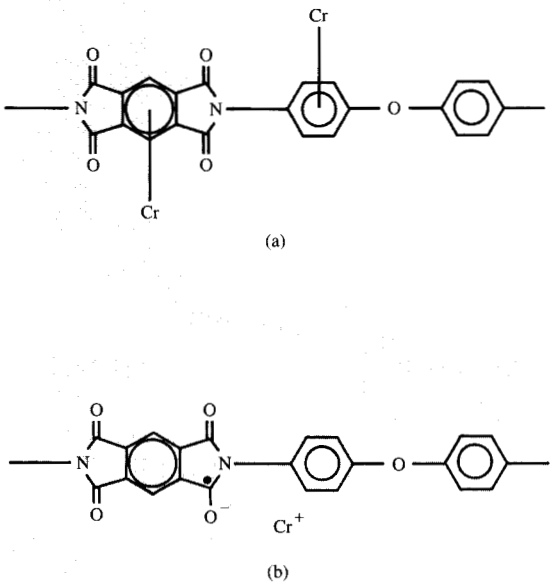


Figure 1

Possible reaction products of chromium metal atoms and PMDA–ODA polyimide: (a) zero-valent chromium-arene complexes; (b) chromium-polyimide redox products.

infrared spectroscopy, transmission electron microscopy (TEM), and by *ab initio* molecular-orbital calculations[1] [2–5]. In general, these studies have shown that chromium differs from copper in that it is much more chemically reactive with the polymer surface. In fact, it has been proposed that the formation of chemical bonds between chromium atoms and the polymer surface gives rise to the observed increase in adhesion of the metal film to the polymer. While several studies have shown evidence for reaction of chromium with the polyimide surface, the detailed mechanism of this reaction and its ultimate reaction products remain poorly understood. Furthermore, although chemical reactivity appears to correlate with improved adhesion, the proposed relationship between adhesion and the direct formation of chemical bonds between the metal and polymer is speculative. In the present study, we have used a combination of surface spectroscopic techniques and experimental chemical model studies in an attempt to better understand the intimate reaction mechanisms which occur upon deposition of electropositive metals such as chromium onto the surface of polyimide films.

On the basis of established organometallic and coordination chemistry, what are the likely products of the reaction of chromium metal atoms with a polymer surface as rich in functionality as polyimide? One possibility is the formation of zero-valent chromium complexes with the arene rings in the polymer. Such π-arene chromium complexes with monomeric arenes are well known in organometallic chemistry and have been widely studied [6]. Complexes of this sort have also been found for polymeric and oligomeric arenes, and have been generated by the reaction of metal atoms with polymer solutions [7, 8]. In the case of polyimide, arene complexes might form at either the arene ring of the PMDA part of the polymer or at the more electron-rich ODA part of the polymer, as shown in **Figure 1(a)**. Though molecular-orbital calculations suggest that the PMDA ring is more favored for reaction by about 1 eV (neglecting final-state effects),[2] chromium-arene complexes of electron-rich arenes are known to be more stable than those of arenes bearing electron-withdrawing groups [9]. Another likely possibility is that chromium, a relatively electropositive metal, can act as a reducing agent and transfer an electron to the polyimide, resulting in a reduced species of the sort shown in **Figure 1(b)**. In fact, the redox chemistry of PMDA–ODA polyimide has recently been studied, and PMDA radical anion [similar to that shown in Figure 1(b)] and dianion species have been generated electrochemically and characterized [10]. In the work described below, we have attempted to ascertain whether either of these possible reaction mechanisms applies for chromium deposition onto polyimide films, by obtaining positive spectroscopic and chemical evidence for the presence of either reduced polyimide species or chromium-arene complexes.

Experimental methods

The XPS spectra of the metal and polymer core levels were taken on a modified Hewlett-Packard 5950B spectrometer with a monochromatic Al Kα X-ray source and a multichannel detector based on the resistive anode principle. The energy resolution of the instrument was 0.8 eV, as determined on the Au 4f core levels. An ultrahigh-vacuum (UHV) e-beam source, differentially pumped, was used for the deposition of chromium. The dose was monitored by a quartz crystal monitor with a sensitivity of 0.1 nm/Hz. For the deposition of cesium we used a zeolite cartridge; an electron microprobe was used to quantify the total amount of cesium present. The UHV system was equipped with a differentially pumped gas-dosing setup for CO exposure studies. The base pressure was 1×10^{-10} torr. To prevent possible accumulation of adsorbates on the surface, the data acquisition time for studies of sequential metal depositions was kept short, sacrificing statistics at times. Control experiments at different metal coverages showed very little residual gas effect after prolonged data accumulation.

Samples for synchrotron-radiation-excited spectroscopy were prepared by spin-coating polymer solutions onto silicon

[1] R. C. White, R. Haight, B. D. Silverman, and P. S. Ho, submitted to *Appl. Phys. Lett.*

[2] B. D. Silverman, IBM T. J. Watson Research Center, Yorktown Heights, NY, personal communication.

wafers, then degassing or curing the polymers *in vacuo*, as appropriate [5]. Photoemission spectra were taken of the clean polymers; then the samples were subjected to successive depositions of chromium. Chromium depositions were performed by exposing the sample to a resistively heated chromium-filled tungsten basket which was surrounded by a water-cooled shroud.

Core-level photoemission spectra were measured using soft X-rays at a 6m/10m toroidal grating monochromator and high-resolution display spectrometer beamline at the National Synchrotron Light Source [11, 12]. Surface-sensitive carbon 1s photoemission spectra were taken using a photon energy of 339 eV. The electron spectrometer had a large angular acceptance (1.8 steradian) centered on the sample normal. The incident radiation was p-polarized and struck the surface at an angle of approximately 5°. The overall instrumental resolution was approximately 0.45 eV. A least-squares fitting routine was used to analyze the data and resolve them into individual peaks. For the high-resolution carbon 1s spectra, a Gaussian lineshape was convoluted with a Lorentzian of full width at half maximum of 0.1 eV to represent the core-lifetime broadening of the carbon 1s level.

Surface-sensitive near-edge X-ray absorption spectroscopy (NEXAFS) spectra were obtained by recording the secondary-electron yield within an 8-eV window as the incident photon energy was ramped across the carbon K-edge [13]. The partial photoelectric yield has been shown to be proportional to the absorption coefficient if the escape depth of the detected electrons is small compared with the photon absorption length [14]. The center value of the electron energy bandpass was set to 42 eV, to minimize escape depth of the detected secondary electrons and thus maximize surface sensitivity.

For chemical studies, UV-visible spectra were recorded on a Perkin-Elmer Lambda 3B spectrophotometer. Fourier-transform infrared spectra were obtained using an IBM Instruments IR44 spectrometer. Resolution was 2.0 cm^{-1}. The model compound PMDA–BA (pyromellitimido bis n-butyl amine) was synthesized by the following method. PMDA (10 g, 46 mmol) was dissolved in 200 ml of DMAc. Upon the addition of 12 ml of n-butylamine (121 mmol), a white precipitate formed which redissolved upon heating. After heating for two hours at 125°C, a crystalline material precipitated. The mixture was cooled to room temperature, diluted with water, and extracted with three 100-ml portions of chloroform. Solvent removal followed by recrystallization from acetone afforded 10 g (75% yield) of PMDA–BA: m.p. 226–227°C; IR ($CHCl_3$, CaF_2) ν(C=O) 1773 (s), 1725 (w), 1394 (w) cm^{-1}; UV-Vis (DMF) 266, 318 nm.

Tris(acetonitrile)chromium tricarbonyl was prepared in the standard manner, by refluxing 1.0 g of hexacarbonylchromium in 60 ml of acetonitrile overnight. Solvent removal, under vacuum, gave bright-yellow crystals characteristic of the the tris(acetonitrile) complex: IR (CH_3CN, CaF_2) ν(CO) 1918 (s), 1795 (s) cm^{-1}.

Reactions with $Cr(CO)_6$ and $Cr(CO)_3(CH_3CN)_3$ were carried out according to the following procedures. PMDA–BA (0.2 g, 0.6 mmol) and hexacarbonylchromium (0.26 g, 1.2 mmol) were dissolved in a mixture containing 5 ml of THF in 55 ml of p-dioxane. The solution was degassed thoroughly prior to refluxing. After heating for 235 hours under nitrogen, both solvent and unreacted $Cr(CO)_6$ were removed under vacuum. The resulting dark-green air-sensitive solid was further manipulated in a nitrogen glove box. Infrared and UV-visible spectroscopy were used to characterize the products: IR (THF, CaF_2) ν(C=O) 1621, 1590 cm^{-1}; IR (DMF, CaF_2) ν(C=O) 1591, 1569, 1534, 1333 cm^{-1}; UV-Vis (DMF) 714, 647, 413, 319, 265 nm. After exposure to oxygen, characterization was repeated: IR (THF, CaF_2) ν(C=O) 1773, 1725, 1394 cm^{-1}; UV-Vis (DMF) 317, 310, 266 nm.

PMDA–BA (0.5 g, 1.5 mmol) was added to a solution containing 0.3 g (1.1 mmol) of $Cr(CH_3CN)_3(CO)_3$ in 75 ml of THF. After degassing, the solution was refluxed for 18 hours under nitrogen. Solvent removal (*in vacuo*) again led to a dark-green precipitate which gave a green solution when dissolved in DMF: UV-Vis (DMF) 712, 645, 412, 316, 265. After exposure to oxygen: UV-Vis (DMF) 317, 309, 266 nm.

Cyclic voltammetry (CV) and bulk electrolysis experiments were carried out using a three-compartment cell with working and counter compartments separated by a fine-porosity fritted disk. All experiments were performed under a nitrogen blanket. Polyimide films were produced for these electrochemical experiments by casting or spin-coating the precursor polyamic acid solution onto conductive substrates. Imide cyclization was achieved either by heating the films to 400°C for 30 min or through a chemical dehydration process involving immersion in a 1:1 mixture of acetic anhydride and pyridine similar to that reported previously. Both thick (3–12-μm) and thin (0.1–1-μm) polyimide films were prepared for this study. PMDA–BA model compounds were prepared as described above. Solutions were made from anhydrous solvents and 0.1M tetrabutylammonium tetrafluoroborate (TBAFB) as supporting electrolyte. Potentials were referenced against the saturated calomel electrode (SCE). Cyclic voltammograms were performed for the PMDA–ODA polyimide-coated electrodes and for solutions of the PMDA–BA model compound. PMDA–ODA exhibited two reduction waves, at potentials of −0.72 V and −1.33 V, which corresponded to the radical anion species and the dianion species, respectively. PMDA–BA also exhibited two reduction waves, at potentials of −0.71 V and −1.43 V, again corresponding to the radical anion and dianion species. Spectroscopic data for the observed reduced species were obtained. For PMDA–ODA radical anion: UV (acetonitrile) 724, 659, 418 nm. For PMDA–ODA dianion: UV (solvent) 555, 525 nm. For PMDA–BA radical anion:

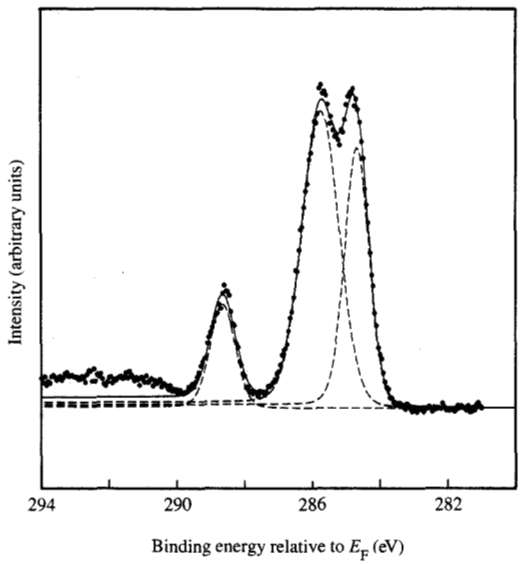


Figure 2

Carbon 1s synchrotron XPS spectrum of a PMDA–ODA polyimide film obtained at 339 eV incident photon energy: Peaks are centered at 288.6 eV, 285.7 eV, and 284.6 eV.

IR (THF) 1656, 1647, 1435, 1350 cm^{-1}; UV (acetonitrile) 720, 654 nm. For PMDA–BA dianion: IR (THF) 1605, 1567, 1517, 1320 cm^{-1}; UV (acetonitrile) 554, 520 nm.

Results and discussion

The carbon 1s XPS spectrum of a PMDA–ODA polyimide film before chromium deposition is shown in **Figure 2**. The assignments of the three observed peaks in the spectrum were made in accordance with those previously published by Buchwalter and Baise [15]. The peak at highest binding energy (288.6 eV) is attributed to the carbonyl carbon atoms; the two large overlapping peaks at lower binding energies are assigned to the aromatic carbons in the polymer. Those carbons of the dianhydride PMDA ring and those attached to heteroatoms in the ODA rings appear at higher binding energy (285.7 eV); the remainder of the carbon atoms give rise to the peak at lowest binding energy (284.6 eV). The deposition of chromium metal on the surface of this polyimide film caused changes in the carbon 1s XPS spectrum which are shown in **Figure 3**. It should be noted that the most dramatic and immediate change in the spectrum occurs at the carbonyl group; with the deposition of very small amounts of chromium metal the carbonyl carbon 1s peak is almost eliminated. In addition, the peak attributed to PMDA carbon atoms is shifted to lower binding energy, suggesting a chemical change affecting the entire PMDA ring. Finally, at higher coverages of chromium, a new peak at very low binding energy (282.6 eV) appears. This new peak has been proposed by other workers to be due to the formation of chromium arene interactions with the ODA rings.[1] It does, however, also correspond to literature values for the binding energy of chromium carbides [16, 17], as is discussed below.

Because polyimide is a complex polymer containing many possible sites of reaction for chromium, we have studied other, simpler polymers to model the individual functional groups in polyimide. Portions of these results have been reported previously and are reviewed only briefly here [5]. The model polymers studied are shown in **Figure 4**, along with the structure of PMDA–ODA polyimide. Poly(vinyl methyl ketone) (PVMK) was chosen to allow the study of carbonyl groups in the absence of any arene rings, to

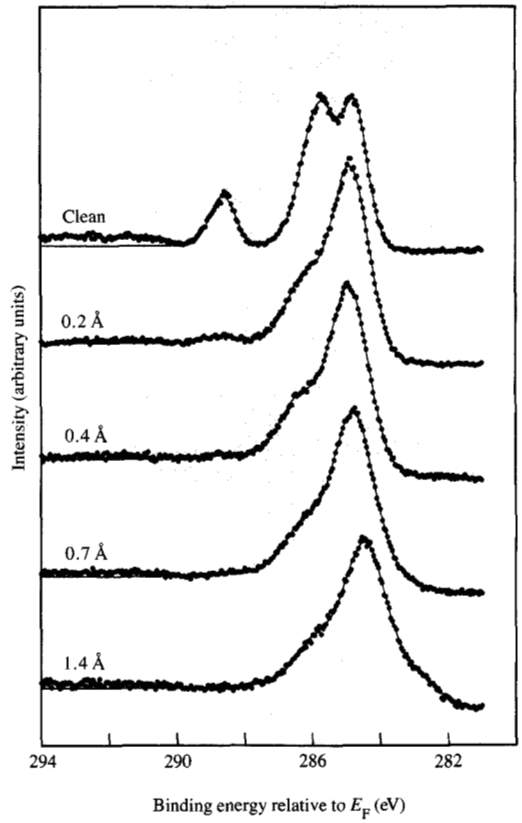


Figure 3

Carbon 1s synchrotron XPS spectra of a PMDA–ODA polyimide film, obtained after successive deposition of chromium metal onto its surface. Coverages were determined using a quartz crystal monitor which was calibrated by Rutherford backscattering.

eliminate the possibility of arene complex formation. Poly(dimethyl phenylene oxide) (PMPO) was chosen to model the arene functionality of the ODA portion of polyimide, to eliminate the possibility of carbonyl reduction chemistry occurring. Poly(pyromellitimidomethylene bis cyclohexylamine) (PMDA–MBCA) was chosen in order to study the action of chromium on the PMDA portion of the polyimide while eliminating the possibility of reaction with the arene or ether groups of the diamine portion. Both polymers which contained carbonyl groups showed a dramatic attenuation of the carbon 1s carbonyl peak on deposition of chromium, similar to that observed for PMDA–ODA. The PMPO polymer, which did not contain a carbonyl functionality, showed only gradual attenuation of the original spectrum upon deposition of chromium, with no new peaks appearing until the achievement of fairly high chromium coverages.

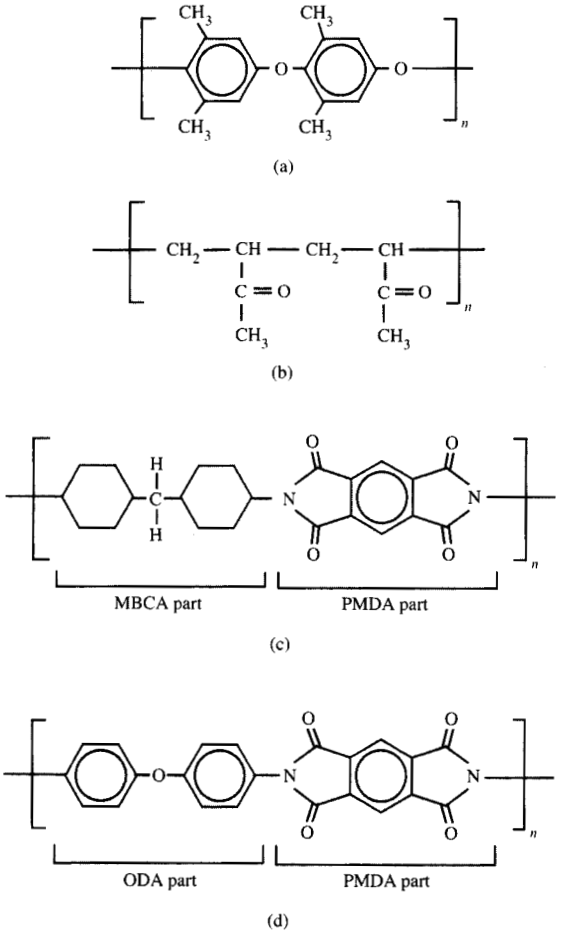


Figure 4

Structures of (a) poly(dimethyl phenylene oxide) or PMPO (two repeat units); (b) poly(vinyl methyl ketone) or PVMK (two repeat units); (c) (PMDA–MBCA (methylene bis-cyclohexyl amine) polyimide (one repeat unit); (d) PMDA–ODA polyimide (one repeat unit).

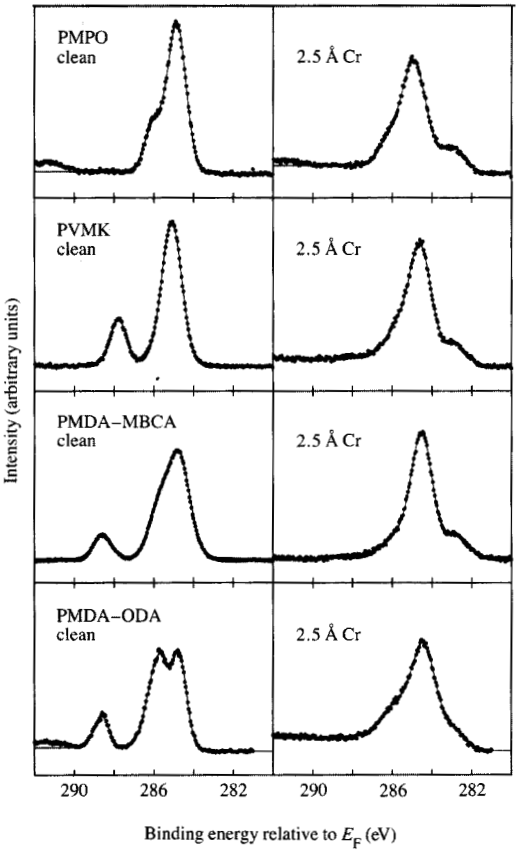


Figure 5

Synchrotron XPS spectra of model polymers and PMDA–ODA with and without chromium present. In all cases, the peak at low binding energy occurred at 282.6 eV.

Deposition of chromium onto all the polymers gave rise at these higher coverages to the formation of a new XPS peak at a binding energy of 282.6 eV. This is illustrated in **Figure 5**, in which the spectra of the clean polymers are shown, together with spectra taken after a layer of chromium 2.5 Å thick was deposited. This is a very low binding energy for carbon, and indicates that the carbon atoms which give rise to this peak are very electron-rich. In fact, this binding energy corresponds to that observed for chromium carbide [16, 17] and is in the same spectral region as other metal carbides [18]. Low-binding-energy peaks attributed to metal carbides have also been observed as a result of the deposition

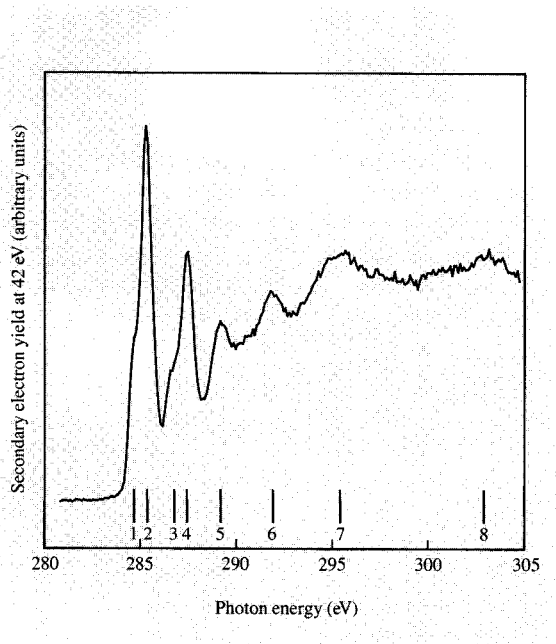


Figure 6

Carbon K-edge NEXAFS spectrum of PMDA–ODA polyimide.

of other electropositive metals on the surface of polymers. Bodo and Sundgren [19] observed a peak at 281.4 eV as a result of deposition of titanium on polyethylene surfaces, which they attribute to formation of titanium carbide. Deposition of titanium onto polyimide surfaces was reported by Ohuchi and Freilich [20], who observed formation of a peak at similarly low binding energy when more than 35% of a monolayer of metal was deposited. This new peak was again attributed to the formation of titanium carbide products, an assignment which was supported by Auger electron spectroscopy. Bartha et al. [21] observed a peak at 282.2 eV as a result of deposition of aluminum on PMDA–ODA polyimide surfaces. This was attributed to formation of Al–C–O complexes rather than aluminum carbide. Chou and Hurst[3] have previously studied the chromium–polyimide system and identified the same low-binding-energy peak that we observe for all the polymers studied as chromium carbide. This was confirmed by Auger electron spectroscopy and by TEM, which showed clearly the presence of chromium carbide in the interface. More recently, it has been proposed by White et al.[1] that in the chromium–polyimide system a chromium–arene interaction with the aromatic diamine portion of the PMDA–ODA polymer gives rise to the peak at 282.6 eV; this is supported by theoretical studies which show that a model structure of this type might be expected to give rise to a low-binding-energy peak in the XPS. The appearance of the same peak (as shown in Figure 5) for the PMDA–MBCA polymer (which contains no aromatic groups in the diamine portion) and for the PVMK polymer (which contains no aromatic groups at all) argues against this assignment. In addition, if the low-binding-energy peak were due to the formation of an arene complex with the ODA rings, one would expect to see this peak immediately in the reaction of chromium with PMPO; this is not observed. Finally, the appearance of peaks in this low-binding-energy region occurs ubiquitously in systems where electropositive metals are reacted with polymer surfaces, whether or not these polymers contain aromatic groups likely to form π-arene complexes and whether or not the metals have electronic configurations suitable for formation of stable π-arene complexes. Hence, we instead attribute this peak to the formation of a metal carbide, or carbide-like species, consistent with what has been previously observed for other metal–polymer systems. In addition to metal carbides, chromium nitride and oxide species have been shown by examination of the nitrogen and oxygen 1s spectra to form at similar coverages [5, 22].

PMDA–ODA polyimide and the model polymers discussed above have also been studied using near-edge X-ray absorption fine-structure (NEXAFS) spectroscopy [23]. Where XPS may be used to probe changes in the chemical environment of the atoms of the polymer, NEXAFS provides a sensitive probe of how these chemical changes affect the lowest unoccupied molecular orbitals of the polymer. As these orbitals are profoundly affected by formation of π-arene chromium complexes, the use of NEXAFS should be a particularly useful technique for observing these intermediates, if they are present. The carbon K-edge NEXAFS spectrum for a PMDA–ODA polyimide film prior to the deposition of chromium is shown in **Figure 6**. In analyzing the spectrum, the PMDA–ODA polyimide has been treated as two distinct subunits (diamine and dianhydride), between which there is expected to be little orbital overlap. This assumption is supported by crystal structure data [24], which have shown there to be a 60° torsional angle between the two units, and by electrochemical and spectroscopic studies, which showed little or no transmission of electronic effects through the imide nitrogen.[4] Peak assignments have been based on comparisons to the spectra of model polymers and to published spectra of simple organic molecules; Kovac et al. [23] offer a more detailed discussion. Peak 1 (Figure 6) is attributed to transitions from the carbon 1s core levels of the PMDA arene ring to the π^* lowest unoccupied molecular orbital (LUMO) for that π-system, which extends over both

[3] N. Chou and J. Hurst, IBM T. J. Watson Research Center, Yorktown Heights, NY, personal communication.

[4] M. J. Goldberg and A. Viehbeck, IBM T. J. Watson Research Center, Yorktown Heights, NY, unpublished results.

the arene ring and the carbonyl groups. Peak 2 is assigned to the transition from the 1s orbital of ODA carbons not bonded to heteroatoms to the π^* LUMO of the ODA portion of the polymer. Peak 3 is attributed to the transition from the 1s orbitals of the remaining ODA carbons (those bonded to oxygen or nitrogen) to the same π^* LUMO of ODA. Peak 4 is the π^* resonance for the carbonyl carbon-atom core electrons. Peak 5 is a result of transitions of both the ODA and PMDA carbon core electrons to the second lowest π^* orbitals in both those units. Peaks 6 through 8 have been assigned to σ^* resonances which are not of significant relevance to the present discussion; the reader is referred to the literature [23] for details.

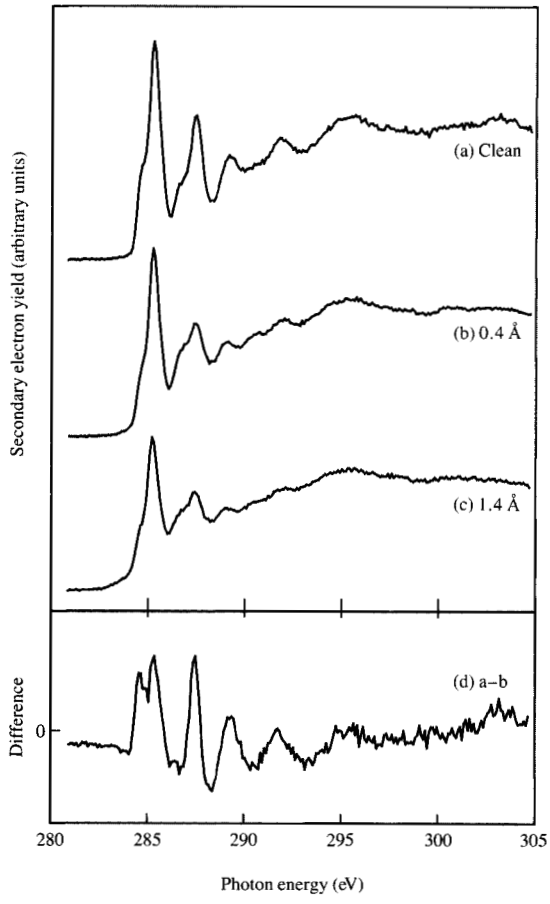


Figure 7

Carbon K-edge NEXAFS spectra of (a) PMDA–ODA polyimide film; (b), (c) the same PMDA–ODA polyimide film after successive deposition of chromium onto its surface. Chromium coverage was determined as described in Figure 3. In (d), the difference (a)–(b) is shown; each plot was normalized to equal integrated intensity.

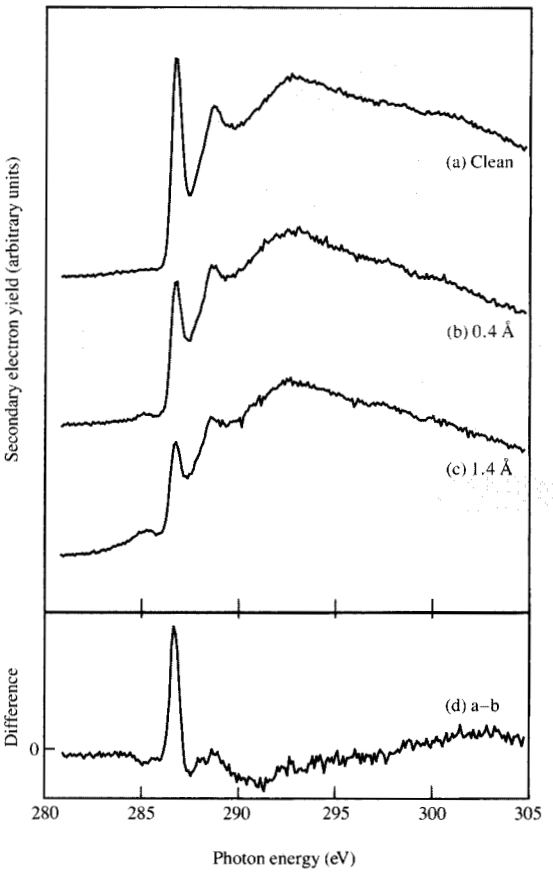


Figure 8

Carbon K-edge NEXAFS spectra of (a) PVMK; (b), (c) PVMK after successive deposition of chromium onto its surface. In (d), the difference (a)–(b) is shown; each plot was normalized to equal integrated intensity.

Deposition of chromium onto the PMDA–ODA polyimide surface (**Figure 7**) resulted in a significant decrease in the intensities of peaks 1 and 4 relative to the other peaks in the spectrum. In particular, peak 4 showed the largest difference, of about 20%, after deposition of only an equivalent of 0.4 Å of chromium. This observation is consistent with those made of the XPS spectra of chromium on PMDA–ODA, and indicates that the PMDA carbonyl groups are the initial sites of reaction with chromium at low coverages. The corresponding NEXAFS spectra for PVMK are given in **Figure 8**, which shows both the spectrum of clean PVMK and those for successive deposition of chromium. Clean PVMK shows two predominant features. The more intense peak at 286.7 eV has been assigned to the carbon-1s-to-π^* transition for electrons from the carbonyl

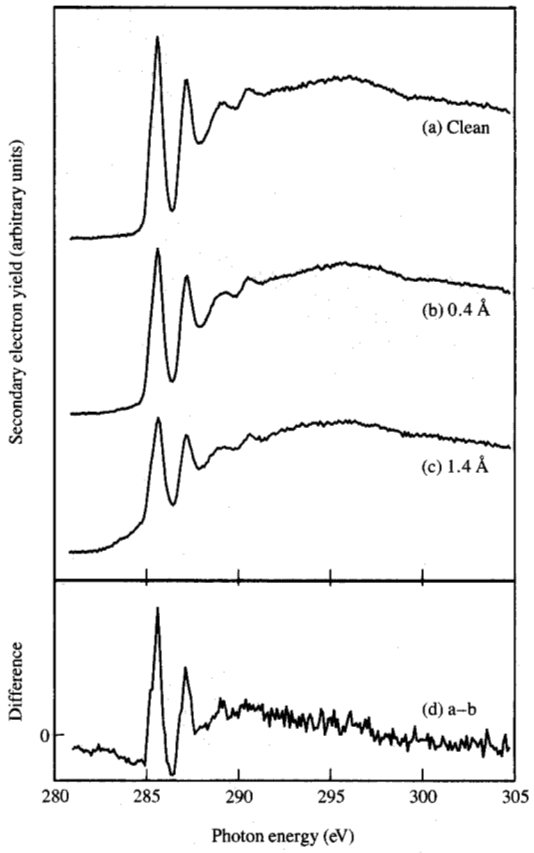


Figure 9

Carbon K-edge NEXAFS spectra of (a) PMPO; (b), (c) PMPO after successive deposition of chromium onto its surface. In (d), the difference (a)–(b) is shown; each plot was normalized to equal integrated intensity.

carbon-atom cores. The second feature, at 288.7 eV, has been assigned to carbon-1s-to-3p/π^* transitions for the aliphatic carbons in PVMK. Several broad resonances appearing at higher energies have been assigned to σ^*-shape resonances. Deposition of chromium onto PVMK caused a rapid decrease in the C=O π^* peak, as seen in the difference spectrum of Figure 8, indicating reaction of the metal with the carbonyl group, as is observed for PMDA–ODA.

Figure 9 shows the corresponding spectra for PMPO, clean and with chromium deposited. The spectrum of clean PMPO contains four peaks which can be attributed to carbon 1s electron transitions to the first- and second-lowest empty π^* orbitals of the aromatic rings. If chromium were to form a complex with these arene rings, electron transfer would occur from the filled d-orbitals of chromium to the lower-energy π^* orbital of the aromatic polymer. Significant changes in the energy of the lowest unoccupied orbitals would be expected upon complex formation, and thus we would expect the NEXAFS spectrum to be quite altered. In fact, what is observed, as can be seen in the difference spectrum of Figure 9, is only a gradual attenuation of the signal because of the increased coverage of the polymer by the evaporated metal film. These results again suggest that interaction of the metal is predominantly with the dianhydride portion of the polyimide, and in particular with the carbonyl functionality. No evidence was found to support the formation of π-arene chromium complexes in any system.

An important chemical difference between the two possible intermediates we have suggested is that the chromium metal in the arene complex intermediate is in the zero-valent state, while in the reduced polyimide intermediate, chromium has been oxidized. Therefore, an experiment was carried out which was designed to demonstrate whether the chromium–polyimide intermediates behaved chemically like zero-valent or oxidized chromium complexes. Zero-valent complexes would be expected to be reactive with good donor ligands, such as carbon monoxide, in either of two ways. First, mono-arene chromium complexes would be highly coordinatively unsaturated, and would be expected to add CO ligands to satisfy the 18-electron rule, forming a stable arene chromium tricarbonyl complex. The new CO ligands would be readily detected in the XPS spectrum of the reacted surface. Such a reaction has been observed when chromium atoms were co-condensed with styrene at low temperatures, and subsequently allowed to react with CO; styrene chromium tricarbonyl was the isolated product [25]. Alternatively, an arene complex formed from polyimide might be expected to be relatively unstable, and could result in displacement of the arene by CO ligands, giving volatile chromium hexacarbonyl as a reaction product. Bis(naphthalene) chromium, for example, readily undergoes ligand displacement in the presence of CO, to give first naphthalene chromium tricarbonyl, and finally chromium hexacarbonyl [26]. If arene displacement were to occur in the case of chromium on polyimide, the changes observed in the XPS spectrum of polyimide as a result of chromium deposition would be expected to be reversible, and the original polyimide spectrum should be regenerated upon exposure to CO. Reduced polyimide species coordinated or ionically bound to chromium ions would be expected to show no reactivity with a donor ligand such as carbon monoxide.

Figure 10 shows first the result of reaction of a PMDA–ODA film with chromium, then the result of treatment of that same film with CO. After deposition of a small amount of chromium, the characteristic decrease in the carbonyl peak was observed, indicating that the initial chromium–

polyimide reaction had taken place. Carbon monoxide was then bled into the chamber until a pressure of 1 torr was reached. After exposure for five minutes, another spectrum was taken. As can be seen in Figure 10, there was no change in the spectrum after exposure to CO, indicating that no reaction of CO with the film occurred, either by displacement of the chromium by CO or by coordination of CO as a ligand by chromium. Similar results were observed for treatment of the chromium-coated PMDA–MBCA polyimide with CO. These results suggest that zero-valent chromium–arene complexes are not present as products of the chromium–polyimide reaction. However, this experiment does not provide positive evidence for the alternative suggested above, in which polyimide is reduced by chromium atoms with the concurrent oxidation of chromium.

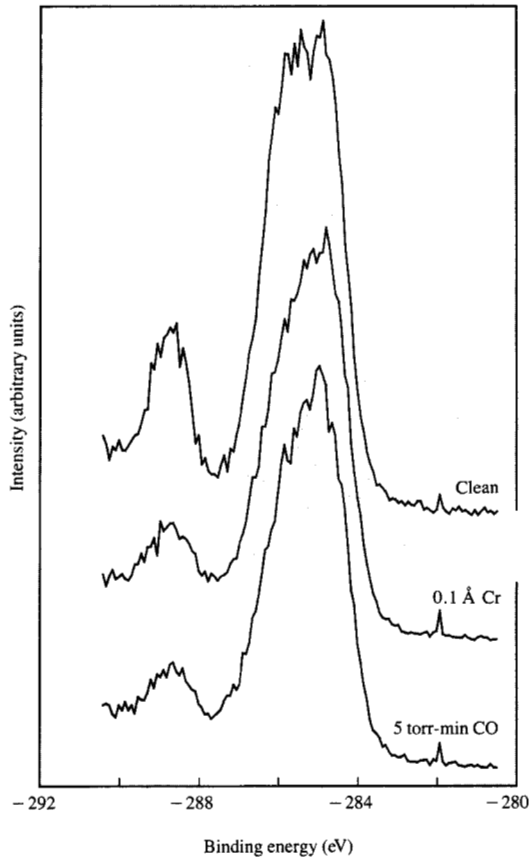


Figure 10

Reaction of chromium-modified PMDA–ODA polyimide film with CO: Carbon 1s laboratory XPS spectrum of a clean PMDA–ODA polyimide film, the same film after deposition of the equivalent of 0.1 Å of chromium onto its surface, and finally after subsequent exposure to 5 torr-min of CO vapor.

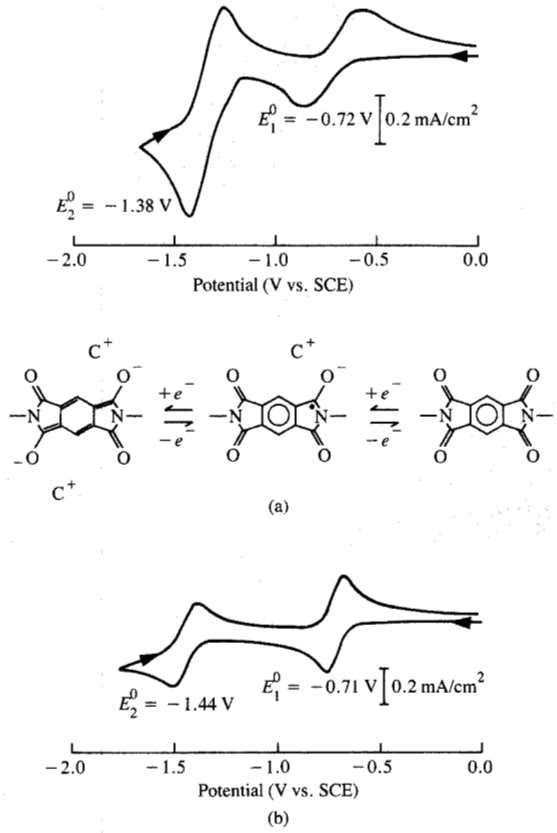


Figure 11

Cyclic voltammograms showing electrochemical reduction of (a) PMDA–ODA polyimide film coated on an electrode; and (b) PMDA–BA model compound in acetonitrile solution. The chemical structures are given for the formation of PMDA radical anion and PMDA dianion.

As mentioned earlier, the electrochemical reduction of polyimide films has been studied and the reaction products characterized [10]. Reduction of polyimide occurs in the presence of suitable counter-ions to give first a radical anion at reduction potential −0.72 V vs. SCE, then a dianion at a reduction potential of −1.38 V vs. SCE [**Figure 11(a)**]. While it is difficult to compare the electrochemical reduction of polyimide in solution to the reduction of a polyimide surface by a gas-phase reducing agent (chromium metal), oxidation potentials for chromium suggest that chromium may be sufficiently reducing to generate the radical anion polyimide species. To compare the XPS spectrum of a known reduced film with that of a film on which chromium had been deposited, reduced-polyimide films were generated electrochemically by methods similar to those reported by Mazur et al. [10(a,b)]. Tetra-n-butyl ammonium cation, the

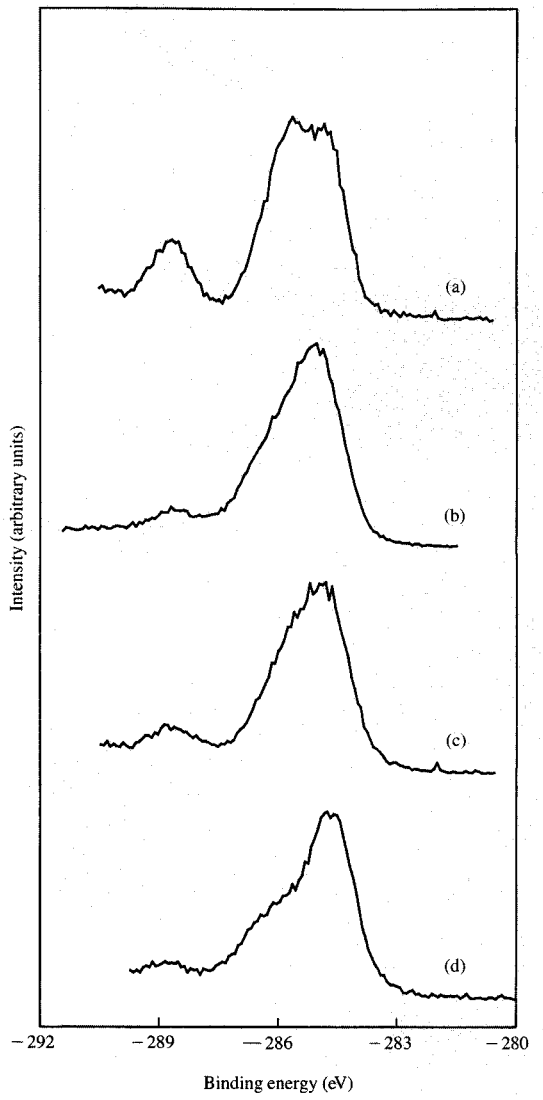


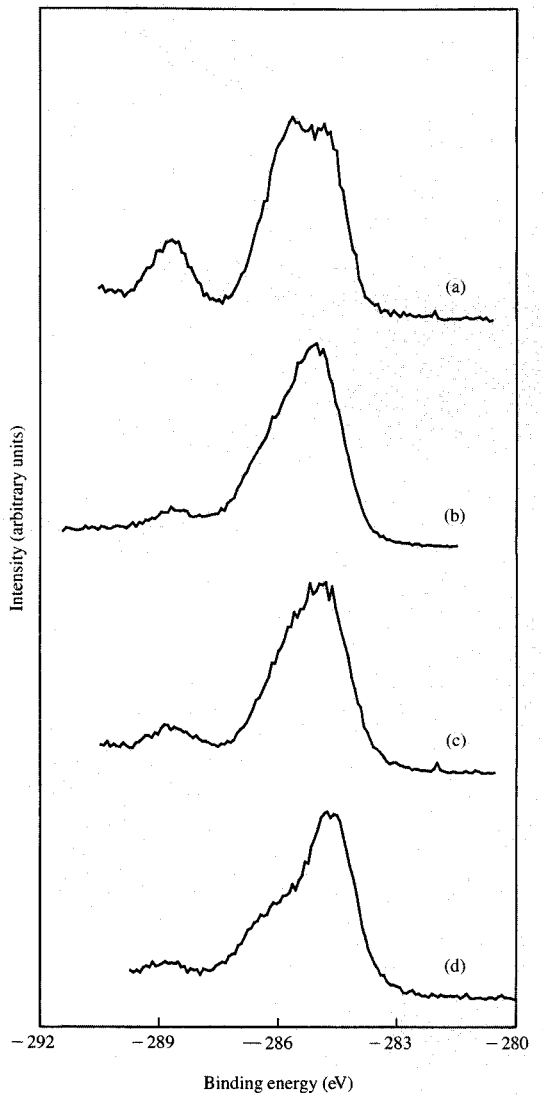
Figure 12

Carbon 1s laboratory XPS spectra of (a) PMDA–ODA polyimide film; (b) electrochemically reduced PMDA–ODA polyimide film in the radical anion form; (c) PMDA–ODA polyimide film after deposition of the equivalent of 0.5 Å of chromium onto its surface; (d) PMDA–ODA polyimide film after deposition of a comparable amount of cesium onto its surface.

electrolyte cation, was present as the counter-ion for the reduced-polyimide species. Figure 11(a) shows the cyclic voltammogram that results from cycling a PMDA–ODA-coated electrode to negative potentials in the presence of an electrolyte solution that swells the film. The two reduction waves can be clearly seen, corresponding to the radical anion and dianion species as identified by Mazur. The reduced films were stable as long as they were stringently protected from oxygen; therefore, reduced films were generated and mounted on the XPS sample holder under anaerobic conditions in a dry box and were transferred to the spectrometer under nitrogen in a glove bag. Laboratory XPS spectroscopy of the electrochemically reduced films gave the spectrum shown in **Figure 12(b)**, which can be compared with the spectrum of a neutral PMDA–ODA film [**Figure 12(a)**]. It should be noted that the changes in the spectrum of the reduced film appear essentially identical to those observed when chromium is deposited onto the surface of clean polyimide [**Figure 12(c)**]; that is, the carbonyl peak is greatly diminished, and the higher-binding-energy PMDA aromatic peak shifts to lower binding energy.

Another method of reducing organic films is to react them with chemical reducing agents such as the alkali metals, which are commonly used for this purpose. In the following experiments, for experimental simplicity, cesium was chosen for deposition onto a polyimide film. However, similar results would be expected with more commonly used alkali metals such as lithium or sodium. Cesium atoms are strongly reducing, having a first ionization potential of 3.89 volts, as measured by vacuum ultraviolet spectroscopy [27]. This low potential results from cesium having a single 6s electron outside a noble gas (xenon) core, causing that electron to be easily removable to leave a very stable monocation. The chemistry of cesium is thus predominantly ionic, with bonds having some slight covalent character when bonded to organic molecules [28]. In any case, the electronic configuration of cesium is much different from that of chromium, for which covalent bonds to carbon can be formed by donation of its d-electrons to empty orbitals of the organic, and by corresponding back-bonding of the organic π-electrons into the remaining empty d-orbitals. Chromium thus can form π-arene-type complexes (and can also act as a reducing agent), while cesium is essentially limited to reduction chemistry.

To compare the effect of cesium deposition onto polyimide with that of chromium and of electrochemical film reduction, laboratory XPS spectra were taken of a PMDA–ODA film onto which cesium had been deposited in the spectrometer chamber. **Figure 12(d)** shows the resulting spectrum. Once again, as in the previous cases, the carbonyl peak is seen to be greatly diminished, and the high-binding-energy aromatic peak of PMDA is shifted to lower binding energy. One minor difference appears as a shoulder on the high-binding-energy side of the aromatic peak, which is less pronounced in either the spectrum of chromium-on-polyimide or of the electrochemically reduced films. This may be the result of a difference in the ionic-covalent character of the metal–O–C bond. In any case, the similarities among the three spectra provide strong evidence that chromium deposition on polyimide results in electron transfer from the metal and concomitant reduction of the PMDA moiety.



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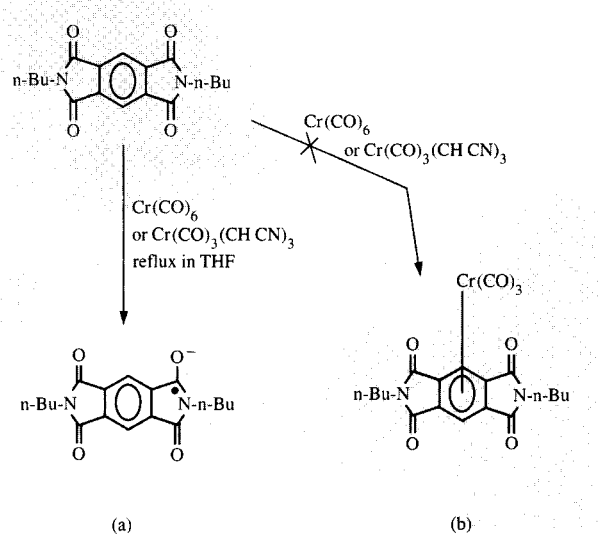

Figure 13

Reaction of PMDA–BA model compound with chromium complexes: (a) product of reaction is reduced radical anion form of PMDA–BA: (b) expected arene chromium tricarbonyl product (none was observed).

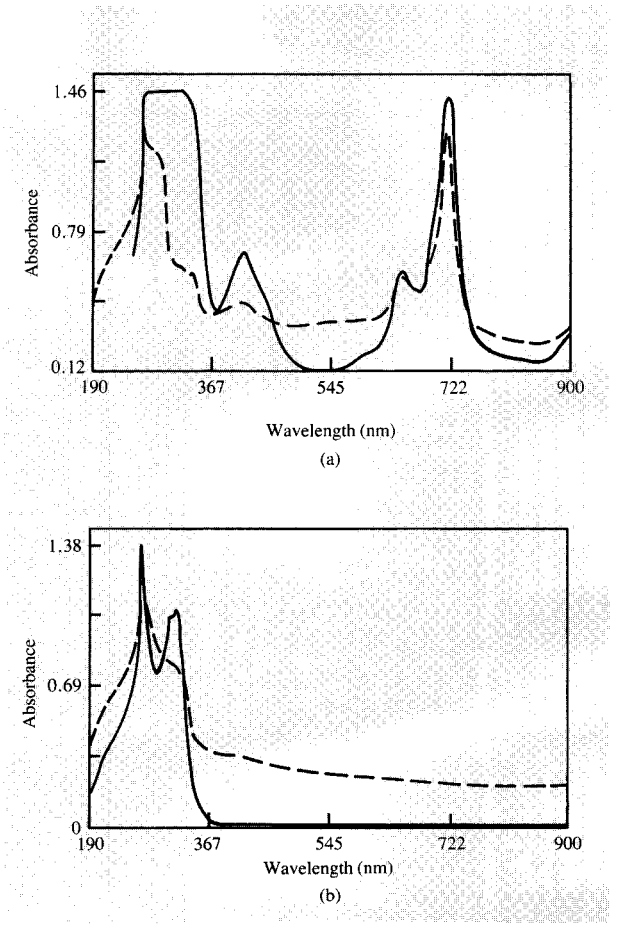

Figure 14

UV-visible spectra of (a) PMDA–BA electrochemically reduced (solid line) and after reaction with $Cr(CO)_6$ (dashed line); (b) after subsequent air oxidation.

Model compound studies can be generally useful in understanding the chemistry of complex polymeric systems such as polyimide. Since the site of reaction was identified, as described above, to be the PMDA moiety of the PMDA–ODA polymer, an attempt was made to synthesize chromium complexes from a model for the PMDA group. In particular, synthetic methods were used to attempt to generate and characterize chromium–PMDA arene complexes. The model compound chosen to represent the PMDA group in polyimide was the bis-imide PMDA-n-butyl amine (PMDA–BA), whose structure is shown in **Figure 13**. This model compound exhibits reduction chemistry very similar to that observed for the PMDA group in the polyimide, as can be seen from the cyclic voltammogram shown in Figure 11(b). The compound PMDA–BA was reacted in THF with the chromium compounds $Cr(CO)_6$ and $Cr(CO)_3(CH_3CN)_3$ (Figure 13). These reactions are commonly used for the synthesis of (arene)chromium tricarbonyl complexes. None of the expected product, (PMDA–NBA)$Cr(CO)_3$, was observed. Instead, the PMDA–NBA underwent reduction to give a radical anion species, which could be characterized by UV-visible spectroscopy and by its electrochemical behavior. **Figure 14(a)** compares the UV-visible spectrum of PMDA–BA which was reduced electrochemically with that of PMDA–BA which was reacted with $Cr(CO)_6$; the two spectra are essentially the same. As further evidence of reduction, both solutions were demonstrated to be susceptible to re-oxidation by oxygen, as shown in **Figure 14(b)**, regenerating the same spectrum, which is that of neutral PMDA–BA. We conclude from these results that even in a solution with relatively stabilized zero-valent chromium, the chemical driving force for reaction with PMDA–bis-imide compounds is for reduction of the carbonyl groups with concomitant oxidation of chromium, and not for formation of stable π-arene zero-valent chromium complexes.

Conclusions

Using a combination of chemical and surface-spectroscopic techniques, we have shown that polyimide films are quite reactive with vacuum-deposited chromium metal. Reaction

appears to take place in several stages which are chromium-coverage-dependent. The focus of this study has been on the initial stage of the reaction. Initial electron transfer from the chromium to the polyimide occurs with very small amounts of chromium (much less than monolayer coverage). This results in a polyimide radical anion species in which the unpaired electron is delocalized over the dianhydride portion of the polyimide structure, but is not appreciably delocalized over the diamine portion. Surface-spectroscopy results (both XPS and NEXAFS) are consistent with this mechanism, showing the carbonyl to be the primary site of reaction, with some delocalization effects on the PMDA portion of the polyimide, but with little or no effect on the diamine portion of the polymer. The lack of chemical reactivity of the chromium-treated film with donor ligands also supports this mechanism, in which chromium is oxidized (with concomitant polyimide reduction) and not zero-valent. A comparison of chromium-treated films with electrochemically reduced films of known structure provides further evidence for the reduction of the polyimide by the chromium. Chemical reduction of the film by vacuum-deposition of cesium results in changes which are similar to those observed upon chromium deposition. Finally, studies designed to produce and characterize PMDA–chromium arene complexes also resulted in reduction of the model compounds used in the study. Neither chemical nor surface-spectroscopic experiments have shown any evidence for the formation of arene chromium complexes with polyimide in any of the systems studied. While such intermediates cannot be entirely ruled out, it does not appear likely that these are the intermediates responsible for the initial changes observed in the polyimide XPS spectrum.

Following film reduction, a second stage of reaction occurs with continued deposition of chromium. This phase of reaction is less well understood, but results in the formation of chromium nitride, oxide, and carbide species. Initial reduction of the film may activate the polymer toward formation of these species; however, it is apparently not required—for example, the aromatic ether polymer PMPO shows formation of carbides upon chromium deposition, even though no carbonyl reduction is possible in this case. The correlation of the initial reduction of the polymer to strength of adhesion has not been made. Either the formation of chemical bonds between the metal and polymer or the alteration of the polymer surface to improve mechanical interactions may give rise to the observed improved adhesion. In any case, it seems that the improvement in adhesion may result from a complex sequence of reactions and probably does not occur in a simple one-step reaction of the metal with the intact polymer. The chemical structure of the polymer chains interacting with chromium at the surface is probably degraded, giving rise to the carbide, oxide, and nitride species observed at higher chromium coverage. These species may play more of a role in adhesion than has heretofore been suspected, and further studies are in progress to elucidate their mechanism of formation and their role in film adhesion.

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