Characterization of the Interface between Pyromellitic Dianhydride/Oxydianiline Polyimide and Silver Using Surface-Enhanced Raman Scattering

J. T. Young, W. H. Tsai, and F. J. Boerio*

Department of Materials Science and Engineering, University of Cincinnati, Cincinnati, Ohio 45221

Received May 7, 1991; Revised Manuscript Received October 7, 1991

ABSTRACT: The molecular structure of the interface formed by curing the polyamic acid of pyromellitic dianhydride (PMDA) and oxydianiline (ODA) against rough silver substrates was determined using surface-enhanced Raman scattering (SERS) and reflection–absorption infrared spectroscopy (RAIR). SERS spectra obtained after films of the polyamic acid were cured against rough silver substrates were independent of the thickness of the films, demonstrating that SERS was surface-selective and that the SERS signal originated from the interface, not the bulk of the films. SERS spectra of the polyimide were more similar to SERS spectra of the polyamic acid than to normal Raman spectra of the polyimide, indicating that curing of the polymer was inhibited by interaction with the substrate, probably through formation of carboxylate salts between the acid groups of the polyamic acid and silver ions of the substrate. There were significant differences in the relative intensities of the bands in the normal Raman and SERS spectra of the polyimide which were related to preferential orientation of segments of the polymer molecules. It was concluded that the PMDA moieties were adsorbed onto the silver surface edge-on with the carbonyl bonds perpendicular to the surface. Some evidence for formation of isoimide or degradation products containing C=N bonds in the interface was obtained from the SERS spectra. Results obtained from RAIR were consistent with those obtained from SERS. However, the infrared results provided additional information indicating that the ODA moieties were oriented mostly parallel to the silver surface.

I. Introduction

Polyimides are widely used as dielectrics in microelectronics and as matrix materials in composite materials due to their excellent thermal stability, chemical resistance, and low dielectric constant. In order to develop strong, environmentally stable adhesive bonds between polyimides and substrates such as graphite and metals, it is necessary to understand the nature of chemical and physical processes occurring at the interface.

Numerous investigations concerned with the structure of interfaces between polyimides and metals have been reported. Most of these have concerned metal-on-polyimide interfaces formed by deposition of metals onto polyimides from pyromellitic dianhydride (PMDA) and oxydianiline (ODA).[1–17] It has generally been observed that metals such as aluminum and chromium, which have strongly negative free energies of vapor-phase oxidation, form an interfacial oxide with the carbonyl oxygen atoms on the polyimide. However, other metals such as copper and silver interact only weakly with PMDA/ODA polyimides and tend to diffuse into the polymer during deposition rather than react with functional groups on the surface.

Polyimide-on-metal interfaces formed by curing the polyamic acids of monomers such as PMDA and ODA against metals have been less widely studied.[18–27] Kim et al.[18,19] used transmission electron microscopy (TEM) to investigate interfaces formed by spin-coating the polyamic acid of PMDA and ODA onto copper substrates and thermally curing to obtain the polyimide. It was suggested that the polyamic acid reacted with copper to form a complex which decomposed during thermal curing, resulting in formation of copper-rich particles distributed in the polyimide 800–2000 Å away from the copper surface. When copper was deposited on the polyimide film, the interface was very sharp and copper-rich particles were not found in the polyimide. The peel strength of polyimide/copper adhesive joints was much higher than that of copper/polyimide joints, since the former case involved chemical bonding between copper and the polyimide.

Burrell et al.[20] utilized X-ray photoelectron spectroscopy (XPS) and reflection–absorption infrared spectroscopy (RAIR) to investigate relatively thick polyimide films (1000–5000 Å) prepared by spin-coating the polyamic acid of PMDA and ODA onto copper and aluminum substrates and then curing the films by heating in air at 200 °C for 30 min. Polyamic acid films deposited on aluminum substrates were completely cured, but copper carboxylate complexes, which inhibited curing, were formed when polyamic acid was deposited onto copper substrates.

Linde[21] used RAIR to determine the structure of thin films (40 Å) formed by depositing the polyamic acid of PMDA and ODA onto reactive metals such as copper and silver and unreactive metals including gold, aluminum, and titanium. Polyamic acid was adsorbed onto silver mostly through PMDA moieties which were oriented perpendicular to the surface and in which the acid groups were meta to each other. One of the acid groups reacted with the substrate to form a carboxylate salt. The carbonyl group in the other acid group was oriented perpendicular to the substrate. Heating these films to 300 °C in nitrogen for 8 min resulted in destruction of the polymer.

Grunze and Lamb[22,23] used XPS and RAIR to investigate mixtures of PMDA and ODA vapor-deposited onto polycrystalline silver surfaces. PMDA and ODA were both chemisorbed on the silver surface through oxygen atoms. Codeposition of PMDA and ODA followed by heat treatment led to formation of thermally stable polyimide films. Adhesion of the polyimide films to the silver substrate involved fragments of PMDA and ODA which were initially chemisorbed on the surface.

Very little information has been obtained using Raman spectroscopy to investigate interfaces between polyimides and metal substrates. Perry and Campion[24] used unenhanced Raman spectroscopy to investigate the adsorp-

0024-9297/92/2225-0887$03.00/0

tion of PMDA and ODA onto Ag(110) at 140 K in ultrahigh vacuum. They found that ODA was physisorbed onto the cold silver substrate but PMDA was dissociatively chemisorbed. Bands which were not observed in the Raman spectra of bulk PMDA appeared near 1414 and 1504 cm^{-1} in the Raman spectra of PMDA adsorbed onto cold silver and were assigned to a bidentate surface carboxylate. Heating a 30-Å film of codosed PMDA and ODA to 473 K resulted in formation of bands near 1391 and 1788 cm^{-1} that were characteristic of imide groups, indicating polymerization of the monomers.

The purpose of this paper is to describe the use of surface-enhanced Raman scattering (SERS) to determine the molecular structure of interfaces formed when the polyamic acid of PMDA and ODA is cured against silver substrates. SERS is a phenomenon in which the Raman scattering cross section of molecules adjacent to the roughened surfaces of metals such as silver, copper, and gold is enhanced as much as 10^6 compared to its value for normal Raman scattering. The enhancement for molecules more than a few molecular layers from the metal surface is negligible. As a result, SERS is surface-selective and can be used for nondestructive characterization of polyimide/silver interfaces. Most other analytical techniques which have been used to investigate polyimide interfaces, such as XPS and RAIR, require either that the polyimide film or the substrate be very thin or that they be separated.

SERS spectra of polyimide films cured against rough silver substrates were independent of the thickness of the films, indicating that the SERS signal was characteristic of the interface rather than the bulk of the polyimide films. Significant differences were observed between normal Raman and SERS spectra of the polyimide. Those differences were related to cure inhibition by formation of carboxylate salts between acid groups in the polymer and silver ions in the substrate, preferential orientation of the PMDA moieties, and formation of C=N bonds due to isoimide species or degradation products at the interface.

II. Experimental Section

Samples were prepared for SERS investigations as described below. Glass slides were immersed in 0.1 N NaOH and in 0.1 N HCl aqueous solutions for 1 h. The slides were then rinsed in distilled–deionized water, blown dry with nitrogen, cleaned ultrasonically in absolute ethanol several times, and blown dry with nitrogen again.

The glass slides were placed in a vacuum chamber which was purged with nitrogen and pumped down to 10^{-6} Torr using sorption, sublimation, and ion pumps. Silver wire was wrapped around a tungsten filament which was resistively heated to evaporate island films onto the glass substrates at a rate of about 1 Å/s. A quartz crystal oscillator thickness monitor was used to control the thickness of the island films at about 40 Å.

The polyamic acid of pyromellitic dianhydride (PMDA) and oxydianiline (ODA) was obtained from Du Pont Corp. Thin films of polyamic acid were deposited on the silver island films by spin-coating from solutions in *N*-methylpyrrolidone (NMP) and then cured to form the polyimide.

Polyamic acids can be either thermally or chemically imidized. Initially we were concerned that the morphology of the silver island films would be unstable at the relatively high temperatures (200 °C) required to thermally cure polyamic acids to polyimides, resulting in a significant loss of enhancement. Therefore, a combination of thermal and chemical curing processes was used. Subsequently, we found that the morphology of the silver island films was sufficiently stable to enable thermal curing to be carried out in a nitrogen atmosphere at 200 °C. However, we did not observe any differences in SERS spectra of polyimides obtained by chemical and thermal curing or by thermal curing only.

Polyamic acid films deposited on silver island substrates were dried at 100 °C for 15 min to remove the solvent. The films were thermally cured by heating at 200 °C for 10 min and then chemically cured by immersion in a 1:1 mixture of acetic anhydride and pyridine for 2 h. Finally, the specimens were dried by heating at 90 °C for an additional 20 min.

The thickness of the polyamic acid films deposited on the silver island substrates was estimated by ellipsometry. Thick (several hundred angstroms) films of silver were evaporated onto glass slides. Films of polyamic acid were spun onto the silver mirrors from the same solutions and at the same speeds as were used to prepare the SERS samples. The thickness of the films was measured using a Rudolph Research Model 436 ellipsometer to examine the silver substrates before deposition of the polyamic acid films and after the films were deposited and heated at 100 °C for 15 min to remove the solvent. The thickness of the films after curing was not expected to differ significantly for the thin films investigated here and was not measured.[27]

SERS spectra were obtained using a spectrometer equipped with a Spex 1401 double monochromator, an ITT FW130 photomultiplier tube, Harshaw photon-counting electronics, and a Spectra-Physics Model 165 argon ion laser. The slit settings of the monochromator provided a spectral resolution of 10 cm^{-1} for the SERS spectra. The green line of the laser (5145 Å in wavelength) was incident on the sample at an angle of about 65° relative to the normal to the sample surface for SERS experiments and was s-polarized. Scattered light was collected using an *f*/0.95 collection lens and focused onto the entrance slits of the monochromator. Spectra were obtained using a scan speed of 50 cm^{-1}/min and a time constant of either 2 or 10 s. Plasma lines were removed from the spectra by the placement of a narrow-band-pass filter between the laser and sample. In many of the spectra, a considerable background, which was removed by zero suppression, was observed.

Normal Raman spectra were obtained from a small amount of powdered sample supported in a glass capillary tube using the instrument described above. All of the instrumental parameters were the same as used for the SERS spectra except that the slits were set for a spectral width of 5 cm^{-1}.

Some Raman spectra were acquired using a detection system consisting of a Stanford Research Model 400 gated photon counter interfaced to a Hewlett-Packard Vectra computer. In those cases the scan rate was about 65 cm^{-1}/min. However, the other instrumental parameters were similar to those described above.

Similar techniques were used to obtain reflection–absorption infrared (RAIR) spectra of polyamic acid and polyimide films on silver substrates. Films of polyamic acid were spin-coated onto thick silver films which were evaporated onto glass slides. The polyamic acid films were then cured by the combination thermal/chemical process described above. Infrared spectra of the polyamic acid films before and after curing were obtained using a Perkin-Elmer Model 1800 Fourier transform infrared (FTIR) spectrophotometer and external reflection accessories provided by Harrick Scientific Co. Transmission infrared spectra were obtained used the same spectrophotometer. Samples were prepared by mixing a small amount of powdered sample with potassium bromide powder and then pressing the mixture into a clear pellet under high pressure.

III. Results and Discussion

The normal Raman and infrared spectra of the polyamic acid of PMDA and ODA before and after curing are shown in Figures 1 and 2. For convenience, the observed bands and their suggested assignments are summarized in Tables I and II. The assignments of the infrared bands are similar to those prepared by Ishida et al. for PMDA/ODA polyimides and model compounds[28] and by DiNardo et al. for PMDA/ODA polyamic acid and polyimide.[29] However, we used the Wilson numbering system[30,31] to describe the modes of the substituted benzene rings. Ishida et al. used a different, unspecified numbering system. The Raman assignments were based on the work of Tsai et al.[32] and Ishida et al.[28] on PMDA/ODA model compounds, assignments for the acid groups given by Varsanyi,[33] and the work of Mack et al.[34] on Raman spectra of PMDA/ODA polyimide. Once again, we used the Wilson numbering

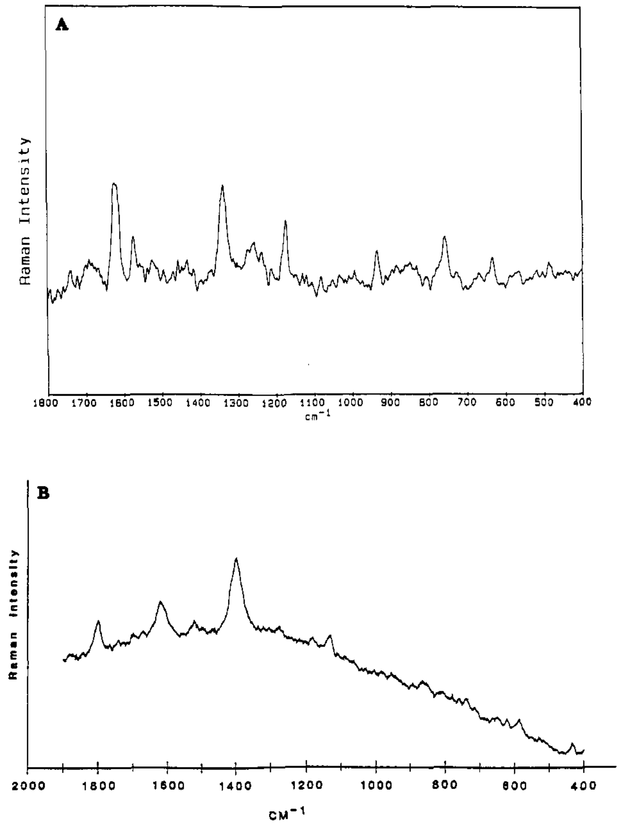

Figure 1.

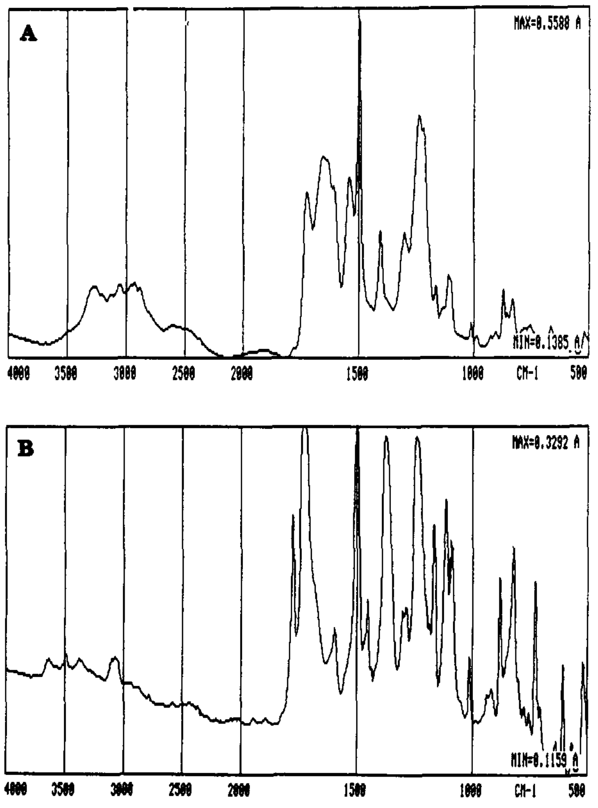

Figure 2.

system to describe the ring modes whereas Ishida et al. used an unspecified numbering system.

Many of the bands observed in the normal Raman spectrum of the polyamic acid were assigned to vibrations of acid and amide functional groups. The remaining bands were associated with vibrational modes of disubstituted and tetrasubstituted benzene rings. Bands near 1698, 940, and 761 cm^{-1} were assigned to the modes ν(C=O), π(OH), and β(C=O) of the acid functional groups, respectively. The weak band near 1574 cm^{-1} was related to the amide II stretching mode. Strong bands near 1623 and 1340 cm^{-1} were associated with the tangential stretching mode ν(8a) of the C_6H_2 and C_6H_4 rings and the stretching mode of the C–N bond, respectively. The band near 732 cm^{-1} was assigned to the radial ring stretching vibration ν(1)–C_6H_4 while other relatively weak bands near 1177, 1012, and 636 cm^{-1} were related to the CH in-plane bending mode ν(9a)–C_6H_4 or the CX stretching mode ν(13)–C_6H_2, the CH in-plane bending mode ν(18a)–C_6H_4, and the radial ring stretching mode ν(6b)–C_6H_4, respectively.

Table I
Preliminary Band Assignments for Polyamic Acid[a]

frequency, cm^{-1}				
Raman	SERS	IR	RAIR	assignment
		3255 (w)		ν(N–H)
		3205 (w)		ν(20)–C_6H_2
		2926 (w)	2921 (w)	ν(OH)
		1720 (s)	1722 (w)	ν(C=O), acid
1698 (w)				ν(C=O), acid
		1670 (s)	1660 (m)	ν(C=O), amide I
1623 (m)				ν(8a)–C_6H_2 and –C_6H_4
	1620 (s)			ν_{as}(COO$^-$), ν(8a)–C_6H_2 and –C_6H_4
		1610 (w)	1609 (w)	ν(8a)
			1570 (w)	ν_{as}(COO$^-$)
1574 (w)	1576 (w)	1545 (m)	1542 (w)	ν(C–N–H), amide II
		1499 (s)	1500 (s)	ν(19a)–C_6H_4
1450 (w)				
	1412 (w)		1400 (w)	ν_s(COO$^-$)
		1407 (m)	1410 (w)	β(OH), acid
1340 (m)	1345 (m)			ν(C–N)
		1303 (m)	1304 (w)	ν(C–OH)
1263 (w)	1269 (w)			ν(C–N–H), amide
		1237 (s)	1240 (w)	υ(C–O–C), ODA
		1216 (m)	1219 (w)	
1177 (w)	1178 (w)	1170 (w)	1170 (w)	υ(9a)–C_6H_4 or ν(13)–C_6H_2
		1113 (m)	1110 (w)	ν(18b)–C_6H_4
1012 (w)		1014 (w)		ν(18a)–C_6H_4
		987 (w)		ν(17a)–C_6H_4
940 (w)				π(OH), acid
		872 (w)		ν(17b)–C_6H_2
	840 (w)		833 (w)	δ(COO$^-$)
761 (m)		754 (w)		β(C=O), acid
732 (w)	733 (w)			ν(1)–C_6H_2
		661 (w)		π(C=O), acid
636 (w)				ν(6b)–C_6H_4

[a] s = strong; m = medium; w = weak.

The normal Raman spectrum of the polyimide, shown in Figure 1B, obtained by curing the polyamic acid was dominated by bands due to the characteristic vibrations of the imide groups. The strongest band in the spectrum was near 1403 cm^{-1} and was assigned to the axial C–N–C stretching mode of the imide groups. Bands near 1802 and 1135 cm^{-1} were assigned to the C=O in-phase stretching mode (imide I) and the C–N–C transverse stretching mode (imide III), respectively. Most of the other bands were related to the vibrations of benzene rings and were assigned by the Wilson numbering system. Thus, the medium intensity band near 1620 cm^{-1} was attributed to the tangential ring stretching mode ν(8a)–C_6H_2 of the substituted benzene rings. The weak band near 1180 cm^{-1} was assigned to the C–H in-plane bending mode ν(9a)–C_6H_4 or the C–X stretching mode ν(13)–C_6H_2.

When the spectra in parts A and B of Figure 1 were compared, significant differences were observed. The disappearance of bands due to acid and amide groups near 1698, 1574, 1340, 940, and 761 cm^{-1} and the appearance

Table II
Preliminary Band Assignments for Polyimide[a]

frequency, cm^{-1}				
Raman	SERS	IR	RAIR	assignment
		3372 (w)		
		3073 (w)		ν(20a)–C_6H_2
1802 (m)	1798 (w)			ν(C=O), in-phase imide I
		1777 (s)	1778 (w)	
		1725 (s)	1730 (s)	ν(C=O), out-of-phase
1623 (m)				ν(8a)–C_6H_2
	1606 (s)			ν(COO^-) and (8a)–C_6H_2 and –C_6H_4
1600 (w)				ν(8a)–C_6H_4
1525 (w)				
		1500 (s)	1500 (m)	ν(19a)–C_6H_4
		1456 (w)		ν(19b)–C_6H_2
1403 (s)	1408 (w)			ν(C–N–C), axial, imide II
		1378 (s)	1379 (w)	
		1291 (w)		ν(7a)–C_6H_4
		1239 (s)	1240 (w)	ν(C–O–C), ODA
1180 (w)	1176 (w)			ν(9a)–C_6H_4 or ν(13)–C_6H_2
		1169 (m)	1169 (w)	ν(C–N–C), transverse, ν(9a)–C_6H_4, ν(13)–C_6H_2
1134 (w)	1142 (w)			ν(C–N–C), transverse, imide III
		1116 (m)	1116 (w)	ν(18b)–C_6H_4
		1093 (w)	1096 (w)	
		1015 (w)		ν(18a)–C_6H_4
		920 (w)	920 (w)	isoimide
		882 (m)		ν(17b)–C_6H_2
865 (w)				ν(1)–C_6H_4
		823 (m)	825 (m)	ν(17b)–C_6H_4
		726 (m)	726 (w)	C–N–C, out-of-plane bending imide IV
736 (w)				ν(1)–C_6H_2
717 (w)				ν(12)–C_6H_4
625 (w)	633 (w)			imide ring, in-plane bending
		605 (w)		ν(12)–C_6H_2
586 (w)	585 (w)			ν(3)–C_6H_2
		518 (w)		ν(16b)–C_6H_4

[a] s = strong; m = medium; w = weak.

of bands characteristic of imide groups near 1802, 1403, and 1135 cm^{-1} indicated that the polyamic acid was fully imidized to form the PMDA/ODA polyimide during the chemical curing process described above.

Transmission infrared spectra of the polyamic acid before and after curing are shown in Figure 2. Bands near 1717, 1303, and 1407 cm^{-1} in the infrared spectra of the polyamic acid before curing (see Figure 2A) were assigned to the C=O stretching, C–O stretching, and C–O–H in-plane bending[29,35] modes of the acid groups, respectively. Bands near 1670 and 1545 cm^{-1} were assigned to vibrational modes of amide groups.[36] The strong, sharp band near 1499 cm^{-1} was assigned to the tangential ring stretching mode ν(19a)–C_6H_4 of the disubstituted rings while the strong, broad band near 1237 cm^{-1} was assigned to a stretching mode of the COC groups in the ODA moieties.

Bands near 1717, 1670, 1545, 1407, and 1303 cm^{-1} all disappeared after curing (see Figure 2B) while bands characteristic of imide groups were observed near 1777, 1725, 1378, 1116, and 726 cm^{-1} after curing.[28,37,38] The bands near 1777 and 1725 cm^{-1} were assigned to C=O stretching modes of the imide groups. Those near 1378, 1116, and 726 cm^{-1} were attributed to the axial and transverse C–N–C stretching modes and the C–N–C out-of-plane deformation mode of the imide groups.

The SERS spectrum of a film of polyamic acid spin-coated onto a silver island film from a 20% solution in NMP is shown in Figure 3. Results obtained from ellipsometry indicated that the film had a thickness of about 1500 Å. Significant differences were observed between the normal Raman (Figure 1A) and SERS spectra of the polyamic acid. The strongest band in the SERS spectrum was near 1620 cm^{-1} and was assigned to a combination of the tangential ring stretching mode ν(8a) of the benzene rings and the asymmetric stretching mode of carboxylate groups.[39-41] The broad band near 1345 cm^{-1} was attributed to the C–N stretching mode of the amide groups. The medium intensity band near 1576 cm^{-1} was assigned to the C–N–H stretching mode. The sharp, medium intensity band near 1178 cm^{-1} was related to the C–H in-plane bending mode ν(9a) of the C_6H_4 rings or to the C–X stretching mode ν(13) of the C_6H_2 ring. Broad bands observed near 1413 and 840 cm^{-1} in SERS spectra of the polyamic acid were assigned to symmetrical stretching and deformation modes of carboxylate groups.[39-41] Bands near 1698, 940, and 761 cm^{-1} which were assigned to vibrations of the acid groups of the polyamic acid (see Figure 1A) were not observed in the SERS spectra. The appearance of bands due to carboxylate salts in the SERS spectra and the disappearance of bands due to acid groups indicated that the polyamic acid was adsorbed onto silver films to form a carboxylate salt.

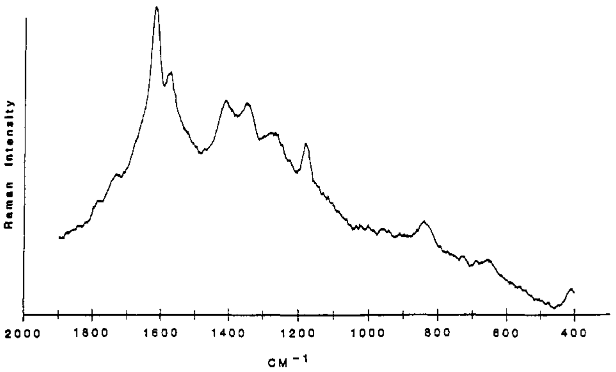

Figure 3.

RAIR spectra obtained from the polyamic acid spun onto silver films from 1, 0.1, and 0.02% solutions in NMP are shown in Figure 4. The thickness of these films was about 133, 37, and 9 Å, respectively. As the thickness of the films decreased, it was observed that the band near 1717 cm^{-1} associated with the C=O stretching mode of the acid groups became weaker, a strong, broad band appeared between 1600 and 1550 cm^{-1}, and the band near 1400 cm^{-1} became stronger and broader. The band near 1400 cm^{-1} contained contributions from the C–O–H in-plane bending mode of the acid groups, but the increase in intensity and broadening of this band as the film thickness decreased was probably related to the appearance of a band related to the symmetric stretching mode of carboxylate groups formed at the interface. Similarly, the broad band between 1600 and 1550 cm^{-1} was related to the asymmetric stretching mode of the carboxylate groups. Formation of bands due to carboxylate groups was consistent with the disappearance of the band near 1717 cm^{-1} related to the C=O stretching mode of the acid groups. Linde et al.[39] investigated the reactivity of thin polyamic acid films as ion-exchange substrates in acquiring various cations from aqueous solutions. IR absorption bands characteristic of the sodium salt were observed near 1600 and 1390 cm^{-1}, providing support for the assignments of carboxylate salts described above.

Brekner et al.[42] investigated the curing mechanism of the polyamic acid of PMDA/ODA and found that polyamic acid films contained up to 30% NMP after drying at 90 °C. However, we do not consider that NMP contributed to the SERS and RAIR spectra of our polyamic acid films

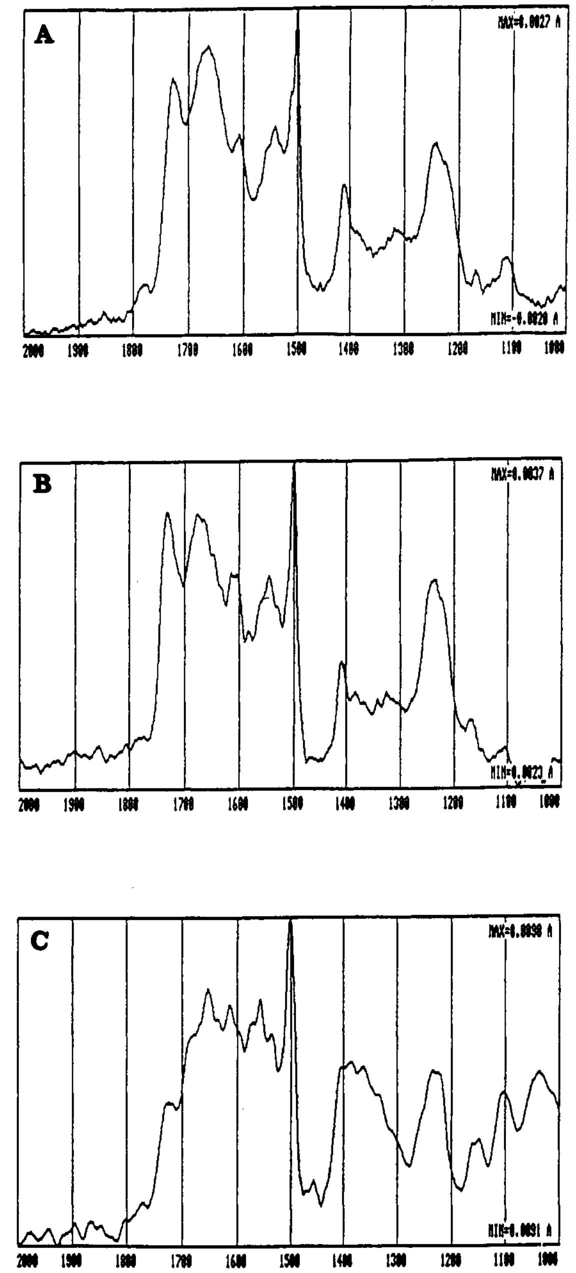

Figure 4.

which were dried at 100 °C for 15 min. The polyamic acid films used in Brekner's investigation were much thicker than those used here and undoubtedly retained more solvent. In addition, the infrared spectrum of NMP has strong bands near 1680, 1400, 1295, 1260, and 1110 cm^{-1}. We observed bands near 1670 and 1110 cm^{-1} in RAIR spectra of polyamic acid which we assigned to vibrations of amide groups and substituted benzene rings. We did not observe bands near 1400, 1295, and 1260 cm^{-1} and concluded that NMP did not contribute significantly to the RAIR or SERS spectra of polyamic acid.

SERS spectra of the polyimide obtained by chemically curing films of polyamic acid adsorbed onto silver island films are shown in Figure 5. The polyimide films were obtained by spin-coating films of polyamic acid that were about 1500, 500, and 120 Å in thickness from 20%, 5%, and 1% solutions in NMP onto silver island films, thermally curing the films at 100 °C for 15 min and at 200 °C in a vacuum oven for an additional 10 min, and finally chemically curing the films in a 1:1 mixture of acetic anhydride and pyridine for 2 h.

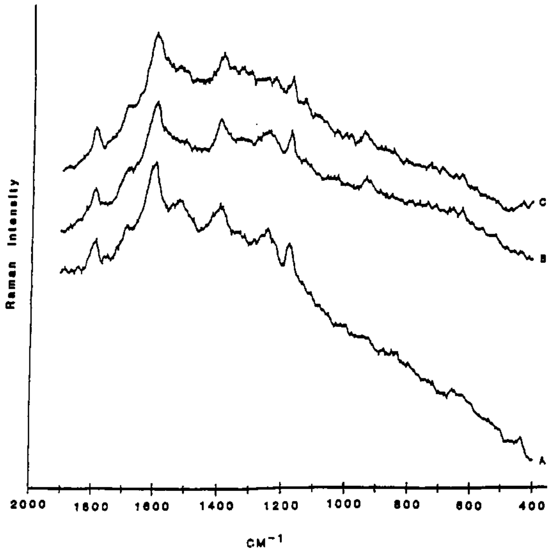

Figure 5.

There are two important aspects to the spectra shown in Figure 5. The first is that the band intensities in all three spectra are very similar even though the thickness of the polyimide films varied by approximately 1 order of magnitude. Since the SERS signal was independent of film thickness, it was obviously characteristic of the interface, not the bulk films.

The second important aspect of the SERS spectra of the polyimide shown in Figure 5 is that the positions and relative intensities of the bands were more similar to those in SERS spectra of the polyamic acid than to those in normal Raman spectra of the polyimide. For example, the band near 1623 cm^{-1}, which had medium intensity in the normal Raman spectrum, was the strongest band in the SERS spectra of the polyimide and polyamic acid. The band near 1403 cm^{-1}, which was the strongest band in the normal Raman spectrum of the polyimide, was relatively weak in the SERS spectra of the polyimide and the polyamic acid. The band near 1345 cm^{-1} in the SERS spectra of the polyamic acid and polyimide was not observed in the normal Raman spectrum of the polyimide. The band near 1176 cm^{-1} was relatively strong and sharp in SERS spectra of the polyimide and polyamic acid but was very weak in the normal Raman spectrum of the polyimide. Considering the similarities between the SERS spectra of the polyimide and the polyamic acid and the differences between the SERS and normal Raman spectra of the polyimide, it was concluded that curing of the polyamic acid on the silver surface was inhibited, probably by formation of carboxylate salts with silver ions in the substrate.

It was evident from the appearance of bands near 1802 and 1403 cm^{-1} in the SERS spectra of the polyimide that some curing had occurred. These bands were assigned to the carbonyl and axial C–N–C stretching modes of the imide groups and would not have been observed if curing was completely suppressed. However, there was considerable evidence in the SERS spectra that some cure inhibition did occur at the silver surface. The band observed near 1345 cm^{-1} in SERS spectra of the polyimide and polyamic acid was assigned to the C–N stretching mode of amide groups. This band was not observed in the normal Raman spectrum of the polyimide where it was replaced by the band near 1403 cm^{-1} which was related to the C–N–C axial stretching mode. Considering the similarities between the SERS spectra of the polyimide and the polyamic acid and the presence of the band near

1345 cm^{-1} in the SERS spectrum of the polyimide, it was concluded that only partial curing of polyamic acid to polyimide occurred at the silver surface.

Orientation effects may also contribute to the differences between SERS and normal Raman spectra of the polyimide. Moskovits developed a theory of Raman scattering by molecules near metal surfaces.[43] According to the theory, bands corresponding to vibrational modes involving atomic motions which are mostly perpendicular to the metal surface are expected to be relatively strong. Bands corresponding to vibrational modes involving atomic motions which are mostly parallel to the surface are expected to be relatively weak. If the polyimide was adsorbed with an edge-on configuration in which the carbonyl bonds were approximately perpendicular to the surface, the band near 1802 cm^{-1} corresponding to the stretching mode of the carbonyl groups would be relatively strong in the SERS spectra. The band near 1403 cm^{-1} corresponding to the axial C–N–C stretching mode would involve atomic motions parallel to the surface and would be relatively weak in the SERS spectra. In fact, this is exactly what was observed, indicating that the cured polyimide was oriented with an edge-on conformation in which the carbonyl groups were perpendicular to the surface.

As indicated above, the intensity of the band near 1606 cm^{-1} was greater in the SERS spectra of the polyimide and the polyamic acid than in the normal Raman spectrum of the polyimide. In the normal Raman spectrum of the polyimide, this band was attributed to ν(8a), a tangential stretching mode of the substituted benzene rings. However, in the SERS spectra of the polyimide and polyamic acid, a band related to the asymmetric stretching mode of carboxylate groups probably overlapped, contributing to the intensity.

Two possible assignments for the band near 1180 cm^{-1} in the SERS spectra of the polyimide and polyamic acid were considered. One was to ν(9a)–C_6H_4, a C–H in-plane bending mode of the disubstituted benzene ring. Another was to mode ν(13)–C_6H_2, the C–X stretching mode of the tetrasubstituted ring. The latter assignment seems more likely for the following reasons. The band near 1180 cm^{-1} was much stronger in the SERS spectra of the polyimide and the polyamic acid than in the normal Raman spectrum of the polyimide. Assuming that the PMDA moieties were adsorbed edge-on, the atomic motions for mode ν(13)–C_6H_2 would be mostly perpendicular to the silver substrate and the corresponding band in the SERS spectrum would be relatively strong. If the PMDA moieties were adsorbed edge-on, the atomic motions for mode ν(9a)–C_6H_4 would be mostly parallel to the substrate and the corresponding band in the SERS spectrum would be relatively weak.

RAIR spectra of thin films of the polyimide which were prepared by spin-coating the polyamic acid onto silver films from 1, 0.1, and 0.02% solutions in NMP and then chemically curing the films are shown in Figure 6. Differences in the relative intensities of several bands were observed when the RAIR and transmission infrared spectra were compared. For example, the bands near 1500, 1379, and 1240 cm^{-1} were much weaker than the band near 1730 cm^{-1} in the RAIR spectra even though they had nearly the same intensity in the transmission infrared spectra. These differences were undoubtedly related to orientation effects and inhibition of curing at the interface.

It is well-known that bands corresponding to vibrational modes having transition moments perpendicular to the substrate appear with enhanced intensity in RAIR spectra while those with transition moments parallel to the surface appear with reduced intensity. Assuming that the PMDA moieties were adsorbed with the edge-on orientation, the band near 1730 cm^{-1} was expected to increase in intensity relative to the band near 1378 cm^{-1} as the PMDA/ODA film thickness decreased, since the transition moment for the C=O stretching mode would be perpendicular to the surface and that for the axial C–N–C stretching mode would be parallel. However, for cure inhibition, the relative intensities of the bands near 1780 and 1379 cm^{-1} were both expected to decrease as the film thickness decreased.

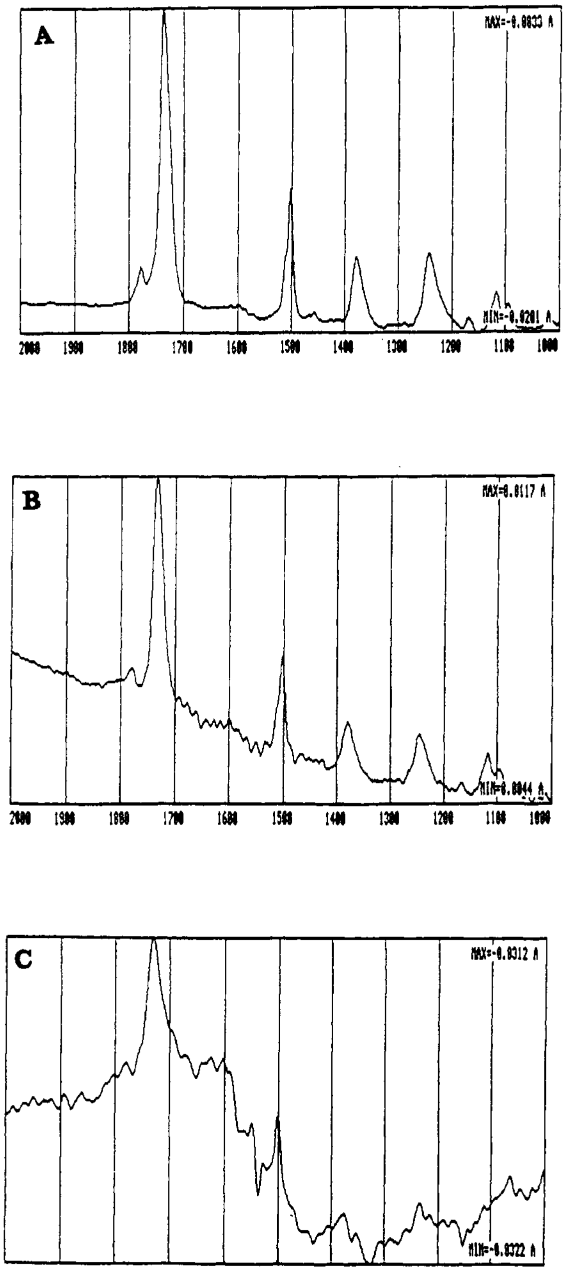

Figure 6.

Reference to Figure 6 indicates that the band near 1730 cm^{-1} was always much stronger that the band near 1378 cm^{-1} in RAIR spectra of PMDA/ODA polyimide, indicating that the differences in the relative intensities between the RAIR and transmission infrared spectra of the polyimide were mostly due to orientation effects and that the PMDA moieties were oriented edge-on with respect to the surface. The bands near 1500 and 1240 cm^{-1}, which were assigned to the tangential ring stretching mode ν(19a)–C_6H_2 and the C–O–C stretching mode of the ODA moieties, were mostly parallel to the surface. Considering that the relative intensities of the bands near 1500, 1378, and 1240 cm^{-1}

did not change much relative to that near 1730 cm^{-1} as the film thickness decreased, it was concluded that preferential orientation of the polyimide molecules on the surface extended into the bulk of the polyimide at least several molecular layers.

The large intensity of the band near 1730 cm^{-1} in the RAIR spectra indicated that considerable curing occurred in all of the polyimide films. However, weak bands related to carboxylate groups were observed near 1610 and 1400 cm^{-1} in the RAIR spectrum of the thinnest PMDA/ODA films (see Figure 6C), indicating that some inhibition of curing occurred. It seems likely that only a few molecular layers of carboxylate salts were formed adjacent to the silver surface, while the preferential orientation of the PMDA and ODA moieties extended at least several molecular layers into the bulk of the polyimide.

The orientation of the PMDA and ODA moieties that is proposed here would require the long axes of the polymer molecules to be arranged parallel to the silver surface. Similar orientations have been suggested by others. Russell et al.[44] investigated the orientation of PMDA/ODA polyimide films which were formed by chemically or thermally imidizing polyamic acid films which were spin-coated onto quartz or Pyrex substrates. They found that the long axes of the molecules were oriented parallel to the plane of the films and that chemically imidized films, such as those used here, were more highly oriented than thermally imidized films. The proposed structure of the polyimide at the surface of the silver substrate would also require the plane of the rings in the ODA moieties to be inclined with respect to the plane of the PMDA rings. Such a model has been proposed by Silverman et al.,[45] who suggested that the angle between the PMDA and ODA rings was 60°.

We have obtained results which are somewhat similar to those described above in a recent investigation concerned with the molecular structure of interfaces formed by curing the polyamic acid of PMDA/ODA against copper substrates in a nitrogen environment.[46] Copper carboxylates which inhibited curing were formed when polyamic acid was deposited onto copper substrates. However, the extent of copper carboxylate formation was greater than that of silver carboxylates, and copper carboxylates salts extended several hundred angstroms away from the copper surface and into the bulk polymer.

Similar results were also obtained by Linde,[21] who used reflection–absorption infrared spectroscopy (RAIR) to determine the structure of thin films (40 Å) formed by depositing the polyamic acid of PMDA/ODA on silver substrates. It was suggested that PAA was adsorbed onto silver mostly through PMDA moieties which were oriented perpendicular to the surface and in which the acid groups were meta to each other. One of the acid groups reacted with the substrate to form a carboxylate salt. The carbonyl group in the other acid group was oriented perpendicular to the substrate.

However, Linde obtained results different from those described here when he cured polyamic acids against silver substrates. Linde found that curing polyamic acid films at 300 °C in nitrogen for 8 min resulted in degradation of the films. However, no destruction of the polyamic acid films occurred under the curing conditions (thermal cure at 200 °C in vacuum for 10 min and chemical cure for 2 h) used in the present study. Instead, a few molecular layers of carboxylate salts were formed adjacent to the silver surface and the oriented polyimide extended at least several molecular layers into the bulk polymer. These results indicate that the structure of polyimide films cured against metal substrates depends strongly on the curing conditions, including temperature, time, and environment.

Weak bands were observed near 1698 and 945 cm^{-1} in the normal Raman spectrum of PMDA/ODA polyimide (see Figure 1B). Corresponding bands were observed near 1695 and 940 cm^{-1} in the SERS spectra of PMDA/ODA (see Figure 5). These bands are probably related to a small amount of isoimide or degradation product formed during the curing process. We favor assignment of the bands near 1695 and 945 cm^{-1} in SERS spectra of PMDA/ODA to isoimide for the reasons described below.

The stretching mode of C=N groups is usually located between 1620 and 1690 cm^{-1}.[47] Mack et al.[34] used Raman spectroscopy to study polyimide films formed by the thermal imidization of vacuum-codeposited layers of PMDA and ODA on polycrystalline copper surfaces. It was found that the precise composition of the films depended on the ratio of the PMDA and ODA flux rates during deposition. A new Raman band associated with isoimide formation during curing was observed in this region, confirming the assignment of the C=N stretching mode. However, Mack et al. did not show the region below 1100 cm^{-1} in their Raman spectrum.

Formation of isoimide species was also evident from the observation of a band near 920 cm^{-1} in IR and RAIR spectra of PMDA/ODA. The same band was observed by Buchwalter et al.,[48] who used XPS and IR to investigate the imidization of polyamic acid and polyamic ester films. They observed a band attributed to isoimide near 920 cm^{-1} in IR spectra of polyamic acid films which were cured at 150 °C, immersed into a 1:2 (by volume) solution of trifluoroacetic anhydride and pyridine for 20 min, rinsed with methylene chloride, and dried at 85 °C for 10–15 min.

As mentioned above, the band near 1698 cm^{-1} was stronger in the SERS spectra of polyimide than in the normal Raman spectra of polyimide. This result implied that more isoimide moieties were formed in the interface than in the bulk of the polyimide.

It could be argued that the SERS results presented here are representative only of SERS-active sites and not the surface in general. However, similar conclusions were reached regarding carboxylate formation at the interface and orientation of structural moieties in the polyimide using SERS and RAIR, which is representative of the entire surface. The similarity of the SERS and RAIR results indicates that the SERS results presented here are representative of the entire surface.

IV. Conclusions

The molecular structure of thin films formed by spin-coating the polyamic acid of pyromellitic dianhydride and oxydianiline (PMDA/ODA) onto silver substrates and chemically curing the films to obtain the polyimide was determined using surface-enhanced Raman scattering (SERS) and reflection–absorption infrared spectroscopy (RAIR). SERS spectra of polyimide films cured onto silver substrates were independent of the thickness of the films, indicating that SERS was an interfacial, not bulk, effect which can be used effectively to characterize interfaces between polymers and SERS-active metals.

SERS spectra of the polyimide were more similar to SERS spectra of the polyamic acid than to normal Raman spectra of the polyimide, indicating that curing of the polyamic acid was inhibited by interaction with the silver substrate. Thus, bands appeared near 1802 and 1403 cm^{-1} in the SERS spectra of the polyamic acid cured against silver. These bands were assigned to the C=O stretching the C–N–C axial stretching modes of imide groups, indicating that some curing had occurred. However, a band near 1345 cm^{-1}, which was assigned to the C–N stretching mode of the amide groups in the polyamic acid, did not completely disappear from the SERS spectra of the polyamic acid cured against silver, indicating that some cure inhibition had occurred, probably by formation of carboxylate salts with silver ions at the interface. The relatively great intensity of the band near 1802 cm^{-1} and the relatively small intensity of the band near 1403 cm^{-1} were taken as evidence that the PMDA moieties were oriented edge-on with the C=O bonds perpendicular to the surface.

Results obtained from infrared spectroscopy were consistent with the proposed orientation of the PMDA moieties on the silver surface. However, the results from infrared spectroscopy provided information that the ODA moieties were oriented mostly parallel to the surface. A band near 1695 cm^{-1} due to isoimide species or degradation products was more prominent in the SERS spectra than in the normal Raman spectra, providing further evidence that the molecular structure of the polymer at the interface was considerably different than that in the bulk.

Acknowledgment. This research was supported in part by grants from the IBM Corp. and the Office of Naval Research. The polyamic acid samples were provided by Du Pont Corp.

References and Notes

(1) Chou, N. J.; Tang, C. H. *J. Vac. Sci. Technol.* **1984**, *A2*, 751.
(2) Ho, P. S.; Hahn, P. O.; Bartha, J. W.; Rubloff, G. W.; LeGoues, F. K.; Silverman, B. D. *J. Vac. Sci. Technol.* **1985**, *A3*, 739.
(3) Freilich, S. C.; Ohuchi, F. S. *Polymer* **1987**, *28*, 1908.
(4) Chou, N. J.; Tang, C. H. In *Surface and Colloid Science in Computer Technology*; Mittal, K. L., Ed.; Plenum Press: New York, 1987.
(5) Bartha, J. W.; Hahn, P. O.; LeGoues, F. K.; Ho, P. S. *J. Vac. Sci. Technol.* **1985**, *A3*, 1390.
(6) LeGoues, F. K.; Silverman, B. D.; Ho, P. S. *J. Vac. Sci. Technol.* **1988**, *A6*, 2200.
(7) Goldberg, M. J.; Clabes, J. G.; Viehbeck, A.; Kovac, C. A. *Polym. Mater. Sci. Eng.* **1988**, *59*, 199.
(8) Jordan, J. L.; Morar, J. F.; Pollak, R. A. *Phys. Rev.* **1987**, *B36*, 1369.
(9) Jordan, J. L.; Sanda, P. N.; Morar, J. F.; Kovac, C. A.; Himpsel, F. J.; Pollak, R. A. *J. Vac. Sci. Technol.* **1986**, *A4*, 1046.
(10) Clabes, J. G.; Goldberg, M. J.; Viehbeck, A.; Kovac, C. A. *J. Vac. Sci. Technol.* **1988**, *A6*, 985.
(11) Goldberg, M. J.; Clabes, J. G.; Kovac, C. A. *J. Vac. Sci. Technol.* **1988**, *A6*, 991.
(12) Atanasoska, L. J.; Anderson, S. G.; Meyer, H. M.; Lin, Z.; Weaver, J. H. *J. Vac. Sci. Technol.* **1988**, *A5*, 3325.
(13) Pireaux, J. J.; Vermeersch, M.; gregoire, C.; Thiry, P. A.; Caudano, R. *J. Chem. Phys.* **1988**, *88*, 3353.
(14) Dunn, D. S.; Grand, J. L. *J. Vac. Sci. Technol.* **1988**, *A7*, 252.
(15) Mack, R. G.; Grossman, E.; Unertl, W. N. *J. Vac. Sci. Technol.* **1990**, *A8*, 3827.
(16) Strunskus, T.; Hahn, C.; Frankel, D.; Grunze, M. *J. Vac. Sci. Technol.* **1991**, *A9*, 1272.
(17) Buchwalter, L. P. *J. Adhes. Sci. Technol.* **1990**, *204*, 183.
(18) Kim, Y. H.; Walker, G. F.; Kim, J.; Park, J. *J. Adhes. Sci. Technol.* **1987**, *1*, 331.
(19) Kim, Y. H.; Walker, G. F.; Feger, C.; Kowalczyk, S. P. *J. Adhes. Sci. Technol.* **1988**, *2*, 95.
(20) Burrell, M. C.; Codella, P. J.; Fontana, J. A.; McConnell, M. D. *J. Vac. Sci. Technol.* **1989**, *A7*, 55.
(21) Linde, H. G. *J. Appl. Polym. Sci.* **1990**, *40*, 2049.
(22) Grunze, M.; Lamb, R. N. *Chem. Phys. Lett.* **1987**, *133*, 283.
(23) Grunze, M.; Lamb, R. N. *Surf. Sci.* **1988**, *204*, 183.
(24) Perry, S.; Campion, A. *Surf. Sci.* **1990**, *234*, L275.
(25) Iacona, F.; Garilli, M.; Marletta, G.; Puglisi, O.; Pignataro, S. *J. Mater. Res.* **1991**, *6*, 861.
(26) Flament, O.; Russat, J.; Druet, E. *J. Adhes. Sci. Technol.* **1990**, *4*, 109.
(27) Russat, J. *Surf. Interface Anal.* **1988**, *11*, 414.
(28) Ishida, H.; Wellinghoff, S. T.; Baer, E.; Koenig, J. L. *Macromolecules* **1980**, *13*, 826.
(29) DiNardo, N. J.; Demuth, J. E.; Clarke, T. C. *J. Chem. Phys.* **1986**, *85*, 6739.
(30) Wilson, E. B. *Phys. Rev.* **1934**, *45*, 706.
(31) Varsanyi, G. *Vibrational Spectra of Benzene Derivatives*; Academic Press: New York, 1974.
(32) Tsai, W. H.; Young, J. T.; Boerio, F. J.; Hong, P. P. *Langmuir* **1991**, *7*, 745.
(33) Varsanyi, G. *Vibrational Spectra of Benzene Derivatives*; Academic Press: New York, 1974; pp 363–375.
(34) Mack, R. G.; Patterson, H. H.; Cook, M. R.; Carlin, C. M.; *J. Polym. Sci., Polym. Lett.* **1989**, *27*, 25.
(35) Colthup, N. B.; Daly, L. H.; Wiberley, S. E. *Introduction to Infrared and Raman Spectroscopy*; Academic Press: New York, 1975; p 301.
(36) Miyazawa, T.; Shimanonchi, T.; Mizushima, S. I. *J. Chem. Phys.* **1956**, *24*, 408.
(37) Dine-Hart, R. A.; White, W. W. *Makromol. Chem.* **1971**, *143*, 189.
(38) Silverman, B. D. *Macromolecules* **1989**, *22*, 2768.
(39) Linde, H. G.; Gleason, R. T. *J. Polym. Sci., Polym. Phys. Ed.* **1989**, *26*, 1485.
(40) Deacon, G. B.; Philips, R. J. *Coord. Chem. Rev.* **1980**, *33*, 227.
(41) Shevchenko, L. L. *Russ. Chem. Rev. (Engl. Transl.)* **1963**, *32*, 201.
(42) Brekner, M. J.; Feger, C. *J. Polym. Sci., Polym. Chem. Ed.* *1987*, *25*, 2479.
(43) Moskovits, M. *J. Chem. Phys.* **1982**, *77*, 4408.
(44) Russell, T. P.; Gugger, H.; Swalen, J. W. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 1745.
(45) Silverman, B. D.; Sanda, P. N.; Ho, P. S. *J. Polym. Sci., Polym. Chem. Ed.* **1985**, *23*, 2857.
(46) Young, J. T.; Boerio, F. J., to be published.
(47) Colthup, N. B.; Daly, L. H.; Wiberley, S. E. *Introduction to Infrared and Raman Spectroscopy*; Academic Press: New York, 1975; p 327.
(48) Buchwalter, L. P. *J. Vac. Sci. Technol.* **1989**, *A7*, 1772.

Registry No. PMDA/ODA (copolymer), 25038-81-7; PMDA/ODA (SRU), 9043-05-4; Ag, 7440-22-4.