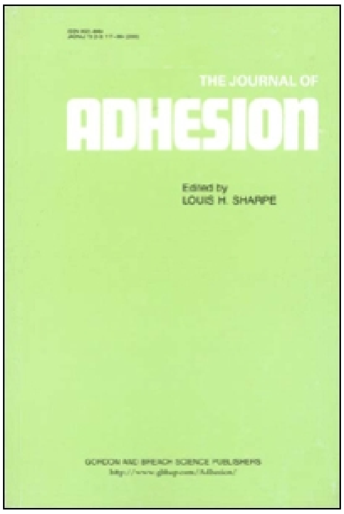

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Surface-Enhanced Raman Scattering As an In-Situ Probe of Polyimide/Silver Interphases*

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The molecular structure of interphases formed by chemically curing the polyamic acid of pyromellitic dianhydride (PMDA) and oxydianiline (ODA) against meta-aminothiophenol (m-ATP)-primed silver substrates was determined using surface-enhanced Raman scattering (SERS) and reflection-absorption infrared spectroscopy (RAIR). It was found that m-ATP was adsorbed dissociatively onto silver substrates through the sulfur atoms. When polyamic acid was deposited onto silver substrates pretreated with m-ATP, acid groups of the polyamic acid combined with amino groups of m-ATP to form ammonium carboxylate salts near the interphase. SERS and RAIR results indicated that the structure of the interphase was significantly different from that of the bulk polymer. Chemical curing of the polyamic acids located in the interphase was suppressed because of the formation of ammonium carboxylate salts. However, the bulk of the polyamic acid films was highly cured to form polyimide. It was also found that more isoimide groups were formed when thin polyamic acid films were chemically cured in acetic anhydride/pyridine solutions than in acetic anhydride/triethylamine solutions.

KEY WORDS PMDA/ODA; polyimide/silver interphase; surface-enhanced Raman scattering; reflection—absorption infrared spectroscopy; meta-aminothiophenol; isoimide.

INTRODUCTION

Polyimides are extensively used in microelectronics and composites due to their excellent thermal and mechanical stability, low dielectric constants, and chemical resistance. Good adhesion of polyimides to other materials such as metals and graphite is essential for applications in microelectronics and composites. As a result, numerous studies have been performed to characterize and control interfaces between polyimides and inorganic materials in order to improve adhesion. Most previous studies have focused on metal/polyimide interfaces formed by deposition of metals onto pyromellitic dianhydride-oxydianiline (PMDA/ODA) polyimide.[1-17] Polyimide/metal interfaces,

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which are formed by curing polyamic acid (PAA) or monomers, such as PMDA and ODA, of polyimide onto a metal substrate, have been less widely studied but have received more attention recently.[18-28]

It was generally found that polyimide/metal adhesive joints exhibited excellent mechanical and dielectric properties but poor adhesion, especially when they were exposed to warm, humid environments. A common technique for improving hydrothermal stability of polyimide/metal and polyimide/silica joints is the application of a silane coupling agent to the adherend surface. Several investigations concerned with interactions between polyimides and aminosilane-primed silica substrates have been reported.[29-33] It was found that covalent siloxane bonds were formed near the interface when aminosilanes were deposited onto silica substrates from aqueous solutions. Amino groups of silane then reacted with acid groups of PAA to form ammonium carboxylate salts which were converted to diamide groups during heat treatment at 120°C. Diamide structures were imidized by heating at temperatures higher than 200°C. Results obtained from peel tests showed that formation of chemical linkages between polyimides and silica substrates through the coupling agent improved adhesion significantly.

However, different results have been reported for the polyimide/metal adhesive system. Linde[34] used reflection—absorption infrared spectroscopy (RAIR) to investigate interactions between polyimides and metals such as Ag, Al, Cu, and Cr which were pretreated with γ-aminopropyltriethoxysilane (γ-APS). It was concluded that amino groups of γ-APS interacted with the metals and that passivating siloxane films were formed above the amine-metal layers. These films restricted the interaction of PAA with amino groups and metals and thus covalent attachment of PAA to the metal surface through the coupling agent did not occur. Instead, imidization occurred in a normal fashion above the siloxane films. Therefore, the use of γ-APS did not enhance adhesion in polyimide/metal adhesive joints.

In order to improve adhesion in polyimide/metal systems, it is necessary to choose another type of coupling agent which can interact strongly with the metal and the polymer. Organosulfur compounds such as aminophenyldisulfide and aminothiophenol seem to be promising candidates. This is because strong chemical interactions exist between sulfur atoms and metals such as gold, silver, and copper. As a result, self-assembled monolayers can be prepared by immersing metal substrates into dilute solutions of organosulfur compounds.[35-40] Organofunctional groups on these coupling agents can then react with polymers, forming chemical bridges between the polymer and the metal and leading to improved adhesion.[41]

Recently, Grunze reported somewhat related studies using second harmonic generation to characterize interfaces between polyamic acids from PMDA and 4,4-diaminodiphenylsulfide and metals.[42] However, to our best knowledge, no information concerning the use of organosulfur compounds as coupling agents in polyimide/metal systems has been reported. Therefore, we were interested in using the novel technique known as surface-enhanced Raman scattering (SERS) to characterize interphases between polyimides and organosulfur-primed metal 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 with its value for normal Raman scattering. The enhancement is very large at the interface but decreases rapidly as a function of distance away from the metal surface. The enhancement obtained from molecules that are more than few monolayers away from the metal surface is negligible. As a result, SERS is surface-selective and can be used for non-destructive characterization of polyimide/metal interphases. Most other analytical techniques which have been used to investigate polyimide interfaces, such as X-ray photoelectron spectroscopy (XPS) and RAIR, require that either the polyimide film or the substrate be very thin or that they be separated.

We have already used SERS to investigate the molecular structure of interphases formed by curing the polyamic acid of PMDA and ODA,[43] and the polyamic acid of PMDA and 2,2-bis[4(4-aminophenoxy)-phenyl]-hexafluoropropane (4-BDAF)[44] against silver substrates. It was concluded that acid groups in the PMDA moieties of both polyamic acids formed carboxylate salts with silver ions from the substrate, thus inhibiting curing of the polymer adjacent to the substrate.

Subsequently, we reported SERS and RAIR results obtained from polyimide/Au and polyimide/Cu systems.[45] These results indicated that large amounts of carboxylate salts were formed on the copper surface, resulting in a partial cure of PAA films on copper substrates. However, only trace levels of carboxylates were detected on gold surfaces on which PAA was highly cured. The extent of carboxylate formation on silver substrates was intermediate between those on copper and gold substrates.

Very recently, we used SERS to determine the molecular structure of interphases between model polyimides and organosulfur-primed silver and gold substrates.[46-47] These model systems were formed by depositing phthalic anhydride (PA) onto an 4-aminophenyldisulfide (APDS) pretreated Au substrate or a meta-aminothiophenol (m-ATP) pretreated Ag substrate, followed by chemical curing in acetic anhydride and pyridine or triethylamine. It was concluded that APDS and m-ATP were adsorbed dissociatively onto Au and Ag substrates, respectively. When PA was deposited onto organosulfur-treated metal substrates, anhydride groups of PA reacted with amino groups of coupling agents to form amic acids. Chemical curing of these amic acid films in acetic anhydride/pyridine or acetic anhydride/triethylamine solutions gave mixtures of isoimide and imide. The relative amounts of imide and isoimide formed on metal substrates depended strongly on the catalysts used for the chemical curing and the coupling agents used for different metal substrates. Formation of chemical linkages between PA and metal through APDS and m-ATP indicated that organosulfur compounds may be effective as adhesion promoters for bonding polyimide to metal.

The purpose of this paper is to describe results we have obtained using SERS and RAIR to determine the molecular structure of interphases formed by curing the polyamic acid of PMDA/ODA against m-ATP-primed silver substrates. SERS and RAIR results showed that m-ATP was absorbed dissociatively onto Ag substrates. When PAA was deposited onto m-ATP pretreated Ag substrates, a very thin interphase layer of ammonium carboxylate salt was formed by reacting acid groups of PAA with amino groups of m-ATP. Formation of ammonium carboxylate salts suppressed the curing of PAA at the interphases during treatment with mixtures of acetic anhydride and pyridine or triethylamine. However, the bulk of the polymer films was highly cured. The SERS and RAIR resutls described in this paper are consistent with XPS results which will be published elsewhere.[48]

EXPERIMENTAL

Silver substrates were prepared for SERS investigations as described below. Glass slides were cleaned by immersion in 0.1N NaOH aqueous solutions for 1 hour and rinsed in 0.1N HCl aqueous solutions for another hour. These glass slides were then rinsed ultrasonically in distilled-deionized water, blown dry with nitrogen, cleaned ultrasonically in absolute ethanol several times, and blown dry with nitrogen again.

The clean glass slides were placed immediatelty in a vacuum chamber which was purged with nitrogen and pumped down to 10^{-6} Torr using sorption, sublimation, and ion pumps. Silver wires wrapped around resistively heated tungsten filaments were then slowly heated to evaporate metal island films onto the glass slides at a rate of 1 Å/sec. The thickness of silver island films was controlled at about 45 Å using a quartz crystal oscillator thickness monitor. Meta-aminothiophenol (m-ATP), acetic anhydride, pyridine, and triethylamine were obtained from Aldrich Chemical Co. and used as received. The polyamic acid (PAA) of pyromellitic dianhydride (PMDA) and oxydianiline (ODA) was obtained from DuPont Co. Monolayers of m-ATP were prepared by immersing an Ag island film into a 0.01% solution of m-ATP in acetone for 10 minutes, followed by rinsing with acetone extensively. m-ATP pretreated Ag substrates were immersed in a 1% solution of PAA in dimethyl sulfoxide (DMSO) for 24 hours and then rinsed with DMSO. PAA-coated specimens were heated at 85°C for 15 minutes to remove solvent and then chemically cured in a solution of acetic anhydride and pyridine or triethylamine (1:1 ratio by volume) for 24 hours. Some SERS specimens were prepared by spin-coating PAA from dilute solutions onto m-ATP pretreated Ag island films, heating at 85°C for 15 minutes, and curing in mixtures of acetic anhydride and pyridine or triethylamine for 24 hours.

All SERS spectra were obtained in a nitrogen atmosphere using a spectrometer equipped with a Spex 1401 double monochromator, a Hamamatsu R943-02 photomultiplier, a Stanford Research Model 400 gated photon counter interfaced to a Hewlett-Packard Vectra computer, and a Spectra-Physics Model 165 argon-ion laser. The slit setting of the monochromator provided a spectral resolution of about $10\,\mathrm{cm}^{-1}$ for the SERS spectra. The green line of the laser (5145 Å) with a power between 10 and 50 mW was incident on the sample at an angel of about 65° relative to the normal to the sample surface 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 $23\,\mathrm{cm}^{-1}$ per minute. Plasma lines were removed from the spectra by placing a narrow-bandpass filter between the laser and sample. Normal Raman spectra of m-ATP were obtained from small amounts of m-ATP 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 $5\,\mathrm{cm}^{-1}$.

Similar procedures were used to prepare samples for RAIR experiments, except that thick Ag films were used instead of Ag island films. Thick Ag films (several thousand angstroms) were prepared by thermally evaporating silver onto clean glass slides. RAIR spectra were obtained using a Perkin-Elmer Model 1800 Fourier-transform infrared (FTIR) spectrophotometer and external reflection accessories provided by Harrick Scientific Co. One reflection at an angle of 78° was used in all cases. Spectra were collected in the quantitative mode at a resolution of 4 cm^{-1}. Seven hundred and fifty scans were averaged for each spectrum collected. The spectra presented in this paper are difference spectra obtained by subtracting spectra of bare substrates from spectra of film-covered substrates. Transmission infrared spectra of m-ATP were obtained using the same spectrophotometer. Specimens were prepared by placing a small amount of m-ATP liquid between two KBr pellets.

The thickness of the organic films deposited onto silver substrates was determined by ellipsometry. Organic films were deposited onto thick silver films using the same procedures as those used to prepare RAIR specimens. The thickness of the films was determined using a Rudolph Research Model 436 ellipsometer to examine the metal substrates before and after deposition of the organic films. The thickness of the polymer films prepared by spin-coating from 2, 0.4, and 0.08% solutions onto m-ATP pre-treated Ag substrates, followed by chemical curing, was approximately 200, 60 and 30 Å, respectively.

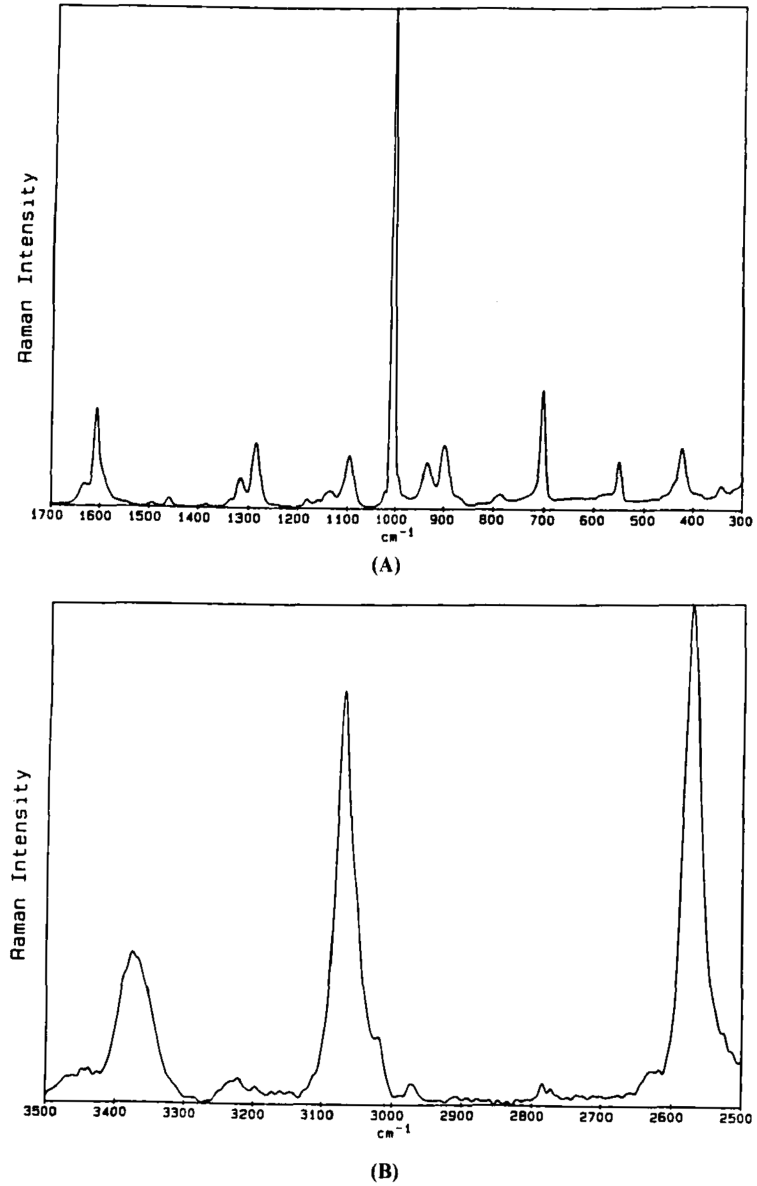
RESULTS AND DISCUSSIONS

The normal Raman spectrum obtained from meta-aminothiophenol (m-ATP) is shown in Figure 1. The observed bands and their assignments are summarized in Table I. Bands near 1637 and 3370 cm^{-1} were assigned to the deformation and the stretching modes of NH_2 groups, respectively.[49] Bands near 934 and 2580 cm^{-1} were attributed to the bending and the stretching modes of S-H groups, respectively. The remaining

TABLE I
Tentative band assignments for meta-aminothiophenol (m-ATP)

NR (cm^{-1})	IR (cm^{-1})	SERS (cm^{-1})	RAIR (cm^{-1})	Assignments
	3432(M)			$\nu_{as}(NH_2)$
3370(M)	3356(M)	3370(W)		$\nu_s(NH_2)$
3080(M)	3053(W)	3080(W)		ν(2), C—H stretching
2580(M)	2556(W)			ν(S—H)
1630(W)	1618(M)	1630(W)	1618(M)	$\beta_s(NH_2)$
1608(M)	1595(S)	1597(S)	1590(S)	ν(8b), C—C stretching
	1478(S)		1478(S)	ν(19b), C—C stretching
1460(W)	1445(W)	1460(W)	1445(W)	ν(19a), C—C stretching
	1321(W)		1320(W)	
1317(W)	1301(W)	1315(M)	1297(W)	ν(14), C—C stretching
1285(W)	1269(W)		1269(W)	ν(13), C-X stretching
	1166(W)		1166(W)	ν(9b), C—H in-plane bending
1095(W)	1081(W)	1085(M)	1075(W)	ν(18a), C-X in-plane bending
1007(S)	992(W)	1005(S)	992(W)	ν(12), radial skeletal vib.
934(W)	924(W)			β(S—H)
899(W)	880(W)	896(W)	880(W)	ν(6b), radial skeletal vib.
	850(W)			ν(17b), C—H out-of-plane vib.
785(W)	771(W)		769(W)	ν(11), C—H out-of-plane vib.
703(W)	685(W)	700(W)	685(W)	ν(1), radial skeletal vib.
549(W)				ν(16a), out-of-plane skeletal vib.
422(W)		424(W)		ν(7b), C-X stretching

S: strong; M: medium; W: weak.



FUGURE 1 Normal Raman spectra obtained from meta-aminothiophenol (m-ATP) between (A)-300–1700 cm^{-1} and (B)-2500–3500 cm^{-1}.

bands were related to vibrational modes of meta-substituted benzene rings and were assigned using the Wilson numbering system.[50–51] For instance, strong bands near 1608, 1095, 1007, and 703 cm^{-1} were assigned to the C—C stretching mode ν(8b), the C—H bending mode ν(18a), and ring breathing modes ν(12) and ν(1), respectively. No distinct aryl-S vibrations were observed due to coupling of C—S modes with ring modes.

SERS spectra obtained from m-ATP monolayers adsorbed onto Ag island films are presented in Figure 2. Several differences were observed between the normal Raman and SERS spectra of m-ATP. Bands associated with S—H groups near 2580 and 934 cm^{-1} disappeared in the SERS spectra of m-ATP. Bands near 1608 and 1095 cm^{-1}, which were assigned to the C—C stretching mode ν(8b) and the C-X in-plane bending

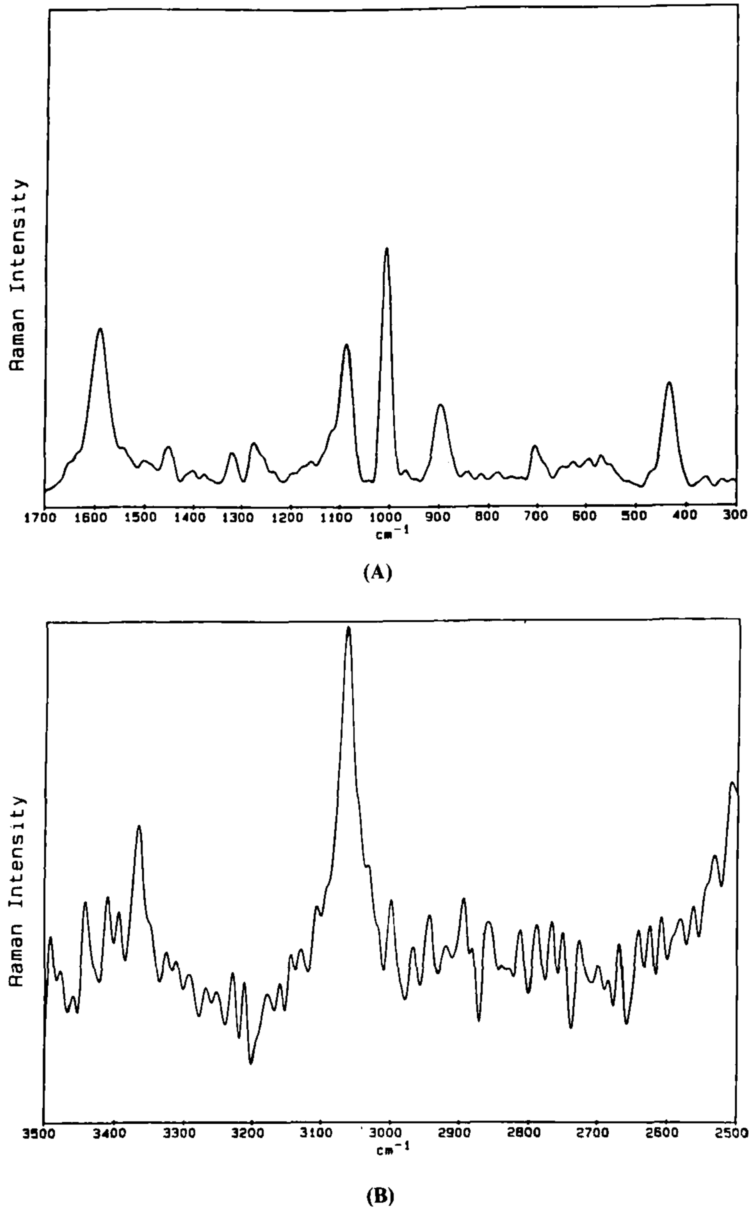


FIGURE 2 SERS spectra obtained from m-ATP monolayers adsorbed onto an Ag island film between (A)-300–1700 cm^{-1} and (B)-2500–3500 cm^{-1}.

mode $\nu(18a)$, respectively, shifted to about 1597 and 1085 cm^{-1} and increased in intensity in SERS spectra of m-ATP. The band near 422 cm^{-1} assigned to the C-X stretching mode $\nu(7b)$ also increased in intensity. Disappearance of bands due to S—H vibrations and the shift of substituent-sensitive ring modes such as $\nu(8b)$ and $\nu(18a)$ indicated that cleavage of S—H bonds occurred and m-ATP was adsorbed dissociatively on Ag substrates through the S atoms.

No clear bands due to S—Ag bonding were observed between 150–400 cm^{-1} in SERS spectra of m-ATP. However, formation of S-metal bonds between organosulfur and Ag has been reported by Sandroff and Herschbach,[52] Joo *et al.*,[53-54] and Yim *et al.*[55] who used SERS to investigate the interactions of organosulfur compounds with Ag sub- strates. These authors also observed the cleavage of S—H bonds and the shift of sub- stituent-sensitive ring modes in their SERS spectra,[52-55] supporting the SERS results described above.

Results obtained from infrared spectroscopy were consistent with SERS results. The transmission infrared and RAIR spectra of m-ATP are shown in Figures 3 and 4, respectively. The observed bands and their assignments are also summarized in Table I. In the transmission IR spectrum of m-ATP (see Figure 3), bands near 2556 and 924 cm^{-1} were assigned to the stretching and bending modes of S—H groups. These bands disappeared in the RAIR spectra of m-ATP monolayers (see Figure 4). Bands near 1595 and 1081 cm^{-1} which were assigned to $\nu(8b)$ and $\nu(18a)$ modes of benzene ring, respectively, shifted downward to about 1590 and 1077 cm^{-1} in the RAIR spectra of m-ATP. These results again suggested that m-ATP was adsorbed dissociatively onto Ag substrates through the S atoms.

As mentioned before, we also used XPS to confirm results obtained from SERS and RAIR. In the high-resolution S(2p) spectrum obtained from m-ATP monolayers adsorbed onto Ag substrates,[48] a broad and asymmetric peak with a binding energy maximum near 162.4 eV was observed. This peak was assigned to the thiolate species,[56-57] indicating that S—Ag bonds were indeed formed between the m-ATP and the Ag substrate.

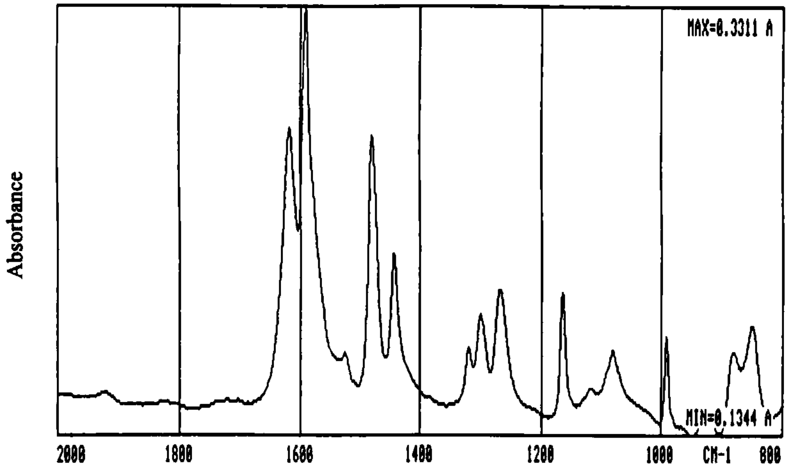


FIGURE 3 Transmission IR spectra obtained from m-ATP.

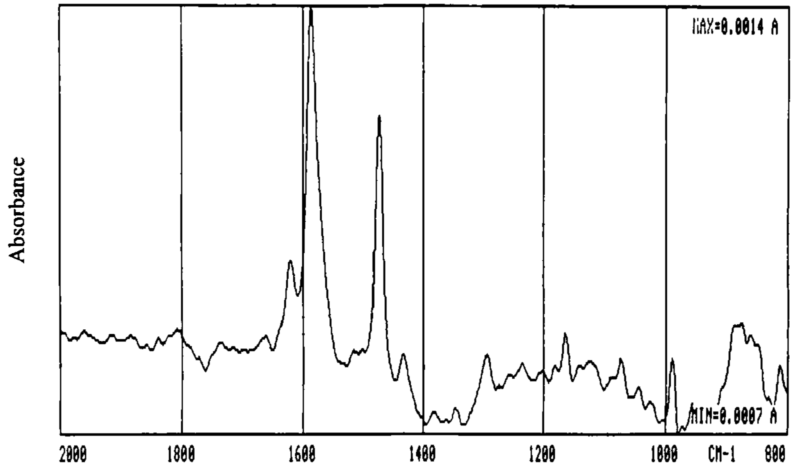


FIGURE 4 RAIR spectra obtained from m-ATP monolayers adsorbed onto a thick Ag film.

Since SERS was a highly sensitive technique, one might ask why the vibration due to S—Ag bonding was not seen in the SERS spectra. As mentioned above, the band due to the S—Ag stretching mode should appear between 200 and 400 cm^{-1} in the Raman spectra. This band was intrinsically weak and usually buried in the strong background due to Rayleigh scattering. Joo *et al.*[54] investigated the adsorption behavior of benzenethiol on a silver sol using SERS. An extremely weak shoulder near 237 cm^{-1} was observed in the SERS spectra of benzenethiol and was assigned to the S—Ag stretching mode. The signal-to-noise ratio in our SERS spectra was probably not good enough to distinguish such a weak shoulder from noise. However, XPS results undoubtedly showed that S—Ag bonds were formed upon adsorption of the m-ATP on Ag substrates.[48]

Figure 5 shows SERS spectra obtained from a sample prepared by immersing a m-ATP pretreated Ag island film in a 1% polyamic acid (PAA) solution for 24 hours, followed by rinsing with dimethyl sulfoxide (DMSO). When this spectrum was compared with the SERS spectrum of m-ATP monolayer (see Figure 2), significant differences were observed. Several new bands were observed in SERS spectra of PAA/m-ATP/Ag. For example, bands near 1340 and 1540 cm^{-1} were related to amide groups,[43-45] indicating that PAA was present on the m-ATP-treated substrates. Bands characteristic of protonated amino groups (NH_3^+) were observed near 1495, 2670, and 2945 cm^{-1} in SERS spectra of PAA/m-ATP/Ag.[49,51] Bands associated with carboxylate groups (COO^-) were also observed near 1390 and 830 cm^{-1} in Figure 5. Observation of bands due to NH_3^+ and COO^- indicated that acid groups of PAA reacted with amino groups of m-ATP to form ammonium carboxylate salts.

The SERS spectrum obtained from a DMSO-rinsed PAA/m-ATP/Ag sample after chemically curing in acetic anhydride and pyridine is shown in Figure 6. This spectrum was similar to the SERS spectra of PAA/m-ATP/Ag samples before curing (see Figure 5). Bands associated with amide, NH_3^+, and COO^- groups were still present in the SERS spectra after chemical curing, indicating that formation of ammonium

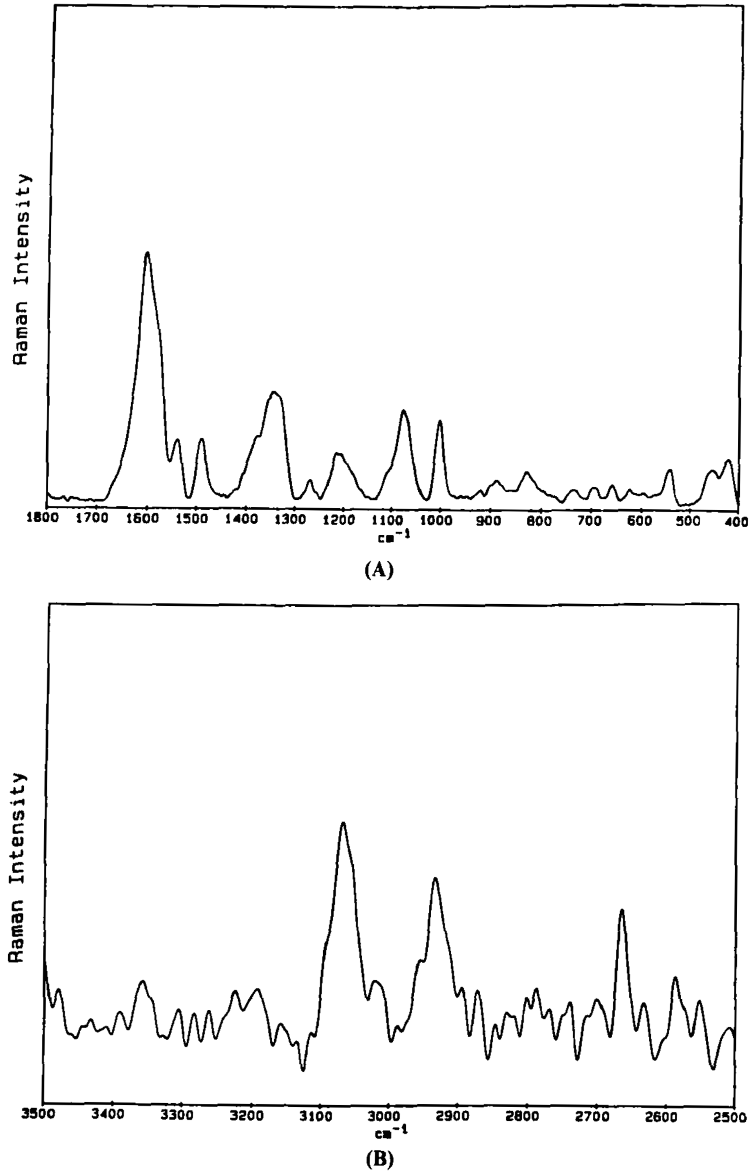


FIGURE 5 SERS spectra obtained between (A)-400–1800 cm^{-1} and (B)-2500–3500 cm^{-1} from a sample prepared by immersing a m-ATP pretreated Ag island film into a 1%solution of PAA in dimethyl sulfoxide (DMSO) for 24 hours, followed by rinsing extensively with DMSO.

carboxylate salts inhibited the imidization of PAA near the interphase. However, the remaining amic acid groups of polymer chains in the bulk were probably imidized. This was evident from the observation of the band related to imide groups near 1800 cm^{-1} in Figure 6.[43–45] Since SERS is an interfacial effect, vibrational modes of those functional groups located further away from the metal surface would appeared with

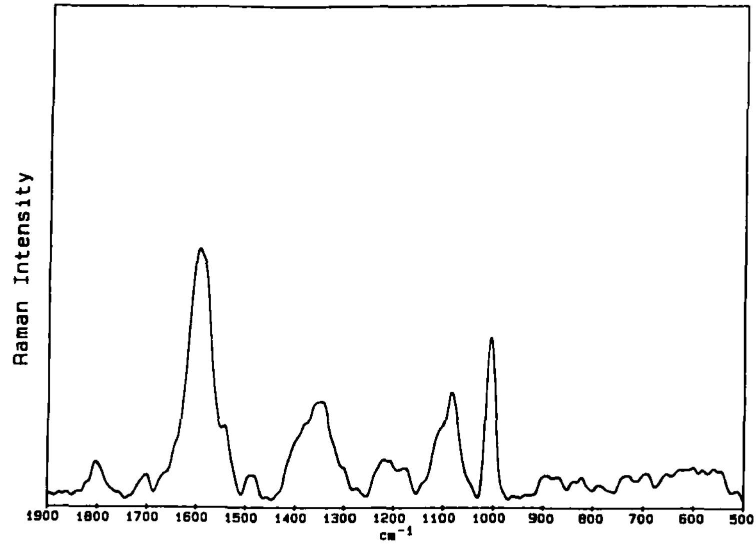


FIGURE 6 SERS spectra obtained from a sample prepared by immersing a m-ATP pretreated Ag island film into a 1% solution of PAA for 24 hours, rinsing with DMSO, and curing the films in mixtures of acetic anhydride and pyridine for 24 hours.

less intensity. The small intensity of the band near 1800 cm^{-1} indicated that imide groups were formed in the bulk portion rather than the interphase.

SERS spectra obtained from PAA/m-ATP/Ag samples prepared by spin-coating PAA onto m-ATP pretreated Ag substrates from 2%solutions and then curing in acetic anhydride/pyridine solutions for 24 hours is shown in Figure 7. The thickness of these polymer films was approximately 200 Å as measured by ellipsometry. This spectrum was very similar to the SERS spectrum obtained from a DMSO-rinsed PAA/m-ATP/Ag sample after curing (see Figure 6), indicating that SERS spectra were independent of the thickness of the polymer film and that the SERS signal originated from the interphase, not from the bulk of the films.

The SERS spectrum obtained from a PAA/m-ATP/Ag sample after curing in mixtures of acetic anhydride and triethylamine is shown in Figure 8. This spectrum was very similar to those obtained from PAA/m-ATP/Ag samples cured in mixtures of acetic anhydride and pyridine (see Figures 6 and 7). Bands due to ammonium carboxylates and amides were observed in this spectrum, indicating that the interfacial region of the films was not cured during treatment with mixtures of acetic anhydride and triethylamine.

However, some differences were observed when the SERS spectrum shown in Figure 8 was compared with those shown in Figures 6 and 7. There was an additional band near 1700 cm^{-1} in SERS spectra of PAA/m-ATP/Ag samples cured in acetic anhydride and pyridine (see Figures 6 and 7). This band was attributed to the C=N stretching mode of isoimide groups,[43-44] indicating that some isoimide species were formed when PAA was cured in acetic anhydride/pyridine solutions. In a previous

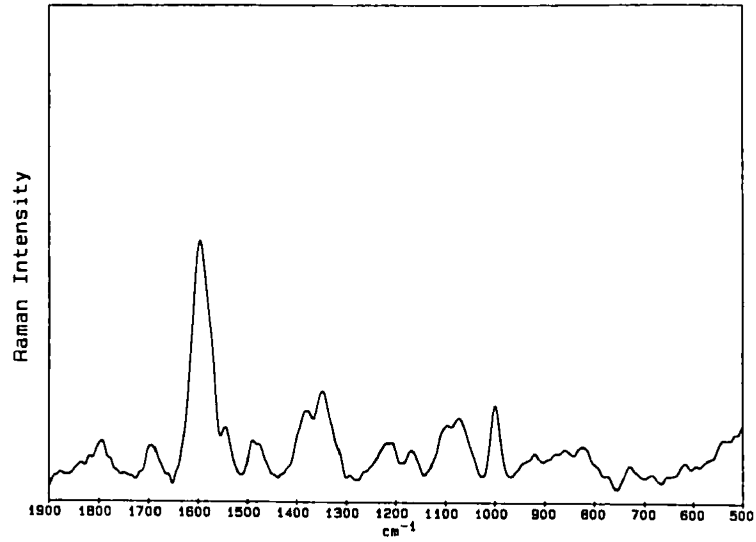


FIGURE 7 SERS spectra obtained from a sample prepared by spin-coating PAA films onto a m-ATP pretreated Ag island film from a 2%solution and curing the films in mixtures of acetic anhydride and pyridine for 24 hours.

investigation[43], we showed that isoimide was formed when PAA was chemically cured against Ag substrates in acetic anhydride/pyridine solutions. However, the products depended strongly on the catalyst used in the curing processes. The band due to isoimide near 1700 cm^{-1} was very weak in the SERS spectrum shown in Figure 8, indicating that less isoimide was formed when PAA was cured in acetic anhydride/triethylamine solutions. The presence of a strong base such as triethylamine generated acetate ions which induced isomerization of isoimide to imide. This isoimide-imide rearrangement in the presence of acetate ions has been proposed by several groups.[58-59]

RAIR spectra obtained from thick polymer films are characteristic of the bulk polymer, while RAIR spectra obtained from thin polymer films are characteristic of the interphase. Therefore, a series of RAIR experiments were performed for various thickness of PAA films cured against m-ATP pretreated Ag substrates.

Figure 9 shows RAIR spectra obtained from samples prepared by spin-coating PAA films onto m-ATP pretreated Ag substrates from 2, 0.4, and 0.08% solutions and heating at 85°C for 15 minutes to remove the solvent. As expected, the spectrum obtained from the thickest film (see Figure 9A) was dominated by bands characteristic of polyamic acid. For example, bands near 1670 and 1545 cm^{-1} were related to vibrations of amide groups, while those near 1720 and 1407 cm^{-1} were related to vibrations of acid groups. The strong band near 1500 cm^{-1} was due to the C—C stretching mode $\nu(19a)$ of ODA rings, while that near 1240 cm^{-1} was assigned to the stretching mode of C—O—C groups. When the thickness of the PAA films decreased, bands characteristic of m-ATP were expected to increase in intensity. Indeed, bands

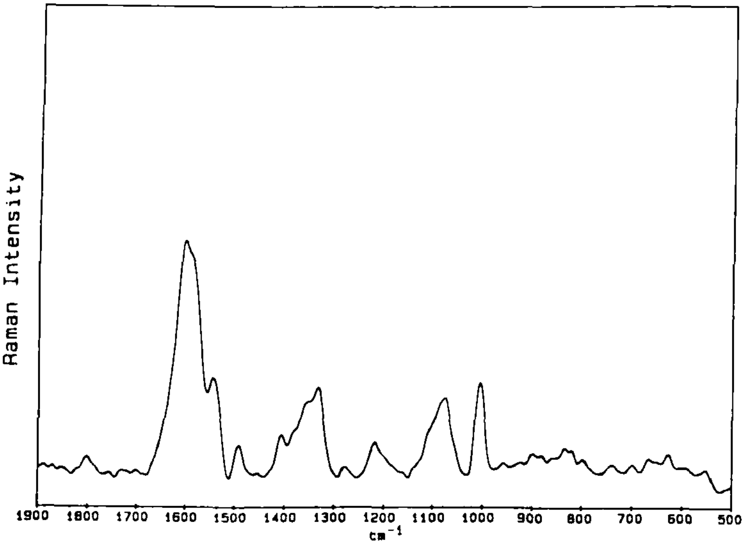


FIGURE 8 SERS spectra obtained from a sample prepared by immersing a m-ATP pretreated Ag island film into a 1% solution of PAA for 24 hours, rinsing with DMSO, and curing the films in mixtures of acetic anhydride and triethylamine for 24 hours.

near 1590 and 1478 cm^{-1} which were assigned to the ν(8b) and ν(19b) modes of m-ATP benzene rings increased in intensity (see Figure 9C). However, the band near 1720 cm^{-1} due to carbonyl stretching of acid groups decreased in intensity as the film became thinner, probably indicating that some acid groups of PAA interacted with amino groups of m-ATP to form ammonium carboxylate salts. Formation of ammonium carboxylates was also supported by the decrease in intensity of the band near 1610 cm^{-1} which was assigned to the deformation mode of NH_2 groups and the ν(8a) mode of PMDA benzene rings.

Figure 10 shows the RAIR spectrum obtained from a PAA/m-ATP/Ag sample prepared by immersing a m-ATP pretreated Ag substrate into a 1% PAA solution and then rinsing with DMSO to remove physisorbed polyamic acid. Obviously, this spectrum was dominated by bands near 1592 and 1478 cm^{-1} which were assigned to m-ATP, indicating that the spectrum was characteristic of the film/substrate interphase. In this spectrum, the band near 1618 cm^{-1} which was assigned to the deformation mode of NH_2 groups was very weak. Bands near 1718, 1670, and 1545 cm^{-1} assigned to acid and amide groups of PAA were also weak but were still present in Figure 10. The band assigned to the C—C stretching mode ν(19a) of ODA rings was also observed near 1500 cm^{-1} in Figure 10. The decrease in intensity of the band near 1618 cm^{-1} and the observation of bands due to PAA in the RAIR spectra of rinsed samples implied that some amino groups of m-ATP reacted with acid groups of PAA.

No distinct bands related to ammonium carboxylate salts were observed in the RAIR spectrum of PAA/m-ATP/Ag shown in Figure 10. Bands characteristic of symmetric and asymmetric deformation modes of NH_3^+ groups were usually observed

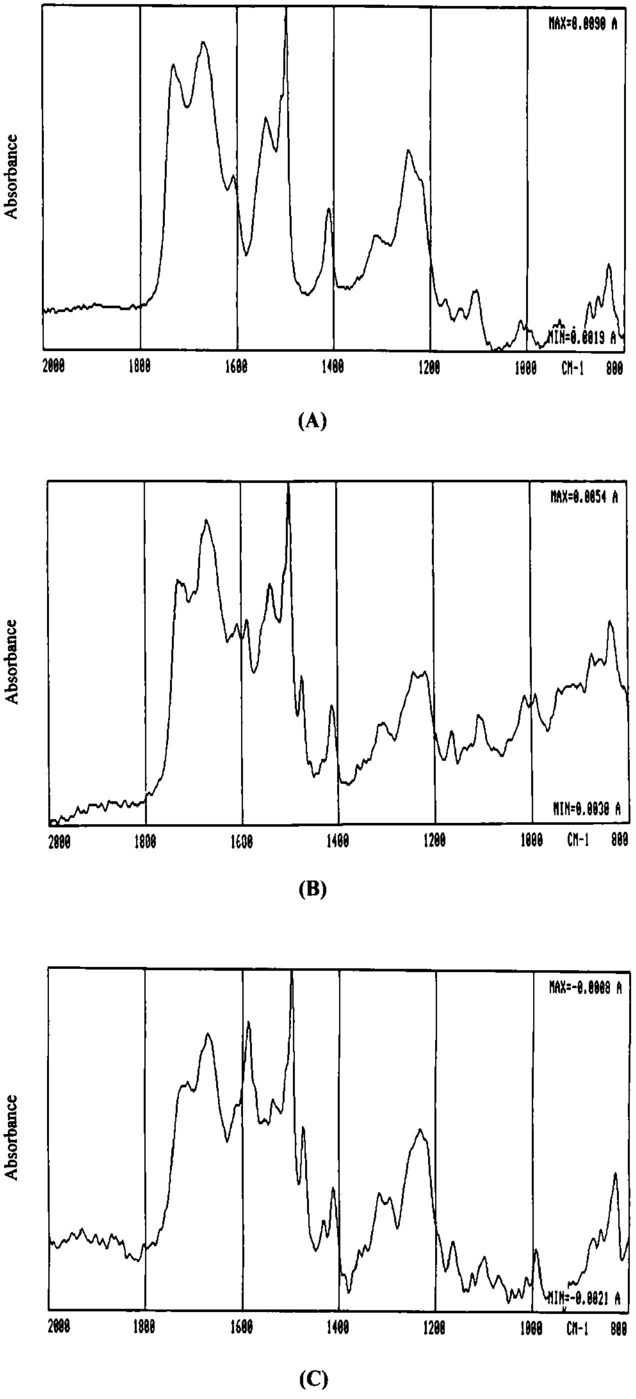


FIGURE 9 RAIR spectra obtained from samples prepared by spin-coating PAA films onto m-ATP pretreated Ag substrates from (A)-2, (B)-0.4, and (C)-0.08%solutions.

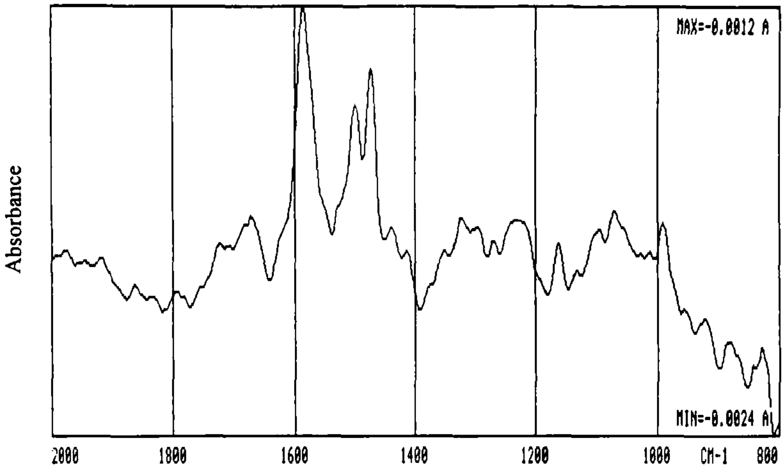
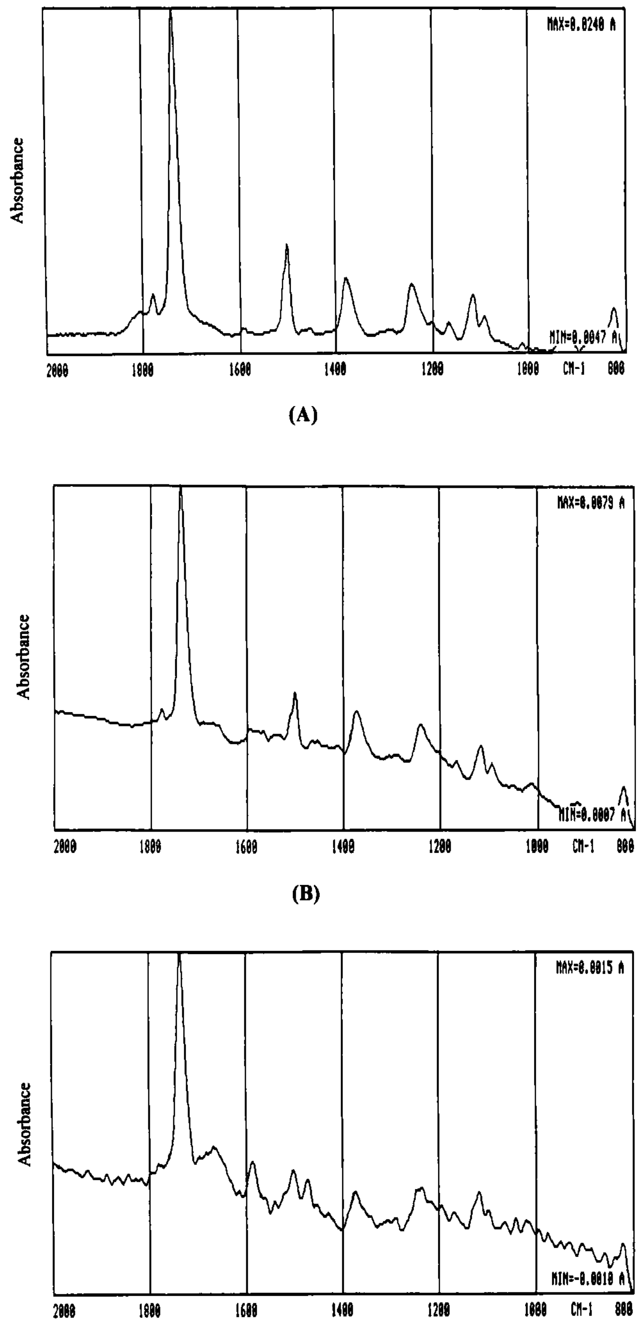


FIGURE 10 RAIR spectra obtained from a sample prepared by immersing a m-ATP pretreated Ag substrate into a 1% solution of PAA for 24 hours and rinsing extensively with DMSO.

near 1500–1530 and 1590–1620 cm^{-1} in the IR spectrum, while bands associated with symmetric and asymmetric stretching modes of COO$^-$ were usually observed near 1380–1430 and 1570–1615 cm^{-1}.[49,51] These bands were probably coupled with bands near 1590 and 1500 cm^{-1} which were assigned to the ν(8b) of m-ATP and the ν(19a) of ODA, respectively. However, bands related to ammonium carboxylates were clearly observed in the SERS spectra of PAA/m-ATP/Ag (see Figure 5), indicating that ammonium carboxylate salts did form near the interphase. Considering the absence of distinct bands due to ammonium carboxylates and the weak intensities of bands due to PAA in the RAIR spectrum shown in Figure 10, it is likely that only a very thin interfacial layer of ammonium carboxylate was formed.

RAIR spectra obtained from samples prepared by spin-coating PAA onto m-ATP pretreated Ag substrates from 2, 0.4, 0.08% solutions, heating at 85°C for 15 minutes, and chemically curing in mixtures of acetic anhydride and pyridine are shown in Figure 11. As mentioned before, the thickness of these polymer films was approximately 200, 60, and 30 Å, respectively. As expected, in the case of the thickest film (see Figure 11A), the spectra were dominated by bands due to imide groups. For instance, bands near 1778, 1730, 1379, and 1130 cm^{-1} were assigned to the in-phase C=O stretching, out-of-phase C=O stretching, C—N—C axial stretching, and C—N—C trans verse stretching modes, respectively.[43] The band near 1240 cm^{-1} was assigned to the stretching mode of C—O—C groups. Observation of strong bands due to imide vibrations suggested that the bulk of the polymer films was highly cured.

When the film thickness decreased, bands near 1592 and 1478 cm^{-1} which were characteristic of m-ATP increased in intensity (see Figures 11B and 11C). The broad band near 1675 cm^{-1} also became stronger. The trend of these changes was even more pronounced in the RAIR spectrum obtained from a sample prepared by immersing a m-ATP treated Ag substrate into 1% PAA solutions, rinsing with DMSO, and curing in acetic anhydride and pyridine (see Figure 12). In this spectrum, bands characteristic



(A)

(B)

(C)

FIGURE 11 RAIR spectra obtained from samples prepared by spin-coating PAA films onto m-ATP pretreated Ag substrates from (A)-2, (B)-0.4 and (C)-0.08% solutions, followed by curing the films in mixtures of acetic anhydride and pyridine.

of m-ATP near 1592 and 1478 cm^{-1} were very strong, while the band near 1730 cm^{-1} due to imide carbonyl stretching was weaker. The band associated with amide groups near 1675 cm^{-1} also increased in intensity. Observation of the band due to amide groups and the decrease in intensity of the band due to imide indicated that some PAA was not cured at the interphase. Inhibition of the curing near the interphase was likely due to the formation of ammonium carboxylate salts. These results were consistent with SERS results described above.

Another series of RAIR experiments were performed by curing PAA films of various thickness against m-ATP pretreated Ag substrates in acetic anhydride and triethylamine solutions. RAIR spectra obtained from PAA films spin-coated onto m-ATP-primed Ag substrates from 2, 0.4, 0.08% solutions and then cured in acetic anhydride/triethylamine solutions are shown in Figure 13. RAIR spectra obtained after curing solvent-rinsed PAA/m-ATP/Ag samples in acetic anhydride/triethylamine solutions are shown in Figure 14. Again, for the thickest films (see Figure 13A), the spectrum was dominated by strong bands due to imide groups, indicating that the bulk of the polymer was highly cured. As the polymer film became thinner, bands characteristic of m-ATP near 1592 and 1478 cm^{-1} became stronger. The broad band near 1675 cm^{-1} assigned to amide groups also increased in intensity and was well-resolved in the spectrum of the thinnest film (see Figure 14). These results again suggested that there existed a thin interfacial layer which was partially cured because of the formation of ammonium carboxylate and that the molecular structure of this interfacial layer was different from that of the bulk of the polymer.

However, a difference was observed between RAIR spectra of rinsed PAA/m-ATP/Ag samples cured in acetic anhydride/pyridine and acetic anhydride/triethylamine solutions (see Figures 12 and 14). Bands near 1675 and 1240 cm^{-1} in Figure 12 were stronger than the corresponding bands in Figure 14. The band near 1675 cm^{-1} was

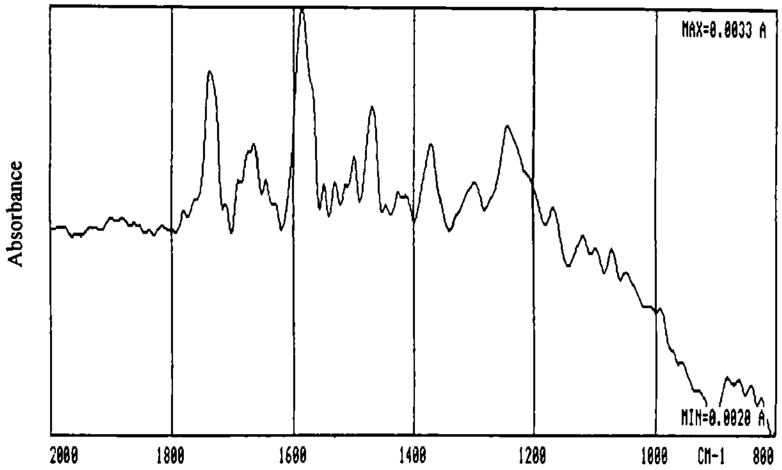


FIGURE 12 RAIR spectra obtained from a sample prepared by immersing a m-ATP pretreated Ag substrate into a 1% solution of PAA for 24 hours, rinsing with DMSO, and curing the films in mixtures of acetic anhydride and pyridine for 24 hours.

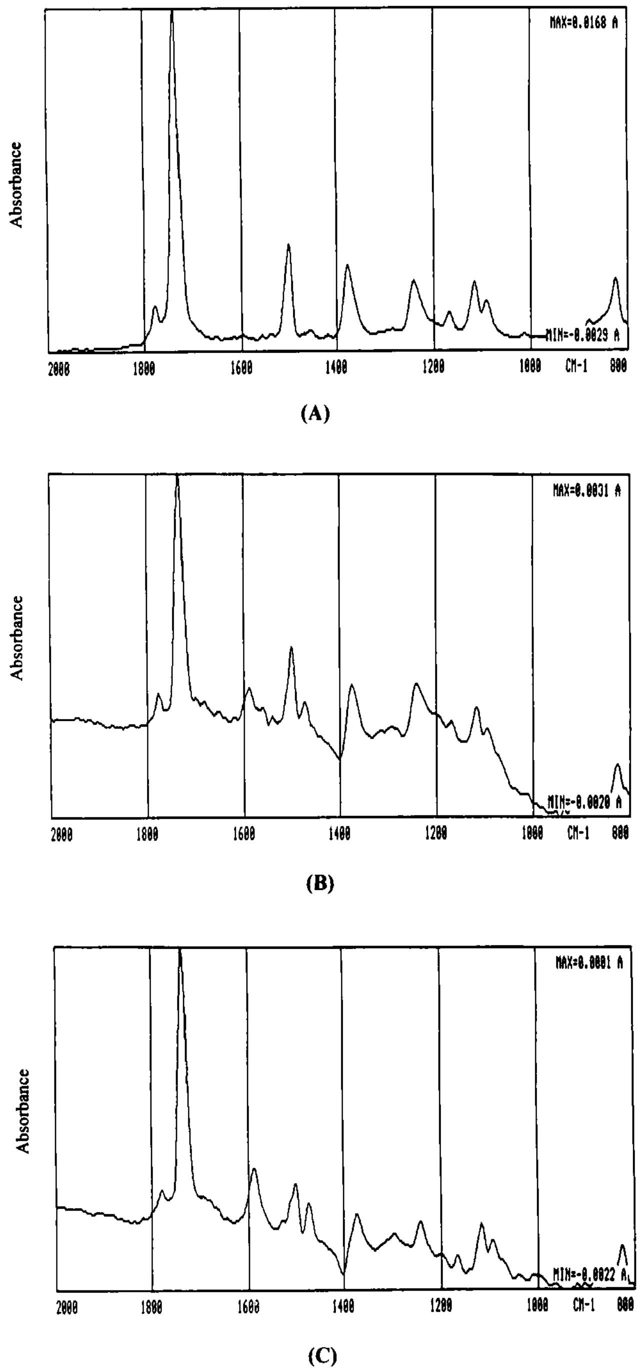


FIGURE 13 RAIR spectra obtained from samples prepared by spin-coating PAA films onto m-ATP pretreated Ag substrates from (A)-2, (B)-0.4 and (C)-0.08%solutions and then curing the films in mixtures of acetic anhydride and triethylamine.

FIGURE 14 RAIR spectra obtained from a sample prepared by immersing a m-ATP pretreated Ag substrate into a 1% solution of PAA for 24 hours, rinsing with DMSO, and curing the films in mixtures of acetic anhydride and triethylamine for 24 hours.

attributed to the C=O stretching mode of amide groups and the C=N stretching mode of isoimide groups.[47] Similarly, the band near 1240 cm^{-1} was assigned to the C—O—C stretching modes of ODA and isoimide. The greater intensities of these two bands in Figure 12 indicated that more isoimide species were formed when PAA was cured in the presence of pyridine. These results were in good agreement with SERS results.

Orszagh *et al.* have investigated chemical cyclization mechanisms of the polyamic acid obtained from PMDA and benzidine.[60] They synthesized the ammonium salt of polyamic acid by reacting polyamic acid with 5% ammonia solutions. No cyclization was observed when the ammonium salt of polyamic acid was treated with the dehydrating agents (mixtures of acetic anhydride and pyridine). It was thus concluded that, for polyamic acid, the first attack of the dehydrating agents occurred at the secondary amide linkage. These results were consistent with our SERS and RAIR results which indicated that the curing of polyamic acids was suppressed by the formation of ammonium carboxylate salts near the interphase.

However, different results were obtained by Kakimoto *et al.*[61] and Sotobayashi *et al.*[62] who deposited mono- and multilayers of polyimide onto quartz and highly oriented pyrolytic graphite (HOPG) substrates using the Langmuir-Blodgett (LB) technique. These polyimide films were prepared by depositing monoloayers of polyamic acid alkylamine salt at the air-water interface onto substrates using the LB technique, and then treating with a mixture of acetic anhydride and pyridine. Infrared spectra obtained from 200 LB layers (about 800 Å) of polyamic acid alkylamine salts before and after chemical curing showed that the imidization proceeded almost completely with the removal of the long-chain alkylamine.[60] These results seem contradictory to our results described above. The reason for this disagreement is still unknown.

However, there were some differences between the LB film system and the PAA/m-ATP/Ag system. In the case of LB films, polyamic acid alkylamine salts (tertiary amine) possessed long alkyl side chains, while the thin interfacial layer of ammonium salts (primary amine) formed in our system were connected to the benzene rings which were chemisorbed on Ag substrates through the S atoms. It is probably that the steric effect of tertiary amines in the LB film system might prevent alkylamine from forming a tightly bonded ion pair with the acid group. Therefore, the polyamic acid alkylamine salts can be easily cured during the treatment with acetic anhydride and pyridine. Moreover, the primary ammonium salts formed in our system had more protons available for hydrogen bonding compared with tertiary amine salts. Formation of hydrogen bonds might stabilize the ammonium salts, resulting in the curing suppression of interfacial PAA films in our system. It is also possible that the resonance effect from m-ATP benzene rings might also stabilize the ammonium salts and thus inhibit the curing of PAA at the interphase. Further investigations are needed to demonstrate these possibilities. However, we did have considerable evidence indicating that the curing of PAA located at the interphase was suppressed by the formation of ammonium carboxylate salt. Bands characteristic of ammonium carboxylate salt and amide were observed in the SERS spectra of PAA/m-ATP/Ag before and after chemical curing. RAIR spectra obtained from thin PAA films cured against m-ATP treated Ag substrates also showed that curing of the PAA near the interphase was inhibited.

It is reasonable to ask if the inhibition of curing resulted from the formation of Ag carboxylates. It has been shown before the Ag carboxylates were formed at the interphase when polyamic acids were deposited onto Ag substrates.[43-45] Formation of Ag carboxylates also inhibited the curing of polyamic acid. Unfortunately, it is impossible to distinguish metal carboxylate from ammonium carboxylate in the SERS and RAIR spectra shown in the present paper, because the bands due to both carboxylates were very close. However, our previous results obtained from PA/m-ATP/Ag systems showed that m-ATP monolayers prepared by immersing Ag substrates in dilute solutions of m-ATP can substantially cover the Ag surface.[47] No evidence was observed indicating that metal carboxylates were formed by reacting Ag ions with phthalic anhydride or acid groups. Therefore, it seems unlikely that acid groups in the much larger molecules such as PAA can diffuse through the m-ATP layer and react with Ag substrates to form metal carboxylate salts.

SERS and RAIR results described above are in good agreement with our XPS results which will be published separately.[48] Further investigations regarding the effect of organosulfur coupling agents on the adhesion in polyimide/metal joints are underway in our laboratory.

CONCLUSIONS

The molecular structure of interphases formed by chemically curing the polyamic acid of PMDA-ODA against m-ATP-primed Ag substrates was determined using SERS and RAIR. It was concluded that m-ATP was chemisorbed onto Ag substrates through the S atom. No clear bands due to S—Ag bonding were observed in the SERS and RAIR spectra. However, XPS results provided direct evidence that S—Ag bonds were formed upon adsorption of the m-ATP onto Ag substrates.[48] When PAA was applied to m-ATP pretreated silver substrates, acid groups of PAA combined with amino groups of m-ATP to form ammonium carboxylate salts. SERS and RAIR results showed that a thin interfacial layer between PAA and m-ATP-treated Ag substrate was not cured during treatment with mixtures of acetic anhydride and pyridine or triethylamine. However, RAIR results showed that the bulk of the films was highly cured. It was also found that more isoimide species were formed when PAA films were chemically cured in acetic anhydride/pyridine solutions than in acetic anhydride/triethylamine.

Acknowledgements

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