

# Polyamic Acid Interactions at Metal Surfaces

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## Synopsis

Pyromellitic dianhydride-oxydianiline (PMDA-ODA)-derived polyamic acid-metal interactions were delineated by grazing incidence infrared spectroscopy on mirror surfaces. Vast differences were observed between unreactive gold, titanium, chromium, and aluminum, and reactive copper and silver, where copper and silver form amic acid salts. Other polymer-metal interactions were observed with unreactive metals where aromatic ether rings appear to align on the metal surface. Further, reactive *meta* and *para* diacid carboxylates appear to assume different surface conformations. Heating the surface-bound metal salts destroys the polymer interface, but nonsalt films, formed from amic acid or amic ester, appears to establish near planar aromatic ether conformations on the metal surfaces, with resultant orthogonal imide links.

## INTRODUCTION

Polyamic acids (PAA) are used as precursors to polyimide dielectric layers in a number of integrated circuit applications. The interactions and adhesion of these polymers to metal surfaces strongly influences the integrity of metal lands and surface interconnects, composed within these semiconductor devices. Understanding the nature of these bonding and interacting processes is essential to basic device reliability. Although we recently reported on the interaction of polyamic acids with various cations and certain metallic surfaces,<sup>1</sup> we describe here the interactions of a pyromellitic dianhydride (PMDA)-oxydianiline (ODA)-based polyamic acid system with copper, silver, gold, titanium, aluminum, and chromium surfaces, as detected by grazing incidence Fourier transform infrared analysis (GIFT-IR).

Grazing incidence Fourier transform infrared spectroscopy has already been used to detail the structure and interaction of monolayer organic/metal interfaces including alkyl carboxylic acids.<sup>2-4</sup> This powerful technique uses incident radiation oriented to irradiate a metal mirror substrate at a sharp grazing angle (about 75°).<sup>5</sup> Radiation polarized parallel to the plane of incidence has a net electric field component normal to the reflecting surface; thus, dipoles normal to the surface will have strong absorption of this energy, and thin organic films on this surface will exhibit polarized infrared absorptions. Spectra collected after passing the reflected energy through a polarizing prism give information on the orientation of functional groups in such surface films.

## EXPERIMENTAL

Reflective metal surfaces were prepared by vacuum evaporation of pure copper, silver, gold, titanium, aluminum, or chromium onto the surfaces of polished

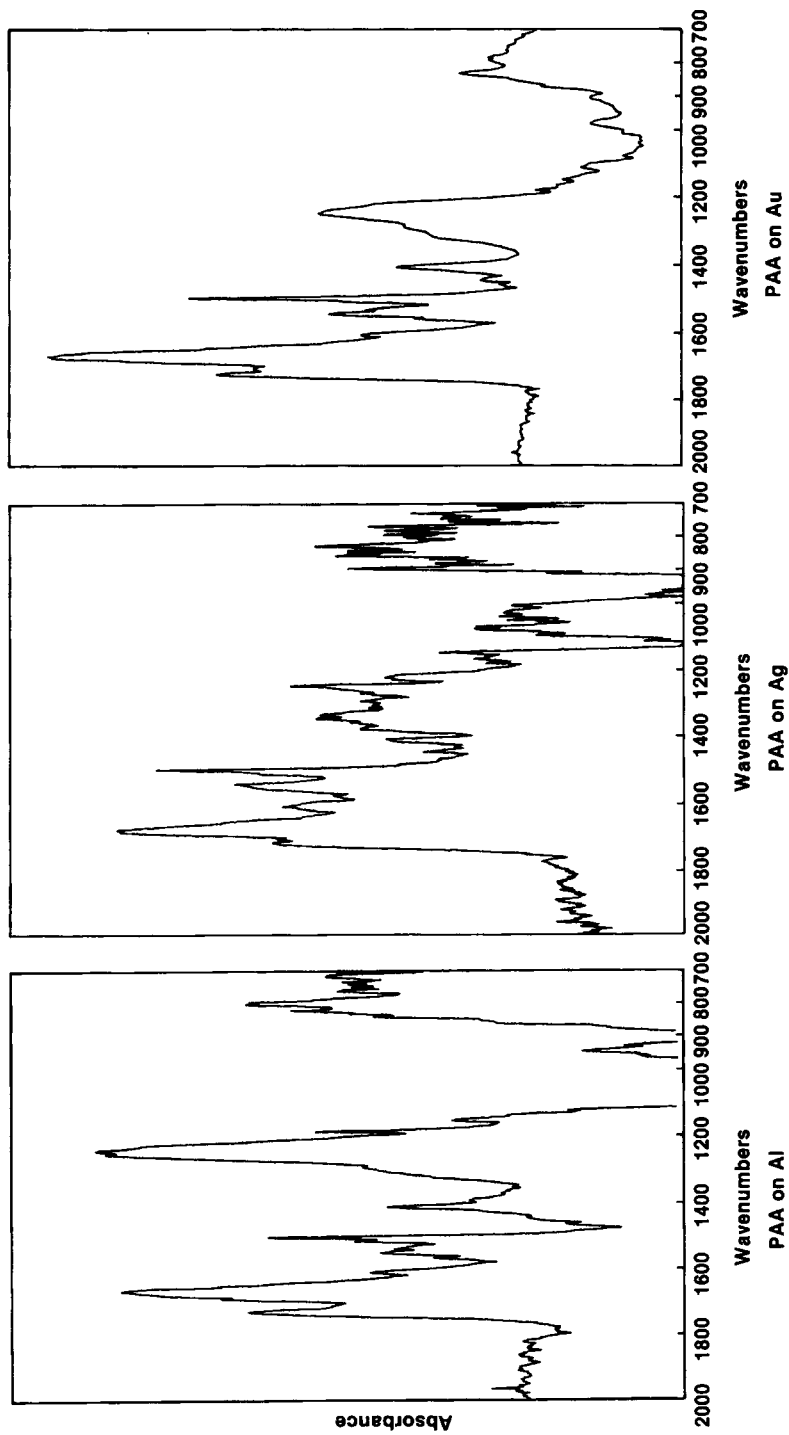


Fig. 1. GIFT-IR spectra of PMDA-ODA amic acid on metal surfaces.

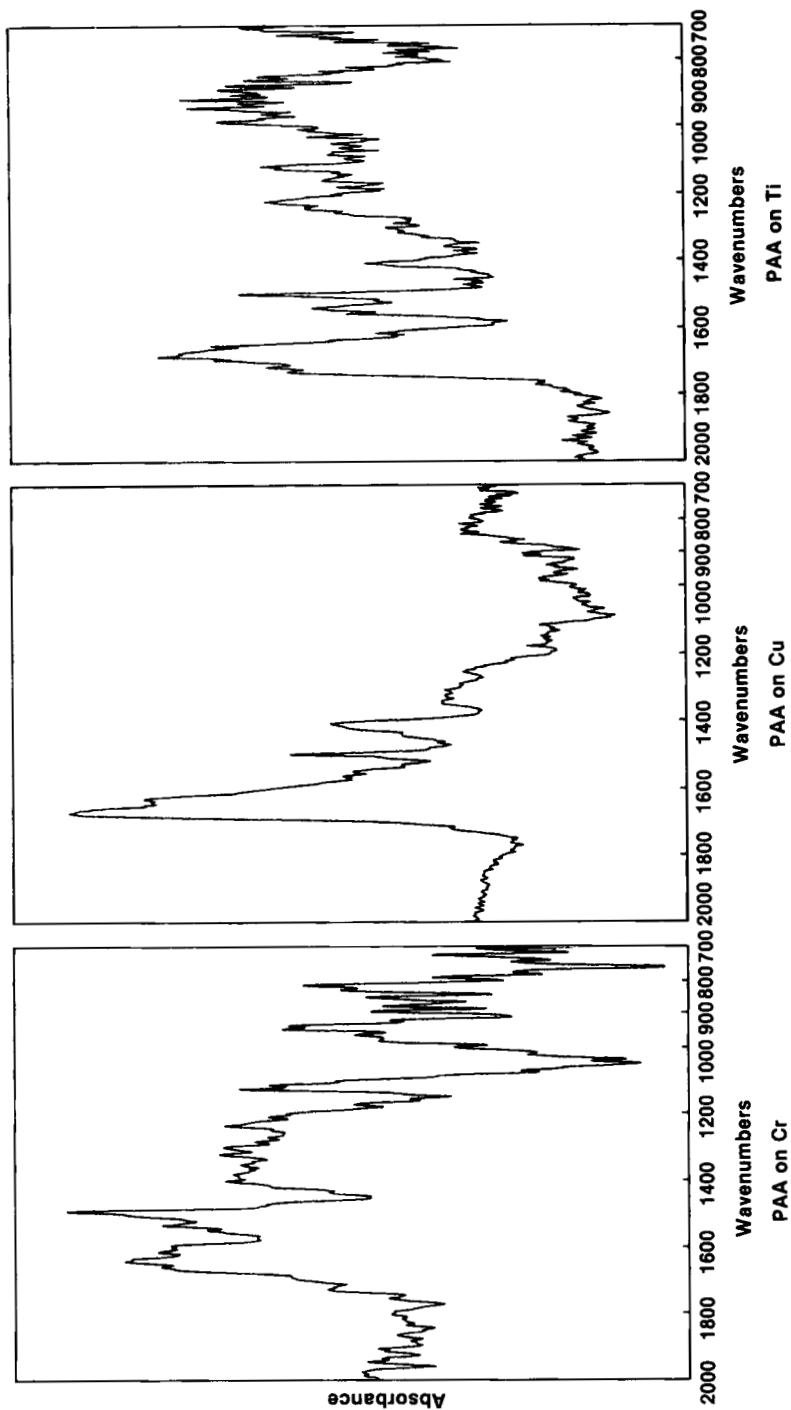


Fig. 1. (Continued from the previous page.)

silicon wafers. Polyamic acid films were deposited by spin application (4000 rpm) of a 6% solids solution of a commercial PMDA-ODA polymer (DuPont product 5057) diluted with *N*-methylpyrrolidinone (NMP). Treated surfaces were puddled with fresh NMP and allowed to soak for 5 min, and the NMP solution removed by spinning (4000 rpm, 1 min). Some wafers were subsequently puddled with deionized water and again spun dry; this process has been shown to remove NMP from thin films of polyamic acids.<sup>1</sup> Film thicknesses were about 40 Å as measured by ESCA.<sup>10</sup> \* Phthalic acid films were prepared by dipping metal wafer films in warm aqueous phthalic acid solutions (for a period of 1 h) and rinsing with tetrahydrofuran. Amic acid interactions were compared to neutral ester interactions by similar treatment of metalized wafers with a solution of polyamic ethyl ester polymer.

Spectra were recorded at 75° incidence using a Harrick Scientific Inc. reflection accessory with germanium polarizer in the beam of a Digilab FTS-14C FT-IR, operated in the single-beam mode at resolution 4 cm<sup>-1</sup>. Sampling was at 2000 scans under nitrogen purge. A nontreated metal film was used to reference each treated film.

Reference films of polyamic acid salts were prepared as described elsewhere<sup>1</sup> and were recorded in the direct transmission configuration. Spectra are presented in absorbance.

## RESULTS

Infrared spectra for PMDA-ODA polyamic acids adsorbed on metals were characterized by absorption in the acid carboxyl (1720 cm<sup>-1</sup>), amide carbonyl (1680 cm<sup>-1</sup>), PMDA aromatic ring (1610 cm<sup>-1</sup>), asymmetric carboxylate carbonyl (1550 cm<sup>-1</sup>), ODA aromatic ring (1500 cm<sup>-1</sup>), and symmetric carboxylate carbonyl (1410 cm<sup>-1</sup>) regions.<sup>6,9</sup> Amic esters contain a 1720 cm<sup>-1</sup> ester carbonyl in place of the acid functionality. After analysis, samples were immersed in deionized water (to remove possible NMP) and rerun; the samples appeared unaltered, indicating little NMP remained after initial application. Results generally demonstrate oriented carboxylic acids or esters on metal surfaces.

Specifically, PAA films on gold, titanium, and aluminum each display a moderate acid carboxyl, a strong amide carbonyl, a weak PMDA aromatic ring, a weak amide II band, a moderate ODA aromatic ring absorption, and a weak 1410 cm<sup>-1</sup> absorption.

Carboxylate absorptions appear stronger on copper and silver, indicating that in these cases the mode of attachment of the polymer to the metal is through an acid-derived metal salt. The spectra of the acids reveal significant differences in each case (Fig. 1) and should be compared to a thin polyamic acid film and cation-derived salt films, observed by direct transmission on silicon (Fig. 2). Unfortunately, a 1410 cm<sup>-1</sup> absorption is present in the parent polyamic acid (and ester), complicating the symmetric stretch of the carboxylate salts; this 1410 cm<sup>-1</sup> parent absorption is assigned to some form of O—C—N—H bond vibration.<sup>9</sup> Similarly, the amide II band masks asymmetric carboxylate at 1550 cm<sup>-1</sup>.

\* Here, signal averaged a 4 mm sq sample area and, assuming an escape depth of 50 Å, representative films measured: Cu 50 Å (high); Ag 40 Å (av); Cr 15 Å (low).

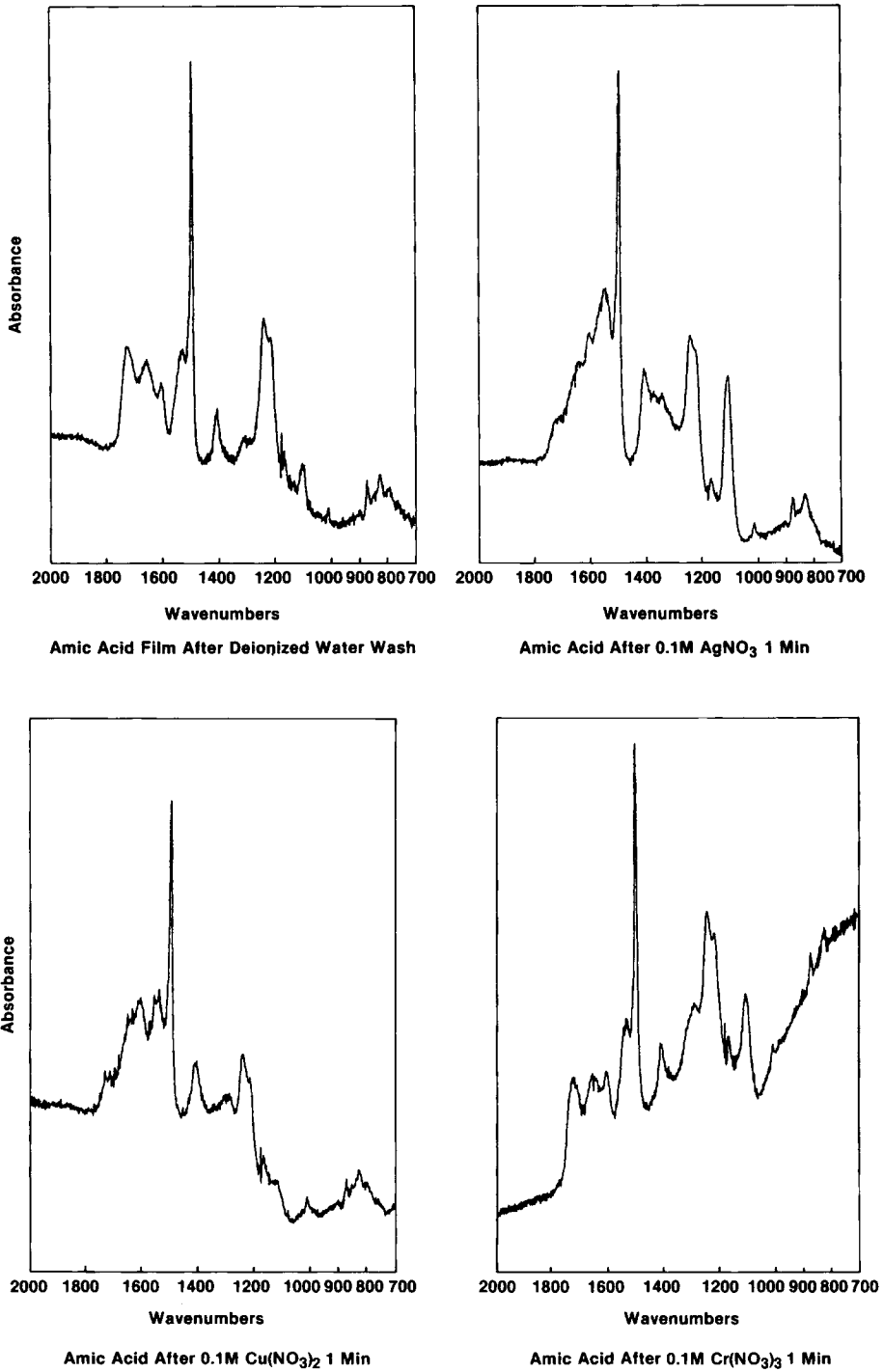


Fig. 2. Transmission FT-IR spectra of thin amic acid films after treatment with water or aqueous cation nitrates.

The planar silver film demonstrates a moderate acid carbonyl, a strong amide carbonyl, a moderate PMDA ring absorption, a moderate asymmetric carboxylate salt stretch, a relatively strong ODA aromatic ring, and a very weak symmetric carboxylate absorption. Random Ag salt films display a moderate asymmetric salt absorption and a very strong ODA aromatic ring stretch.

In contrast, the thin copper film reveals a very weak to nonexistent carboxylic acid carbonyl, a very strong amide carbonyl, a strong PMDA ring absorption, a moderate asymmetric carboxylate, a relatively strong ODA aromatic ring, and a relatively strong symmetric carboxylate.

Chromium displays a weak acid carboxylate, a shifted but moderate amide carbonyl ( $1640\text{ cm}^{-1}$ ), a moderate PMDA ring stretch, a moderate asymmetric salt carboxylate, a strong ODA aromatic ring, and a weak symmetric carboxylate. These absorptions are dissimilar to the PAA-Au, Ti, Al interaction and indicate altered environments of the amide and ODA aromatic rings.

## DISCUSSION

### PMDA-ODA Interactions on Nonreactive Surfaces

Spectra of PAA on Au, Ti, or Al reveal little aromatic ring functionality associated with the ODA moiety. Since carbonyl components are active (in the plane perpendicular to the surface), the aryl ether rings must be preferentially oriented largely parallel to the plane of the surface; in fact, thicker films on these metals ( $300\text{--}500\text{ \AA}$ ) reveal strong aryl ether functionality, indicating random orientation of this group. A very thin amic acid film on Au ( $< 30\text{ \AA}$ ) reveals almost no aryl ether at all (Fig. 3).

Thin amic ester films on gold, titanium, and aluminum give results almost identical to amic acids (Fig. 4), with a moderate to strong ester carbonyl, a strong amide carbonyl, and subdued aryl ether aromatic ring absorption. Copper, although not apparently reactive with the amic ester, gives both ester and amide carbonyl activity, but also displays a significant ODA-derived aromatic ring absorption, revealing less planar ring ordering on this surface.

These spectra therefore reveal a nonpolar interaction that appears to align aromatic ether rings nearly parallel to the metal surface and PMDA-derived rings perpendicular to the surface (Fig. 5). This conformation causes a dramatic intensity loss in the  $1500\text{ cm}^{-1}$  absorption, reducing it from the most intense absorption in unaligned films to a very weak absorption at metal interfaces.

Thermal imidization of these films shows continued alignment of aryl ethers, where the  $1500\text{ cm}^{-1}$  absorption is dwarfed by the strong asymmetric imide carbonyl (Fig. 6), which remains perpendicular to the metal plane on gold and titanium, but remains unaligned on chromium (see below).

Ethyl esters also preferentially orientate with aryl ether rings approximately parallel to the metal surface and infrared inactive, but with orthogonal ester and amide carbonyls (Fig. 7).

The very thin chromium-PAA interface differs significantly: Acid carbonyl is present but weak; amide carbonyl is shifted to  $1640\text{ cm}^{-1}$  and is only moderately intense; and the PMDA aromatic ring is moderate, as are both the amide II and  $1410\text{ cm}^{-1}$  absorptions, but the ODA aromatic ring is strong. Low signal to noise indicates a thin region of significant disorder, with configurations

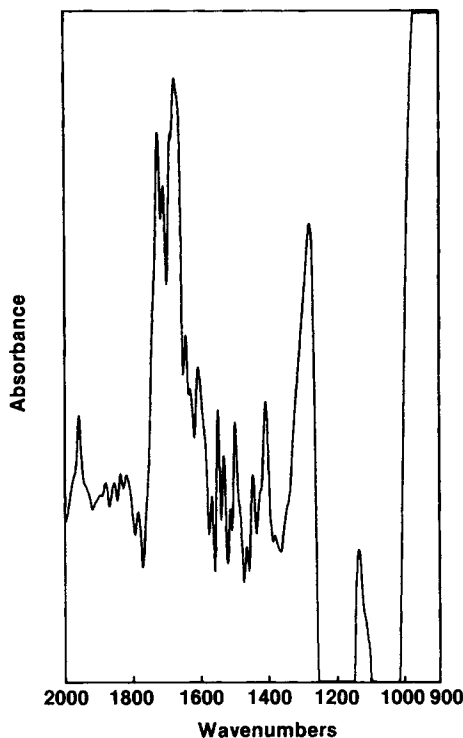


Fig. 3. GIFT-IR spectrum of a very thin amic acid film on gold.

where ODA rings are normal to the mirror plane. This configuration is not significantly altered by thermal imidization.

### PMDA-ODA Interactions on Reactive Surfaces

Polyamic acids formed from direct reaction of PMDA and ODA contain a random but equal number of *meta* and *para* diacid (and diamide) groups formed during anhydride opening. The acid salts formed during amic acid-metal reaction will therefore orient the nonreacting acid group either *meta* or *para* to the reacting group, and surface species will appear as Figure 8(a) or 8(b). The interpretation of infrared spectra of such surface species were aided by the analysis of the salts formed by isophthalic (*meta*) and terephthalic (*para*) acids on copper. These spectra, which appear as Figure 9, give specific insight into the symmetric and asymmetric carboxylate absorptions on this surface.

As expected, the spectrum of isophthalic acid-copper reveals a strong acid carbonyl, a strong aromatic ring absorption, a moderate asymmetric salt, and a very strong symmetric salt stretch. These absorptions are consistent with the acid carbonyl and ring being parallel with the electronic field vector (normal to the surface). The carboxylate absorptions indicate the symmetric stretch is enhanced, whereas the asymmetric stretch is largely out of the plane of the electronic field vector; contributions from 8c are not evident (but are probably not infrared active). In contrast, terephthalic acid displays only a weak carbonyl

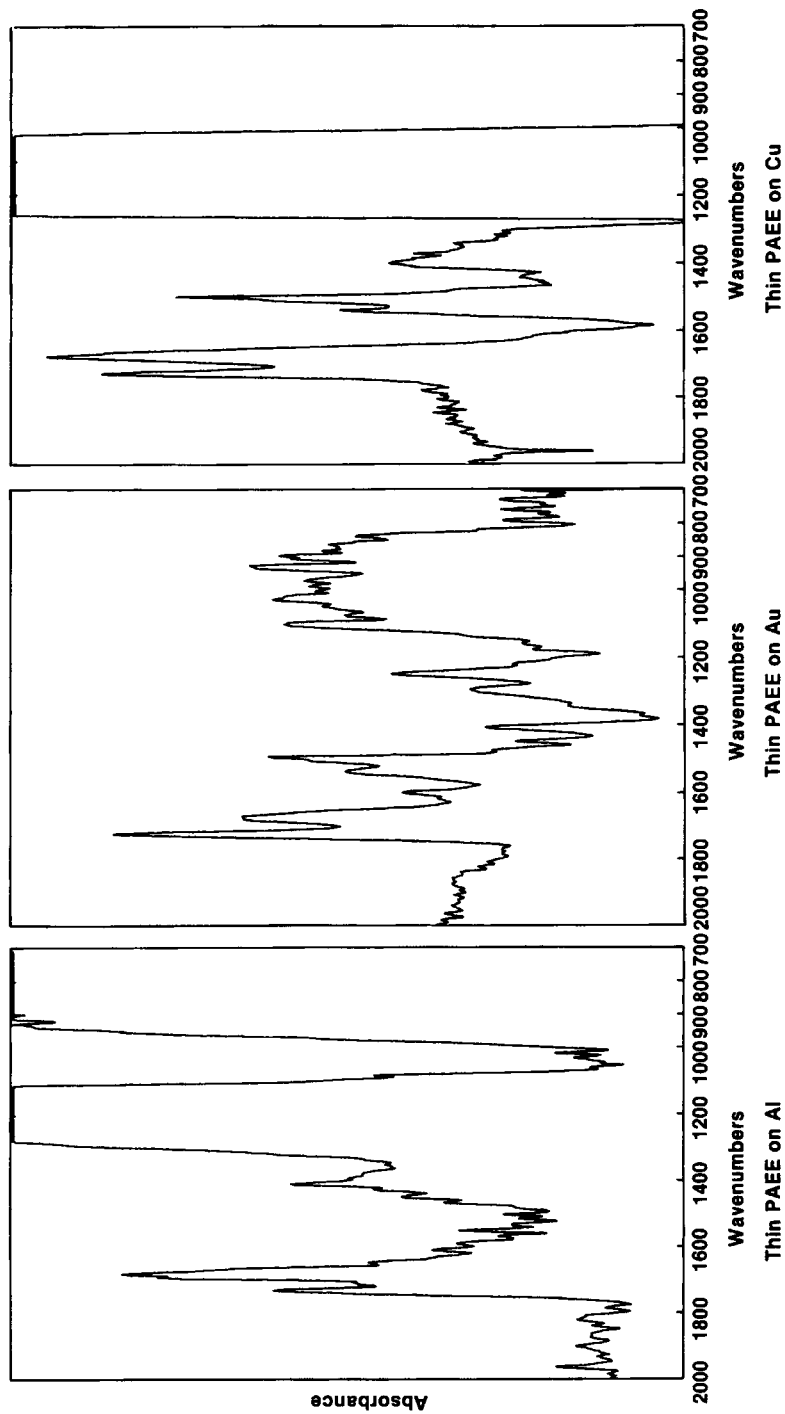


Fig. 4. GIFT-IR of amic ester films on selected metal surfaces.



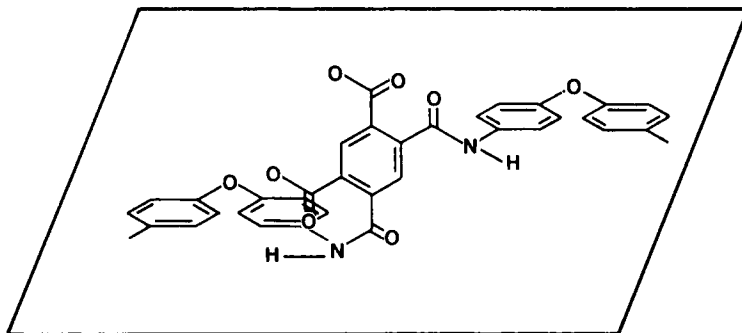


Fig. 5. Probable orientation of aligned amic acid film on nonreactive metals.

whose transitional moment is out of the plane of the field vector (as expected). Surprisingly, however, although the aromatic ring absorption is very weak (*p*-substitution), the asymmetric carboxylate contribution is strong and the symmetric carboxylate is only moderate. These data indicate a contribution from significantly different carboxylate orientations [**8(d)**] or unexpected asymmetric resonance in this salt. When these spectra are compared to amic acid salts, prepared directly with cations in solution,<sup>1</sup> interesting conformational assignments can be deduced at the amic acid-metal interfaces.

### Conformational Interactions

The silver amic acid salt surface displays the expected (*meta*) carboxylic acid and PMDA ring normal to the metal plane; enhanced normal amides are evident [three contribute in a 1 : 1 mix of **8(a)** and **8(b)**]; *para*, asymmetric, acid carboxylate is strong, analogous to terephthalic acid (on Cu). The ODA aromatic rings appear twisted out of perpendicular to the mirror plane (and may well be oriented somewhat parallel to this plane) since they contribute only a relatively weak absorption; the symmetric carboxylate is unexplainably weak. Thus, the silver interface appears as a mixture of carboxylate salts with contributions from **8(a)**, perhaps **8(b)**, and possibly **8(d)**. Heating at 300°C destroys this polymer film.

The copper-amic acid salt interface is drastically different. Amide carbonyl dominates the spectrum with accompanying aromatic ring resonance, indicating the PMDA ring is normal to the mirror plane. Both asymmetric and symmetric carboxylate are similar to the *para* (terephthalic-type) acid salt, and the aromatic ODA rings again appear out of perpendicular to the mirror plane. Significantly, almost no free carboxylic acid is evident; thus, the major contribution to the spectrum is conformation **8(b)**. The fate of the *meta*-linked acids is unclear, but they do not appear normal to the mirror plane.

Interestingly, analogous cuprous carboxylate salts frequently appear as intermediates, where acids and Cu<sub>2</sub>O are present.<sup>7</sup> Many of these carboxylates are dimeric in both liquid and solid states,<sup>8</sup> coordinating one carboxylate to two Cu<sup>+</sup> ions. Such special interactions may account for spacing or packing differences of the carboxylate coordination complex with ions on the Cu surface, where **8(c)** may exist as shown, or in the plane perpendicular to the page (and

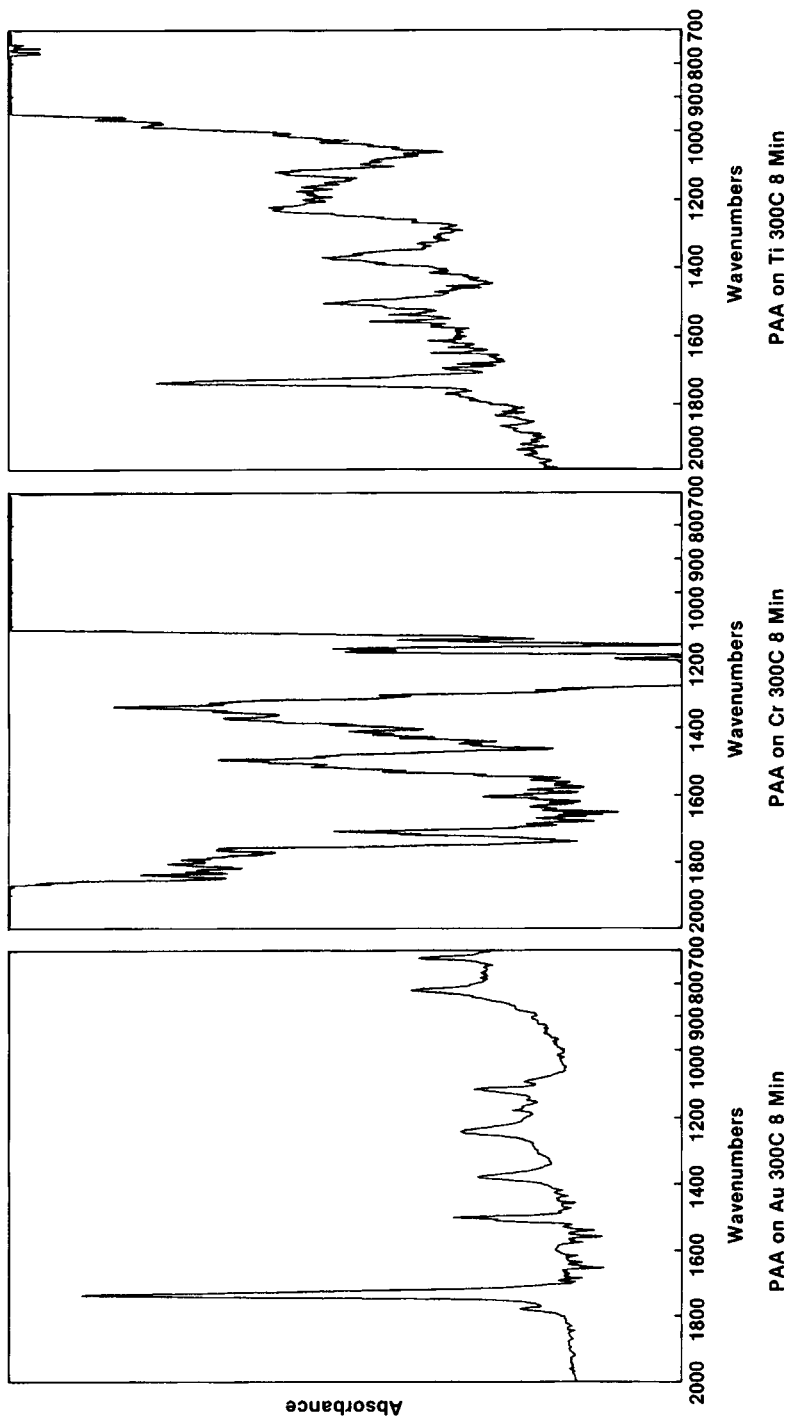


Fig. 6. GIFT-IR of thermally imidized PAA films on certain metal surfaces.

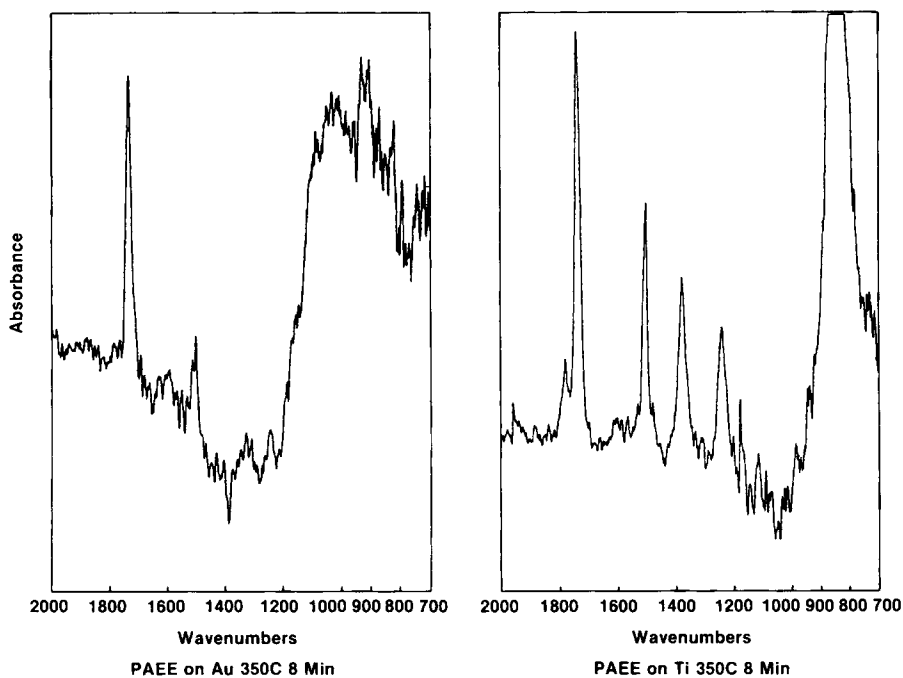


Fig. 7. GIFT-IR of thermally imidized polyamic ester films on certain metal surfaces.

lying on the mirror surface). Heating the Cu salt film to 300°C (8 min in nitrogen) imidizes the free carboxylic acids, presenting a new film (Fig. 10) with imide carbonyl ( $1725\text{ cm}^{-1}$ ) in the field perpendicular to the mirror plane.

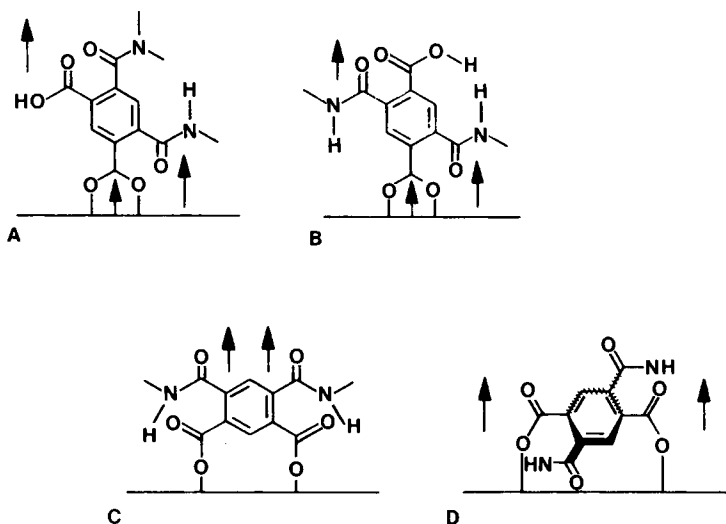


Fig. 8. Oriented conformations of various polyamic acid carboxylates: (a) *meta* orthogonal mono carboxylate; (b) *para* orthogonal mono carboxylate; (c) *meta* orthogonal dicarboxylate; (d) *ortho* planar dicarboxylate.

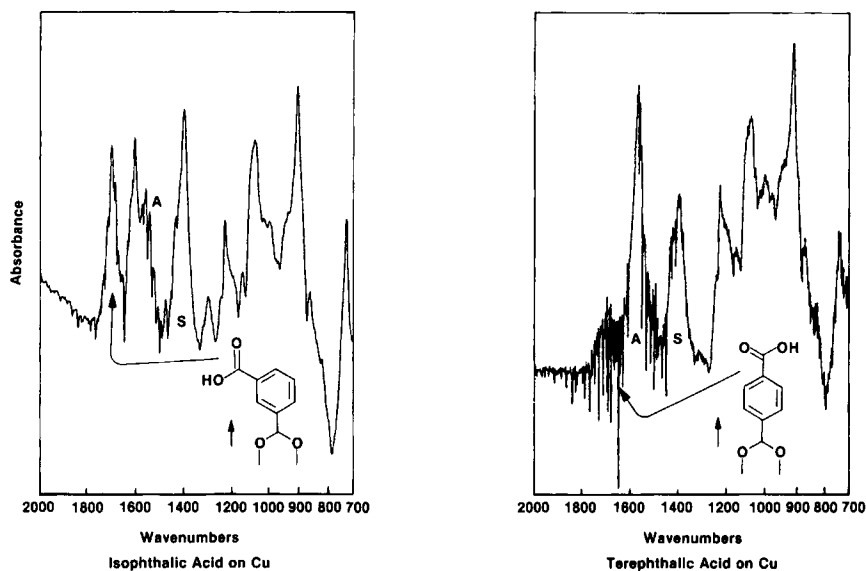


Fig. 9. GIFT-IR spectra of phthalic acids on copper.

This spectrum also displays an altered amide carbonyl ( $1690\text{ cm}^{-1}$ ) and a strong PMDA ring absorption, but few traces of either symmetric or asymmetric carboxylate; the ODA ring absorption is moderately strong. The presence of amide

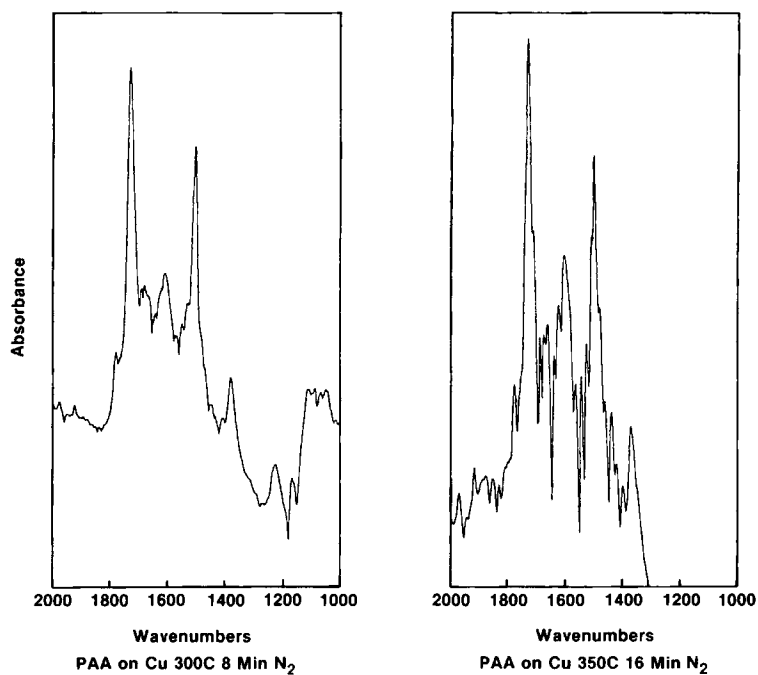


Fig. 10. GIFT-IR spectra of the heated copper-PAA salt surface.

indicates latent salt functionality undetected by the electronic field component and therefore not aligned with the amide and amide ring absorptions. Geometric configurations consistent with these absorptions are (1) non-*ortho* (separated) amide and acid groups, where separation is a result of (noncyclic) transimidization (here the acid carbonyl is either buried in the imide carbonyl stretch or is not in the electronic field plane), or (2) structures like **8(c)**. The existence of infrared inactive salt groups, with infrared active amides, strongly suggests contributions from **8(c)** on copper. Further heating of this film (8 min, 350°C in nitrogen) destroys the polymer, probably through copper-catalyzed decarboxylation.<sup>7</sup>

The differences observed in these spectra suggest four separate modes of attachment or metal coordination:

1. Disordered amic acids where random ODA alignment perpendicular to the metal plane is a contributing conformation; this arrangement appears on chromium.
2. Ordered amic acids or esters, where aryl ethers appear largely parallel to the metal surface and amides and acids align perpendicular to the surface; this conformation appears on Au, Ti, and Al and on Cu with the amic ester.
3. Perpendicularly oriented *meta* **8(a)** (and *para*) acid salts, interconnected by largely unaligned ODA linkages that also contain aligned asymmetric carboxylate linkages, which may originate from *para* surface dicarboxylates [**8(d)**], as seen on silver.
4. Perpendicularly oriented *para* acid salts **8(b)**, interconnected by largely unaligned ODA linkages that probably contain *meta* surface dicarboxylates [**8(c)**] that contribute aligned amide (but not free acid) absorptions, as seen on copper.

Although the origins of these orderings is not detailed, it appears that contributions from dicarboxylates may strongly influence subsequent geometric positioning of amic acids on metal surfaces and override the tendency for aryl ether ring interactions, which appear to position ODA segments generally parallel to the surface.

An additional important difference is seen on copper, where reactive amic acid forms a salt that decomposes on heating, but the ethyl ester does not. Variations also exist in thermally imidized films on Al where the amic acid yields a conformation with significant ODA ( $1500\text{ cm}^{-1}$ ) absorption, but the ester derived imide displays a contrasting  $1600\text{ cm}^{-1}$  ring absorption (Fig. 11).

## CONCLUSIONS

Metal surfaces of Ag and Cu bond polyamic acids as metal carboxylate salts, but each coordinates the amic acids in a different fashion. Although the origin of this ordering is not detailed, conformation seems strongly dependent on the configuration of acid groups. Of the other metals tested, chromium has the weakest interaction and greatest disorder with a large number of ODA com-

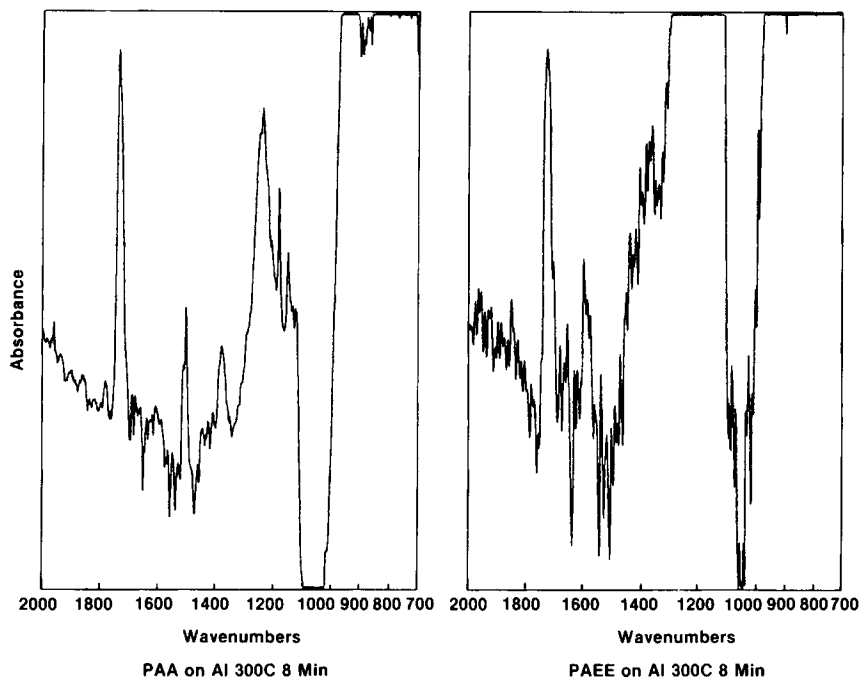


Fig. 11. GIFT-IR comparison of thermally imidized amic acid and amic ester films on aluminum.

ponent aromatic rings perpendicular to the mirror plane. Gold, titanium, and aluminum are unreactive but coordinate aryl ether rings nearly parallel to the metal surface, with interconnecting amic acid or ester rings perpendicular to the surface. This order is maintained during thermal imidization. Silver has a higher ordering with significant *meta* acid-carboxylate configuration perpendicular to the mirror plane; ODA rings are largely out of perpendicular to this plane. Copper produces an ordered interface with largely *para* configuration perpendicular to the mirror plane; again ODA rings are nonorthogonal. Heating imidizes the copper salt-free acids at 300°C, but 350°C destroys the polymer interface. Heating the silver salt to 300°C also destroys the interface. Polyamic ester interactions are similar on Au, Al, and Cu. Since Cu is unreactive, copper salts are not produced and the polymer is not subjected to decarboxylation during imidization.

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### References

1. H. Linde and R. Gleason, *J. Polym. Sci. Polym. Phys. Ed.*, **26**, 1485-1497 (1989).
2. (a) F. J. Boerio, *Assoc. Finish. Process. SME*, **FC 79-663**, 1-6 (1979). (b) F. J. Boerio, J. P. Boerio, and R. C. Bozian, *Appl. Surf. Sci.*, **31**, 42-58 (1988).
3. J. F. Rabolt, F. C. Burns, N. E. Schlotter, and J. D. Swalen, *J. Chem. Phys.*, **78**, 946-952 (1983).

4. (a) N. E. Schlotter, T. Bright, and D. L. Allara, *SPIE*, **553**, 494-495 (1985). (b) M. D. Porter, *Anal. Chem.*, **60**, 1143A-1155A (1988).
5. N. J. Harrick, *Am. Lab.*, **18**(11), 78-81 (1986).
6. H. Ishita, S. T. Wellinghoff, E. Baer, and J. L. Koenig, *Macromolecules*, **13**, 826-834 (1980).
7. J. March, *Advanced Organic Chemistry*, 2nd Ed., McGraw-Hill, New York, 1977, pp. 367, 514-515.
8. F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, New York, J. Wiley & Sons, 1962, pp. 754-756.
9. M. Avram and G. H. Mateescu, *Infrared Spectroscopy*, Wiley-Interscience, New York, 1972, pp. 444, 447.
10. ESCA analysis, to appear separately.

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