

AD-A197 240

DTIC FILE COPY

(4)

1. REPORT 8		ACCESSION NO.		3. RECIPIENT'S CATALOG NUMBER	
4. TITLE (and Subtitle) A Raman Spectroscopic Study of Vapor Deposited Poly[N,N'-bis(phenoxyphenyl)pyromellitimide] Films		5. TYPE OF REPORT & PERIOD COVERED Technical Report #8		6. PERFORMING ORG. REPORT NUMBER	
7. AUTHOR(s) R. G. Mack, H. H. Patterson, M. R. Cook and C. M. Carlin		8. CONTRACT OR GRANT NUMBER(s) N00014-85-K-0641			
9. PERFORMING ORGANIZATION NAME AND ADDRESS Laboratory for Surface Science & Technology 9 Barrows Hall University of Maine, Orono, ME 04469		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR#629-849			
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Chemistry Program Arlington, VA 22217		12. REPORT DATE June 30, 1988		13. NUMBER OF PAGES 16	
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report) unclassified		15a. DECLASSIFICATION DOWNGRADING SCHEDULE	
16. DISTRIBUTION STATEMENT (of this Report) This document has been approved for public release and sale; its distribution is unlimited.					
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)					
18. SUPPLEMENTARY NOTES Accepted for publication in Journal of Polymer Science					
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Raman, poly[N,N'-bis(phenoxyphenyl)pyromellitimide], co-deposition, 4,4'-oxydianiline, pyromellitic dianhydride, polycrystalline copper, polyimide, solution-cast					
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) See first page					

DTIC
ELECTE
JUL 29 1988

E

OFFICE OF NAVAL RESEARCH

Contract N00014-85-K-0641

R&T Code 413a001

Technical Report No. 8

A Raman Spectroscopic Study of Vapor Deposited
Poly[N,N'-bis(phenoxyphenyl)pyromellitimide] Films

by

R. G. Mack, H. H. Patterson, M. R. Cook and C. M. Carlin



Accepted for Publication in
Journal of Polymer Science

Laboratory for Surface Science & Technology
9 Barrows Hall
University of Maine
Orono, ME 04469

30 June 1988

Accession For	
NTIS GRA&I	☒
DTIC TAB	☐
Unannounced	☐
Justification	
By _____	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	

Reproduction in whole or in part is permitted for
any purpose of the United States Government

This document has been approved for public release
and sale; its distribution is unlimited

A Raman Spectroscopic Study of Vapor Deposited
Poly[N,N'-bis(phenoxyphenyl)pyromellitimide] Films

by

R. G. Mack, H. H. Patterson, M. R. Cook and C. M. Carlin

Laboratory for Surface Science and Technology
9, Barrows Hall,
University of Maine,
Orono, ME 04469.

Synopsis

Raman spectra have been obtained for thin (ca. 200 nm) poly[N,N'-bis(phenoxyphenyl)pyromellitimide] films produced by co-deposition of 4,4'-oxydianiline and pyromellitic dianhydride onto polycrystalline copper substrates from the vapor phase. It is demonstrated that even severe overdosing with one of the starting materials produces material which, after curing, is spectroscopically identifiable as polyimide. The details of the spectra obtained are, however, variable according to the dosing and curing conditions and, in some cases, are substantially different from those characteristic of solution-cast films. These differences are attributed to the presence of reaction products formed by the attack on imide carbonyls by unreacted amines in the matrix to form branched polymer chains. *1 modes, 2 peaks*

INTRODUCTION

The growth of thin polyimide films on solid substrates by means of the controlled deposition of aromatic dianhydride and diamine precursor species from the vapor phase was first demonstrated by Salem *et al.*¹ This vapor deposition polymerization (VDP) process has a number of potential advantages over the solvent-based methods normally used in commercial applications, such as the fabrication of polyimide interlevel dielectrics for very large scale integration (VLSI) microelectronic devices^{2,3}, and offers the possibility of producing more uniform films with more precisely controllable properties than is possible with conventional spin-coating technology. The nature of the adhesion and bonding of ultra-thin VDP polyimide films to metal surfaces has been addressed in x-ray photoelectron spectroscopy (XPS) and infrared absorption experiments carried out by Grunze and his co-workers⁴⁻⁶. XPS has also been used by these authors to examine the stoichiometry and chemical bonding in the outer regions of thicker (≥ 8 nm) VDP films on polycrystalline Ag⁷.

In this paper we report the results of a Raman spectroscopic study of *ca.* 200 nm poly[N,N'-bis(phenoxyphenyl)pyromellitimide] (PI) films formed by the imidization of vacuum co-deposited layers of 4,4'-oxydianiline (ODA) and pyromellitic dianhydride (PMDA) on polycrystalline Cu samples. These studies support the finding of reference 1 that the VDP process produces polyamic acid curable to polyimide, but reveal that the precise composition of the films is variable and depends on the ratio of the individual PMDA and ODA flux rates during deposition. A large initial excess of ODA, in particular, leads to the appearance of new and intense Raman bands when the sample is cured. These bands, which also appear weakly in samples prepared using more nearly equal PMDA and ODA flux rates, are attributed to the formation of branches and/or cross-links by the nucleophilic attack of free amine groups on imide carbonyls at temperatures in excess of 250°C.

EXPERIMENTAL

The experimental work was carried out in an ultra-high vacuum (UHV) chamber capable of base pressures of below 2×10^{-10} torr. Cu

sample foils were cut from 0.1 mm thick sheet (99.99% purity, Alfa Products) and mounted on a moveable manipulator stage. They were cleaned by repeated cycles of Ar ion bombardment and heating to temperatures in excess of 650°C. No direct electron spectroscopic monitoring of the surface cleanliness was possible *in-situ* in these experiments, but samples prepared in the same way in a second UHV system showed no trace of residual contamination at the sensitivity level of Auger electron spectroscopy.

Exposure of the sample foils to the PI starting materials was achieved using a mechanically retractable vapor doser containing high purity PMDA and ODA (zone refined, Aldrich Gold Label) loaded into quartz tubes and covered with aluminum end caps containing small orifices. The quartz tubes were held in ceramic formers and could be heated by passing current through Ta coils wrapped around them. Their temperatures were monitored by means of thermocouples inserted into the interior cavities of the ceramic formers.

To perform a deposition, the source materials were first heated to above 150°C to drive off absorbed water and then equilibrated at the required dosing temperature (typically between 70°C and 130°C). The doser was isolated from the main sample chamber by a gate valve during this process and was separately pumped to avoid any cross-contamination. To make an exposure, the gate valve was opened and the doser head translated into the experimental chamber directly in front of the sample holder. The thickness and, to a lesser extent, the uniformity of the resulting overlayer could be controlled by varying the temperatures of the PMDA and ODA ovens and the total exposure time. However, the extent of this control was constrained by thermal conduction between the ovens, which limited the maximum temperature differential between them to $\pm 20^\circ\text{C}$. The thicknesses of the cured films were subsequently estimated by *ex-situ* ellipsometry measurements.

Additional, reference data were obtained for solid PMDA and ODA (zone-refined, Aldrich Gold Label) and for bulk PAA and PI samples prepared in our own laboratory. PAA was synthesized by the method of Sroog *et al.*⁸ and coated directly onto clean, air-oxidized Si wafer substrates. Solvent prepared PMDA-ODA polyimide was prepared

by thermal curing of such PAA samples by heating them successively for one hour at temperatures of 150°C, 250°C and 350°C.

The light source used was a Spectra-Physics (model 2020) Ar ion laser operated at 457.9 nm. A prism monochromator and interference filter were employed to eliminate plasma lines. Data were recorded using a holographic grating double monochromator (Instruments SA, model H6-2000), a cooled photomultiplier tube and a pulse counting photometer system. The monochromator and photometer were interfaced to a personal computer (Apple IIe) for automated spectral scanning and digitization. The monochromator was operated with a resolution of approximately 2 cm^{-1} , well below the intrinsic width of the Raman bands for polyimide⁹. The power at the laser was adjusted to 100 mW and the beam was focused into a 0.1 mm diameter spot on the sample. Because of attenuation in the optical path, the actual power at the specimen surface was reduced to approximately 15 mW. No evidence for any thermal or photochemical degradation of PI was detected at these power levels and spectra obtained from reference samples after many hours of direct exposure to the laser were indistinguishable from spectra recorded from previously unexposed portions of the same films.

RESULTS

The Raman spectrum of solution prepared PMDA-ODA polyimide over the range 1100 to 1900 cm^{-1} is shown in Figure 1(a) after removal of the intense luminescence background typical of material synthesized in this fashion. This spectrum shows all of the peaks seen in the UV resonance Raman data reported by Ishida *et al.*⁹ for commercial poly(N,N'-bis(phenoxyphenyl)pyromellitimide) with approximately the same relative intensities. Differences in the resonance enhancement of the various modes are evident and due to the different excitation wavelengths used (363.8 nm vs. 457.9 nm in the present work). Peak assignments for both solution prepared PI and VDP material were made with the aid of the analysis presented in reference 9 and are listed in Table 1.

There are several features in Figure 1(a) that are relevant to the following discussion and should be noted. The asymmetric band at 1386 cm^{-1} is characteristic of the imidized polymer and, upon

curing, replaces a moderately intense C-N stretch at about 1340 cm^{-1} observed in the Raman spectrum of PAA. The symmetric C=O stretch at 1787 cm^{-1} is both intense and narrow in comparison to the other bands in the spectrum. The broad feature centered near 1610 cm^{-1} is a combination of the aromatic C=C stretches for the central pyromellitimide ring and the phenoxyphenyl parts of the molecule. Following Ishida *et al.*, the main peak at 1610 cm^{-1} is assigned to ν_{16} for the pyromellitimide and the shoulder near 1595 cm^{-1} to ν_{16} for the phenoxyphenyl moiety.

Italic "v" represents Greek "nu"

A typical spectrum for vapor deposited PI over the same energy range is shown in Figure 1(b). Several differences between this spectrum and that shown in Figure 1(a) are apparent. Most significantly, there is a marked increase in the intensity of the shoulder on the low energy side of the 1610 cm^{-1} C=C stretch and the imide C-N stretch is shifted in energy from 1386 cm^{-1} to 1396 cm^{-1} . The latter, which has been observed in all of the VDP films studied to date, is suggestive of a change in conjugation affecting the imide linkages in the polymer. A similar effect has been observed when solution prepared PI is annealed in order to improve crystallinity⁹. The intensity changes in the 1610 cm^{-1} band indicate an excess of phenoxyphenyl moieties in the VDP film. However, any such excess is necessarily in the form of chemically bound rather than unreacted ODA as both bulk crystalline ODA and thin layers of non-crystalline, vapor deposited ODA exhibit strong Raman bands at 1622 cm^{-1} , well above the C=C stretch in PI. Other noteworthy differences between the spectra in Figure 1 concern the pyromellitimide ν_{13} band near 1456 cm^{-1} and the broad feature between 1650 cm^{-1} and 1660 cm^{-1} , both of which are more intense in the VDP data, and a slight weakening of the carbonyl band at 1787 cm^{-1} . Again, these changes appear to be characteristic of PI prepared by the VDP process.

Figure 2 shows the results of an experiment in which the PMDA and ODA evaporation sources were maintained at approximately equal temperatures (ca. 125°C) during evaporation. The vapor pressure of ODA is about 100 times that of PMDA under these conditions¹⁰, thus implying highly non-stoichiometric arrival rates. The lower spectrum (2(a)) was recorded from a spot on the sample surface close to the bottom edge of the film and closest to the ODA oven. Figure 2(b) was recorded under identical conditions from a spot near the

center of the sample and approximately equidistant from both ovens, while the spectrum in Figure 2(c) shows a spot near the top of the film, closer to the PMDA oven.

There is a clear progression of band intensity changes across the sample in these spectra. The films appear to be more ODA rich toward the bottom of the film, as evidenced by the more intense C=C stretch (ν_{16}) at 1597 cm^{-1} . The pyromellitimide ν_{13} band at 1460 cm^{-1} exhibits the opposite progression. The intensities of the new bands at 1656 cm^{-1} and 1742 cm^{-1} follow a similar progression, being approximately twice as strong at the bottom of the sample. Referenced to the combined ν_{16} peak, the integrated intensities of these two bands vary from 0.25 - 0.45 and 0.06 - 0.14, respectively. They are therefore identifiable with variations in the overall composition of the film and, as described below, are believed to be due to the formation of new species that arise from reaction of the excess phenoxyphenyl moieties. As in the case of the 1597 cm^{-1} band, these features cannot be attributed to unreacted ODA since the spectrum of bulk ODA exhibits no peaks in this region.

DISCUSSION

The chemical composition of PI films produced by the VDP process has not yet been precisely and unambiguously described. The literature contains several references^{1,4-7} to the presence of excess ODA or PMDA groups that are attributed to unreacted starting material, terminal groups, or various branching and cross-linking structures. In addition, Salem et al.¹ have reported that as much as 26% of the nitrogen in stoichiometrically dosed PI may exist as the isoimide. The evidence for this observation is based primarily on the presence of a split N 1s level in XPS data. However, similar data observed by Lamb et al.⁷ have been attributed to the presence of unreacted amine groups.

The expected reaction pathway for the synthesis of PAA from co-deposited PMDA and ODA and its subsequent imidization to form PI is shown below. Spectroscopic data have shown that ODA and PMDA react spontaneously on the surface at room temperature to produce polyamic acid^{1,4-7}. The Raman spectrum of vapor deposited PAA (not shown) is characterized by a strong C-N stretch band near 1340 cm^{-1} and a

Insert
Xns 1
after this
point

notable absence of carbonyl bands between 1650 and 1900 cm^{-1} . The lack of observable C=O bands may be due in part to band broadening caused by intra- and/or intermolecular hydrogen bonding as well as to the existence of multiple environments within the film. The presence of a weak band near 1396 cm^{-1} indicates that partial imidization occurs at or near room temperature. Curing the film at 150°C for 30 minutes leads to an increase in the intensity of this feature, consistent with continued imidization. Subsequent curing at 250 and 350°C leads to a further increase in the intensity of the 1396 cm^{-1} band and, ultimately, to the complete loss of the amide C-N stretch.

The observation of new Raman features at 1656 cm^{-1} and 1742 cm^{-1} with intensities which depend on the relative arrival rates of PMDA and ODA suggests that certain dosing conditions may produce material containing functional groups not normally expected in PI. The specific conditions which led to the spectra in Figure 2, namely excess ODA and location dependent flux variations, further indicate that ODA enrichment is responsible for these additional peaks. Spectra taken during the curing of the vapor deposited PAA (not shown) reveal that the new bands begin to emerge from the background at temperatures between 150°C and 250°C, the same temperature range over which imidization is found to be completed in nominally stoichiometric films^{1,7}. The isomerization to isoimide is ruled out, since isoimide is known to rearrange to imide at high temperatures¹¹ and not the reverse.

The possibility that the 1656 cm^{-1} feature is an amide carbonyl stretch is apparently inconsistent with the absence of a detectable amide C-N stretch between 1330 cm^{-1} and 1350 cm^{-1} , since the latter is very pronounced in the Raman spectrum of PAA. The alternative possibility that this band is due to an C=N stretch¹² is, however, fully consistent with the spectroscopic evidence. The way in which such functionalities might come about can be understood as follows. Under the conditions of high relative ODA flux used in this experiment, the initial reaction of PMDA and ODA on the surface might be expected to favor the formation of relatively short polymer chains (trimers containing a single PMDA and two ODA moieties represent a possible limiting case). This, in turn, would produce a high concentration of terminal amine groups and thus the possibility

of intermolecular nucleophilic attack of the imide carbonyls at elevated temperatures.

Typically, the reaction between an imide and primary amine would be expected to produce two amides or, in the case of PI, a diamide (product I, below). While this mechanism would lead to both cross-linking and increased molecular weight, it is inconsistent with the spectroscopic evidence for the reasons discussed above. In view of the thermal stability of PI, moreover, the ring-opening associated with this reaction may not be energetically favorable. The alternative condensation reaction shown below (product II) is somewhat atypical but is consistent with the Raman data and several other documented spectral characteristics of vapor deposited polyimide. According to this model, the strong peak at 1656 cm^{-1} is attributed to the imine $\text{C}=\text{N}$ stretch and the peak at 1742 cm^{-1} is assigned to a $\text{C}=\text{O}$ stretch which arises through the symmetry reduction associated with imine formation. The variability of the peak and shoulder intensities in the $\text{C}=\text{C}$ stretch region near 1600 cm^{-1} may also contain contributions from changes associated with the formation of the imine.

The occurrence of imine cross-links may not be limited to heavily ODA rich material. Since the initial reaction between PMDA and ODA occurs entirely at the sample surface in the VDP process¹, even films produced under more nearly stoichiometric dosing conditions may initially consist of relatively short PAA chains with a correspondingly high density of ODA and/or PMDA terminal groups. Certainly, PAA molecular weights comparable to those produced by solvent synthesis would not be expected under the conditions of lower molecular mobility operative in a condensed film. This argument is supported by the presence of the residual 1656 cm^{-1} band seen in Figure 1(b), which is typical of films prepared under more balanced PMDA and ODA partial pressures.

Finally, this model may help explain anomalies in other VDP film data such as the intense low binding energy component in the N 1s core level emission reported by Salem et al.¹ The evidence found by Lamb et al. for an excess of ODA and PMDA terminal groups in films cured at 267 and 367°C is also compatible with a model in which the initial dose and cure generate relatively short PI chains.

Insert
Rxn 2
after
this point

REFERENCES

1. J. R. Salem, F. O. Sequeda, J. Duran, D. Y. Lee, and R. M. Yang, *J. Vac. Sci. Technol. A* 4, 369 (1986).
2. S. D. Senturia, in *Polymers for High Technology*, M. J. Bowden and R. S. Turner, Eds., *ACS Symp. Ser.* 364, 428 (1987).
3. R. J. Jensen, in *Polymers for High Technology*, M. J. Bowden and R. S. Turner, Eds., *ACS Symp. Ser.* 364, 466 (1987).
4. M. Grunze and R. N. Lamb, *Chem. Phys. Lett.* 133, 283 (1987).
5. M. Grunze and R. N. Lamb, *J. Vac. Sci. Technol. A* 5, 1685 (1987).
6. M. Grunze, W. N. Unertl, S. Gnanarajan, and J. French, "Chemistry of Adhesion at the Polyimide-Metal Interface," in *Proceedings of the Materials Research Society Symposium on Electronic Packaging Materials Science*, Vol. 108, Boston, December 1987, in press.
7. R. N. Lamb, J. Baxter, M. Grunze, C. W. Kong, and W. N. Unertl, *Langmuir*, 4, 249 (1988).
8. C. E. Sroog, A. L. Endrey, S. V. Abramo, C. E. Berr, W. M. Edwards, and K. L. Olivier, *J. Polym. Sci. A* 3, 1373 (1965).
9. H. Ishida, S. T. Wellinghoff, E. Baer and J. L. Koenig, *Macromolecules* 13, 826 (1980); S. T. Wellinghoff, H. Ishida, J. L. Koenig and E. Baer, *ibid.* 13, 834 (1980).
10. O. Elshazly and M. Grunze, to be published.
11. C. G. McCarty, "syn-anti Isomerizations and Rearrangements," in *The Chemistry of the Carbon-Nitrogen Double Bond*, S. Patai, Ed., Interscience, London, 1970, p. 445.
12. M. C. Tobin, *Laser Raman Spectroscopy*, Wiley-Interscience, New York, 1971.

TABLE 1

Raman peak assignments for VDP and solution prepared PI. The ranges quoted for the VDP entries correspond to the features shown in Figure 2. Values reported in the text are averages unless otherwise stated.

=====		
Polyimide		

VDP	Solution cast	Assignment

1125-1128	1120	(OC) ₂ NC (imide III)
1165-1168	1165	
1240-1242		V _{C=O}
1276-1280		
1394-1397	1386	V _{C=N}
1458-1462	1456(?)	V ₁₃ (1,2,4,5-C ₆ H ₂)
1510-1517	1512	V ₁₃ (1,4-C ₆ H ₄)
1596-1598	1595(sh)	V ₁₆ (1,4-C ₆ H ₄)
1608-1610	1610	V ₁₆ (1,2,4,5-C ₆ H ₂)
1654-1658		V _{C=N}
1742-1743		V _{C=O}
1785-1788	1787	V _{C=O} (sym)
=====		

SUMMARY

The work reported above indicates that Raman spectroscopy is a sensitive technique for the study of thin layers of vapor deposited polyimides. The data suggest that the final composition of the film depends significantly on initial dosing conditions and, specifically, that the presence of excess ODA leads to the formation of short polyimide chains that may be highly branched or cross-linked with imine functionalities. This finding may have substantial implications for the thermal, mechanical, and chemical properties of films produced by vapor deposition methods.

ACKNOWLEDGEMENTS

This work was supported by the Office of Naval Research under contract number N00014-85-K-0641.

FIGURE CAPTIONS

Figure 1: (a) Laser Raman spectrum of solution deposited poly(N,N'-bis(phenoxyphenyl)pyromellitimide) (PI).
(b) Raman spectrum of ca. 200 nm vapor deposited PI film.

Figure 2: Raman spectra of PI prepared by dosing under conditions of excess ODA flux:
a) bottom of sample and nearest ODA oven.
b) center of sample, equidistant from both ovens.
c) top of sample and nearest PMDA oven.

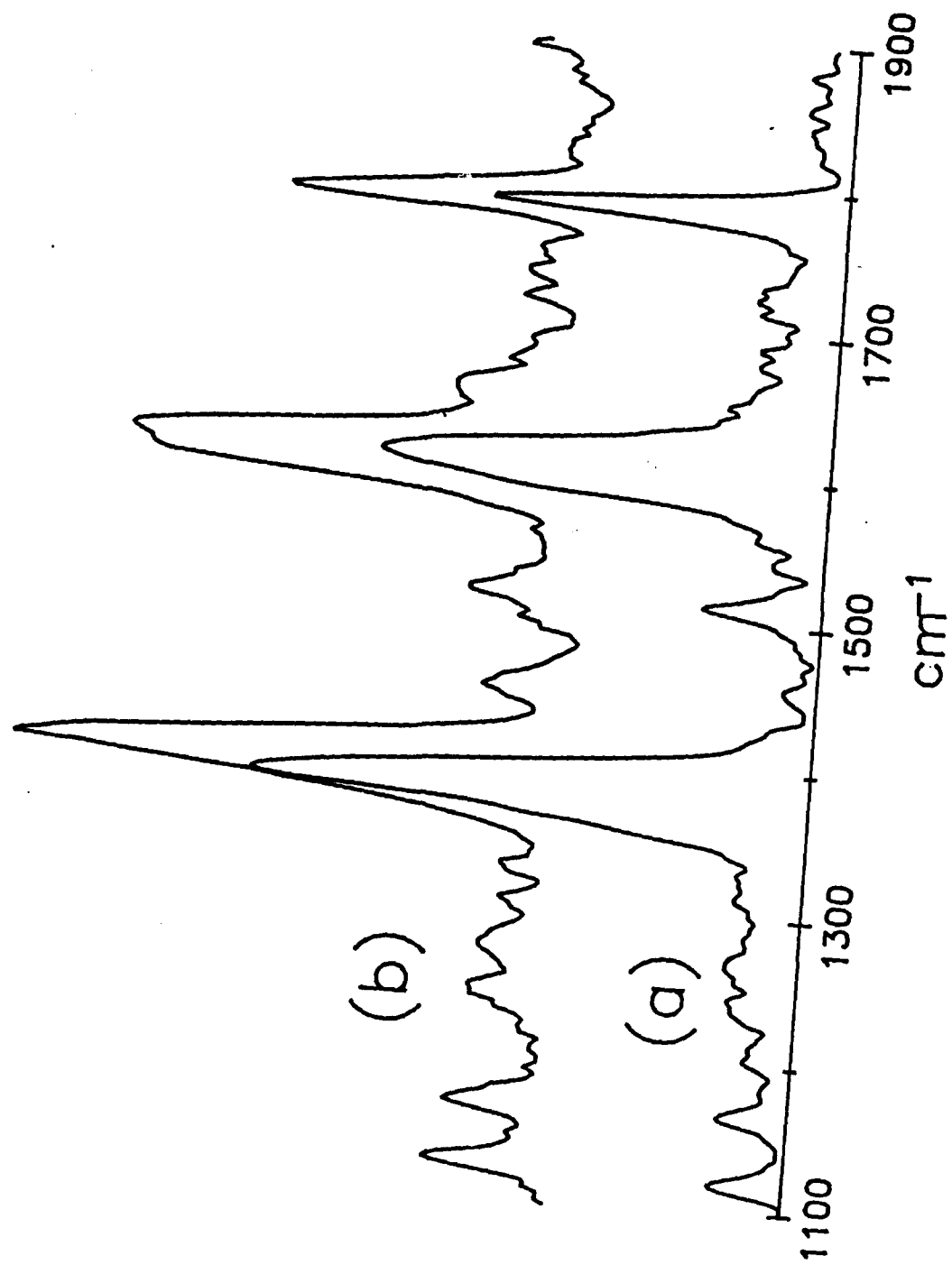


Figure 1

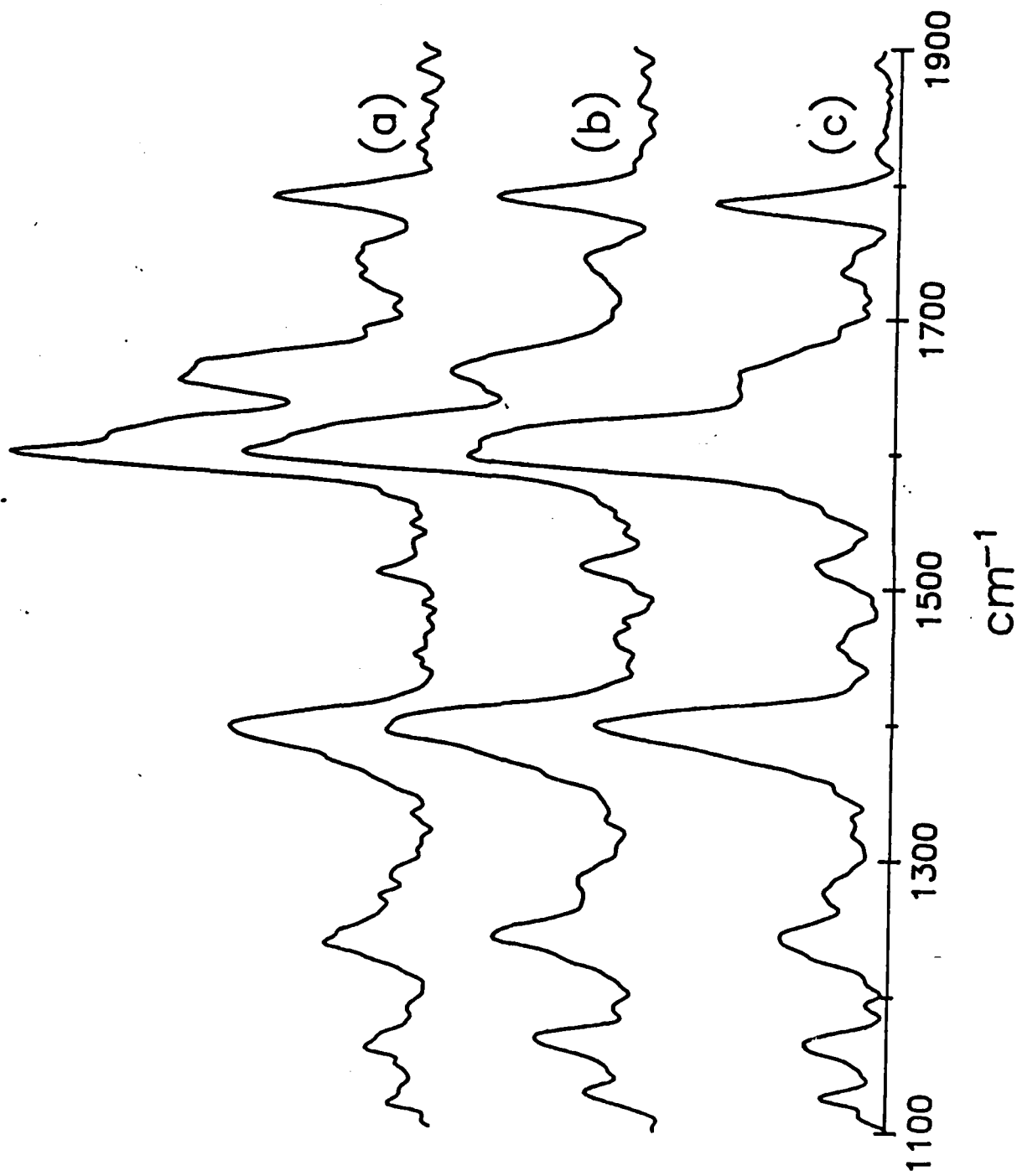
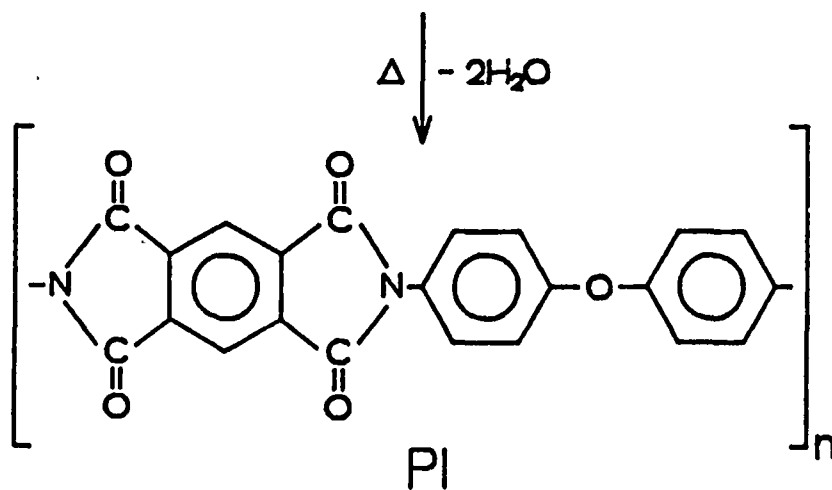
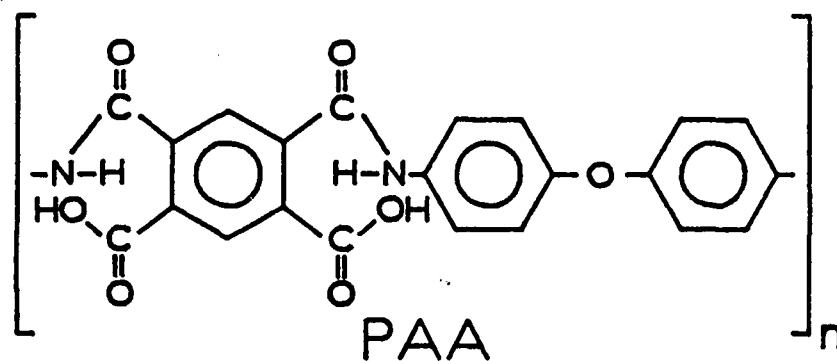
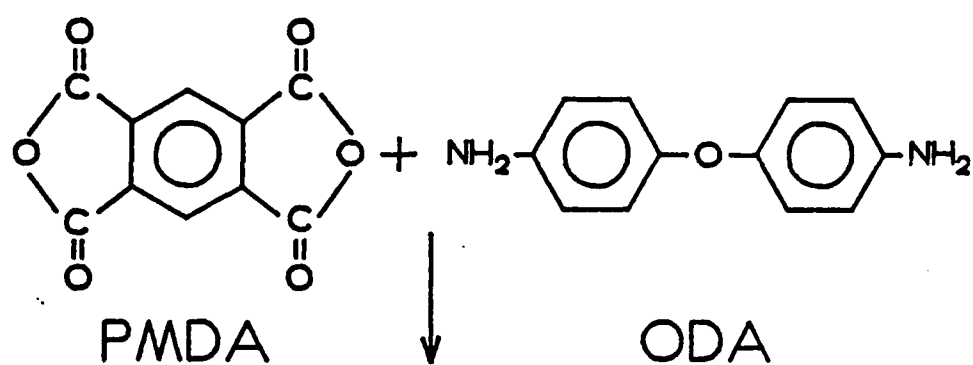
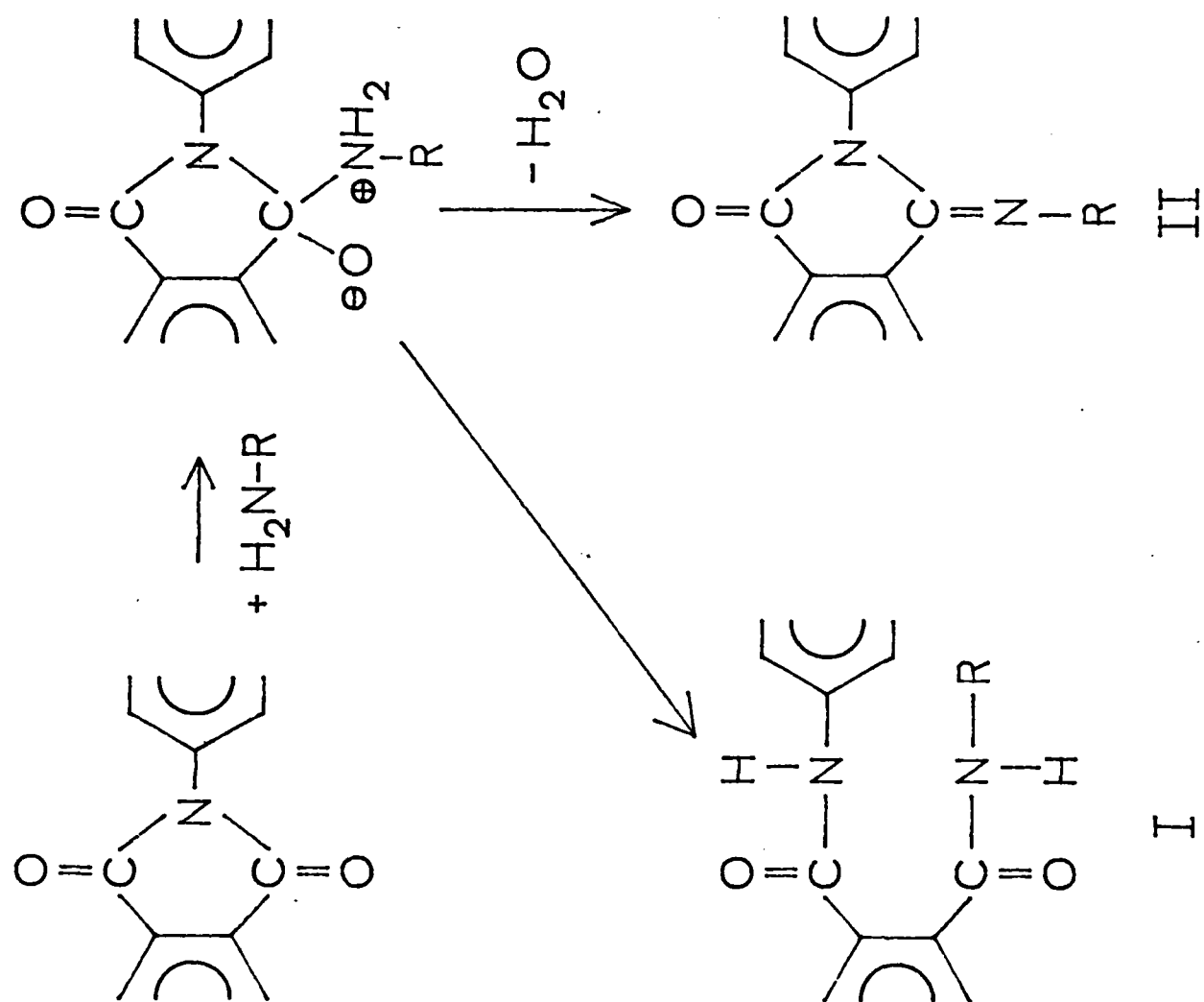


Figure 2





TECHNICAL REPORT DISTRIBUTION LIST, GEN

	<u>No. Copies</u>		<u>No. Copies</u>
Office of Naval Research Attn: Code 413 800 N. Quincy Street Arlington, Virginia 22217	2	Dr. David Young Code 334 NORDA NSTL, Mississippi 39529	1
Dr. Bernard Doua Naval Weapons Support Center Code 5042 Crane, Indiana 47522	1	Naval Weapons Center Attn: Dr. Ron Atkins Chemistry Division China Lake, California 93555	1
Commander, Naval Air Systems Command Attn: Code AIR-931A (Dr. L. Slotter) Washington, D.C. 20361-9310	1	Scientific Advisor Commandant of the Marine Corps Code RD-1 Washington, D.C. 20380	1
Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko Port Hueneme, California 93401	1	U.S. Army Research Office Attn: CRD-AA-IP P. O. Box 12211 Research Triangle Park, NC 27709	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	12	Naval Ocean Systems Center Attn: Dr. S. Yamamoto Marine Sciences Division San Diego, California 91232	1
DTNSRDC Attn: Dr. G. Bosmajian Applied Chemistry Division Annapolis, Maryland 21401	1		
Dr. William Tolles Superintendent Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375	1		