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A Raman Spectroscopic Study of Vapor Deposited
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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.

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-workers[4-6]. 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 Ag[7].

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 ±20 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 polyimide[9]. 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 "ν" represents Greek "nu" ν

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 crystallinity[9]. 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 conditions[10], 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 (v_{16}) at 1597 cm^{-1}. The pyromellitimide v_{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 v_{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.

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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

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 temperatures[11] 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 stretch[12] 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 a 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 C=N stretch and the peak at 1742 cm^{-1} is assigned to a C=O stretch which arises through the symmetry reduction associated with imine formation. The variability of the peak and shoulder intensities in the C=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 process[1], 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.

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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 Packinging 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	$(OC)_2NC$ (imide III)
1165–1168	1165	
1240–1242		ν_{COC}
1276–1280		
1394–1397	1386	ν_{CN}
1458–1462	1456(?)	ν_{13} $(1,2,4,5-C_6H_2)$
1510–1517	1512	ν_{13} $(1,4-C_6H_4)$
1596–1598	1595(sh)	ν_{16} $(1,4-C_6H_4)$
1608–1610	1610	ν_{16} $(1,2,4,5-C_6H_2)$
1654–1658		$\nu_{C=N}$
1742–1743		$\nu_{C=O}$
1785–1788	1787	$\nu_{C=O(sym)}$

==

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.

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.

(b)

(a)

1100   1300   1500   1700   1900
cm⁻¹

Figure 1

(a)

(b)

(c)

1900 1700 1500 1300 1100

cm^{-1}

Figure 2

PMDA + ODA

PAA

$\Delta \mid -2H_2O$

PI
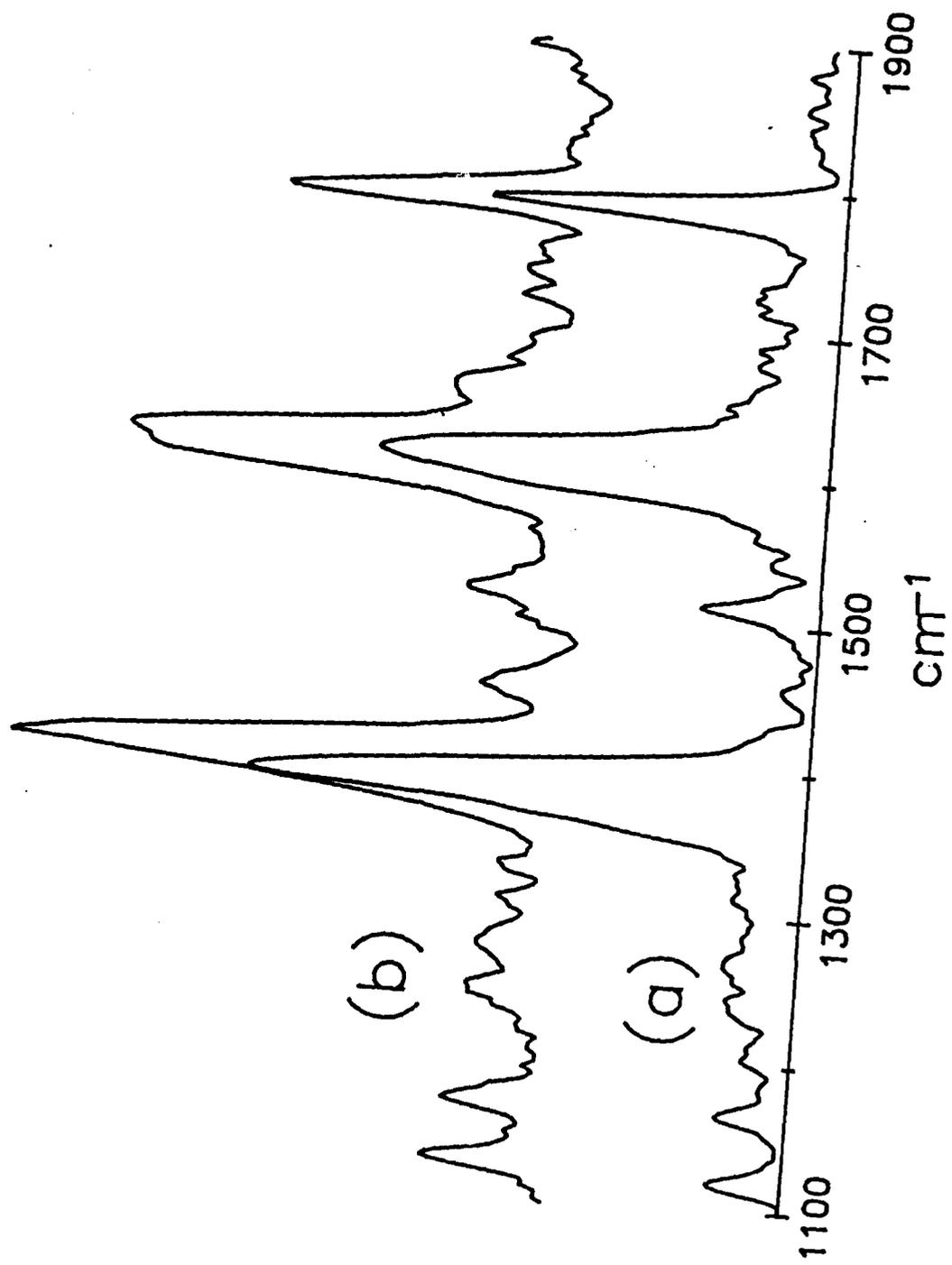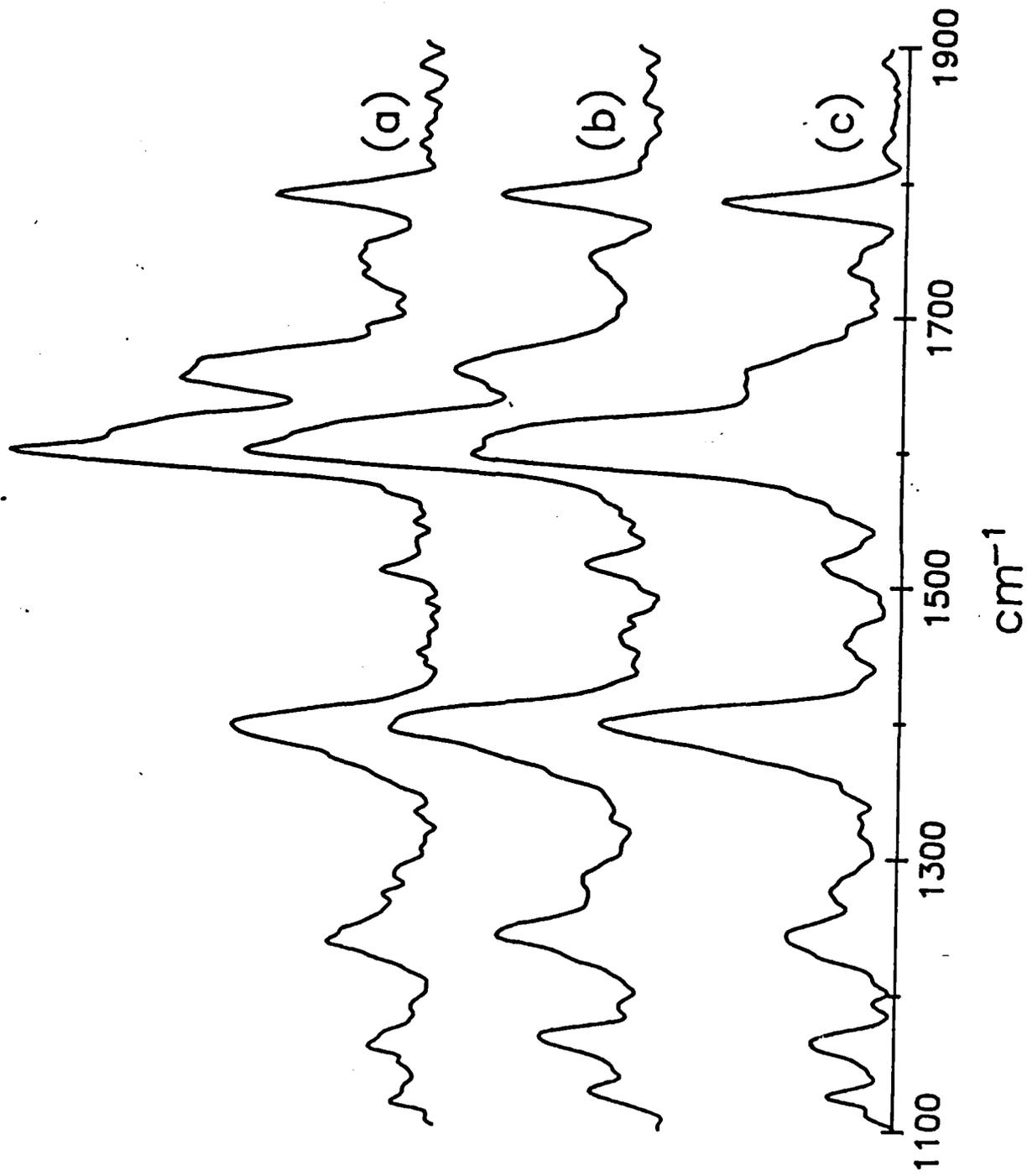
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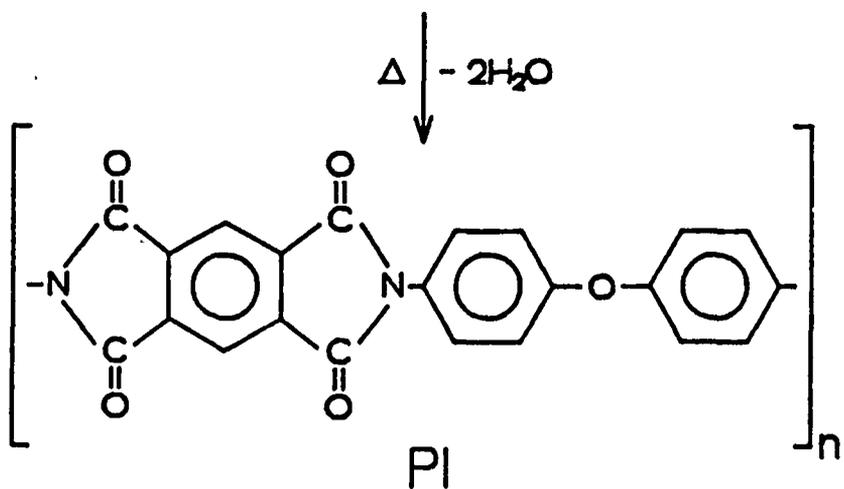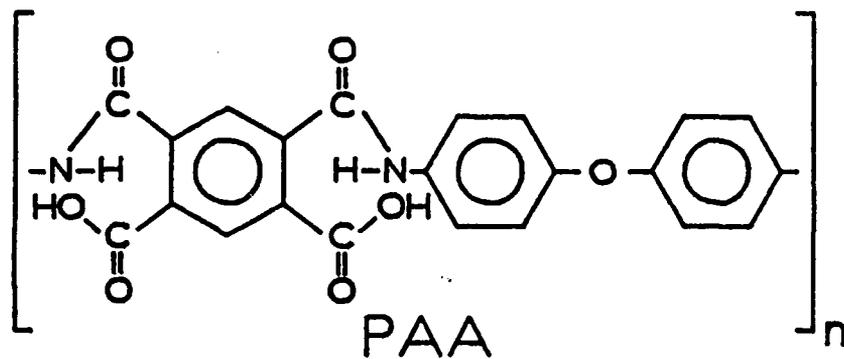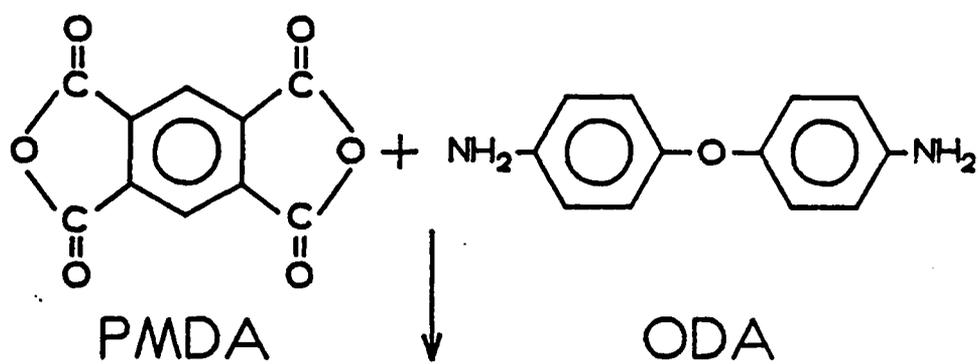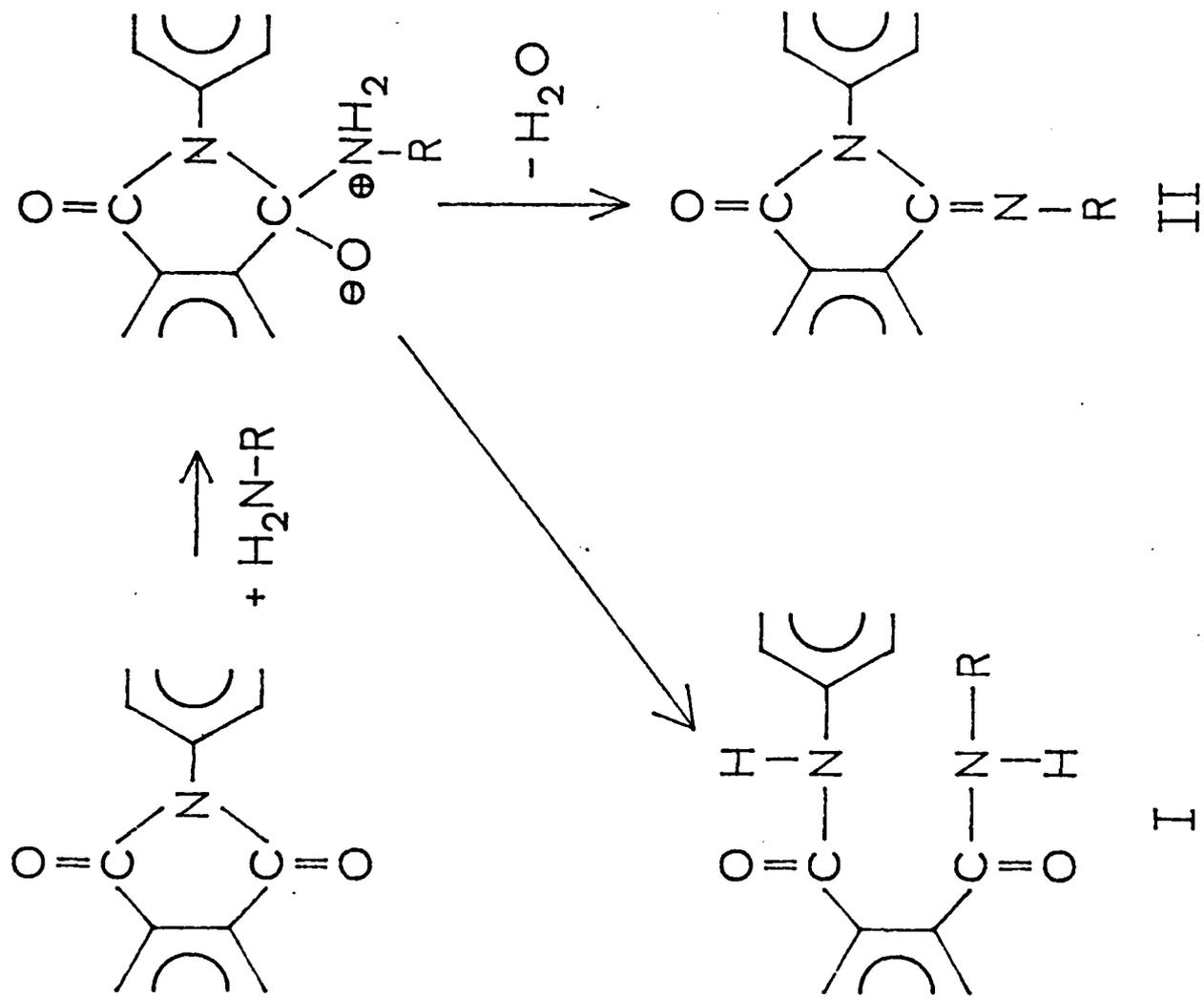
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