

# Combustion Products from Polydiallylamine

## INTRODUCTION

We recently found<sup>1</sup> that anion exchange resins made from polydiallylamine can be used to selectively adsorb complex gold anions from mixed metal solutions such as those found in the mining or electroplating industries. As the resins are cheap and easy to make, and also retain the gold in a highly purified form at a high capacity (>50% by weight), the most economic technique for gold recovery is to ash the metal saturated resin. The possibility of pollution arising from this technique, if carried out on a large scale, prompted us to study the combustion products resulting from the thermal decomposition of polydiallylamine and its gold salts. In conjunction with the standard micropyrolysis of polymer samples, we have previously reported a number of new methods for collecting and analysing the combustion products of polymers, which preserve (by rapid cooling and fast analysis) many of the reactive or unstable compounds released in such reactions.<sup>2,3</sup> Some of the same techniques have now been applied to the combustion of polydiallylamine and its gold salts.

## EXPERIMENTAL

### Samples

Crosslinked polydiallylamine (Sirez Au<sup>1</sup>) was prepared by the redox-initiated ( $K_2S_2O_8/TiCl_3$ ) polymerization of freshly distilled diallylamine [containing 2% 1,6-bis(*N,N*-diallylamino)hexane] as a 30% solution in 80% phosphoric acid at 0°C. The resulting crosslinked resin is thoroughly washed with water and then sodium hydroxide solution (10%) before a final distilled water washing and air drying.

Polydiallylamine resin containing  $\approx 50\%$  by weight gold was prepared by soaking the above resin in a three fold molar excess of gold cyanide solution (2 g/L at pH 8.5) overnight and then filtering the resin, washing with distilled water, and air drying. The samples were dried for 24 h over  $P_2O_5$  before combustion.

### Apparatus

**Pyrolysis.** A Hewlett Packard 18580A Pyroprobe, with coiled platinum probe, was connected to a Finnigan 9500 Gas Chromatograph coupled to a Finnigan 3300F Quadropole Mass Spectrometer with INCOS 2300 Data System. Mass spectra were produced by electron impact ionization using an electron energy of 70 eV and a beam current of 0.5 mA.

**Combustion.** The combustion furnace and collection system used in these experiments has been described in previous papers.<sup>2,3</sup>

### Method

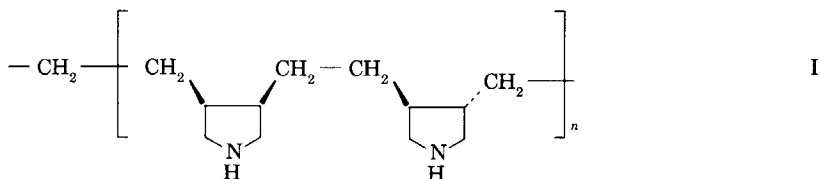
**Pyrolysis.** Five-milligram samples were placed in quartz tubes and pyrolyzed at 900°C for 10 s with ramp setting off. These conditions were shown by preliminary experiments to give the optimum resolution of pyrolysis peaks. The GC was programmed from 60 to 260°C at 10°C/min using a 1.8 × 2mm i.d. packed column containing 3% OV17 on 100/120 GasChrom Q. Nitrogen was used as the carrier gas with a flow rate of 20 mL/min. The mass spectrometer was scanned from 35 to 600 amu at intervals of 3 s. The products from pyrolysis were identified by comparison of their mass spectra with those recorded in the EPA/NIH Mass Spectral Data Base and also by comparison of retention indices with literature values.

**Combustion.** One-gram samples were placed into the oven preheated to 480°C, and air was drawn through the oven and the dry ice traps, at a flow rate of 1 L/min. The contents of the traps were immediately dissolved in the minimum of methanol, the solution was dried with

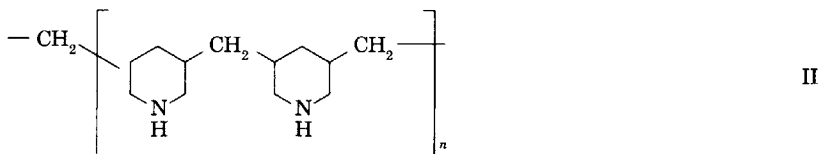
molecular sieves, cooled to  $-18^{\circ}\text{C}$ , and immediately injected into the GC/MS using the same conditions as above.

## RESULTS AND DISCUSSION

Recent  $^{13}\text{C}$  NMR and other evidence<sup>4,5</sup> has confirmed that the polydiallylamine structure contains mainly pyrrolidine rings linked by two methylene units as shown:

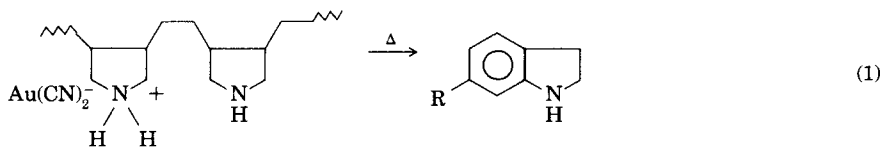


Structure I would be expected to give very different combustion products to the polypiperidine structure (II) originally proposed for polydiallylamine<sup>6</sup> and assumed to be correct for many years. The gold chelating resins formed from polydiallylamine also contain small amounts (1–3%) of difunctional diallylamine residues as a crosslinker.



A list of the products obtained from the pyrolysis and combustion experiments with polydiallylamine resin and its gold salts are shown in Table I. As expected from structure I, many of the major products are substituted pyrroles and indoles. Other basic compounds produced include pyridines and quinolines. Neutral compounds formed include a number of thermally stable molecules found in the pyrolysis products of many hydrocarbon polymers. Such compounds include benzene, xylenes, styrene, and naphthalene. In most cases it was not possible from the mass spectra to identify the actual substitution pattern of the alkyl substituted aromatics.

Although the types of compounds produced on pyrolysis of the free base resin (Fig. 1) and the gold loaded material (Fig. 2) were predominantly the same, there were large differences in relative amounts of different constituents. As seen from the figures, the free resin produced relatively larger quantities of pyrrole compounds (peaks 4, 8, 12, and 13) whereas the gold-loaded material produced greater amounts of the higher boiling materials such as indoles and carbazoles (peaks 29, 30, 31, 32, 25, and 36). The latter compounds would be expected to result from Hoffman type elimination reactions where quaternary amine salts are adjacent to a neutral amino segment as in



At the high gold loadings (50%) used in these experiments the ratio of nitrogen to gold atoms is approximately 2:1. Thus the proportion of the partial structure shown in eq. (1) will be high in the loaded polymer.

Micropyrolysis experiments are not necessarily a good indication of the combustion products obtained by burning large amounts of polymer, but sample collection in the latter case is very

TABLE I  
Identified Pyrolysis Products of Polydiallylamine

Peak No.	Name	Peak No.	Name
1	Methyl cyclopentadiene	20	Methyl pyridine
2	Benzene	21	C <sub>4</sub> pyrrole
3	Methyl benzene	22	Isocyano methyl pyridine
4	Pyrrole	23	Methyl indene
5	Pyridine	24	C <sub>4</sub> pyrrole
6	Xylene	25	Napthalene
7	Benzylamine + C <sub>7</sub> H <sub>14</sub> alkene	26	Methyl naphthalene
8	N-methyl pyrrole	27	Indole
9	Styrene	28	3-Methyl quinoline
10	Methyl pyridine	29	Methyl indole
11	Ethyl methyl benzene	30	Dimethyl indole
12	Dimethyl pyrrole	31	C <sub>3</sub> indole
13	Ethyl pyrrole	32	C <sub>4</sub> indole
14	Methyl styrene	33	C <sub>3</sub> quinoline
15	Methyl pyridine	34	Carbazole
16	C <sub>3</sub> pyrrole	35	Methyl carbazole
17	Methyl pyridine	36	Ethyl carbazole
18	Benzonitrile	37	Methyl phenazine
19	Indene		

difficult. A standard method of sample collection in combustion experiments is by adsorption on a porous solid surface (i.e., OV 101 column) with subsequent flash desorption. This only is applicable if very stable combustion products are obtained. Instead we used the technique of adsorption on cold glass surfaces with subsequent cold solvent removal and column injection. Even here changes in reaction products could be observed. Intermittent sample collection during large scale burns was used to prevent surface heating during collection and subsequent fast analysis helped preserve the sample constituents.

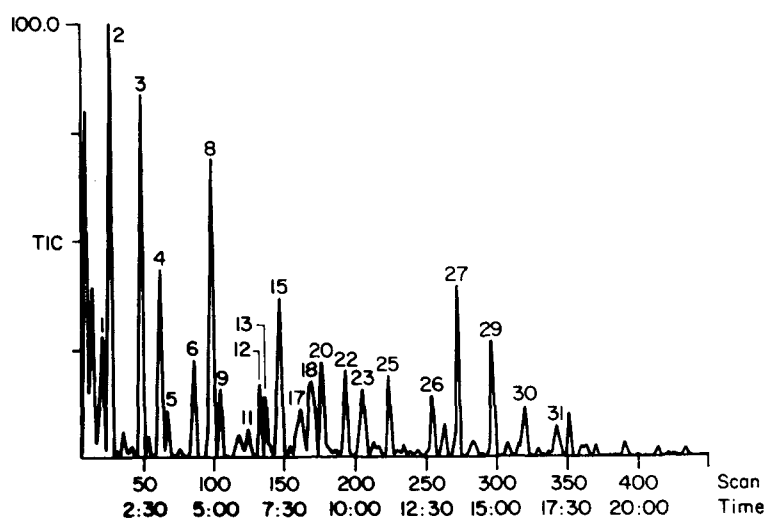


Fig. 1. Total ion chromatogram of polydiallylamine pyrolysis products.

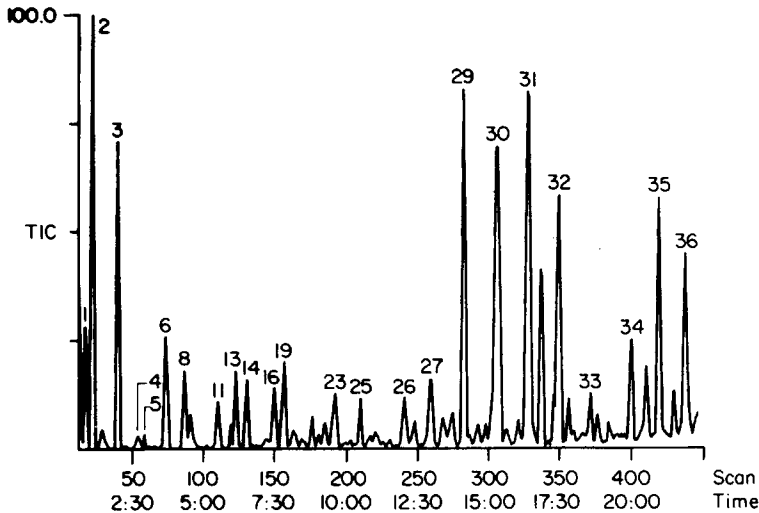


Fig. 2. Total ion chromatogram of polydiallylamine (gold-loaded) pyrolysis products.

Figure 3 shows the product distribution obtained by the combustion of 1 g of polydiallylamine in air at 480°C. This latter value was chosen as a compromise between too slow rates of decomposition at lower temperatures and uncontrollable evolution of gases leading to loss of gold by sputtering at higher temperatures. The products obtained were almost identical to those found in the pyrolysis experiments except for the addition of peak 7 (benzylamine and a  $C_7H_{14}$  hydrocarbon); a few early peaks were swamped by the methanol solvent peak. As with the polydiallylamine pyrolysis results, pyrrole derivatives predominated. However, some of the more complex indole molecules (peak 31, 32, etc.) did increase in relative intensity. This is in line with the finding<sup>7</sup> that slower heating rates lead to a greater yield of high molecular weight products in the thermal decomposition of other polymers. The products and their intensities were reproducible under the same combustion conditions provided the product was kept cold both before and after dissolving in methanol and provided that sample analysis was carried out within hours. Material kept for several hours at room temperature polymerized on glass surfaces, and chromatograms of any remaining methanol soluble products showed considerable changes with extra peaks appearing and others almost disappearing.

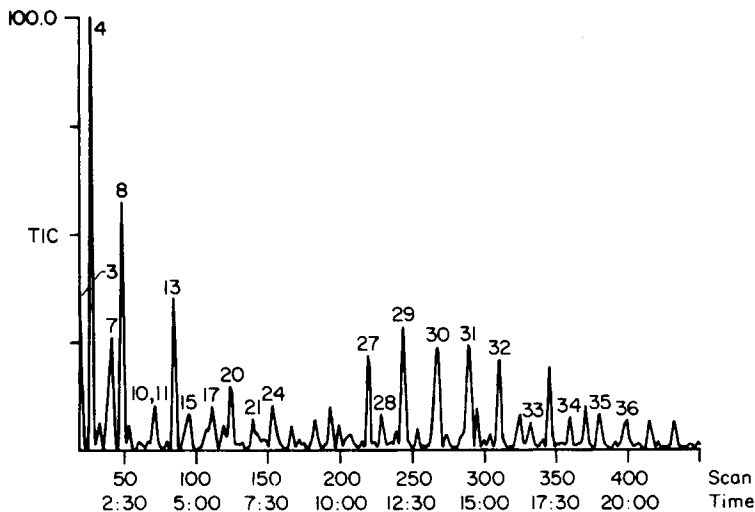


Fig. 3. Total ion chromatogram of polydiallylamine combustion products.

## CONCLUSION

The combustion products of polydiallylamine and its gold salts are mainly heterocyclic amines, with pyrroles and indoles predominating. The nature of the products does not change extensively with gold level in the resin or combustion techniques, although relative product ratios do. It has been possible in small scale experiments to remove these amines, and hence the unpleasant odours given off during the gold recovery operations, by bubbling the combustion effluent through dilute, aqueous acid solutions.

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