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Structural Characterization of the Condensation Polymer of Dipyridine Manganese II Dichloride with 1,3-Di-4-piperidy I propane

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Structural Characterization of the Condensation Polymer of Dipyridine Manganese II Dichloride with 1,3-Di-4-piperidylpropane

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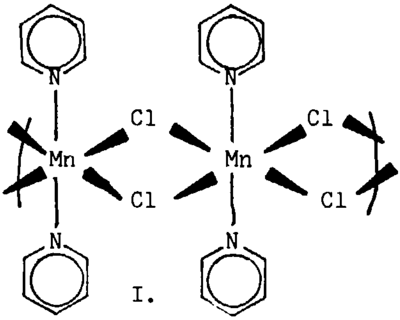
ABSTRACT

The synthesis of polymers derived from the condensation of dipyridine manganese II dichloride with 1,3-di-4-piperidylpropane is described. Structural analysis of the polyamines is detailed utilizing results based on infrared, thermal, elemental and solution analyses.

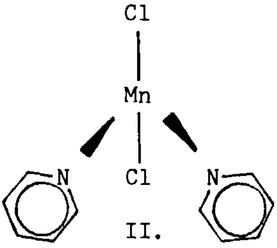
INTRODUCTION

The previous paper describes the construction and operation of a new Thermogravimetric Analyzer-Mass Spectrometer, TG-MS, assembly suitable for identification of the sequence of products resulting from the thermal degradation of polymers. This paper describes the initial synthesis of a manganese polyamine and describes the use of the TG-MS assembly for degradation product identification.

Synthesis of dipyridine manganese II dichloride, Py_2MCl_2, DMC, has been known for a long time (1). Its structure in the solid state has been well studied using x-ray diffraction (2,3), magnetic techniques (2-4) and spectral techniques (mainly infrared, ultraviolet and Raman spectroscopy; 5-12). DMC is octrahedral and is a linear polymer in its solid state (form I) with bridging occurring through the chlorides. Gill, et al. (9) note that while a tetrahedral arrangement is feasible for DMC (Mn II is a d^5 atom) the observed octrahedral structure in the solid state is presumably due to the low electronegativity of the Mn II atom which favors six-coordination.



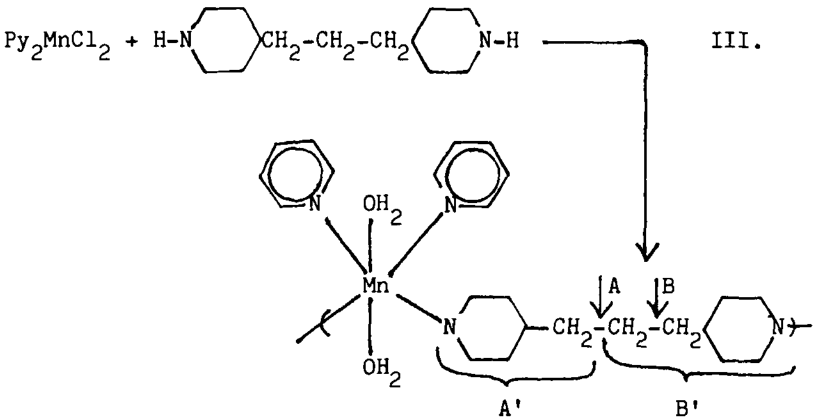
I.



II.

Even though much is reported on the physical properties of the DMC in the solid state little is reported on any reactions or solution properties of DMC. Dash and Ramana Rao (13) concluded from magnetic susceptibility measurements in nitrobenzene that DMC exists in a monomeric tetrahedral configuration of form II.

Here we report the initial synthesis of a manganese II polyamine, for which the degradation data and other analyses are consistent with a structure of form IV.



III.

IV.

EXPERIMENTAL

Dipyridine manganese II dichloride (ROC/RIC, Belleville, N.J.) and 1,3-di-4-piperidylpropane (a gift from Reilly Coal Tar Products; Di-Pip) were used as received without further purification. Reactions were carried out utilizing a one pint Kimex Emulsifying jar fitted onto a Waring Blendor (Model 700). Solutions of triethylphosphate, TEP, containing DMC were added to TEP solutions containing Di-Pip and triethylamine as the added base at stirring speeds around 20,000 rpm. Stirring is stopped and the reaction mixture poured into a beaker and left for about 24 hours. A brown precipitate begins to form after several minutes and continues to form for several hours. The reaction mixture is filtered using centrifugation, and the brown solid product is collected and washed repeatedly with TEP and then with diethylether. The solid is transferred to a preweighed petri dish and dried.

General elemental analyses were carried out utilizing typical wet analysis techniques. The products showed the presence of

Mn and the absence of chloride. Quantitative elemental analyses were carried out by Alfred Bernhardt, Mikroanalytisches Labs and Galbraith Labs, Inc. The results of these analyses for the condensation product between DMC and Di-Pip are consistent with a product of form IV. (Thus, %Mn calc. = 12.1, found 13.5; %H calc. = 8.11, found 8.13.)

Infrared spectra of the product were also obtained utilizing KBr pellets and a Perkin-Elmer 457 Grating Infrared Spectrophotometer. The product shows bands characteristic of the presence of both reactants (Di-Pip and DMC) and of water. The presence of water is indicated by the presence of a strong band in the 3400-3600 cm^{-1} region (reported to be *ca* 3450 cm^{-1} for water in organic compounds and *ca* 3300 to 3400 cm^{-1} for uranyl-water compounds). The presence of DMC is indicated by the presence of such bands as those at 1580 and 1460 cm^{-1} which are characteristic of the aromatic ring stretching vibrations present in pyridinyl containing compounds, and the presence at bands of *ca* 1040 and 1010 cm^{-1} which are characteristic of C-H in-plane deformation. The presence of the Di-Pip moiety is indicated by the presence of such bands as those at 2850 to 2975 cm^{-1} which are characteristic of aliphatic C-H stretching, and the bands about 1390 cm^{-1}, a series of bands in the 1100 to 1030 cm^{-1}, a series of bands in the 1100 to 1030 cm^{-1} region (in addition to those noted above), and bands at 825 and 810 cm^{-1}, all present in both the monomer and polymer. The N-H stretching band at 3225 cm^{-1}, present in the Di-Pip monomer, is not present in the polymer. Bands which are characteristic of the Mn-N and Mn-Cl moieties are currently in dispute, but are below 250 cm^{-1}, the limit of the employed infrared spectrophotometer.

Light scattering measurements were also accomplished for the polymer, utilizing serial dilutions and employing a Brice-Phoenix 2000 Universal Light Scattering Photometer. The dissymetric technique was used to calculate the data. Refractive index increments were determined utilizing a Bausch and Lomb Abbe Refractometer Model 3-L. The product chosen for study had a weight average molecular weight of 2.1×10^6.

Thermal stability of the condensation product was determined using Differential Scanning Calorimetry (DSC), Thermal Gravimetric Analysis (TG) and the combination TG-MS instrument mentioned above. The equipment employed included a duPont 900 Differential Scanning Calorimeter cell, attached onto a duPont 950 Thermal Analyzer Console, a duPont 900 Thermal Gravimetric Analyzer, and a duPont 21-491 Double-Focusing Mass Spectrometer. Details of the TG-MS assembly are presented in the previous paper.

RESULTS AND DISCUSSION

We have been incorporating metals into polymers for a variety of reasons, one being that such compounds are useful as delivery agents in biological systems (14-16). The portion delivered may be either the metal containing moiety, or the organic comonomer, or both. We wished to synthesize manganese-containing polyamines because manganese is an essential metal in many biological systems and there are a number of biologically active diamines which could be incorporated to give polymers of form IV. Further, there are a number of naturally occurring amides, which enhances the probability for biological acceptance and subsequent hydrolysis of manganese polyamines. Here, we will restrict our discussion to the condensation product between DMC and Di-Pip and its physical characterization.

As noted in the previous section, infrared spectroscopy and elemental analysis data for the polymer are consistent with a structure of form IV. In addition, Clark and Williams (8) noted that the frequencies of pyridine ring vibrations in the metal-pyridine complexes, including DMC, are, in general, indicative of the stereochemistry (octrahedral, square planer or tetrahedral) of the metal complex. DMC itself shows a pyridine ring vibration at 627 cm^{-1}. Product IV shows a band at about 620 to 630 cm^{-1}, consistent with an octrahedral structure. Similar aqueous compounds are known to be octrahedral in the solid state. For instance Richards, Quinn and Moros (3) utilized x-ray diffraction and ESR to prove the octrahedral structure of solid $PyHMnCl_3H_2O$.

The TG-MS data is also consistent with a product of form IV. Figure 1 shows plots of weight loss and total ion current as a

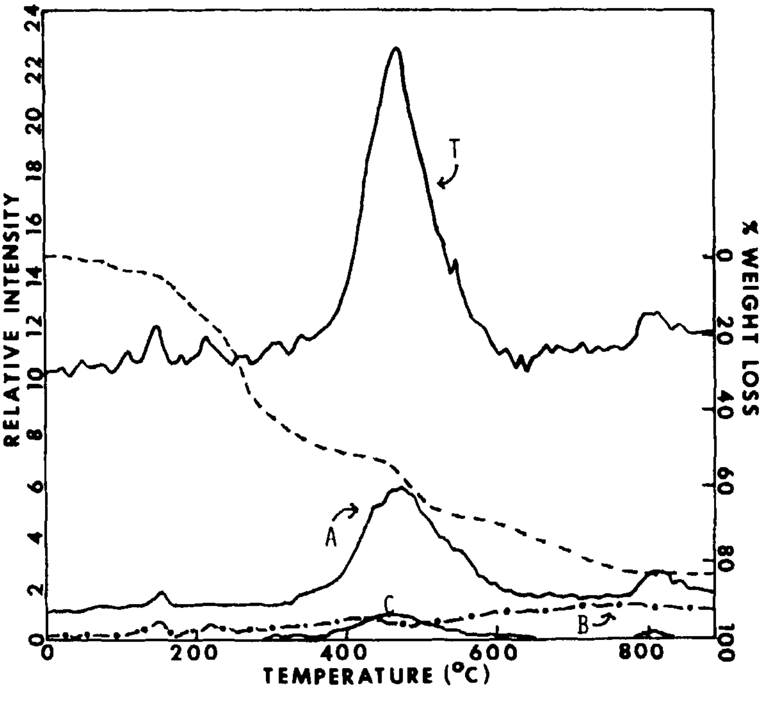


FIGURE 1. TG(---) AND MS(——) PLOTS FOR THE CONDENSATION PRODUCT FROM DIPYRIDINE MANGANESE II DICHLORIDE AND DIPYRIDINE AT AN ACCELERATING VOLTAGE OF 70eV, FLOW RATE OF HELIUM AT 55 ML/MIN FOR A HEATING RATE OF 20 C°/MIN AND A DATA SAMPLING FREQUENCY OF 41 KC. T = TOTAL ION CURRENT. A = PLOT OF M/E 18. B = PLOT OF M/E 44. C = PLOT OF M/E 79.

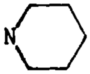
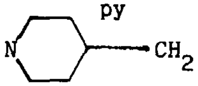
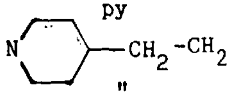
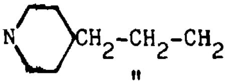
function of temperature for the thermal degradation of the polymer. The plot of total ion current shows four maximums; the first occurs at a temperature of about 160°C, the second at about 250°C, the third and largest at about 460°C and the fourth at about 750°C. The TG thermogram shows five clear breaks (temperature regions where accelerated weight loss occurrs) at temperatures of approximately 130, 150, 250, 470 and 700°C, respectively. The breaks near 150, 250, 470 and 700°C also correspond to the maximums in the total ion current plot.

Initial weight loss upon degradation of the polymer occurs at about 120°C, and at the same time mass spectral peaks indicative of propylene are observed (Figures 1) followed shortly by the appearance of mass spectral peaks characteristic of water. Therefore, initial degradation apparently occurs through breakage of the propylene chain present in the Di-Pip moiety and the evolution of water.

The accelerated weight loss of 65% which occurs in the 200-250 °C range, corresponds with the appearance of a number of mass spectral peaks with relative ion intensities greater than 1%. The greatest accelerated weight loss occurs at about 453°C, concurrent with the appearance of 38 mass spectral ions with normalized intensities greater than 1% (Table 1). No other significant mass peaks are observed from degradation products over the entire 200 to 500 °C temperature region. The relative intensities of the mass spectral peaks detected at m/e 79, 52, 51, 50, 78, 53 and 39 are consistent with the fragmentation pattern of pyridine (17). The Di-Pip moiety apparently produces the fragment ions detected at m/e 119-115, 108-105, 94-91, 82-77, 69-64, 56-54, 43, 41 and 14. Many of these ions could result from several fragmentations of different portions of the Di-Pip moiety, and Table 1 lists the structure of only one set of these possible fragments.

Table 1

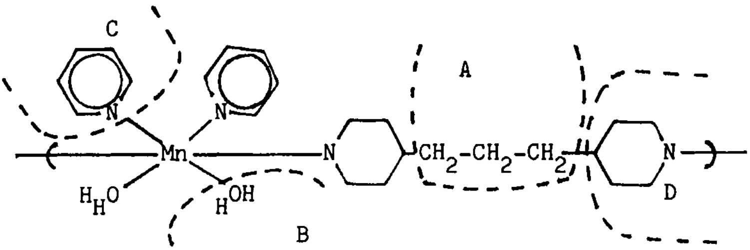
Major Mass Spectral Peaks Observed from the Degradation Products Joined at 453°C from the Condensation Product of Di-Pip with DMC.

m/e	Normalized Intensity	Assignment	m/e	Normalized Intensity	Assignment
14	3.6	CH_2	78	3.3	py
17	20.5	HO	79	15.1	py
18	95.6	H_2O	80	2.2	
26	4.4	HC=CH (py)	81	1.9	py
27	4.5	HC=N (py)	82	2.8	py
39	6.4	HC=CH-CH (py)	91	1.5	
41	4.2	H_2C-CH-CH	92	3.1	py
43	2.2	H_3C-CH_2-CH_2	93	5.3	py
50	3.0	C=C-CH=CH (py)	94	1.1	py
51	5.8	C=CH-CH=CH (py)	105	2.5	
52	12.5	HC=CH-CH=CH (py)	106	4.3	"
53	2.8	HC=CH-CH=N (py)	107	2.1	"
54	2.3	HC-CH_2-CH_2-CH	108	1.5	"
55	5.3	HC-CH_2-CH_2-CH_2	115	1.2	
56	1.7	H_2C-CH_2-CH_2-CH_2	117	1.1	"
64	1.2	HC=CH-C=CH-CH	118	2.3	"
65	2.5	HC=CH-CH=CH-CH	119	1.5	"
66	2.2	HC-CH-CH_2-CH-CH			
67	2.3	HC-CH_2-CH_2-CH-CH			
68	1.4	HC-CH_2-CH_2-CH-CH			
69	2.2	H_2C-CH_2-CH_2-CH-CH_2			
77	2.2	py			

The differentiation between pyridine and the Di-Pip moiety is accomplished by comparing the appearance of m/e 79, 52, 51, 50, 78, 53 and 39 (all mass sequences are given in order of decreasing intensities) associated with the pyridine moiety and m/e 119-117, 108-105 and 91-90 characteristic of the Di-Pip moiety. Masses associated with pyridine are initially detected around 150°C reaching two maximums; one at 450°C and the second about 780°C. Masses associated with the Di-Pip moiety are detected around 350°C reaching a maximum around 460°C. Thus, degradation in the 200 to 500°C range began with the evolution of pyridine followed by the evolution of masses associated with the degradation of the Di-Pip moiety.

If fragmentation occurs in a statistical manner, predictable relationships between certain species should be evident. For instance, breakage of the Di-Pip chain at A or B (IV) should generate equal quantities of fragments A' associated with the quartet of ions at m/e 91-94 and B', associated with the quartet at m/e 105-108. Summation of the intensities of the ions associated with fragments A' and B' (corrected for difference in mass between the two fragments) shows that these agree within 1.5%, which suggests a random bond scission, at least at A and B.

The overall degradation sequence is depicted in Form V where the order of fragmentation is designated by the alphabetical indicator.



V.

The infrared spectra of the residue of the product remaining from the TG-MS analysis shows bands at 1060-1030, 1010, 640-590, 560, 500, 410-411 and 380-270 cm^{-1}. The 1010 cm^{-1} band is characteristic of inplane C-H stretching of pyridine. Other bands present in both the TG-MS residue and the original polymer are associated with DMC (620-570 and 380-270 cm^{-1}). Manganese dioxide, MnO_2, exhibits bands in the neighborhood of 700-450, 410-350 and 340-311 cm^{-1}. Bands present in the residue also correspond to many of the bands characteristic of MnO_2, indicating the possible presence of this compound. The final residue weight was 16% (%MnO_2 theory = 19, %Mn theory = 12). Therefore, the TG-MS residue probably consists of manganese and manganese oxide, with some organic material derived from the pyridine moiety.

In summary, the appearance of mass spectral peaks characteristic of the Di-Pip moiety, water, and pyridine in the mass spectra of the degradation products of the polymer, is consistent with the structure depicted in IV, and is also consistent with results obtained from elemental analysis and infrared spectral studies. While the infrared, elemental analysis and TG-MS data are consistent with structure IV, uncertainties remain with respect to the exact locations of the various ligands about the manganese II atom. Form IV is likely a major structure, since it is reasonable from steric considerations, that the cis or neighboring pyridines remain in these positions, and that when concurrent addition/replacement by either water or the diamine occurs, that such addition occurs to the trans position. Steric requirements are minimized if the trans positions are occupied by the diamines.

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