

Polymer anchored metal complexes

I. Synthesis of 3d-metal complexes of pyromellitic dianhydride-bipyridyl/bipyridylamine polycondensates

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SUMMARY

Pyromellitic dianhydride and dipyridyl/dipyridylamine have been polycondensed in presence of anhydrous $ZnCl_2$ under selective conditions. Fe(III), Cr(III), Co(II), Ni(II) and Cu(II) complexes of the polycondensates have been prepared. Tentative structures for PMDA-DP (DPA)-M complexes have been proposed on the basis of elemental IR and electronic spectral analyses.

INTRODUCTION

Increasing research attention is being paid of late (1) to find out how metal ion complexation can influence the bulk properties of a base polymer. We found (2-5) that thermal stability, dielectric and conductivity characteristics of PVC-DMG-M (M = Fe(III), Co(II), Ni(II) and Cu(II)) are characteristically different from those of the unmodified PVC, depending upon the nature of the metal ion incorporated in the polymer.

Polycondensation reactions may be particularly useful in such studies since they allow of wide structural variations, through use of different functionalized monomer units and ligand moieties.

This article will describe (Scheme 1) the preparation of polymers from pyromellitic dianhydride (PMDA) and dipyridyl (DP) and dipyridylamine (DPA) and their subsequent complexation with Cr(III), Fe(III), Co(II), Ni(II) and Cu(II) ions.

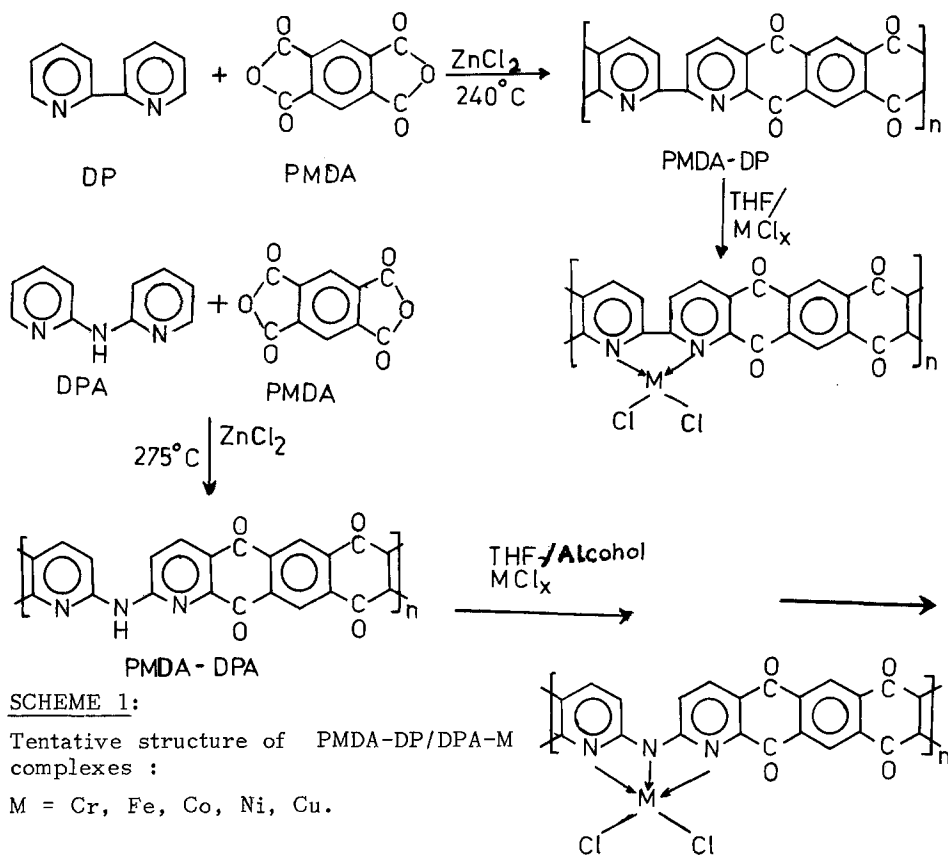
EXPERIMENTAL

Synthesis of PMDA-DP and PMDA-DPA Polycondensate

Pyromellitic dianhydride and DP/DPA (Aldrich, 0.03 mol) were ground together with excess of anhydrous zinc chloride (0.1 mol) and the solid mixture was heated in a Pyrex container gradually to a definite temperature for a definite time under nitrogen with frequent stirring. It was extracted with water, filtered, washed repeatedly with very dilute HCl solution, then again with water and ethanol and finally dried at 60°C (for PMDA-DP) and at 80°C (for PMDA-DPA) in an oven.

Purification of the polymer was done by leaching again the powdered polymer with 0.001N HCl for 3-6 h to remove any trace of

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unreacted Zn salt. Subsequently, the polymers were extracted with water for 2 h, ethanol 2 h, for PMDA-DP and PMDA-DPA. Additional extraction with DMF for 1 h and THF for 2 h was done in the latter case.

Synthesis of 3d-metal complexes of PMDA-DO and PMDA-DPA

1 g each of the polymers was taken in a round-bottomed Pyrex flask provided with a reflux condenser. A 0.05% metal chloride in THF or in THF-alcohol mixture was added to the flask and the mixture stirred for 6 h at 60°C. After a definite reaction time, the metal complex was collected by filtration repeatedly washed with ethanol and THF for 16 h and finally dried at 50°C under vacuum.

Characterization

C and H contents were determined with a Heraeus combustion unit (micro) and N was estimated by micro Duma's method. IR spectra were obtained on a Perkin-Elmer 237B' IR Spectrophotometer in KBr pellets. Solid state reflectance spectra were recorded on a uv-3100 Shimadzu spectrophotometer. BaSO₄ was used as the reference and the wavelength was monitored with 190-1200 nm.

RESULTS AND DISCUSSION

General Feature : PMDA-PP and PMDA-DPA complexes

The condensation between PMDA and DP was carried out under varying reaction conditions such as different PMDA- ligand mole ratios, 1:1, 2:2; temperature 200^o-250-300^oC; and time, 3, 12 and 24 h. The yields varied between 40-85%. The highest yield of 85% was realized with both PMDA-DP and PMDA-DPA using 1:1 mole ratio at 250^oC for 24 h. PMDA/DP : C 68.1 (69.9); H 2.9 (3.2) and N 7.5 (7.8) PMDA/DPA : C 66.3 (67.2); H 2.4 (2.8) and N 11.2 (11.7). All these condensates are insoluble in all solvents and pale white in color.

The estimated percentages of nitrogen, carbon and hydrogen for PMDA-DP and PMDA-DPA indicate that the condensation between PMDA and DP or DPA takes place in 1:1 mole ratio, which supports the proposed structure (Scheme-I).

PMDA-DP and PMDA-DPA exhibit IR-absorption bands at 1636 and 1660 cm⁻¹ respectively which may be assigned (8) to carbonyl stretching. The low carbonyl stretching frequency, implies significant electron delocalization by the pyridine systems on the carbonyl group (9). This also supports the quinonoid structures of these complexes as suggested in Scheme-I. Due to the presence of aromatic ring in PMDA-DP and PMDA-DPA, it is difficult to assign the absorption peak for pyridine ring. In DP or DPA, the IR absorption for pyridine ring appears at 1580 cm⁻¹. In PMDA-DP, only one peak appears at 1590 cm⁻¹ instead of two separate peaks, for pyridine and the aromatic ring. However, in PMDA-DPA, an asymmetric doublet appears at 1600 and 1590 cm⁻¹. The significantly elevated pyridine ring stretching frequency in PMDA-DP and PMDA-DPA can be satisfactorily rationalized in terms of the resonance stabilization, of these complexes which lead to an increase in the ring stretching frequency (9).

General Feature of PMDA-DP and PMDA-DPA Metal Complexes

Almost all the 3d transition metal chloride salts can coordinate readily with the PMDA-DP as well as with the PMDA-DPA in the heterogeneous phase. Fe(III) is the most reactive ion towards PMDA-DP and PMDA-DPA complexes and interestingly FeCl₃ can coordinate with PMDA-DP and PMDA-DPA even in the water medium in presence of a buffer. However, to achieve the maximum coordination of metal salts with these polymeric chelating complexes, the reactions were carried out in THF or THF-alcohol mixture (depending on the solubility of the metal salts) at 50^oC for 6 h.

The 3d transition metal complexes of PMDA-DP and PMDA-DPA exhibit characteristic color which endorses the coordination of metal ions with the PMDA-DP and PMDA-DPA complexes.

Table 1 compares the percentage of metal ions present in the different metal complexes of PMDA-DP and PMDA-DPA with the theoretical percentage of metal ions calculated on the assumption that each metal ion is coordinated to one DP or DPA unit. With respect to PMDA-DP or PMDA-DPA, the order of metal ion loading is Fe(III) > Cu(II) > Cr(III) > Ni(II) > Co(II). Among the metal ions, FeCl₃ is found to coordinate most efficiently (100%) with DP and DPA. With a typical metal ion, the order of complexation with the polymeric ligand is

Table - 1 : Characterization of metal complexes

Polymer	Color	% metal ion		Characteristic IR absorption		λ max. in reflectance spectra (nm)
		Found	Calculated	(cm) ⁻¹	H ₂ O	
PMDA-DP-Fe(III)	brown	11.9	11.07	--	1597, 1493	3387 680
PMDA-DPA-Fe(III)	brown	10.8	10.75	--	1580, 1500	3400 705
PMDA-DP-Cu(II)	green	11.3	13.33	--	1598, 1580, 1498	3454 488
PMDA-DPA-Cu(II)	green	12.1	12.92	1647	1584	-- 520
PMDA-DP-Cr(III)	skyblue	8.12	10.38	--	1597, 1493	3395 590
PMDA-DPA-Cr(III)	grey	9.31	10.08	1660	1580	-- 620
PMDA-DPA-Co(II)	blue	5.38	12.48	--	1580, 1497	3366 580
PMDA-DPA-Co(II)	blue	9.10	12.10	1660	1590, 1497	-- 575
PMDA-DP-Ni(II)	blue	8.61	12.44	--	1552, 1500	3390 532
PMDA-DPA-Ni(II)	pale-blue	9.32	12.06	1680	1590	-- 530

PMDA-DPA > PMDA-DP (when M = Fe, Cu, Co, Ni, Cr)

which is similar to that reported by Hendrickar et al.(10) for polystyrene bound DPA metal complexes.

Characteristic IR absorptions suggest the following features : (a) PMDA-DP-M complexes (where M = Fe, Cr, Cu, Ni and Co) do not exhibit any absorption band in their IR spectra in the frequency range 1600-1800 cm^{-1} for carbonyl or quinone group which is present in PMDA-DP at 1636 cm^{-1} . (b) All these PMDA-DP-M complexes exhibit a very broad IR absorption between 3350-3450 cm^{-1} . The IR spectra for PMDA-DPA-Fe(III) and PMDA-DP-M complexes are similar indicating absence of CO stretching frequency, and broadening of the absorption peaks in the frequency range 3300-3400 cm^{-1} and 1600 cm^{-1} . Other PMDA-DPA-M complexes (M = Cu, Ni, Co and Cr) exhibit the IR absorption at 1660 cm^{-1} for CO group as observed in their base polymer.

The structure of the repeating unit of the PMDA-DP is comparable to that of di-2-pyridyl ketone (DPK) where two dypidine rings are attached via CO group. Work on DPK-metal complexes by Osborne (11) and Feller (9,12) indicates the absence of carbonyl absorption band in certain metal complexes of DPK due to hydration or alcoholation across the ketone double bond, $>C=O + ROH \longrightarrow >C(OH)(OR)$. These authors also suggested that the complexes are N-N chelated.

Due to polymeric nature of PMDA-DP, it is likely to have a more strained structure which may facilitate hydration in presence of almost all transition metal complexes (unlike DPK). The IR spectra of these complexes suggest the hydration (broadening of the peak in the high frequency range). Further, it appears that like DPK, only N,N chelation is possible between metal ions with PMDA-DP. However, in PMDA-DPA (Scheme-I) two pyridine rings are attached with via nitrogen and is likely to form a less strained structure compared to PMDA-DP. Consequently, the tendency of hydration should be less in presence of metal ions which is confirmed by IR spectral data.

The diffuse reflectance spectra of either PMDA-DP or PMDA-DPA metal complexes exhibit broad intense bands in the visible region. The λ_{max} values for these complexes are tabulated in Table-1. Unfortunately, these data are not sufficient for the precise assignment of the transitions undergone during metal-nitrogen interaction. However, by comparing a few available transition data (13) for $[Cu(DP)]^{+2}$, $[Fe(DP)_2Cl_2]^{+}$, $[Cr(DP)NO_2]^{+2}$ with the present result, it may be tentatively suggested that the transitions probably are of d-d origin. Exact geometry of the various complexes anchored on the polymer chain remains an open issue as of now. Relevantly, with DPA which is not attached to a polymer support, tetrahedral complexes with covalently bound chlorides of formulation $M(DPA)Cl_2$ have been isolated (14-16) for M = Co, Fe, Cu. The proposed structures of these complexes (Scheme-I) also are consistent with this notion. However, situation with Cr^{3+}/Fe^{3+} complex where the metal may possess an octahedral geometry is somewhat obscure. It is unlikely that the metal ion already complexed will further coordinate with a second DPA/DP unit hanging from another polymer chain. This is because such a configuration will imply interchain crosslinking and will be difficult to occur during such heterophase reaction (10) (ligand

insoluble - MCl_3 soluble). Also the experimental percentage of metal ions does not agree with such a structure involving ZDP/DPA units. Tentatively, geometry in such cases is possibly maintained through necessary coordination by solvent species (H_2O , alcohol etc.) present in the reaction medium.

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