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Polymer anchored metal complexes

II. Thermal stability, dielectric and conductivity characteristics of 3d-metal complexes of pyromellitic dianhydride-bipyridyl and bipyridylamine polycondensates

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SUMMARY

Thermal stabilities of these polymers are influenced by the nature of the 3d-metal and their initial decomposition temperatures are between 230-290°C in general. The dielectric constant values are essentially independent of the applied frequency and at 10^{4} KHz reveal the trend :

$$\underset{(9.2)}{\text{PMDA-DP-Cr(III)}} > \underset{(8.7)}{\text{PMDA-DP-Fe(III)}} > \underset{(8.1)}{\text{PMDA-DP-Cu(II)}} > \underset{(8.0)}{\text{PMDA-DP}}$$

Values for dielectric loss (tan δ) for these polymers are low (1-4 x 10^{-2} at 10 KHz) and unlike the dielectric constant, are strongly dependent on the applied frequency. The d.c.- conductivities of the polymers are in the range 4.5 x 10^{-8} - 4.7 x 10^{-10} (ohm-cm)$^{-1}$ and depend on the metal ions :

$$Fe^{3+} > Cr^{3+} > Ni^{2+} > Cu^{2+}$$

INTRODUCTION

In an earlier publication (1) we described the preparation and tentative structures of the PMDA-DP/DPA based 3d metal complexes of Fe(III), Cr(III), Co(II), Ni(II) and Cu(II) ions. This article will highlight the thermal stability, dielectric and conductivity characteristics of the various 3d-metal anchored PMDA-DP/DPA polycondensates.

EXPERIMENTAL

Syntheses of PMDA-DP/DPA and the 3d metal complex (M = Fe(III), Cr(III), Ci(II), Ni(II) and Cu(II) have been described earlier (1).

Thermal stability

TGA and DTA were recorded on a Stanton Redcroft Analyzer under the following conditions : heating rate = 10°C/min; reference - Al_2O_3; temperature range 1000°C.

Dielectric measurements

D.C. and tan δ were obtained with a HP A 4192 Impedence Bridge. The samples were used as pellets prepared under 4ton pressure at 25°C. The pellets were silver painted and cured for 24 h before being used for measurements.

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Electrical conductivity

A cell containing a guard-ring and stainless steel electrodes was used with the special mounting device of Keithley-610C resistivity adaptor. The circuit consisted of HP 6144 precision power supply and a Keithley 610C solid state electrometer.

RESULTS AND DISCUSSION

Thermal Stability Characteristics

PMDA-DP and PMDA-DPA : Table 1 indicates the initial decomposition temperatures of both these complexes are almost same (~ 240°C). Beyond this temperature, these polymers suffer continuous weight loss till 100% weight loss at 450°C. The continuous weight loss for PMDA-DPA and PMDA-DP in the temperature range 240-350°C and 240-450°C is accompanied by exothermic DTA peaks at around 253°C and 320°C respectively. These probably represent oxidation via the carbonyl-link in either system (2).

PMDA-DP-M and PMDA-DPA-M Complexes : On incorporation of metal ions, the thermal stabilities of both the PMDA-DP and PMDA-DPA complexes are significantly improved (Table 1). Some general features may be noted: (i) with a typical metal ion, incorporated in either PMDA-DP or PMDA-DPA, the initial decomposition temperature does not vary very significantly, i.e., for Cu(II) complex 260°C, Fe(III) complex 265°C and for the Ni(II) complex 270°C; (ii) with either PMDA-DPA or PMDA-DP, the effect of different metal ions on the stability is in the order : $Fe^{+3} > Ni^{+2} > Cu^{+2}$ upto 40% decomposition in the former case and upto 25% decomposition for the PMDA-DP-M complex. (iii) Beyond this decomposition extent, the order becomes irregular but finally above 70% the limiting stability order again becomes similar in either system $Fe^{+3} > Cu^{+2} > Ni^{+2}$. (iv) All these complexes retain a significant amount of residue (~ 20-25%) even after heating beyond 1000°C. These residues presumably are the oxides of the metal ions ultimately formed in the heating process.

The following general factors seem to contribute to the overall stability of the various complexes (i) stabilities of the metal-ligand complexes themselves manifesting through the metal-ligand bond energy; (ii) the inherent thermal stabilities of the MCl_2 metal chlorides are also to be considered. Relevantly, Biswas and Maitra (3) reported that the stabilities of PVC-DMG-M (M = Fe^{3+}, Co^{2+}, N^{2+} and Cu^{2+}) correlate with the CFSE of these DMGM complexes.

Dielectric Characteristics

The d.c.-frequency data for PMDA-DP, PMDA-DPA and their metal-complexes are presented in Figures 1 and 2 respectively and suggest the following typical features : (i) The dielectric values for PMDA-DP and PMDA-DPA complexes fall between 7-8, which is in the range expected for polar polymers (4). Changing the frequency from 10^3 to 10^7 Hz alters the dielectric values by only 3%. (ii) On incorporation of metal ions in these complexes, the dielectric constant values are slightly enhanced in the above frequency range. (iii) At a particular frequency (ca,, 10 KHz) the dielectric constant values for the PMDA-DP-M complexes depend slightly on the nature of the metal ion in the order :

TABLE 1

Thermal stability behavior of metal containing polymers

Polymer	Temperature, (°C) corresponding to the (%) weight loss					
	Initial	10	20	40	65	80
PMDA-DP	238	265	280	330	410	460
PMDA-DPA	235	260	275	290	325	350
PMDA-DP-Fe(III)	280	310	340	375	600	---
PMDA-DPA-Fe(III)	290	330	360	405	575	---
PMDA-DP-Cu(II)	250	260	300	540	610	---
PMDA-DPA-Cu(II)	265	290	295	380	570	---
PMDA-DP-Ni(II)	255	295	320	400	550	---
PMDA-DPA-Ni(II)	280	320	350	400	500	---

TABLE 2

D.C. conductivity data

Polymer	d.c. conductivity $(\text{ohm-cm})^{-1}$
PMDA-DP	1.1×10^{-9}
PMDA-DPA	0.7×10^{-9}
PMDA-DP-Fe(III)	1.7×10^{-8}
PMDA-DPA-Fe(III)	4.5×10^{-8}
PMDA-DP-Cu(II)	5.0×10^{-10}
PMDA-DPA-Cu(II)	4.7×10^{-10}
PMDA-DP-Cr(III)	5.2×10^{-9}
PMDA-DPA-Cr(III)	7.2×10^{-9}
PMDA-DP-Ni(II)	3.2×10^{-9}
PMDA-DPA-Ni(II)	4.1×10^{-9}

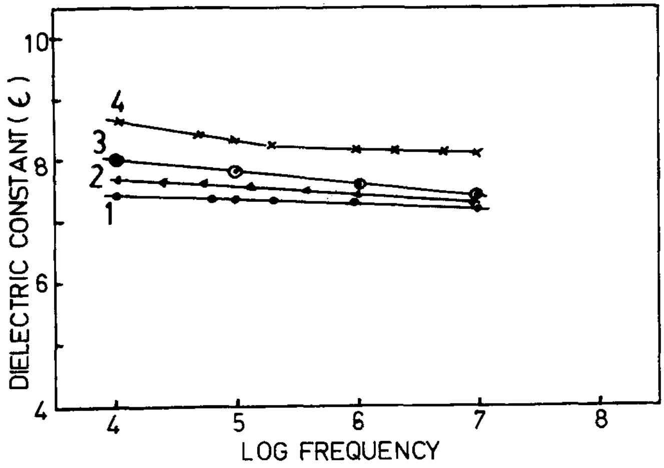

FIG.1 Dielectric constant vs frequency plots for (1) PMDA-DP; (2) PMDA-DP-Cu(II); (3) PMDA-DP-Fe(III); (4) PMDA-DP-Cr(III)

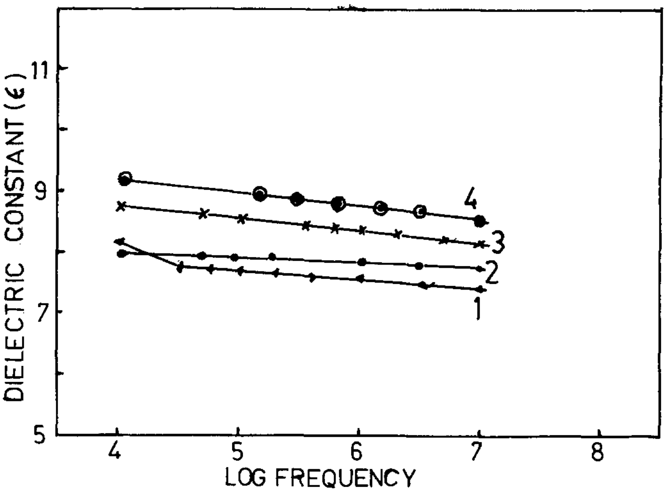

FIG.2 Dielectric constant vs frequency plots for (1) PMDA-DPA; (2) PMDA-DPA-Cr(II); (3) PMDA-DPA-Fe(III); (4) PMDA-DPA-Cr(III)

PMDA-DP-Cr(III) (9.2) $>$ PMDA-DP-Fe(III) (8.7) $>$ PMDA-DP-Cu(II) (8.1) $>$
PMDA-DP (8.0)

A similar trend is also noted for the PMDA-DPA-M complexes. (iv) These polymers exhibit rather low dielectric loss (tan δ: 1-4 x 10^{-2} at 10 KHz which however is strongly dependent on the applied frequency. Thus, a broad relaxation pattern is typically observed even though the dielectric constant is not drastically changed.

The dielectric polarization in the DPA/DP-metal complexes, is not evidently appreciable since the conjugation between the two pyridyl rings in DP or DPA is not favoured structurally. The system is best described as a rubi-conjugated (5) system which apparently should discourage manifestation of high dielectric constant and high conductivity.

The observed order in dielectric constant with the 3d-metal ions is significantly also the order in which the electronegativity (6) of the metal ions changes :

$$Cr^{3+}(1.56) < Fe^{3+}(1.64) < Co^{2+}(1.70) < Cu^{2+}(1.78).$$

This implies that the electronegativity difference between nitrogen and the metal decreases in the series leading to a decreased extent of dielectric polarization as actually observed.

The frequency dependence of the tan δ values in these complexes is marked and is reminiscent of the situation encountered by Biswas et al. in PVC-DMG-metal complex systems and other highly conjugated polymer systems based on carbazole-aromatic anhydride (7) anthracene-anhydride polycondensates ((2) and polysulfones (7). Evidently, the metal complexes possess a rigid structure where dipoles do not find sufficient time to reorient with the direction of the applied frequency of alternation resulting thereby in a broad dielectric relaxation (8).

Conductivity Characteristics

The d.c. conductivity values at 27°C (Table 2) for PMDA-DPA and PMDA-DP are in the order of $\sim 10^{-9}$ which is not affected very drastically on incorporation of the metal ions. The Fe^{3+} complexes of PMDA-DPA or PMDA-DP exhibit 6 to 12 times higher conductivity than these base polymers. The Cr^{3+} and Ni^{2+} complexes show 2 to 5 times higher conductivity than the base polymers. Interestingly, the Cu^{2+} complexes show lower conductivity values than the base polymer. The general trend in the conductivity value is :

$$Fe^{3+} > Cr^{3+} > Ni^{2+} > Cu^{2+}$$

As is well-known, high conductivity in organic solids arises from delocalization of π -electrons in highly conjugated structures or by the formation of C.T. complexes with appropriate donors and acceptors (5,9). Further, rubi-conjugated (5) polymer systems are known to consist of structures which are not completely conjugated and often contain herero atoms. In these types of polymers, delocalization of π-electrons is confined to small and segregated regions of the polymer leading to small (10^{-7} (ohm-cm)$^{-1}$ conductivity (5). PMDA-DP/DPA-M complexes appear to belong to the rubi-conjugated class of polymers, and low conductivity values seem reasonable.

Further, the observation that trivalent metal centers)Fe^{3+}, Cr^{3+}) are particularly effective in enhancing the conductivity value is interesting. A similar behavior has been reported by Bolto and Weiss (9) for the polymeric chloranil-o-phenylene diamine metal complexes where Fe^{3+}, Cr^{3+} induce much enhanced conductivity in the base polymer, due to (i) enhanced interchain cross-linking in the polymer induced by the metal ions and (ii) better acceptor property of the M^{3+} cations. In the present system, the possibility of interchain cross-linking involving nitrogen atoms of two different PMDA-DP/DPA chains is remote since the reactants are insoluble and the reaction is carried out in heterogeneous phase. Relevantly, Hendricker et al. (10) also confirmed this suggestion in their PS-DPA based metal complex systems. It seems therefore, enhanced conductivity in Fe^{3+}, Cr^{3+} containing PMDA-DP/DPA is likely to result from facile charge transfer interaction between N and the complexing metal ions.

Another factor affecting the conductivity is the stability of the metal chelates themselves and it is fairly well-established that the conductivity decreases as the stability increases (5). Reportedly (11, 12) the stability of Cu-chelates exceeds that of the Ni-chelates while the Cu-chelates has a lower conductivity than the Ni-chelate. Irving-William series of stability constants of metal chelates also indicates that the stability of 3d-metal complexes follows the order

$$Mn^{2+} < Fe^{2+} < Vo^{2+} < Ni^{2+} < Cu^{2+} < Zn^{2+}$$

which also confirms the highest stability of the Cu-chelates (13,14). In the light of these observations therefore, the trend that the PMDA-DP/DPA-Cu complex has the lowest conductivity noted with the present system, is fairly consistent.

CONCLUSION

Fe(III), Cr(III), Co(II), Ni(II) and Cu(II) complexes of polycondensates from pyromellitic dianhydride, dipyridyl / dipyridylamine polycondensates show interesting thermal stability dielectric and conductivity characteristics that depend on the nature of the metal ion moiety.

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