Polymer-Anchored Metal Complexes. III. Preparation, Structural, Thermal Stability, Dielectric, and Conductivity Characterization of Polycondensates from Cu(II)–1,10-Phenanthroline and Trimellitic Anhydride/Pyromellitic Dianhydride

MUKUL BISWAS* and **AMIT MUKHERJEE**

Department of Chemistry, Indian Institute of Technology, Kharagpur 721302, India

SYNOPSIS

Trimellitic anhydride and pyromellitic dianhydride have been polycondensed with Cu(II)–phenanthroline complex as a comonomer in the presence of anhydrous $ZnCl_2$ under selective conditions. Elemental diffuse reflectance and infrared spectroscopic and X-ray diffraction (XRD) analysis data of these polymers have been correlated with the tentative structure proposed for these polycondensates. Thermal stability and dielectric and conductivity characteristics of these polycondensates have been evaluated to understand the effect of the ligand and the anhydride moieties on these properties. Unlike the polymer-anchored 3d-metal complexes, these polycondensates fail to initiate the cationic polymerization of *N*-vinylcarbazole. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

The synthesis and structure–property correlation of metal-containing polymers constitute a topic of current global interest.[1] Among the various procedures usually adopted for the preparation of these metal-containing polymers, anchoring of metal complexes[2–7] on a preformed polymer matrix (polystyrene–divinylbenzene, partially chloromethylated) is the most widely used one. In contrast, it may be of interest to design metal-containing polymers where the metal complex may exist in the main-chain backbone of the polymer. In the course of our continuing research in this direction,[8,9,†] we describe now the preparation and structural characterization of polycondensates based on Cu(II)–1,10-phenanthroline dichloride (Cu–Phen), Cl_2 and trimellitic anhydride (TMA), and pyromellitic anhydride (PMDA) along with their thermal stability and dielectric and conductivity behavior. We also compare in this context the polymerization initiating activity of these metal complexes with that of polystyrene–divinylbenzene–dipyridyldiamine–metal complexes (PS–DVB–DPA–M) and polyvinyl chloride–dimethylglyoxime–metal complexes (PVC–DMG–M) prepared by Biswas and co-workers[3–7,10] in regard to the monomer *N*-vinylcarbazole (NVC). Furthermore, by comparing these properties with those of Cu(II)-bipyridyl–X_2–PMDA complexes,[8,9] we intend to show that these properties are variously influenced by (*i*) the nature of the ligand moiety with a fixed metal ion, Cu(II)–Phen–X_2, lower thermodynamic and thermal stability, and higher polarity than Cu(II)–BP–X_2 and (ii) the nature of the anhydride counterpart TMA, PMDA increasing bulkiness and functionality for polycondensation.

EXPERIMENTAL

1,10-Phenanthroline monohydrate (Phen, Aldrich), trimellitic anhydride (TMA, Fluka), and Cu(II) chloride dihydrate (Aldrich) were used as supplied. 1,2,4,5-Benzene tetracarboxylic dianhydride (PMDA, Fluka)

---

[*] To whom correspondence should be addressed.

[†] To be regarded as Parts I and II of this series.

Journal of Applied Polymer Science, Vol. 56, 501–508 (1995)
CCC 0021-8995/95/040501-08

Table I Cu(11)–Phen–Anhydride Copolycondensate

Complex/Polymer	Time (h)	Temp. (°C)	Color	Yield (%)	N% (Found)	Cu% (Found)	Diffuse Reflectance, $\lambda_{\max}$ (nm)
Cu–Phen	—	—	Green	—	—	—	751
Experiment 1							
(i) Cu–Phen–PMDA[a]	6	230 ± 10	Blue	63	6.3	7.04	756
(ii) Cu–Phen–PMDA[b]	6	230 ± 10	Blue	65			
(iii) Cu–Phen–PMDA[b]	6	230 ± 10	Blue	62			
Experiment 2							
Cu–Phen–TMA[a]	6	230 ± 10	Green	78	6.7	7.6	761

[a] The polymers were prepared with anhydride–copper complex–ZnCl$_2$ ratios of 1 : 1 : 4.2 for PMDA and 1 : 1 : 3.2 for TMA, respectively. Molar equivalent of ZnCl$_2$ was deliberately kept in excess of the other reactants to allow for its possible consumption in side reactions with the anhydrides. See Ref. 12.

[b] The polycondensation reaction carried out with 2 : 1 and 3 : 1 molar ratio of PMDA and Cu–Phen complex, respectively, showed variation in yield of ±3%.

was purified by sublimation under reduced pressure. *N*-vinyl carbazole (NVC, BASF) was used directly as supplied. Zinc chloride (Aldrich) was dried in a vacuum oven at 60°C for 24 h prior to use. The solvents used were of reagent quality.

Preparation of Cu–Phen–Anhydride Copolycondensates

The anhydride and the Cu–Phen complex[11] were ground together intimately in the presence of excess ZnCl$_2$ in the appropriate molar ratio (Table 1) and the solid mixtures were heated in a Pyrex container at 230 ± 10°C for 6 h under nitrogen atmosphere with frequent stirring. The resultant mixture was extracted in a Soxhlet apparatus for 4 h with the following solvents: water, tetrahydrofuran, chloroform, and ethanol. Product was then vacuum dried at 60°C for 24 h and subsequently characterized.

Polymerization-Initiating Activity of Polycondensates

An intimate mixture of the appropriate mole ratios of NVC and the metal catalysts was reacted under nitrogen in a Pyrex tube at 70°C for a definite period of time (Table II). Afterward the mass was extracted with toluene, and the solution was filtered off the insoluble catalyst and was precipitated in methanol. The polymer was filtered, washed with hot methanol[13] several times to wash out the monomer, and subsequently dried. Control runs were taken for all the systems.

CHARACTERIZATION

Infrared (IR) spectra were taken on a Perkin-Elmer model 889 spectrophotometer in KBr pellets. However, far-IR spectra were obtained in nujol mulls.

Table II Polymerization Initiating Activity of Metal–Polymer Complexes

System No.	Catalyst/Metal Complex	Temp. (°C)	Conversion (%) to PNVC In 10 min	Conversion (%) to PNVC In 30 min
1	PS-DVB-DPA-Fe(III)[a]	70	18	
2	PS-DVB-DPA-Co(II)[a]	70	8	
3	PS-DVB-DPA-Cu(II)[a]	70	11	
4	PVC–DMG–M(II)[b]	25	—	69.3–89.5
5	Cu–Phen–PMDA[a]	70		
6	Cu–Phen–TMA[a]	70		
7	Cu–Phen[a]	70		

[a] NVC: catalyst ratio was 1 : 6.

[b] Reproted in Ref. 7.

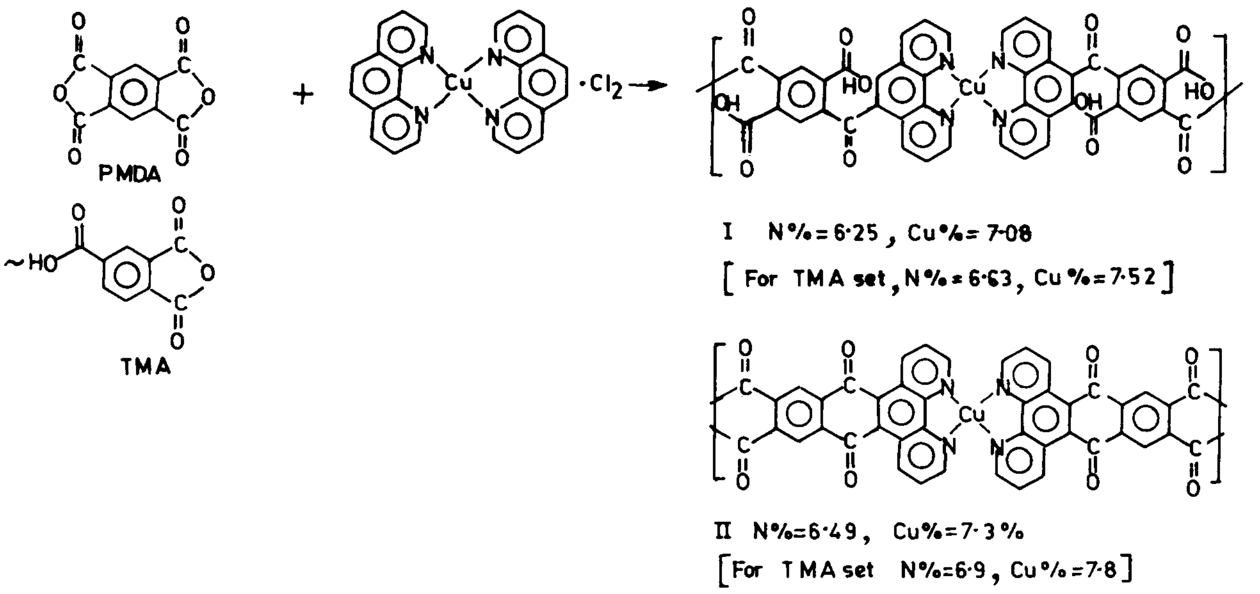

Figure 1 Tentative structure of Cu-Phen-PMDA copolycondensate in semiquiononic (I) and quiononic (II) forms.

Diffuse reflectance spectra were recorded on a Shimadzu UV-VIS-NIR MPC 3100 spectrophotometer using $BaSO_4$ as the reference. Elemental analysis of N and Cu were performed by standard procedures.

X-ray diffractograms of all the samples were recorded in a Phillips PW 1729/PM 8120 diffractometer with CuK radiation. A Gouy magnetic balance was used to determine the magnetic characteristics of the individual complex and all the polycondensates.

Thermogravimetry (TG) and differential thermal analysis (DTA) were performed on a Shimadzu DT-40 thermal analyzer in air at a heating rate of 15°C/min.

Direct current (DC) electrical conductivities were measured with a Kiethley-610C resistivity adapter. The samples were used as pellets prepared under 5.0–6.0 tons pressure at room temperature, silver painted, and cured for 24 h before being used for measurement.

The dielectric constant and loss factor (tan δ) were obtained with a HIOKI 3530 LCR fitted with

Table III Absorption Characteristics

Compound/Polymer	IR Absorption Bands with Probable Assignments (cm^{-1})
PMDA	926, 1235 [C—O str. vib. for —C—(CO)—O—(CO)—C—]; 762 (oop* bending of ring C—H); 1502 (skeletal C=C str.); 1771, 1854 (C=O str. vib. for cyclic anhydrides); 3011 (Ar C—H str.)
TMA	923, 1241 (C—O str. vib. for —C—(CO)—O—(CO)—C—); 772 (oop bending of ring C—H); 1499, 1575 (skeletal C=C str.); 1708 (C=O str. for aryl conjugated acids); 1784, 1850 (C=O str.), vib. for cyclic anhydrides; 3067 (aromatic C—H str., superimposed on broad O—H bands)
Cu-Phen	311 (Cu—N vib.); 779 (oop bending of ring C—H); 1339 (C—N str. vib.); 1585, 1508 (skeletal C=C str.); 3045 (Ar C—H str.)
Cu-Phen-PMDA	307 (Cu—N vib.); 789 (oop bending of ring (C—H); 1315 (C—N str. vib.); 1503, 1585 (skeletal C=C str.); 1699 (C=O str.) vib.); 3023 (Ar C=H str.); 3400 (O=H str. vib.)
Cu-Phen-TMA	308 (Cu—N vib.); 772 (oop bending of ring C—H); 1345 (C—N str. vib.); 1580, 1505 (skeletal C=C str. vib.); 1701 (C=O str. vib.); 3067 (Ar C—H str.); 3400 (O—H str. vib.)

* oop: out-of-plane.

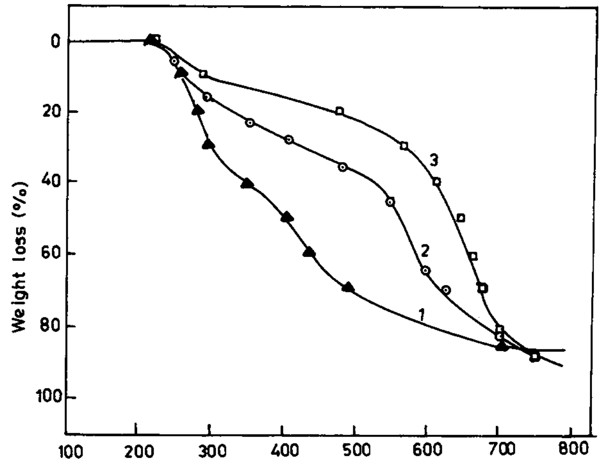

Figure 2 Comparative thermal stability of Cu-BP-PMDA (2), Cu-Phen-PMDA (1), and Cu-Phen-TMA (3).

a 9261 test fixture. The samples were used as pellets prepared under 5.0–6.0 tons pressure at room temperature. The pellets were silver painted and cured prior to measurement. The pellets were sandwiched under pressure between two copper plates having dimensions equal to the pellet. From the two copper plates two electrodes were taken in the form of coiled insulated wire and inserted in to the 9261 test fixture.

RESULTS AND DISCUSSION

All the polycondensates (Table I) possess characteristic color, are insoluble in all solvents including dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO), and are partly soluble in concentrated H_2SO_4. The elemental analysis data for Cu and N are consistent with the mode of reaction suggested (Fig. 1). The paramagnetic behavior of the polycondensates further implies that Cu maintains its +2 oxidation state in the polymers. All these polycondensates exhibit polycrystalline X-ray diffraction (XRD) pattern with some of the interplanar spacings matching with those of the corresponding anhydrides and the Cu-Phen complex moieties.

Diffuse Reflectance Spectra

All the polycondensates including the Cu-Phen complex exhibit distinct peaks in the 750–765-nm range (Table 1). The Cu(II) complexes with ligands such as tetradentate tetraamines and ethylene diamine show absorption in the region 470–560 nm and those with Schiff's bases around 500–760 nm. These complexes are reported to exhibit square-planar configurations.[14] However, with bulkier ligands, such as in the present case with 1,10-phenanthroline or 2,2′-bipyridine, square-planar configuration of the Cu complexes is reportedly[15,16] discouraged on steric grounds in favor of five or six coordinated configurations.[17] It is relevant to mention that $[Cu(Phen)_2CN_3]NO$ shows λ_m at about 740 nm.[18] Chlorine being a weaker ligand than CN in the spectrochemical series, it is expected that λ_{max} for the chlorides of Cu-Phen complex and its copolycondensates will exhibit a higher value compared to λ_{max} for the CN ligand.

Infrared Absorption Characteristics

The anhydride $-C-(CO)-O-(CO)-C-$ stretching bands,[19] exhibited in all the anhydrides, are absent or very weakly manifested in the polycondensates. This implies that this particular group has taken part in the polycondensation process leading to the suggested quinonic or semiquinonic structures (Fig. 1) as endorsed by the presence of strong carbonyl stretching (Table III). A distinct absorption also appears around 3400 cm^{-1} in all the polycondensates, including the thermally treated polymers. This is tentatively ascribed to $O-H$ stretching from the respective acid moieties present in TMA and likely to be formed in PMDA during reaction. Further, such $O-H$ groups may exist as intermolecularly hydrogen-bonded entities involving different polymer chains, leading eventually to a more thermally stable crosslinked structure. This appears to be one of the reasons why Cu-Phen-

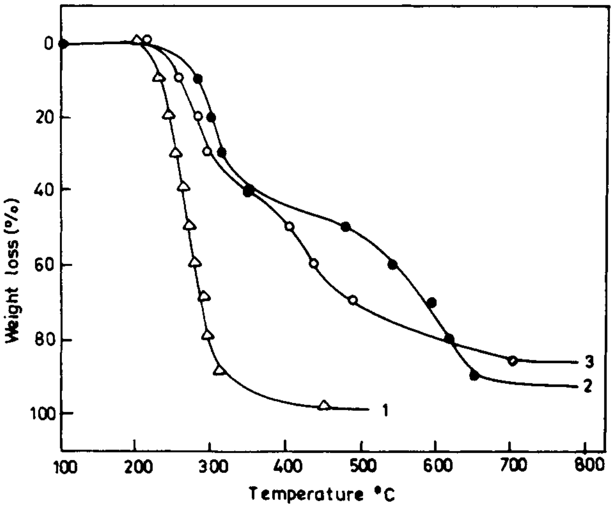

Figure 3 Comparative thermal stability of PMDA (1), Cu-Phen (2), and Cu-Phen-PMDA (3).

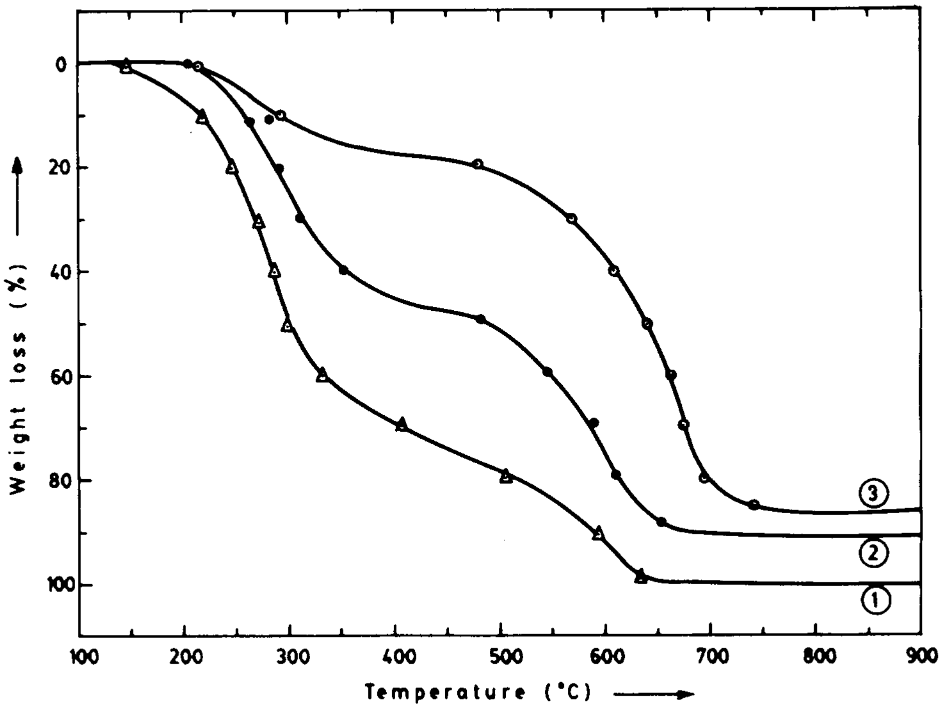

Figure 4 Comparative thermal stability of TMA (1), Cu-Phen (2), and Cu-Phen-TMA (3).

TMA is more stable thermally (Fig. 2) than Cu-Phen-PMDA, as discussed later in the text.

The polycondensates also show a peak of medium intensity in the region of 1315–1345 cm^{-1} due to C—N stretching of the phenanthroline ring (1339 cm^{-1}).

Absorptions due to metal-nitrogen vibration[20,21] are manifest in all the polymers (301–307 cm^{-1}) including the pure metal complex (311 cm^{-1}).

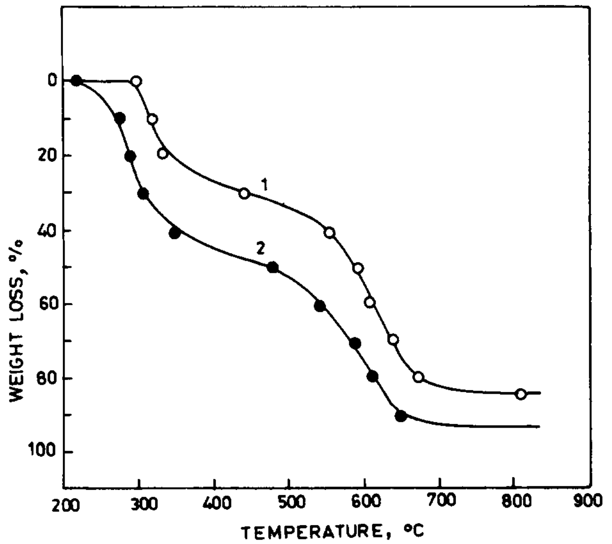

Figure 5 Comparative thermal stability of Cu-BP (1) and Cu-Phen (2).

Thermal Stability

The thermograms of Cu-Phen-TMA/PMDA polycondensate reveal order in stability as follows: Cu-Phen-TMA > Cu-Phen-PMDA (Fig. 2). The relative thermal stabilities of PMDA, Cu-Phen, and Cu-Phen-PMDA are in the order PMDA < Cu-Phen-PMDA < Cu-Phen (Fig. 3), while the corresponding trend for the TMA set is TMA < Cu-Phen < Cu-Phen-TMA (Fig. 4).

The relative stability order of the these polymers is perhaps expected, since structurally TMA will face less steric hindrance in forming a polycondensate than PMDA. Restricted chain growth in the case of PMDA implies lesser thermal stability. In addition, interchain crosslink formation will also be restricted in the bulkier anhydrides, leading to decreased stability of the polymer.

With a fixed metal ion and an anhydride (PMDA), the ligand also appears to influence the stability: Cu-BP-PMDA > Cu-Phen-PMDA (Fig. 2). The relative stability of these polycondensates should be expected to be substantially influenced by the thermodynamic stability of the individual reactants, especially of the metal complexes. This contention is fully endorsed by the stability constants of the Cu-BP ($\log K = 5.75$) and Cu-Phen ($\log K = 4.54$) complexes reported by Condike and Martell,[22] indicating the order Cu-BP > Cu-Phen, which is the same as their thermal stability order (Fig. 5).

Table IV DTA Characteristic Peaks

Compound/ Copolycondensate	Peak Temperature (°C)	
	Endothermic	Exothermic
PMDA	215	
	250	
	275	
TMA	170	
	220	
	270	375
Cu–Phen	105	
	305	
	320	
		345
		420
		550
Cu–Phen–PMDA		260
		275
		335
		355
		420
Cu–Phen–TMA		235–440
		655

DTA Characteristics

Table IV suggests the following features: (i) All the anhydrides, as well as the Cu–Phen–Cl_2 complex, exhibit endothermic peaks in the initial decomposition regions. However, the polycondensates show strong exothermic peaks as soon as they start decomposing; evidently new bond formation is indicated. (ii) The exothermic peak at about 345°C for Cu–Phen is detected in all the polycondensates around 345–395°C. (iii) The peaks at 260°C for Cu–Phen–PMDA (weight loss ~ 13%) and at around 235–440°C (broad) for Cu–Phen–TMA (weight loss ~ 21%) are probably due to loss of carbonyl groups as evident from IR and electron spectroscopy chemical analysis (ESCA) observations discussed below. However, a quantitative correlation of the weight loss with the carbonyl group loss, while tempting, is not justified in view of the tentative nature of the proposed structure. (iv) The exothermic peak around 335–395°C noted for Cu–Phen–PMDA and Cu–Phen–TMA (somewhat broad) appears to match with the corresponding Cu–Phen complex. These may be due to some common oxidative degradation processes involving the phenanthroline moiety. (v) The final exotherms at temperature above 450°C corresponding to significant weight losses (~ 40%) and observed in all the polycondensates evidently represent oxidative degradation of the polymer matrix as a whole.

In accordance with the above discussion, the IR spectra of the thermally degraded polycondensates after exposure at 250–270°C for 20 min confirmed the drastic reduction of the carbonyl stretching frequency in all cases. At the same time residual carbonyl frequency tends to shift to the higher frequency side (1730 cm^{-1} for Cu–Phen–TMA, 1744 cm^{-1} for Cu–Phen–PMDA), possibly due to degradation of the conjugated structure of the polycondensate. Comparative ESCA analysis of Cu–Phen–PMDA (at ambient temperature and at 250–270°C) also indicated a sharp reduction in the oxygen peak.[23] Significantly here, too, complete loss of oxygen is not observed.

Dielectric Properties

Table V presents the dielectric constant and dielectric loss (tan δ) values of Cu–Phen, Cu–Phen–PMDA, Cu–Phen–TMA, Cu–BP, and Cu–BP–PMDA. The following features are of interest: (i) The variations in the dielectric constant values for Cu–Phen–PMDA and Cu–Phen–TMA at any particular frequency are not significantly different and reveal only a 10% decrease, corresponding to a frequency change from 10^3 Hz (average dielectric constant: 32) to 10^6 Hz (average dielectric constant: 27.8). (ii) The dielectric loss is low for all the polycondensates and is practically independent of

Table V Dielectric Constant and Dielectric Loss Values[a] of Metal–Polymer Complexes

Frequency, × 10^3 (Hz)	Cu–Phen–PMDA	Cu–Phen–TMA	Cu–BP–PMDA[b]	Cu–Phen	Cu–BP
1	30.2 (0.03)	30.93 (0.04)	—	53.27	15.52
10	29.92 (0.02)	29.76 (0.01)	7.75 (0.110)	35.28 (0.90)	14.31 (0.08)
100	28.47 (0.05)	28.92 (0.04)	7.59 (0.01)	28.28 (0.21)	13.20 (0.06)
1000	26.81 (0.04)	27.71 (0.04)	7.41 (0.006)	25.17 (0.07)	12.38 (0.04)

[a] Numbers in parentheses.

[b] From Ref. 9.

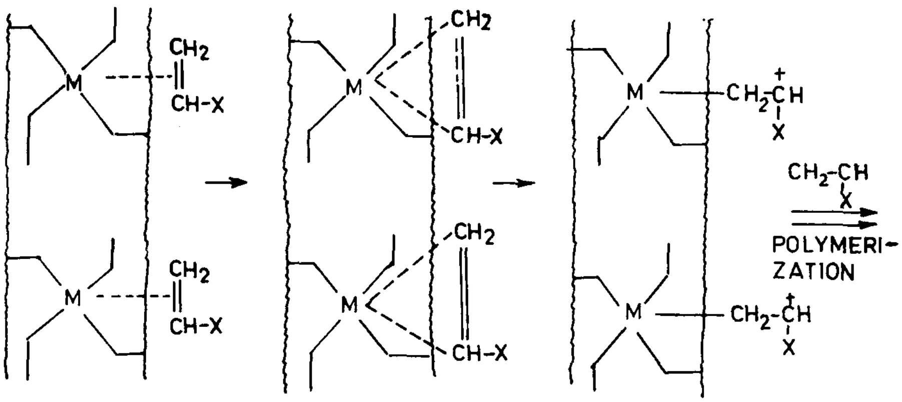

Figure 6 Mechanism of polymerization of NVC by metal-anchored polymeric systems.

the applied frequency. (iii) Interestingly, Cu–Phen exhibits comparatively higher dielectric constant values in the range 10^3–10^6 Hz compared to Cu–Phen–PMDA/Cu–Phen–TMA. The usual fall in the dielectric constant with frequency is common for all the polymers. (iv) Incorporation of PMDA or TMA moiety to Cu–Phen lowers the dielectric constant values. (v) A change of the ligand, e.g., Cu–Phen to Cu–BP, lowers the dielectric constant as well as the loss parameter.

The broad pattern of dielectric constant and tan δ variation with frequency is typical of other metal-bearing nitrogen heterocyclic copolycondensates[8,9] and presumably is related to interfacial polarization.[24] The difference in the higher dielectric parameter for Cu–Phen compared to Cu–BP is consistent with the higher polarity of the ligand moiety. In fact Phen is certainly more polar (μ = 3.65D) compared to BP (μ = 0.69D).[25]

Conductivity

The DC conductivity values of Cu–Phen anhydride complexes are in the order: Cu–Phen–PMDA (3.4×10^{-10} Ω^{-1} cm^{-1}) > Cu–Phen–TMA (2.5×10^{-12} Ω^{-1} cm^{-1}), respectively, which is not particularly different from that exhibited by Cu–BP–PMDA,[9] 5×10^{-10} Ω^{-1} cm^{-1}. Of relevance is the fact that Phen reportedly exhibits conductivity in the range 10^{-13}–10^{-15} Ω^{-1} cm^{-1}. Doping with iodine for 2 h did not improve the conductivity significantly.

Polymerization-Initiating Activity of Metal–Polymer Complexes

In earlier publications Biswas and Moitra[5,7] demonstrated that the 3d-metal complexes of DMG can initiate the solution polymerization of NVC. In view of this, it was of interest to find out the efficiency of PS–DVB anchored 3d-DPA metal complexes reported by Mukherjee and Biswas[3,4] and of the copolycondensates Cu–Phen–anhydride reported now. It is commonly believed with the 3d-complexes, NVC polymerization is initiated through a π complex between the 3d-metal ion center and the vinylic double bond, with the subsequent formation of a carbocationic center[27–31] (Fig. 6).

The failure of metal-bearing polycondensates (Table II) to initiate such polymerization may be due to steric restrictions faced by the bulky NVC moiety inhibiting access to the metal centers which remain coordinated and surrounded by two other bulkier groups like Phen. It is relevant to mention in this respect that due to steric reasons Phen does not form the tris(hydroxymethyl)aminomethane (Tris–) metal complexes.[16]

In support of this contention, the pure Phen–metal complexes revealed no initiating activity toward NVC polymerization. Moreover, as will be disclosed in a future publication, ESCA analysis will also reveal the environment surrounding the metal of the polycondensates to be almost similar to Phen–Metal complexes.

In regard to polymer-anchored metal complexes such as PS–DVB–DPA–M, the NVC moiety may have access to the three-dimensional metal centers. The metal ions are hanging from the polymer chains coordinated by a DPA moiety, the other coordination sites being occupied by smaller solvent molecules. Therefore, NVC moiety can interact with the centers without facing the steric constraints, as in the case of the polycondensates.

CONCLUSION

Thermal stability and dielectric properties of metal-bearing polycondensates with aromatic anhydrides

(TMA and PMDA) and the metal-complexed ligand (Cu–BP, Cu–Phen) depend on the nature of the anhydride moiety and the ligand moiety with a particular metal ion. The conductivity values, however, do not change significantly. The polycondensates do not show any polymerization-initiating activity, in contrast to the other metal complex–anchored polymeric systems.

Thanks are due to the authorities of IIT Kharagpur for the use of their facilities.

REFERENCES

1. M. Biswas and A. Mukherjee, *Adv. Polym. Sci.*, **114,** 89 (1994).
2. M. Biswas and A. Mukherjee, *Ind. J. Tech.*, **31,** 393 (1993).
3. A. Mukherjee and M. Biswas, *J. Appl. Polym. Sci.*, **46,** 1453 (1992).
4. A. Mukherjee and M. Biswas, *J. Appl. Polym. Sci.*, **50,** 1485 (1993).
5. M. Biswas and S. Moitra, *J. Appl. Polym. Sci.*, **38,** 1243 (1989).
6. M. Biswas and S. Moitra, *J. Polym. Mater.*, **7,** 89 (1990).
7. M. Biswas, S. Moitra, and T. Uryu, *Polym. Commun.*, **30,** 225 (1989).
8. M. Biswas and A. Majumder, *Polym. Bull.*, **26,** 145 (1991).
9. M. Biswas and A. Majumder, *Polym. Bull.*, **26,** 151 (1991).
10. M. Biswas, S. Moitra, A. S. Brar, and R. G. Mendritta, *Polym. Commun.*, **31,** 237 (1990).
11. C. M. Harris, T. N. Lockyer, and H. Waterman, *Nature,* **192,** 424 (1961).
12. B. S. Furniss, A. J. Hannaford, P. W. G. Smith, and A. J. Tatchell (Eds.), *Vogels Textbook of Practical Organic Chemistry,* 5th ed, ELBS, Longman, UK, 1989.
13. L. P. Ellinger, *Polymer,* **26,** 22 (1985).
14. A. B. P. Lever, *Inorganic Electronic Spectroscopy,* 2nd ed., Elsevier, New York, 1984.
15. B. J. Hathway and D. E. Billing, *Coord. Chem. Rev.*, **5,** 143 (1970).
16. E. D. McKenzie, *Coord. Chem. Rev.*, **6,** 187 (1971).
17. O. P. Anderson, *Inorg. Chem.*, **14,** 730 (1975).
18. M. Wicholas and T. Wolford, *Inorg. Chem.*, **13,** 316 (1974).
19. R. M. Silverstein, G. C. Bassler, and T. C. Morril, *Spectrophotometric Identification of Organic Compounds,* 5th ed., J Wiley, New York, 1991.
20. R. E. Wilde, T. K. K. Srinivasan, and S. N. Ghosh, *J. Inorg. Nucl. Chem.*, **35,** 1017 (1973).
21. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Co-ordination Compounds,* 3rd ed., Wiley, New York, 1978.
22. G. F. Condike and A. E. Martell, *J. Inorg. Nucl. Chem.*, **31,** 2455 (1969).
23. M. Biswas, A. Mukherjee, T. B. Ghosh, to appear.
24. R. Rosen and H. A. Pohl, *J. Polym. Sci.*, **A-1**(4), 1135 (1966).
25. C. W. N. Cumper, R. F. A. Ginman, and A. I. Vogel, *J. Chem. Soc.*, **31,** 2455 (1969).
26. *Chem. Abstr.*, Subject Index, **65,** 8737a (1966).
27. S. Tajuke, K. Nakagawa, and S. Okamura, *J. Polym. Sci. B.* **3,** 923 (1965).
28. S. Tajuke, T. Tjoa, and S. Okamura, *J. Polym. Sci.*, **A-1**(5), 1911 (1967).
29. S. Tajuke, M. Asai, S. Ikeda, and S. Okamura, *J. Polym. Sci. B,* **5,** 453 (1967).
30. H. Scott, G. Miller, and M. Labes, *Tetrahedr. Lett.*, **17,** 1073 (1963).
31. L. P. Ellinger, *Advances in Macromolecular Chemistry,* Vol 1, Academic, New York, 1968.

Received July 12, 1994
Accepted August 26, 1994