

Synthesis and Some Properties of PVC-Bound Dimethylglyoxime Complexes of Co(II), Ni(II), and Cu(II)

MUKUL BISWAS and SUBRATA MOITRA, *Department of
Chemistry, Indian Institute of Technology, Kharagpur 721302, India*

Synopsis

Poly(vinyl chloride) (PVC) has been reacted with dimethylglyoxime (DMG) in THF to form the PVC-DMG complex, which has been characterized by spectroscopic and elemental analyses. The latter indicate that there is one DMG moiety anchored on the PVC chain by displacing every 12th Cl atom in the chain. PVC-DMG has further been reacted with alcoholic solutions of Co(II), Ni(II), and Cu(II) to form the intensely colored PVC-DMG-M(II) complexes. The structures of these complexes have been analyzed by elemental and IR spectral analyses. The overall thermal stability of PVC-DMG-M(II) increases in the order: PVC < PVC-DMG-Cu(II) < PVC-DMG-Ni(II) < PVC-DMG-Co(II). The electrical conductivities are also significantly enhanced in the same order. The permittivities of these complexes are high relative to PVC at low frequency falling gradually with increasing frequency and the dielectric loss-frequency behavior is very broad.

INTRODUCTION

Synthesis of polymer-bound chelating ligands and the selective chelation of specific metal ions is a field of active research.¹ A number of ligands including polydentate amines, crown-ethers, porphyrine, phosphines, bipyridines, and naphthyridines have been bound with mainly polystyrene and polystyrene-divinylbenzene copolymers.²⁻⁶ These studies are mostly concerned with ion-binding and catalytic⁷ aspects. Very little information appears to exist as to whether, and to what extent, such metal ion complexation can influence the properties of the macromolecule. Recently, we were able to modify⁸⁻¹⁰ poly(vinyl chloride) (PVC) by introducing aromatic and heterocyclic moieties through halogen displacement reaction. PVC, thus modified, showed improved overall thermal stability and interesting changes in dielectric property relative to unmodified PVC. The facile chlorine displacement from PVC indicated the possibility of easy anchoring of chelating ligands to PVC matrix and the subsequent synthesis of immobilized transition metal complexes therefrom. In view of the paucity of any information on PVC in this line, we undertook the synthesis of PVC-bound dimethylglyoxime complex (PVC-DMG) and the corresponding Cu(II), Ni(II), and Co(II) complexes of PVC-DMG. This article will describe the synthetic procedure adopted (Fig. 1) and highlight the structural characteristics of PVC-DMG and of PVC-DMG-M(II). In addition, the effect of metal ion complexation on the bulk properties of the base polymer—such as thermal stability, conductivity, and dielectric behavior—will also be discussed.

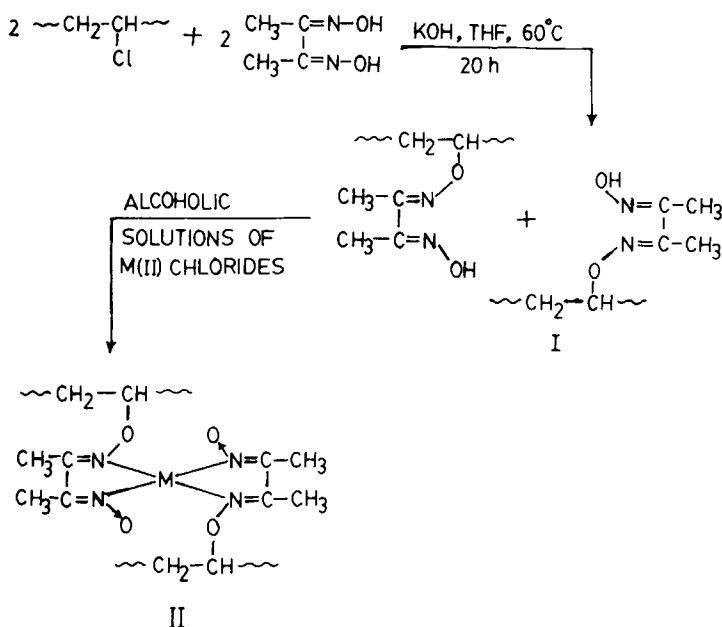


Fig. 1. Reaction scheme for synthesis of PVC-DMG(I) and PVC-DMG-M(II).

EXPERIMENTAL

Material

Commercial PVC ($[\eta] = 1.46$ in DMF) was reprecipitated from THF solution by alcohol several times and finally dried under vacuum at room temperature for 2 days. AR grade $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ were dried in vacuum overnight. DMG (E. Merck) was used as received. All other solvents were of analytical grade and freshly distilled before use.

Synthesis of PVC-DMG Complex

In a 100-mL two-necked Pyrex flask equipped with a stirrer, a condenser, and a nitrogen inlet tube, one gram of PVC was dissolved in 25 mL THF to which 0.5 g of KOH and an excess (3–4 g) of DMG were added. The reaction was continued for (20–60 h) at 60°C , when the color of the reacting solution changed to straw yellow. Addition of methanol to this solution gave a light yellow precipitate. This was filtered and the residue was repeatedly extracted with hot alcohol till the extract did not produce any coloration with a Ni(II) solution (in rectified spirit) confirming complete removal of any unreacted DMG. The light yellow precipitate was reprecipitated several times from THF solution by methanol and finally dried *in vacuo* and subsequently characterized as PVC-DMG.

Synthesis of PVC-DMG-M(II) Complexes

PVC-DMG-M(II) complexes were obtained by adding dropwise different transition metal salt solutions (1% wt/vol in rectified spirit) to 0.25% (wt/vol)

TABLE I
Synthesis and Characterization of PVC-DMG and PVC-DMG-M(II)

Synthesis			Characterization				
Complex	Temp (°C)	Time (h)	Yield (%)	Color	$[\eta]^a$ (dL/g)	M(II) (%)	Solubility characteristics
PVC-DMG	60	20	73	Light	1.49	—	Soluble in THF, C ₆ H ₆ , C ₆ H ₅ CH ₃ , DMF, CHCl ₃
	60	60	75	Yellow			
PVC-DMG-Ni(II)	30	20	41	Rose	1.65	33.7	Very slightly soluble in warm THF, fairly soluble in DMF, insoluble in C ₆ H ₆ , C ₆ H ₅ CH ₃ , CHCl ₃
	60	10	54	Red			
	60	20	68				
PVC-DMG-Co(II)	60	20	62	Brown	1.64	10.6	
PVC-DMG-Cu(II)	60	20	64	Green	1.57	13.4	

^aIn DMF in which all complexes are fairly soluble.

solution of PVC-DMG in THF, till the supernatant clear solution did not produce any colored precipitate. The intensely colored precipitates were filtered, washed with excess of rectified spirit, then with THF to remove any unreacted PVC-DMG, and subsequently dried at 40°C for 4h to constant weight. The relevant synthesis and characterization data for PVC-DMG and PVC-DMG-M(II) complexes are presented in Tables I and II.

Characterization

Elemental Analyses

C, H, and N were estimated in a Heraus standard combustion apparatus. Cl was determined quantitatively gravimetrically as AgCl after fusion with sodium peroxide.

Spectroscopy

Infrared (IR) spectra were recorded on Perkin-Elmer 598 infrared spectrophotometer in KBr pellets. Absorption spectra were obtained on a Cary 17D recording spectrophotometer.

Intrinsic Viscosity

Viscosity measurements were done with 0.1% solutions of PVC-DMG-M(II) in DMF at 25°C using an Ubbelohde viscometer.

Dielectric Measurements

Permittivity (ϵ) and dielectric loss ($\tan \delta$) were recorded at different frequencies on a 4192A LP Impedance 5 Hz-13 MHz Hewlett Packard instrument with silver coated pellets of PVC-DMG-M(II) complexes. The pellets were prepared under 3-4 ton pressure (5 min).

TABLE II
 Absorption and IR Spectra of PVC-DMG and PVC-DMG-M(II)

Complex	Electronic absorption peaks (nm)	IR (cm ⁻¹)	Assignments
PVC-DMG	—	(i) 3300 (ii) 2900 (iii) 1625 (iv) 1420 (v) 1350 (vi) 1250 (vii) 975 (viii) 610	O—H stretching of oxime C—H stretching of —CH ₂ — C=N— stretching of oxime C—H bending of —CH ₂ — C—H bending of —CH ₃ C—O stretching N—O stretching C—Cl stretching
PVC-DMG-Ni(II)	415 [Ni(II)]	(i) 3150 (very broad) (ii) 1650 (iii) 1400 (broad) (iv) 1250 (v) 975 and 900 (vi) 705 (vii) 475	C—H stretching of —CH ₂ — C=N stretching C—H bending of —CH ₂ — C—O stretching —CH ₃ rocking and N—O stretching C—Cl stretching N—Ni stretching
PVC-DMG-Co(II)	272 [Co(II)]	(i) 2900 (ii) 1620 (broad) (iii) 1425 (iv) 1380 (v) 1250 (vi) 975 and 1090 (vii) 470	C—H stretching of —CH ₂ — C=N stretching C—H bending of —CH ₂ — C—H bending of —CH ₃ C—O stretching —CH ₃ rocking and N—O stretching N—Co stretching
PVC-DMG-Cu(II)	515 [Cu(II)]	(i) 3125 (ii) 1625 (iii) 1380 (iv) 1210 (v) 1100 and 950 (vi) 700 (vii) 480	C—H stretching of —CH ₂ — C=N stretching C—H bending of —CH ₃ C—O stretching —CH ₃ rocking and N—O stretching C—Cl stretching N—Cu stretching

Electrical Conductivity

Electrical conductivities were obtained by using a cell containing guard ring and electrodes made of stainless steel disc. The special mounting device of Keithley 6105 resistivity adaptor was used for the measurements. The circuit consisted of HP 6144 precision power supply and Keithley 610C solid state electrometer.

Thermogravimetric Analysis

TG analyses were carried out on an Ulvac Sinkuriko analyzer, Model TGD-5000 (heating rate = 5°C/min; temperature range 0–1500°C in air).

RESULTS AND DISCUSSION**Synthesis of PVC-DMG and PVC-DMG-M(II)**

Table I presents the relevant data on the synthesis and some general properties of PVC-DMG and the corresponding complexes of Co(II), Ni(II), and Cu(II). PVC-DMG was isolated as a pale yellow solid after several reprecipitations from THF solution by methanol. Since PVC is also soluble in THF, it may be likely that PVC-DMG, thus isolated, may contain some unreacted PVC. However, we used an excess of DMG for complexation and varied the reaction time sufficiently widely (20–60 h, Table I) and realized a constant yield. So, we assume that, under these conditions, there would not be any unreacted PVC, along with PVC-DMG.

The elemental analysis data for PVC-DMG are C = 42.12 (51.06), H = 5.22 (6.38), and N = 2.23 (19.86), the values in parenthesis being the theoretical data calculated on the assumption that the DMG units react with every Cl atom in a PVC chain. Further, the theoretical percentage of oxygen in PVC-DMG(I) should be 24.67, while the same on the basis of the experimental nitrogen content should be 2.55. It follows then that the residual Cl in I should be 47.89%. Calculations on the basis of these experimental data further indicate that, on an average, one DMG unit displaces every 12th Cl atom in a PVC chain, which also suggests the elemental Cl percentage to be 47.13. Experimental Cl percentage in I is 46.32 which endorses the above contention concerning I.

The reaction of PVC-DMG with Co(II), Ni(II), and Cu(II) ions proceeds smoothly with the formation of precipitates with characteristic colors (Table I). The yields depend on time and temperature and, as revealed by the data for PVC-DMG-M(II) system, reached a limiting value at 60 h, at 60°C.

The decreased solubility of PVC-DMG-M(II) is consistent with the formation of metal-ion-incorporated crosslinked PVC-DMG moiety(II). The higher intrinsic viscosity values of PVC-DMG-M(II) relative to PVC-DMG also indicates such a possibility.

IR Absorption Spectra

The formation of PVC-DMG(I) is also endorsed by an analysis of IR absorptions (Table II). The formation of $\begin{array}{c} | \\ -\text{C}-\text{O} \\ | \end{array}$ linkage, and the presence of C—CH₃ and N—O moieties in PVC-DMG of structure I are confirmed by the expected absorptions. Significantly, O—H stretching at 3300 cm⁻¹ endorses the presence of a free O—H moiety as in I.¹¹

In PVC-DMG-M(II) complexes, the IR absorptions are in agreement with the tentative structure II. In all these complexes, the absorption at 3300 cm⁻¹ due to the free OH moiety is absent which is expected if it is involved in

complexation with the metals as suggested in II. The presence of N-metal stretching frequencies in all the PVC-DMG-M(II) complexes also endorses incorporation of M(II) in PVC-DMG as in II.

Electronic Absorption Spectra

All the PVC-DMG-M(II) complexes exhibit characteristic electronic absorption maxima (Table II), which agree with the reported absorptions for the respective metal ions.¹²

Structure of PVC-DMG-M(II)

The tentative structures for PVC-DMG(I) and PVC-DMG-M(II) [II] appear to be consistent with the various experimental findings on I and II. Two different PVC-DMG chains have been supposed to participate in complexation with M(II) as in II, which implies a crosslinked structure as endorsed by the higher intrinsic viscosity values for PVC-DMG-M(II). The

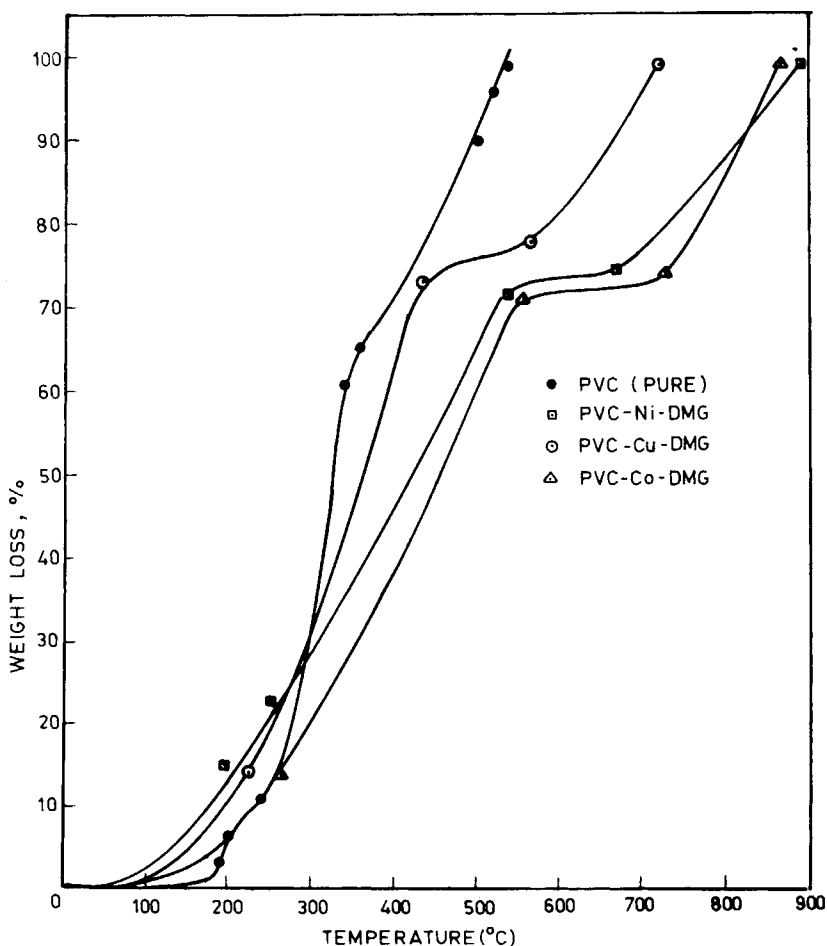


Fig. 2. Weight loss-temperature curves for PVC-DMG-M(II).

TABLE III
Crystal Field Stabilization Energies of Co(II), Ni(II), and Cu(II)
in Square Planar Field

Metal ion	Outer electronic configuration	CFSE (Δ_{sq})
Co(II)	$3d^7$	-1.8
Ni(II)	$3d^8$	-1.2
Cu(II)	$3d^9$	-0.6

alternate possibility in which M(II) might complex with the DMG units hanging from a single PVC chain on every 12th $-\text{CH}_2-\text{CH}-$ unit would lead to a strained structure and possibly may be ruled out.

Thermal Stability

Figure 2 presents the thermograms of the various PVC-DMG-M(II) complexes along with the one for unmodified PVC. The initial decomposition temperature of unmodified PVC (ca. 200°C) is somewhat lowered in the modified PVC-DMG-M(II). However, it is possible that this small weight loss (3-10%) is due to loss of solvents/water from the modified matrix. Beyond ca. 250-300°C (12-20% weight loss), PVC-DMG-M(II) complexes start gaining in stability in the order: PVC < PVC-DMG-Cu(II) < PVC-DMG-Ni(II) < PVC-DMG-Co(II).

This trend is not parallel to the trend noted for the incorporation of metal ions in these complexes. On the other hand, the crystal field stabilization energies of the DMG-M(II) complexes show a parallel variation, as shown in Table III. This feature may be interpreted to imply that interchain crosslinking, as suggested in Figure 1, is not the main factor responsible for improvement of the thermal stability of PVC. The inherent stability of the metal complexes, anchored upon the PVC chains, also contributes to the thermal stability because the applied thermal energy will be involved in rupturing the polymer-ligand-metal bonds.

The interchain crosslinking postulated in Figure 1 for II is believed to be partly responsible for the decreased solubility of PVC-DMG-M(II) in usual solvents for PVC (Table I). The $[\eta]$ values for PVC-DMG-M(II) are somewhat larger than that for unmodified PVC. This supports the contention that PVC-DMG-M(II) is more crosslinked than unmodified PVC.

Electrical Conductivity

Table IV presents the electrical conductivity data of the PVC-DMG-M(II) complexes. Interestingly, conductivities appreciably increase relative to PVC in the order PVC < PVC-DMG-Cu(II) < PVC-DMG-Ni(II) < PVC-DMG-Co(II). The enhancement in the conductivity is readily ascribable to the varying extents of charge transfer¹³ between the $3d$ metal ion centers and the electron-rich heteroatoms in DMG. Apparently, ease of such charge transfer will depend upon the availability of $3d$ vacant orbitals which follows the order $\text{Co}^{+2} (3d^7) > \text{Ni}^{+2} (3d^8) > \text{Cu}^{+2} (3d^9)$.

TABLE IV
 Electrical Conductivity of PVC-DMG-M(II)

Polymer	Diameter (mm)	Thickness (mm)	Voltage (V)	Current (A)	Electrical conductivity ($\Omega^{-1} \text{ cm}^{-1}$)
PVC (pure)	11.6	1.75	20	0.14×10^{-8}	1.68×10^{-11}
PVC-DMG-Cu	11.8	1.95	20	6.1×10^{-8}	5.44×10^{-10}
PVC-DMG-Ni	11.65	1.55	20	0.6×10^{-6}	4.36×10^{-9}
PVC-DMG-Co	11.75	2.00	20	9.0×10^{-4}	8.30×10^{-6}

Dielectric Characteristics

Figure 3 reveals that at low frequency (10 kHz–100 Hz) the permittivities obey the trend PVC \ll PVC-DMG-Cu(II) \ll PVC-DMG-Ni(II) \ll PVC-DMG-Co(II). The permittivities fall monotonously with the applied frequency.¹⁴

The dielectric loss ($\tan \delta$) parameter also falls steadily with the applied frequency. However, PVC-DMG-Co(II) exhibits a comparatively large fall in $\tan \delta$ from 2.5 to 0.2 in the frequency range (100 kHz–10 MHz), while PVC-DMG-Ni(II) shows a smooth fall in $\tan \delta$ from 0.1 to 0.05 in the same frequency range. Notably, $\tan \delta$ -frequency curves for PVC-DMG-Ni(II) or PVC-DMG-Co(II) do not reveal any maxima at the point of inflection in the dielectric constant frequency curve. Further, $\tan \delta_{\max}$ does occur for PVC-DMG-Cu(II) at a frequency which does not correspond to the inflection point in the permittivity-frequency curve.

A very similar trend has been observed by us with PVC modified by meta-aminophenol,⁸ carbazole,¹⁵ and anthraquinone/anthracene¹⁶ moieties. In all these cases, the permittivity values for the modified PVC polymers are appreciably higher than PVC at low frequency, falling sharply with increasing frequency. At the same time, $\tan \delta$ shows a broad relaxation at high frequency.

The introduction of polar groups in PVC will cause them to orient when placed in an electric field. If these groups are flexibly attached to the polymer chain, they will orient easily and rapidly. If the polymer is rigid, and the polar groups are rigidly attached, they will orient slowly with difficulty.

In an alternating electric field, the polar groups in the polymer will orient and give high permittivity only when the frequency of alteration is low enough to permit motion and orientation of these groups. With increasing frequency in the alteration of electric field, the polar groups will be able to orient less and less rapidly—and at still higher frequencies, they will be able to orient hardly at all. As a result the polymer will exhibit low permittivity.

As for the broad nature of loss tangent parameter, it seems that loss of electric energy by conversion to thermal energy is too small to be detected at low frequency. It shows up only at some intermediate frequency in the transition region, where the polar groups are able to orient at the rate and frequency of alteration in the electric field.

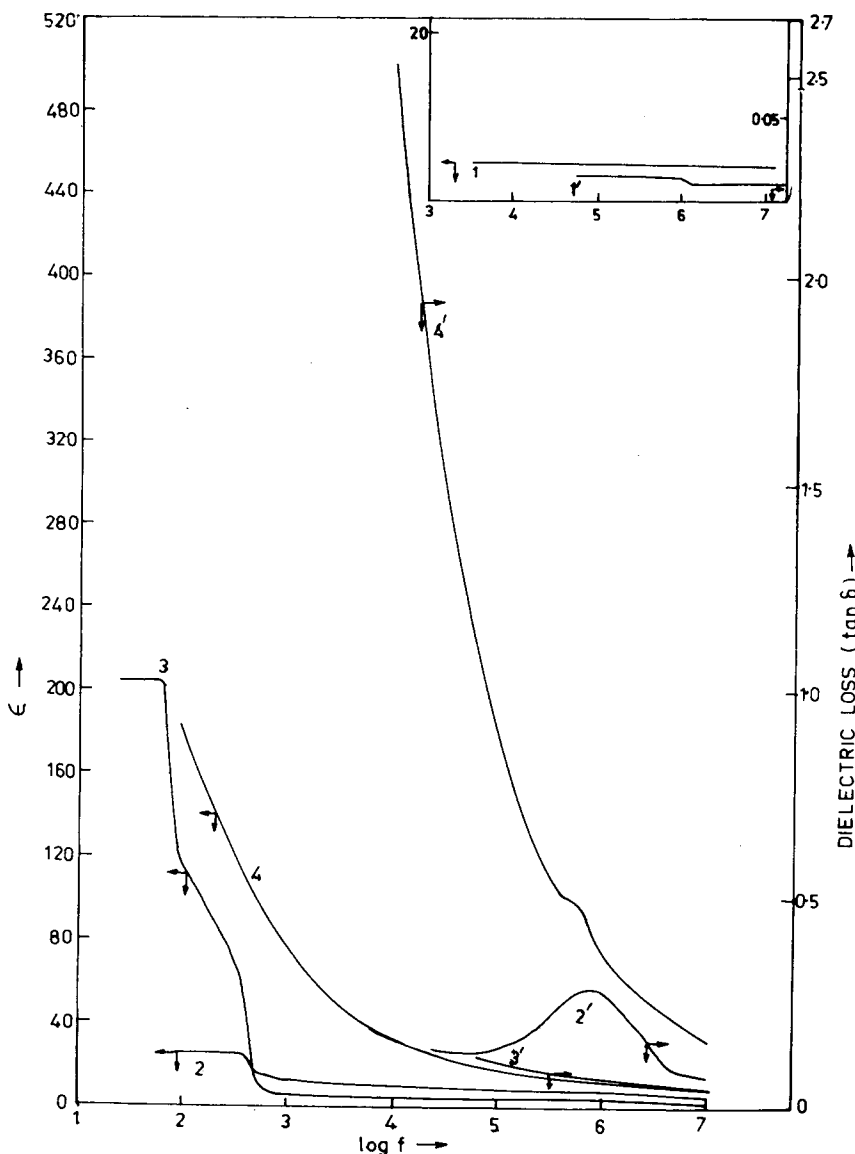


Fig. 3. Variation of permittivity (ϵ) and dielectric loss ($\tan \delta$) of PVC-DMG-M(II) with applied frequency: (1, 1') PVC; (2, 2') PVC-DMG-Cu; (3, 3') PVC-DMG-Ni; (4, 4') PVC-DMG-Co.

CONCLUSION

PVC bound DMG complex can be synthesized by Cl displacement reaction between PVC and DMG in alkaline condition. Subsequent complexation of PVC-DMG with Co(II), Ni(II) and Cu(II) yields intensely colored PVC-DMG-M(II) complexes which exhibit improved overall thermal stability, improved conductivity, and interesting dielectric property relative to unmodified PVC.

Thanks are due to the authorities of I.I.T., Kharagpur for facilities.

References

1. M. R. Kratz and D. G. Hendricker, *Polymer*, **27**, 1641 (1986).
2. L. R. Melby, *J. Am. Chem. Soc.*, **97**, 4044 (1975).
3. C. J. Federson and H. K. Frensdorff, *Angew Chem., Int. Ed. Engl.*, **11**, 16 (1972).
4. L. D. Rollman, *J. Am. Chem. Soc.*, **97**, 2132 (1975).
5. R. S. Drago, J. Gaul, A. Zombeck, and D. K. Staub, *J. Am. Chem. Soc.*, **102**, 1033 (1980).
6. C. U. Pittman Jr. and R. M. Hanes, *J. Am. Chem. Soc.*, **98**, 5402 (1976).
7. C. U. Pittmann, *Polymer Supported Reactions in Organic Synthesis*, P. Hodge and D. C. Sherrington, Eds., Wiley, New York, 1980, Chap. 5.
8. M. Biswas and S. Moitra, *Polym. Prepr.*, **27**, 76 (1986).
9. M. Biswas and S. Moitra, *Polym. Bull.*, **17**, 361 (1987).
10. M. Biswas and S. Moitra, *Chemical Reactions on Polymers*, Anaheim, ACS Symposium Series, Am. Chem. Soc., Washington, DC, 1986.
11. C. B. Singh and B. Sahoo, *J. Inorg. Nucl. Chem.*, **36**, 1259 (1974).
12. F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 2nd ed., Wiley Eastern, New Delhi, 1967, pp. 872, 885, and 901.
13. D. A. Seanor, *Electrical Properties of Polymers in Polymer Science*, A. D. Jenkins, Ed., North-Holland, London, 1972, Vol. 1, Chap. 17.
14. (a) J. M. Pochhan, R. G. Crystal and (b) C. W. Reed, in *Dielectric Properties of Polymers*, F. E. Karasz, Ed., Plenum, New York, 1972, pp. 316 and 343.
15. M. Biswas and P. Mitra, *Angew. Makromol. Chem.*, (1988), to appear.
16. M. Biswas and A. Mazumdar, *J. Appl. Polym. Sci.*, (1988), to appear.

Received May 3, 1988

Accepted August 30, 1988