Synthesis and Characterization of Poly(vinyl Carbazole) Complexes with Copper(II) Chloride in THF Solution

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Synopsis

Several polymer-metal complexes were prepared by reacting poly(vinyl carbazole) (PNVC) with copper(II) chloride, $CuCl_2.2H_2O$, in refluxing tetrahydrofurane (THF) for mole ratios of $CuCl_2.2H_2O$ to monomeric unit (Cu:PNVC ratio) ranging between 0.086 and 4.98. Complexes were characterized by infrared (IR) and elemental analysis. Thermal behavior of complexes was studied by differential thermal analysis (DTA). It appears that THF behaves as a specific solvent for complexation of PNVC with copper(II) chloride.

INTRODUCTION

In recent years, the study of polymer metal complexes has been of great interest[1] for several reasons. Thus, polymer-metal complexes may be used as models for the metalloenzymes,[1,2] in coating of electrodes,[3] as catalysts,[4] for their magnetic properties[5] and as catalyst-sensitizers for the photodissociation of water.[6,7]

Poly(vinyl carbazole) (PNVC) has been used as donor in complexes with low molecular weight compounds such as iodine, tetracyanoquinodimethane, and 2,4,7-trinitro-9-fluorenone (TNF). Thus, the PNVC: TNF 1:1 complex has been used as a photoconductive layer in electrophotography.[8-10] This fact has prompted the synthesis of new complexes of PNVC with low molecular weight compounds, as well as new polymers derived from PNVC in order to obtain complexes with low molecular weight acceptors.[11,12] This paper reports the synthesis and characterization of PNVC complexes with copper(II) chloride.

EXPERIMENTAL

Materials

Vinylcarbazole (Fluka puriss) was purified by successive crystallization from methanol; its purity was checked by infrared (IR) and differential thermal analysis (DTA). Diaquo copper(II) chloride was supplied by Panreac (puriss) and used without further purification. Tetrahydrofurane (THF) (Fluka puriss)

was purified by repeated vacuum distillation, retaining the middle cut each time. Benzene (Merck p.a.) and methanol (Fluka puriss) were fractionally distilled before using.

PNVC SAMPLE

PNVC was obtained by radical polymerization in benzene using 1,2-azobis-isobutyronitrile (AIBN) as initiator. It was precipitated in methanol, purified by reprecipitation and fractionated from benzene solution with methanol into eleven fractions. The first fraction was chosen for experiments. Its molecular weight ($\overline{M}_v$) calculated by viscometry in THF at 298 K using the Mark-Houwink-Sakurada equation $[\eta] = 14.4.10^{-5}. M^{0.65}$(13) was 323.000.

$(C_{14}H_{11}N)_N$(193)$_N$ Calc. C   87.0   H   5.7   N   7.2
                                    Found C   87.2   H   5.4   N   7.1

Infrared Spectra. IR spectra were recorded as KBr discs, on Unicam SP1000 Spectrophotometer.

Thermal Stability. Thermal stabilities of the complexes were studied by means of a Mettler TA 2000 differential thermal analyzer system.

Atomic Absorption. The amount of copper incorporated in the complex was determined with a Perkin-Elmer atomic absorption spectrophotometer (model 560). In order to enable the determination of copper in aqueous solutions, the complexes were decomposed by heating weighed samples with H_2SO_4 (50%) and afterwards diluting them in water to a concentration suitable for measurements.

Synthesis of Metallopolymers. Appropriate stoichiometric amounts of PNVC and $CuCl_2.2H_2O$ were mixed in THF and heated under reflux with stirring. The initial green color changed gradually to gold; later the solutions sharply changed their color to a dark green. This fact was observed between 0.5 and 3 minutes after beginning the reaction. Then, reflux was continued for 15 or 20 minutes. For high Cu : PNVC mole ratios, a small green precipitate was formed which could not be recovered. Solutions were filtered and precipitated in methanol. The material obtained was isolated by removal of the residual solvent under vacuum. All complexes were green with intensity increasing as the Cu : PNVC mole ratio increases.

Composition of reaction mixtures and elemental analyses of the complexes are given in Table I.

RESULTS AND DISCUSSION

After precipitation from the reaction mixture, the complexes are insoluble in THF, suggesting formation of crosslinks. Complexes are also insoluble in benzene, chloroform, chlorobenzene, acetone, dimethyl sulfoxide, ethyl ether, cyclohexanone, acetonitrile, nitrobenzene, 1,3-dichlorobenzene, and 1,2-dichloroethane.

Sample B is soluble in tetrachloroethane and the complex is stable in solution as it can be recovered by precipitation in methanol.

Sample A is soluble in THF. Its elemental analysis is close to that of PNVC as well as its thermal behavior, suggesting that there is a minimum Cu : PNVC mole ratio for crosslinking.

TABLE I

Composition of Reaction Mixtures and Elemental Analyses of
the Products (Time of Reaction Ranged Between 15 and 20 min)

Mole ratio Cu : PNVC in reaction mixture	Sample	Elemental analysis			Amounts of reactants		
		C	H	N	$CuCl_2.2H_2O$ (mg)	PNVC (mg)	THF (mL)
0.086	A	86.2	6.0	6.9	12.4	162.8	50
0.28	B	72.6	5.9	5.6	22.0	100.0	50
0.56	C	66.5	5.3	5.0	50.0	100.0	50
0.88	D	—	—	—	150.8	192.8	75
1.70	E	46.6	4.8	3.6	150.0	100.0	50
2.26	F	42.8	4.4	3.0	200.0	100.0	75
4.98	G	26.8	3.3	1.8	269.5	61.2	75

Solubility and therefore crosslinking is influenced by the time of reaction. Thus, a trial with Cu : PNVC mole ratio for sample C was carried out at two times of reaction, viz. 5(C1) and 10 minutes (C2), respectively. C1 is soluble in THF and 1,2-dichloroethane, whereas C2 is swollen in 1,2-dichloroethane and is slightly soluble in tetrachloroethane. The color of both samples was clearer than the C sample, indicating that the amount of copper incorporated depends also on the time of reaction.

Influence of the Solvent in Complexation

We have tried to obtain the PNVC-Cu(II) complexes in solvents other than THF but without success. Solvents used in these trials as well as reaction conditions can be found in Table II.

It seems that THF behaves as a specific solvent for complexation of PNVC with copper chloride. The reason for this is not clear, although it may be related to the fact that THF forms a complex with Cu(II). In fact, the reaction under reflux between THF and $CuCl_2.2H_2O$ produces exactly the same changes of color as that between PNVC and $CuCl_2.2H_2O$ in THF, with one difference only: at the end an intense bluish-green precipitate is produced, whereas the reaction with PNVC gave a product most of which remained in solution. Nevertheless, 1,4-dioxane also forms an orange colored complex with $CuCl_2.2H_2O$, but complexation between PNVC and $CuCl_2.2H_2O$ does not take place in 1,4-dioxane.

TABLE II

Trials to Obtain the PNVC-Cu(II) Complex

Solvent	Amounts of reactants/mg		Time of reaction (hr)	Result
	PNVC	$CuCl_2.2H_2O$		
THF	See Table I			Positive
p-dioxane (50 mL)	100	200	2.75	Negative
DCE (50 mL)/MeOH (7 mL)	118	100	4.50	Negative
$CHCl_3$ (100 mL)/MeOH (35 mL)	118	115	0.75	Negative

All reactions were carried out under reflux DCE = 1,2-dichloroethane.

TABLE III

Empirical Formulae of the PNVC-Cu(II) Complexes and Their
Copper Contents from Atomic Absorption

| | | % Copper | | Cu : PNVC mole ratio |
Sample	Probable Formula	Calc.	Found	in the complex
B	$|(C_{14}H_{11}N)(C_4H_8O)_{0.27}(CuCl_2)_{0.27}|_n$	7.0	7.3 ± 0.2	0.27
C	$|(C_{14}H_{11}N)(C_4H_8O)_{0.36}(CuCl_2)_{0.44}|_n$	10.1	9.8 ± 0.2	0.44
E	$|(C_{14}H_{11}N)(C_4H_8O)_{0.23}(CuCl_2.2H_2O)_{1.03}|_n$	17.0	18.0 ± 0.2	1.03
F	$|(C_{14}H_{11}N)(C_4H_8O)_{0.61}(CuCl_2.2H_2O)_{1.30}|_n$	18.1	18.6 ± 0.2	1.31
G	$|(C_{14}H_{11}N)(C_4H_8O)_{0.94}(CuCl_2.2H_2O)_{3.13}|_n$	25.0	25.8 ± 0.2	3.13

Infrared Spectra

The complexes were also characterized by IR, as some bands of many polymers show shifts upon coordination.[1] We have obtained the IR spectra of $CuCl_2.2H_2O$, PNVC and of the complex THF-Cu(II) synthesized here (C: 11.8 H: 2.7).

IR spectra of the complexes do not show any significant shift with respect to that of PNVC, indicating that linking between the polymer and copper may be taking place only through the tertiary nitrogen of the carbazole side group.

As we shall see below (Table III), THF forms part of these complexes. It is puzzling that their spectra do not show at all the strong and sharp bands of THF at 935 cm^{-1} and 1100 cm^{-1}. We cannot explain the absence of these bands from the spectrum of the THF-Cu(II) complex.

The band of the complexes at 1610 cm^{-1} is broader than that of PNVC which may be an indication of the presence of THF and copper as in this region both the THF-Cu(II) complex and $CuCl_2.2H_2O$ exhibit a very broad band.

Above 1700 cm^{-1} spectra of the complexes show two differences from that of the polymer. On the one hand, samples E, F, and G have a broad band clearly located at 3400 cm^{-1}, indicating the presence of water which has its origin in the coordination water of $CuCl_2.2H_2O$. On the other hand, in samples B, C and E two broad and one weak but clearly defined bands are observed at 1750 and 1790 cm^{-1}; they are difficult to assign.

Structure of PNVC-Cu(II) Complexes

From elemental analysis, atomic absorption and IR spectra, it is possible to obtain the empirical formulae of PNVC-Cu(II) complexes. Formulae for the different samples studied here as well as Cu : PNVC mole ratios in the complex (calculated from elemental analysis) and copper contents as obtained by atomic absorption can be seen in Table III.

Insolubility of these complexes indicates existence of crosslinking of polymer chains suggesting the presence of structures such as that in Figure 1(a). It is also possible that there are intramolecular links such as the structure shown in Figure 1(b). Our data allow only speculation about the structure of these complexes. UV/VIS and X-ray diffraction studies would be necessary but unfortunately, the insolubility of these complexes prevents the measurements; the X-ray diffraction technique is out of our reach.
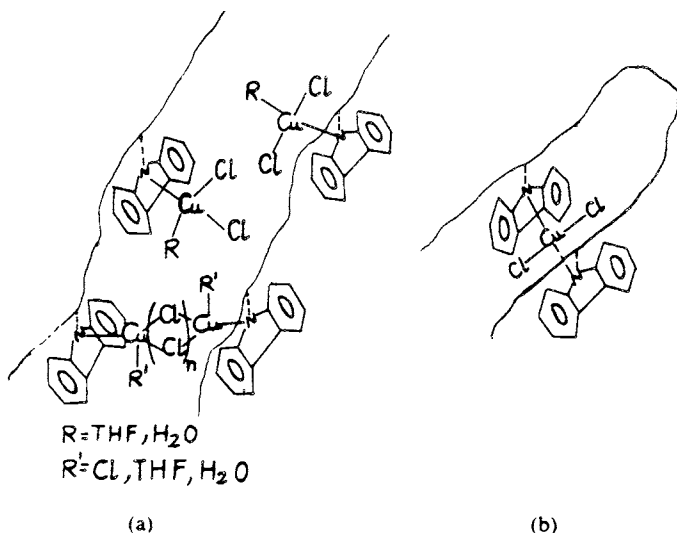
R=THF,H₂O

R'=Cl,THF,H₂O

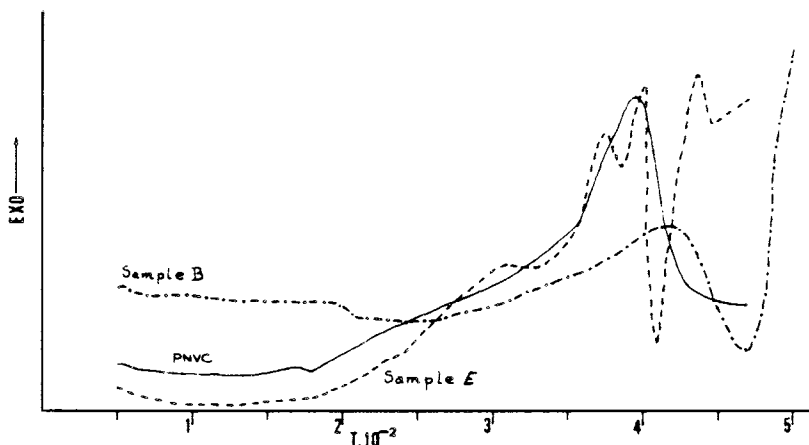(a)   (b)

Fig. 1. Structure of different PNVC-Cu(II) complexes.

Fig. 2. Thermograms of some samples studied in this work. (-.-) PNVC sample B. (---) sample E. Heating rate 10°C/min in all cases. Sensitivity: 100 μV for PNVC sample and 200 μV for the other sample.

Thermal Analysis

Thermal behavior of PNVC and two of its complexes (samples B and E) as a function of temperature is shown in Figure 2. The glass transition temperature of PNVC (close to 473 K) does not appear in the thermograms of the complexes probably because their decomposition begins between 423 and 473 K.

Thermogravimetric curves of PNVC, samples of PNVC-Cu(II) complex, and THF-Cu(II) complex (C: 11.8; H: 2.7), have been plotted in Figure 3. As can be seen, the thermal stability of PNVC-Cu(II) complexes is lower than that of PNVC. Thus, the threshold temperature for significant weight loss for the PNVC-Cu(II) complexes is close to 373 K, (i.e., about 250° below the temperature for PNVC). On the other hand, thermogravimetric curves of the com-
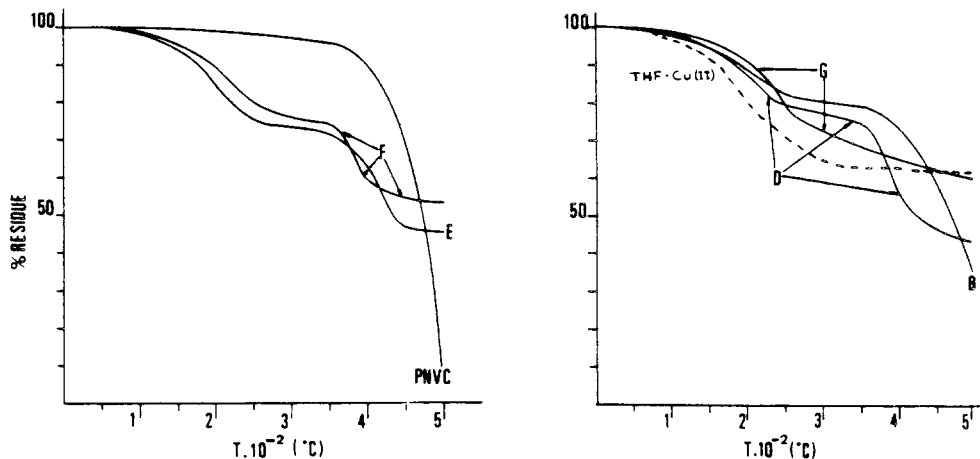
Fig. 3. Thermogravimetric curves for PNVC and samples of PNVC-Cu(II) complex in air as well as for THF-Cu(II) complex synthesized in this work (- - - -).

plexes are similar to that of THF-Cu(II) complex up to 623 K. In our opinion, this indicates that the degradation of these complexes begins at the complexing sites, the weight loss below 623 K being due to elimination of water and THF molecules. This fact is supported by the IR spectra of the complexes which, at least up to 623 K, show the typical bands of PNVC, indicating that its degradation has not begun. Above 673 K, degradation of the macromolecular chain of PNVC begins.

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