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Copper Chloride Complexes with Poly(2-vinylpyridine): Preparation and Redox Properties[†]

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ABSTRACT: Soluble copper chloride complexes with poly(2-vinylpyridine) (P2VPy) were prepared in a methanol–water solution. Solubility was achieved with the proper solvent system, due to the sterically hindered environment of the ligand, allowing only one pyridine moiety to complex each copper cation. Partial reduction of the cupric cation occurred during sample preparation, as observed by X-ray photoelectron spectroscopy (XPS) and magnetic susceptibility measurements. These complexes were thermally decomposed to form metallic copper. The first step in the formation of metallic copper is the complete reduction of Cu^{II} to Cu^{I}, as observed by XPS and magnetic susceptibility measurements. This reaction occurs in the temperature range from 150 to 180 °C, with the loss of water observed by thermogravimetric analysis and pyrolysis mass spectroscopy and the oxidation of the pyridine rings. The final step in the formation of copper metal occurs during the decomposition of the polymer at temperatures above 320 °C, resulting in a composite of copper and carbon.

I. Introduction

Polymer precursors offer significant processing advantages over conventional methods for the direct formation of conductive paths in electronic circuits. Examples of such materials include novolac photoresist, as a precursor to the lithographic definition of carbon patterns,[1] and cuprous complexes dispersed in poly(vinylpyrrolidone), as precursors to the laser writing of copper lines.[2]

A major impediment to the widespread use of metal–polymer precursors for the preparation of inorganic films and fibers is the solubility of the precursor. In order to exploit the processing advantages of polymers, high molecular weight linear materials are required since cross-linked networks are not soluble. Numerous metal containing polymers have been reported,[3] but few of these materials exhibit significant solubility. Several techniques can be used in order to avoid cross-linking and other reactions that lead to low solubility. These include the use of dilute solutions, copolymerization with monomers of enhanced solubility, and the utilization of sterically bulky ligands to block coordination sites.

In this paper, we first describe the synthesis of soluble complexes between copper chloride and P2VPy. Solubility was achieved through the selection of a sterically hindered polymeric ligand and the proper solvent system.

To design materials as precursors to metallic copper, it is important to understand the relevant thermal decomposition processes. The effect of copper complexation on the thermal stability of the P2VPy matrix is reported separately.[4] Characterization of the reduction of Cu^{II} to Cu^{0}, and the corresponding oxidation reactions, constitutes the second aspect of this paper. A two-step process was observed, where a chemically stable Cu^{I}–P2VPy complex was formed at ≈180 °C. Above 320 °C, the cuprous complex was reduced to metallic copper during the thermal decomposition of the polymer.

II. Experimental Section

II.1. Materials. 2-Picoline was purchased from Aldrich, distilled under reduced pressure (≈25 mm of Hg) at 84 °C and characterized by infrared spectroscopy (IR) before use. Poly(2-vinylpyridine) (P2VPy) was purchased from Aldrich Chemical Co. (low molecular weight) and from Polysciences Inc. with a nominal molecular weight of 300 000–400 000. In both cases, the polymer was purified by two precipitations from ethanol into deionized water, ground to a fine powder, dried under vacuum,

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Table I
Reactant Specifications for the Preparation of $CuCl_2$-P2VPy Complexes

complex Cu:Py ratio	$CuCl_2 \cdot 2H_2O$ (mol)	P2VPy (mol)	solvent (mL)
1:4	1.25×10^{-3}	5.00×10^{-3}	22
1:2	2.50×10^{-3}	5.00×10^{-3}	84
1:1	5.00×10^{-3}	5.00×10^{-3}	225

and characterized by nuclear magnetic resonance (NMR) and IR. A molecular weight of 36 000 was determined for the purified Aldrich polymer by viscosity measurements at 25 °C in ethanol. Poly(4-vinylpyridine) (P4VPy) was used as received from Aldrich. $CuCl_2 \cdot 2H_2O$ (ACS purity) was used as received from Mallinckrodt and characterized by X-ray diffraction.

II.2. Preparation of Model Compounds

II.2.1. Cu(2-picoline)$_2$Cl$_2$. The complex was prepared according to published methods.[5,6] Distilled methanol, absolute ethanol, and 95% ethanol were used as solvents but all yielded the same blue crystals, as determined by X-ray diffraction (see section II.12). The X-ray powder patterns contained all the peaks reported in ref 6 plus numerous additional peaks. However, all observed peaks could be indexed by calculating plane (*d*) spacings using standard formulas for the triclinic system[7] and reported crystallographic parameters.[8] The material that was used for additional study was prepared by the dropwise addition of 2.00 mL (2.03×10^{-2} mol) of freshly distilled 2-picoline dissolved in 30 mL of distilled methanol to a warmed, stirred, solution of 1.3665 g (1.016×10^{-2} mol) of anhydrous $CuCl_2$ in 30 mL of methanol. After several minutes of stirring, the solution was filtered to remove a green precipitate and was allowed to stand at room temperature for several hours. The solution was filtered again and placed in a freezer overnight. Blue crystals (several millimeters in size) were formed which were filtered, washed with ether, dried under vacuum, and ground to a fine powder.

II.2.2. Cu(2-picoline)Cl$_2$. 2-Picoline (0.50 mL, 5.08×10^{-3} mol) was added to a warmed, stirred solution of 0.8653 g (5.08×10^{-3} mol) of $CuCl_2 \cdot 2H_2O$ in 30 mL of ethanol. Crystals were formed immediately. The suspension was allowed to stand at room temperature for approximately 12 h before the green powder was filtered, dried under vacuum, and ground to a fine powder. X-ray diffraction showed only three weak peaks.

It was desired to prepare a solution of this complex so that it could be isolated by the same techniques as for the polymer complexes, described below. A solution of 0.20 mL (2.03×10^{-3} mol) of 2-picoline in 25 mL of distilled methanol was added dropwise to a stirred solution of 0.3461 g (2.03×10^{-3} mol) of $CuCl_2 \cdot 2H_2O$ in 25 mL of methanol, to form a dark green solution. After 24 h of stirring, the complex was isolated by freezing the solution in liquid nitrogen and removing the solvent under a vacuum of $\approx$100 μm of Hg as the solution thawed. A red tar was the principle product, along with small amounts of green and blue material.

II.3. Preparation of Polymer Complexes. Complexes of different ratios of Cu to pyridine moiety were formed by the dropwise addition of a $CuCl_2$ solution to a solution of the polymer. Low molecular weight P2VPy was used in all cases. Soluble complexes were formed when a mixed solvent of 95% CH_3OH and 5% H_2O was used. Due to decreasing solubility of the complex with increasing copper concentration, the concentration of reagents was varied as shown in Table I. After 24 h stirring, the complexes were isolated by freezing the solutions in liquid nitrogen and removing the solvent under a vacuum of $\approx$100 μm of Hg as the solution thawed. The resulting solids were ground to a fine powder in an agate mortar and pestle and stored in a nitrogen purged dessicator. Complexes prepared in pure methanol were only slightly soluble and resulted in the precipitation of a fine green powder which was isolated by either filtration or removal of the solvent under vacuum as described above.

II.4. Thermal Decomposition. In addition to the decomposition studies of the complexes within specific instruments (e.g. TGA, DSC, MS), decomposition was also performed under a purified nitrogen ambient in a Lindburg tube furnace with a mullite muffle to prepare thin films for spectroscopic studies and bulk material for chemical analysis. Temperature uniformity in the sample zone was maintained to within 2 °C of the set point. A graphite lined boat was required to remove the last traces of oxygen. The samples were heated at a nominal rate of 10 °C/min to a set temperature which was maintained for 1 h. The furnace was allowed to cool to room temperature over approximately 7 h.

II.5. Analysis. Chemical analysis of the complexes, as well as chars, was performed by Schwartzkopf Laboratories, Woodside, NY. Samples weighing $\approx$300 mg were placed in a porcelain crucible and pyrolyzed to 180 °C in a Lindburg furnace as described in the preceding section. The resulting sample was ground to a fine powder before analysis.

II.6. Electronic Spectra. Electronic spectra were recorded on either a Perkin-Elmer Model 575 or Lambda 9 spectrophotometer. Films were prepared on either quartz or CaF_2 substrates by pipetting a few drops of solution on the substrate and evaporating the solvent under vacuum.

The method of continuous variation[9] (Job's method) was employed to determine the ligand to metal ratio in the $CuCl_2$ system, using a total solution concentration of 10^{-2} M. A series of $CuCl_2$ solutions was used to generate a curve from which the background correction factors were determined, as $CuCl_2$ does not follow Beer's law in this region.

II.7. Infrared Spectra. Infrared spectra were recorded on a Perkin-Elmer Model 680 grating spectrophotometer or Niclolet Model 5DX Fourier transform spectrophotometer as mulls in Nujol or fluorolube on KBr or as films prepared on CaF_2 substrates as described above.

II.8. Magnetic Susceptibility. The magnetic susceptibility of the copper complexes was measured from 4.2 to 300 K by the Faraday method.[10] In all cases, the susceptibility (χ) followed the Curie–Weiss expression $\chi_g = C_g/(T + \Theta) + \chi_0$ for $T \geq \Theta$, where χ_g is the paramagnetic susceptibility, C_g is the Curie constant, T is temperature, Θ is the Weiss constant, and χ_0 is the diamagnetic contribution. The data were fit to the above expression to obtain C_g, Θ, and χ_0 as previously described.[11] The average effective moment per Cu atom (μ_{eff}) was obtained from C_g by the equation $\mu_{eff} = [8C_g(MW)]^{1/2}$, where MW is the molecular weight of the complex.

II.9. Thermogravimetric Analysis (TGA). The TGA experiments were performed on a Perkin-Elmer TGS-2 thermobalance in N_2 purified by passing the gas over molecular sieves, followed by an Oxyclear purifyer, purchased from Diamond Tool and Die. A flow rate of $\approx$30 cm^3/min and a sample size of either 10 or 30 mg were employed. Selected experiments were conducted in an atmosphere of 4% H_2 in N_2, which was purified as described above. A heating rate of 10 °C/min was used except where noted. The materials were dried by heating in N_2 for 2 h at 30 °C in the thermobalance to remove $\approx$2 wt % absorbed water before beginning the experiments.

II.10. Differential Scanning Calorimetry (DSC). DSC was performed on a Perkin-Elmer DSC-4 calorimeter in 99.999% N_2 (purchased from Matheson Co.) at a flow rate of $\approx$30 cm^3/min and heating rate of 10 °C/min. Samples were weighed into aluminum volatile sample pans which were crimped closed and then punctured with a pin. Samples of P2VPy were heated to 200 °C and cooled to 50 °C before glass transition temperatures were measured.

II.11. X-ray Photoelectron Spectroscopy (XPS). Copper chloride–P2VPy complexes (1:1 and 1:2 Cu:P2VPy ratios) were characterized by XPS. Thin film samples were prepared on silicon substrates at room temperature. One sample of each composition was pyrolyzed at 180 °C, as previously described, before introduction into the spectrometer. XPS spectra were acquired with a Perkin-Elmer hemispherical spectrometer operated in the small area mode. The incident radiation was the Mg Kα line with the source operated at 300 W (15 kV, 200-mA emission) and at a distance of $\approx$1.5 cm between the source and the sample surface. The binding energy scale is referenced to the Au($4f_{7/2}$) transition at 84.0 eV. Multiplex spectra were taken with a pass energy of 19 eV and a step size of 0.1 eV. The accuracy of binding energies reported is conservatively estimated at ±0.2 eV, with the C(1S) peak in P2VPy taken as 285.0 eV.

A 90° photoelectron emission angle with a 1-mm diameter analyzed area was used to minimize contributions of adsorbed surface species to the spectra and maximize the contribution from

Table II
Elemental Analysis Results of the As Prepared Complexes and P2VPy Compared to Calculated Values

compd	ratio		wt % C	wt % H	wt % N	wt % Cu	wt % Cl
P2VPy		obsd	78.4	6.6	12.9		
		calcd	80.0	6.7	13.3		
$CuCl_2$–P2VPy	1:4	obsd	57.4	5.3	10.5	10.6	12.6
95% methanol		calcd	58.7	5.2	9.8	11.1	12.4
	1:2	obsd	45.4	4.6	7.5	17.5	19.2
		calcd	46.3	4.4	7.7	17.5	19.6
	1:1	obsd	31.6	3.7	5.1	23.9	27.0
		calcd	32.6	3.5	5.4	24.7	27.6
$CuCl_2$–P2VPy	1:2	obsd	46.3	4.2	7.6	18.4	20.0
100% methanol		calcd	48.1	4.2	8.0	18.2	20.3

the bulk film. Ion bombardment could not be used effectively in this study to remove surface contamination as Cu^{II} could be reduced,[12] and changes to the polymer structure could occur. The time elapsed between the preparation of the samples and their introduction into the vacuum system was kept to a minimum (several hours) to reduce the possibility of reactions with the atmosphere.

Sample heating from the X-ray source was a consideration in these studies. The procedure for acquiring spectra on the pyrolyzed samples was to acquire a survey scan and then multiplex over the regions for the Cu(2P), Cl(2P), C(1S), N(1S), and O(1S) transitions. Multiplexed spectra for the pyrolyzed samples were taken at 90° and 45° exit angles, to determine the extent of adsorbed gas or surface reactions in the spectra. The unbaked samples were analyzed only in the multiplexed mode at a 90° exit angle in order to minimize heating from the X-ray source.

II.12. X-ray Diffraction. The composition of the polymer complexes was investigated by X-ray diffraction, using a Phillips automated powder diffractometer. Samples were prepared either as powders (e.g. from the products of TGA experiments) or as films on oxidized silicon substrates.

III. Results

III.1. Preparation of Polymer Complexes. Three products were isolated from P2VPy with copper to pyridine ratios of 1:4, 1:2, and 1:1. The solutions of all three complexes were green and yielded either green (1:4 and 1:2) or yellow-brown (1:1) hygroscopic powders. Films prepared by evaporating the solutions under vacuum were transparent and of the same color as the powders. The complexes could be redissolved after isolation.

The complexes between $CuCl_2$ and P2VPy, regardless of P2VPy:copper ratio, turned deep red in color after pyrolysis at 180 °C. These films are chemically stable and would not revert to the green form even after exposure to a humid ambient for 30 days. Pyrolysis of these films at 800 °C resulted in discontinuous films with a gray-copper color.

Addition of cupric chloride solutions to P4VPy solutions formed blue cross-linked insoluble gels.

III.2. Analysis. Results from the chemical analysis of the various complexes are in good agreement with theoretical values as shown in Table II. Note that the weight percent values observed for carbon are low for all samples analyzed, including the uncomplexed P2VPy. The effect of pyrolyzing the 1:2 copper chloride complex to 180 °C on the composition of the complex is shown in Table III. The calculated values for the pyrolyzed sample are based on the composition $CuCl_2(C_7H_7N)_2$.

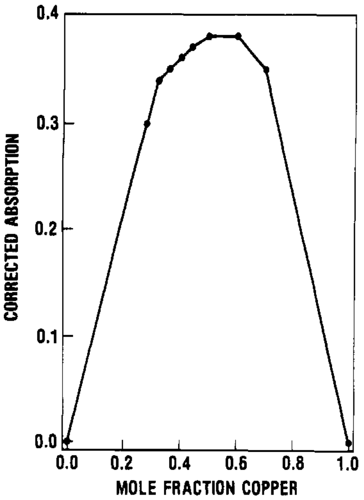

Figure 1. Continuous variation plot (Job's plot) for the $CuCl_2$–P2VPy system in 95:5 $MeOH$–H_2O. Mole fraction $CuCl_2$ is plotted vs corrected absorption.

III.3. Electronic Spectra. Upon addition of $CuCl_2$ to P2VPy, the solution turned deep green. Differences in the UV–visible spectra were manifested as a shoulder at approximately 370 nm and a shift in the visible absorption from 865 to 850 nm. The method of continuous variation (Job's method) was employed by using the new, 370-nm, absorption. The results, as shown in Figure 1, indicate a 1:1 complex formed between copper chloride and pyridine moieties.

The shape of the solid state transmission spectra are dependent upon the Cu:Py ratio. For the 1:4 and 1:2 samples, the solid-state spectra are unchanged from the spectra recorded in solution. In the case of the 1:1 sample, the films show a more complex visible spectra with peaks observed at 1750, 970, 830, 605, and 390 nm. Significant changes were observed after heating films on quartz at 200 °C in N_2. All three samples exhibited spectra with shoulders of increasing intensity at 610 and 510 nm and a maximum between 400 and 200 nm.

III.4. Infrared Spectra

III.4.1. Copper Chloride Complexes with 2-Picoline. The infrared spectra of the 1:2 and 1:1 complexes with 2-picoline are qualitatively similar with two additional peaks observed for the 1:1 complex at 600 and 579 cm^{-1} and peak shifts on the order of 1–5 cm^{-1}. Large shifts are observed, however, for the red tar isolated from the 1:1 preparation by removal of the solvent under vacuum. The spectra of the tar is compared to the green form of the 1:1 product in Figure 2. These shifts would be consistent with a partially reduced copper complex.

III.4.2. Copper Chloride Complexes with P2VPy. The infrared spectra of the 1:2 ($CuCl_2$–P2VPy) complex is compared to that of P2VPy, $P2VPy^+HCl^-$, and a monomeric analogue, $Cu(2\text{-ethylpyridine})_2Cl_2$,[13] in Table IV. Two regions are of particular interest: vibrations due to O–H and those of the pyridine ring.

The symmetric and antisymmetric O–H stretch[15] is attributed to the two vibrations observed at 3450 and 3360

Table III
Elemental Analysis Results for the 1:2 $CuCl_2$–P2VPy Complex Prepared in 95:5 Methanol–Water, As Prepared and after Reduction at 180 °C, Compared to Calculated Values

compd	ratio	temp, °C		wt % C	wt % H	wt % N	wt % Cu	wt % Cl
$CuCl_2$–P2VPy	1:2	180	obsd	47.3	4.3	7.7	17.4	19.9
95% methanol			calcd	48.8	4.1	8.1	18.4	20.6
		25	obsd	45.4	4.6	7.5	17.5	19.2
			calcd	46.3	4.4	7.7	17.5	19.6

Table IV
Infrared Bands (cm^{-1}) for P2VPy and Its Complex with $CuCl_2$ Compared to Monomeric Analogues

$P2VPy^+HCl^-$ [14]	P2VPy	1:2 complex	$Cu(2\text{-ethylpyridine})_2Cl_2$ [13]	2-ethylpyridine[13]	assignts[13,14]
3420		3450			OH
3250		3360			OH
3100	3090	3100			
3045	3070	3065	3076	3072	ring CH
	3015		3029	3006	ring CH
2940	2940	2940	2972, 2941	2970	asym CH_2
	2860		2887, 2827	2873	sym CH_2
2600					
2060, 2000					$C{=}N^+H$
1620		1622			quart. ring/H_2O
	1595	1610, 1595	1612	1595	ring
	1570	1570	1574	1573	ring
1540		1540			quart. ring
1470	1476	1470	1486	1479	ring
1410	1435	1438	1441, 1428	1438	ring
1380	1375		1387	1372	ring
1300	1305	1310	1299	1300	CH
1250		1250	1257, 1240	1251	CH_2
1215	1205		1218	1221	
1170	1150	1165	1166	1147	CH
1100	1092	1100	1121, 1086	1106	CH
1050	1050		1058	1050	CH
1000	995	1030, 1000	1035, 1014	995	ring
960	960	950	967	959	CH
	890	915, 895	896	885	CH
775	747	770	773	749	CH
625	625	649, 625	654	626	C–C–C
550	555	550	567	571	C–C
		520			H_2O
	409	430, 400	435	406	C–C

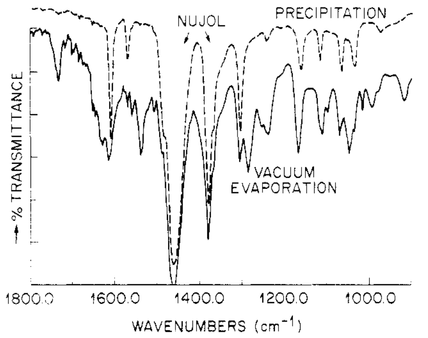

Figure 2. Fourier transform infrared spectra of the $CuCl_2$(2-picoline) complex isolated by precipitation (dashed line) and by removal of the solvent under vacuum (solid line).

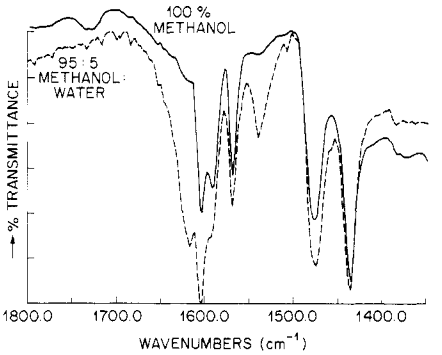

Figure 3. Fourier transform infrared spectra of the 1:2 $CuCl_2$–P2VPy complex prepared in 100% methanol (solid line) and 95:5 methanol–water (dashed line).

cm^{-1} for the P2VPy complexes. Only broad, weak absorptions are observed for P2VPy in this region. A very strong band at 1622 cm^{-1} could be attributable to either complexed water or a quarternized pyridine ring vibration, as discussed below.

The second area of interest is that of the pyridine ring vibrations. For the P2VPy complexes, vibrations at 1595, 1570, 1476, and 1435 cm^{-1} decrease in intensity with increasing copper concentration. New peaks, observed at 1610 and 1030 cm^{-1}, are attributed to complex formation. Other new bands at 1622 and 1540 cm^{-1}, which also increase with increasing amounts of $CuCl_2$, may be partially explained by water but may also be attributed to quarternized pyridine ring vibrations.[14] The spectra of the 1:2 complexes prepared in 95% and 100% methanol are shown from 1800–1350 cm^{-1} in Figure 3.

For the 1:2 complexes prepared in pure methanol, the bands at 1622 and 1540 cm^{-1} decrease in significance relative to the complex prepared in 95% methanol, regardless of isolation technique. No other differences from the spectra of the 1:2 complex isolated from 95:5 methanol–water were observed.

Films of $P2VPy^+HCl^-$ were prepared with different HCl:P2VPy ratios. These films show a correlation of the 1622 and 1540 cm^{-1} bands with increasing HCl concentration. In addition, bands at 2600, 2060, and 2000 cm^{-1} appear that are attributed to $=N^+H$ vibrations.[14,16] These bands are observed in the copper chloride complexes only when they are prepared as films on CaF_2 substrates. In mulled samples these bands are difficult to observe as they are probably obscured by particle scattering.

Infrared spectra were recorded for the complexes heated at 200 °C for 1 h in N_2. Several changes were observed in the spectra. The O–H bands in the 3400 cm^{-1} region, broaden, while the 1622 and 1540 cm^{-1} bands become narrower and more intense. For the complexes prepared in pure methanol, the bands at 1622 and 1540 cm^{-1} appear *only* after heating to 200 °C. In addition, the band at 1610 shifts to 1605 cm^{-1}, which is attributed to the complexation of Cu^I to the pyridine ring.

III.5. Magnetic Susceptibility

III.5.1. $CuCl_2$(2-picoline)$_2$. The magnetic susceptibility results indicate a room temperature moment of 1.85 μ_B, which is slightly higher than the reported value of 1.78

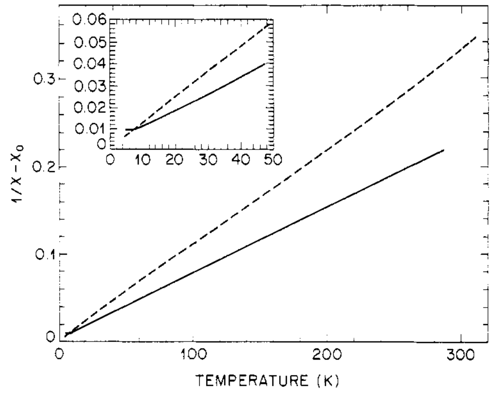

Figure 4. Plot of the inverse of the magnetic susceptibility vs temperature for 1:2 copper chloride complexes with 2-picoline (solid line) and P2VPy (dashed line). Insert shows expansion of the low-temperature regime.

Table V
Magnetic Susceptibility Data for the P2VPy-$CuCl_2$ Complexes, As Prepared and after Pyrolysis at 180 °C in N_2

conditns	complex	fit (K)	$10^6\chi_0$	10^3C_g	Θ	μ_{eff}, μ_B
as prepared	1:4	20–300	–0.088	0.586	4.0	1.66
	1:2	20–300	0.157	0.937	4.0	1.65
	1:1	25–300	0.466	1.31	9.0	1.64
after 180 °C pyrolysis	1:4	20–300	–0.627	0.0035	1.0	0.125
	1:2	20–300	–0.598	0.0041	2.0	0.106
	1:1	20–300	–0.549	0.0054	0.0	0.102

μ_B.[6] Both materials, however exhibit similar behavior of the $1/\chi$ vs temperature curves. The Curie–Weiss law is obeyed between room temperature and approximately 20 K. Below this temperature regime, the materials exhibit antiferromagnetic behavior with a Neel temperature of approximately 6 K, as shown in Figure 4.

III.5.2. Copper Chloride Complexes with P2VPy. Results from the magnetic susceptibility measurements are listed in Table V. Moments for the three P2VPy-$CuCl_2$ complexes are between 1.5 and 1.6 μ_B. These values are low, compared to the spin-only value of 1.73 μ_B or the experimentally observed moments of 1.8–2.0 μ_B for Cu(II) complexes. Curie–Weiss behavior is followed from room temperature to approximately 20 K. Below this temperature, a slight negative inflection is observed in the $1/\chi$ vs T curve. Thus, no indication of antiferromagnetic behavior is observed between 300 and 4 K. Results for the 1:2 complex with P2VPy are compared to the $CuCl_2$(2-picoline)$_2$ complex in Figure 4. The magnetic moments were found to be independent of the technique used to isolate the complexes. All three 1:2 complexes were found to exhibit moments of 1.6 μ_B.

Heating the complexes to 200 °C for 1 h in N_2 changed the color to deep red and lowered the moment appreciably to 0.1 μ_B. This indicates that paramagnetic Cu(II) has been substantially reduced to a diamagnetic form, either Cu(I) or Cu(0).

III.6. Thermogravimetric Analysis (TGA). Significant differences were observed during the thermal decomposition of P2VPy as a result of complexation with copper chloride. A new weight loss event, observed with an extrapolated onset temperature of 150 °C, is attributed to water based on mass spectral data.[17] The weight percent lost increases with increasing copper concentration, as summarized in Table VI. The complexes isolated from distilled methanol show a reduced percentage of weight lost in this temperature regime compared to the complexes prepared in 95:5 methanol–water solution. The weight loss region, for these complexes, spans a greater temperature range than the complexes from 95% methanol, and the onset temperature is lowered by >50 °C. No differences were observed in the subsequent decomposition steps of the polymer.

Table VI
Weight Loss of the P2VPy-$CuCl_2$ Complexes after Drying for 2 h at 30 °C Recorded by TGA in the Temperature Regime from 35 to 220 °C[a]

		wt % H_2O	
complex	MW	calcd	obsd
1:4	572.5	3.1	2.7
1:2	362.5	5.0	5.3
1:1	257.5	7.0	7.3

[a] Values are compared to the calculated quantity of H_2O in the complexes.

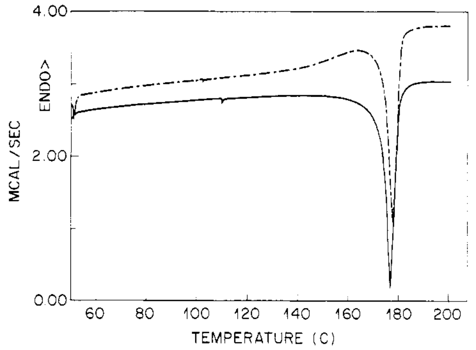

Figure 5. DSC results for the 1:2 $CuCl_2$ complexes isolated from 100% methanol (solid line) and 95:5 methanol–water (broken line). The samples were previously heated to 140 °C and cooled to 50 °C in the calorimeter.

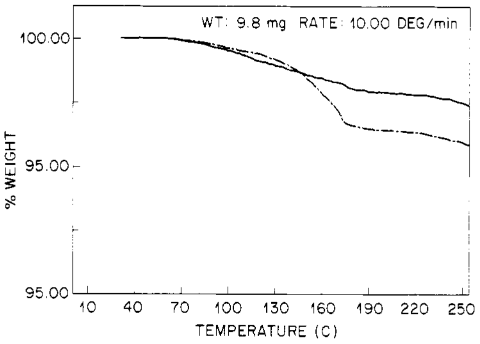

Figure 6. Thermograms of the 1:2 $CuCl_2$ complexes isolated from 100% methanol (solid line) and 95:5 methanol–water (broken line).

Decomposition of the polymer occurred at lower temperatures and via an additional process upon complexation. Details of the effect of cupric salts on the thermal decomposition of P2VPy are discussed elsewhere.[4]

Decomposing the samples at a greater heating rate (150 °C/min) increased the observed onset temperatures but otherwise did not effect the general course of the decomposition. In addition, using a 4:96 H_2–N_2 atmosphere did not significantly alter the TGA results.

III.7. Differential Scanning Calorimetry (DSC). Copper Chloride Complexes with P2VPy. Calorimetry results, performed on the 1:2 complexes isolated from 95% and 100% methanol by vacuum evaporation, are shown in Figure 5. The material isolated from 95% methanol shows a small endothermic peak preceding a sharp, intense exotherm (T_{min} = 175 °C), whereas the material isolated from 100% methanol shows a flat region before the exotherm. The magnitude of the endothermic transition, which is attributed to the evolution of water, is correlated to the original water content of the sample (see Figure 6). Reduction of Cu^{II} to Cu^I is manifested as a sharp, intense,

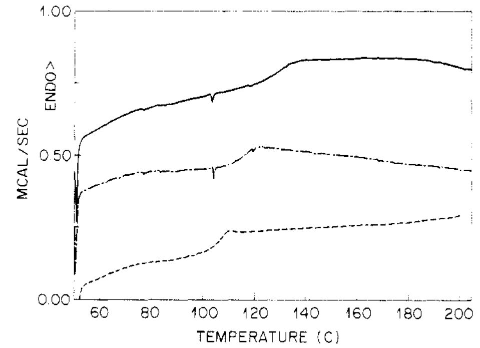

Figure 7. DSC results for the 1:2 $CuCl_2$-P2VPy complex after the complex was reduced (broken line in Figure 5). Top (solid) line is first run, and middle (broken) line is second run after reduction. These curves are compared to results for P2VPy shown in the bottom (dashed) line.

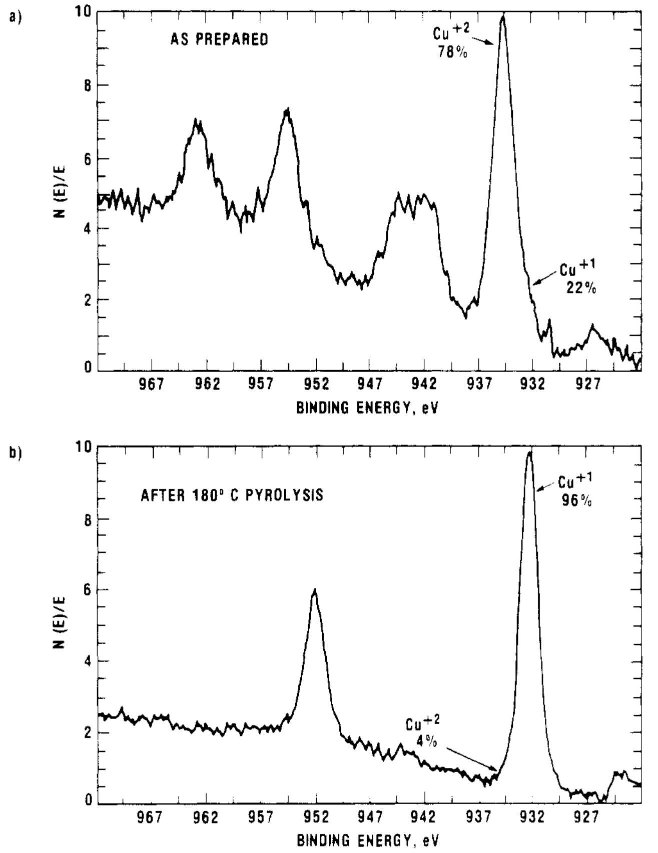

Figure 8. XPS results of the Cu(2P) transitions for the 1:2 $CuCl_2$-P2VPy complex as prepared (a) and after pyrolysis at 180 °C (b).

exotherm. The evolution of water is probably coincident with copper reduction.

The glass transition temperature (T_g) of the original complexes is not observed, even after annealing the samples at 140 °C in the calorimeter. This is probably due to the coincidence of the redox reaction. After the complexes have been reduced (i.e. heated to 200 °C), rerunning the DSC reveals a T_g at 130 °C. Repeating this measurement causes the T_g to decrease to 115 °C. A subsequent repetition has no further effect. These values are 25 and 10 °C higher, respectively, than the T_g of uncomplexed P2VPy (105 °C) as shown in Figure 7.

III.8. X-ray Photoelectron Spectroscopy (XPS). Plots of the Cu(2P) transitions are shown for the 1:2 chloride complex before and after pyrolysis in parts a and b, respectively, of Figure 8. The asymmetry of the Cu($2P_{3/2}$) peak and the presence of the shake-up satellites indicate that Cu^{II} predominates in the as prepared complex (Figure 8a). Computer fits of the Cu($2P_{3/2}$) transition show that 78% of this signal occurs at a binding energy (BE) = 935.0 eV. A second component at 932.8 eV is assigned to the Cu^{I} state on the basis of the Auger parameter[18] (the difference in kinetic energy between an Auger line and a photoelectron line) which was measured at 1847.6 eV. Cu^{I} and Cu^{0} are not distinguishable on the basis of their $2P_{3/2}$ binding energies, but differences in the Auger parameters (1847.8 ± 0.2 eV[18] for cuprous halides and 1851.1 ± 0.3 eV[18] for copper metal) are significant. Peak positions and component fractions are shown in Table VII for the 1:1 and 1:2 complexes.

Table VII
XPS Results for the As Prepared Chloride Complexes

	Cu(2P)			Cl(2P)		N(1S)		C(1S)	
complex		BE	%	BE	%	BE	%	BE	%
1:2	Cu^{I}	932.8	22	197.9	100	398.8	50	285.0	100
	Cu^{II}	935.0	78			399.8	50		
1:1	Cu^{I}	932.6	7	197.8	100	399.6	100	285.0	100
	Cu^{II}	934.7	93						

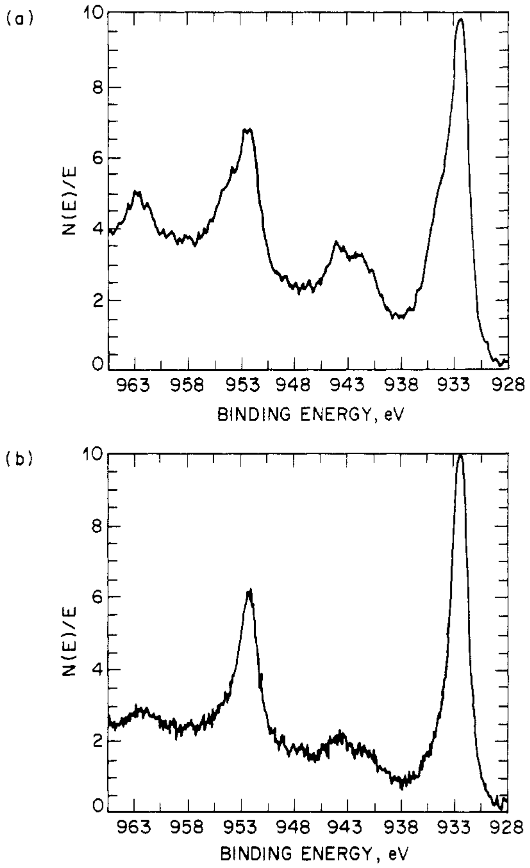

Figure 9. XPS results for the 1:1 complex, after pyrolysis at 180 °C, at exit angles of 45° (a) and 90° (b).

These samples were difficult to analyze as a slow transition from Cu^{II} to Cu^{I} was observed with exposure to X-rays. Consequently, the data in Table VII were acquired as quickly after introduction into the spectrometer as possible, minimizing exposure to the X-ray source prior to multiplexing. Conversion of Cu^{II} to Cu^{I}, observed in previous XPS studies,[19] was attributed to photolysis. In this study, the reduction of copper by heating cannot be distinguished from possible photolysis reactions.

Reduction of Cu^{II} to Cu^{I} is evident after pyrolysis as the low-energy peak at 932.6 eV (again assigned to Cu^{I} on the basis of the Auger parameter) predominates the spectrum (Figure 8b). Only 4% Cu^{II} at 934.8 eV could be determined

Table VIII
XPS Results for the Chloride Complexes after Pyrolysis at 180 °C in N_2

		Cu(2P)		Cl(2P)		N(1S)		C(1S)	
complex		BE	%	BE	%	BE	%	BE	%
1:2	Cu^{I}	932.6	96	197.9	100	398.6	45	285.0	100
	Cu^{II}	934.8	4			399.4	55		
1:1	Cu^{I}	932.5	83	198.4	100	398.6	18	285.0	100
	Cu^{II}	934.6	17			399.6	82		

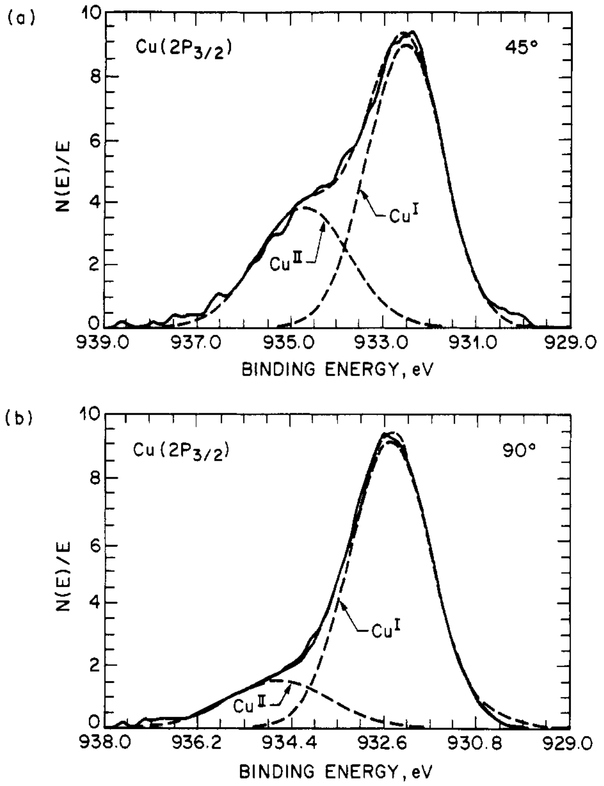

Figure 10. Curve fit results (dashed lines) for the Cu($2P_{3/2}$) transitions (solid lines) shown in Figure 9.

by curve fitting techniques. The loss of the shake-up satellites is also characteristic of the reduction of Cu^{II}. Results for the 1:1 and 1:2 complexes, after pyrolysis to 180 °C, are summarized in Table VIII.

Oxidation of the surface of the pyrolyzed complexes was determined by examination of the spectra as a function of exit angle. Figure 9a shows the XPS spectrum recorded at an exit angle of 45° for the 1:1 complex after pyrolysis to 180 °C. It is clear from the shape of the Cu($2P_{3/2}$) peak and the presence of the shake-up satellites that Cu^{II} contributes significantly to the spectrum at 45°. Computer fits of the Cu($2P_{3/2}$) 45° data (Figure 9a), show that 66% of this signal occurs at BE = 932.5 eV, while 34% occurs at 934.7 eV. The component at 932.5 eV is assigned to Cu^{I} on the basis of the Auger parameter, while the Cu^{II} occurs at 934.7 eV. Rotation of the sample to an exit angle of 90° gives the Cu(2P) spectrum shown in Figure 9b. The vertical scale is increased by 1.6 over that for Figure 9a, and the component of Cu^{I} obtained from a computer fit of the $2P_{3/2}$ transition has increased from 66% at 45° to 83% at 90°. In accord with the observed increase in Cu^{I} component at 90° exit angle, the oxygen signal drops from 8.8 atom % at 45° to 4.7% at 90°. This is consistent with the oxidation of Cu^{I} on the surface.

The curve fits used to obtain the fractions of Cu^{I} and Cu^{II} at 45° and 90° are shown in parts a and b, respectively, of Figure 10. The binding energy shift between the two oxidation states of copper is 2.2 eV, which is in good agreement with reference values[18] and the half-widths of the Cu^{I} components are each 1.9 eV where the Cu^{II} half-widths are 2.4 (45°) and 2.3 eV (90°). The correspondence between the components on the Cu($2P_{3/2}$) transition is considered excellent and is typical of curve fitting for this transition.

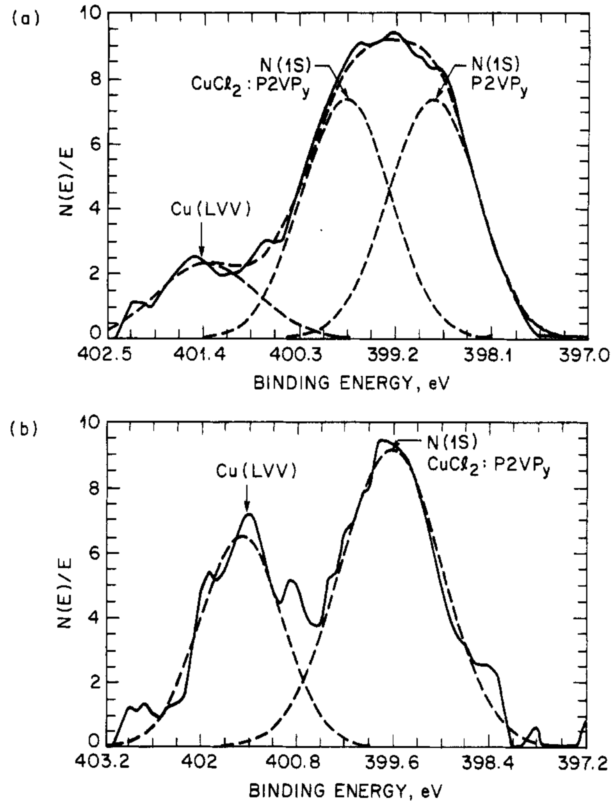

Figure 11. XPS results of the N(1S) transitions and Cu(LVV) Auger peaks (solid lines) and curve fit results (dashed lines) for the 1:2 (a) and 1:1 (b) complexes.

The XPS spectra of the N(1S) and Cl(2P) transitions provide additional information about the electronic processes in these compounds, with the N(1S) spectra being the most straightforward to interpret. In P2VPy, the N(1S) transition was found at 398.8 eV with a half-width of 1.47 eV. Clark and Thomas[20] report this transition at 400 eV whereas Nolberg et al.[21] report 398.6 eV for N(1S) in pyridine. Upon complexation, this value shifts to higher energies. The N(1S) transition is observed at 399.6 eV for the 1:1 complex (Figure 11b) without an increase in peak width, indicating that partial charge transfer from the nitrogen lone pair to copper has occurred. This shift is observed in both the as prepared and pyrolyzed films, where the assigned formal valence is +2 and +1, respectively. In the 1:2 complex, the N(1S) transition is broadened to a half-width of 2.1 eV, which can be decomposed into two peaks with binding energies of 398.8 and 399.8 eV, as shown in Figure 11a. The noncomplexed N(1S) transition occurs at 398.8, in good agreement with the measurement of P2VPy, whereas the peak at 399.8 eV agrees with our observations for the 1:1 complex. Note that the intensity of the Cu LVV Auger transition at BE = 401.5 eV roughly doubles in intensity relative to N(1S) with the doubling of the copper concentration in the complex.

The Cl(2P) binding energy was found to be the same in all of the complexes, regardless of the oxidation state of the copper. The Cl(2P) transition could be fit into the $2P_{1/2}$ and $2P_{3/2}$ components without any indication of additional peaks due to chemical shifts. The unusual aspect of the Cl(2P) transition is that it occurs at BE = 198.0 ± 0.2 eV, which is closer to the BE in CuCl (198.6

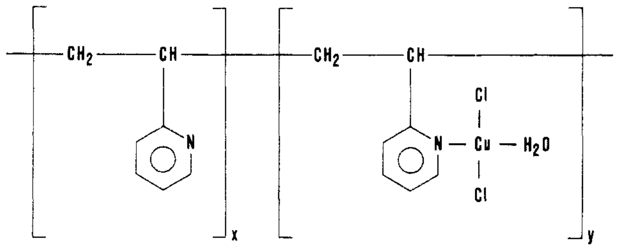

Figure 12. Proposed structure of the $CuCl_2$–P2VPy complex.

eV[22]) than in $CuCl_2$ (BE = 199.2 ± 0.2 eV[18,22]) or poly(vinyl chloride) (BE = 199.9 eV[18]). Measurements of $CuCl_2$ and poly(vinyl chloride) in the spectrometer give values for Cl(2P) at 199.2 and 199.9 eV, respectively, confirming the accuracy of the spectra.

The presence of any carbon–chlorine bonds is improbable due to the good fit of the chlorine peaks and lack of significant shifts in the C(1S) transition. The shift to lower energies may be due to the ligation of the copper. Shifts as large as −2.1 eV were reported for the Cl(2P) transition in ethylenediamine complexes of $CuCl_2$.[19]

III.9. X-ray Diffraction. X-ray diffraction of the complexes as prepared, and after heating to 200 °C for 1 h, shows a broad amorphous band centered at ≈3.8 Å. After heating at 350 °C, however, the sharp, intense bands of metallic copper appear. The diffraction pattern remains unchanged above 350 °C.

IV. Discussion

IV.1. Structure of the Complexes. Although the structure of the polymer complexes is difficult to determine exactly due to their amorphous nature as well as the variable geometry of copper complexes as a class,[23] a general picture can be formed from the available data. The proposed structure of the complex is shown in Figure 12. Each copper atom is coordinated to one pyridine moiety. This configuration is consistent with the Job's plot results, as well as the equivalence between solution and solid-state spectra. Chemical analysis results for the three complexes are in good agreement with the calculated values shown in Table II. In addition, reactions between the sterically unhindered P4VPy and $CuCl_2$ resulted in the complexation of at least two pyridine moieties about each copper atom and insoluble cross-linked gels.

The complexation of only one pyridine ligand by Cu(II) is unusual but is probably due to the severe steric environment of the polymeric ligand. For nonsterically hindered aromatic amines, such as pyridine and 4-methylpyridine, polymeric complexes are formed with $CuCl_2$, where copper is found in a distorted octahedral environment surrounded by two pyridine moieties (2.0 Å) and two Cl's (2.3 Å), with two other Cl's further removed (3.1 Å).[24] With sterically hindered pyridines, such as 2-picoline, two pyridine moieties and two Cl's are able to complex to copper[8,25] in a distorted square-planar arrangement. The two coppers are bridged in this dimer by a chlorine atom occupying the fifth, apical site. This bond is very long (bond length of 3.364 Å[8,25]) and is longer than any other tetragonal-pyramidal dichloro-bridged copper(II) dimer.[8] The long bridge accounts for this material's weakly antiferromagnetic properties. A 1:1 complex formed between 2-picoline and $CuCl_2$ has also been reported,[26] but its structure has not been determined. The lack of structural information may be due to the amorphous nature of this complex, as results reported here indicate.

The low magnetic moments of the polymeric complexes could result from the presence of a diamagnetic impurity, such as Cu(I), with a concentration of 22% (calculated by using the equation $\mu_{\mathrm{eff}} = [8C_g(\mathrm{MW})]^{1/2}$ and assuming a value of $\mu_{\mathrm{eff}} = 1.85\ \mu_B$ for a pure Cu^{II} complex). This percentage is consistent with the XPS results (see Table VII). Pyridine is known to stabilize the cuprous state.[27] The adherence to the Curie–Weiss law, as well as the low Θ values, supports this contention. Low moments in many complexes can be accounted for, however, by coupling between copper atoms bridged by various groups. Magnetic moments in the range of 1.3–1.6 μ_B are commonly observed for binuclear Cu(II) complexes including the acetate bridged $[Cu(OOCCH_2)_2(H_2O)]_2$[28] and the hydroxide-bridged $[Cu(2\text{-aminopyridine})_2(OH)]_2(NO_3)_2$.[29] For the acetates and other hydroxide-bridged copper complexes,[30] distinct antiferromagnetic behavior is observed. Hydroxide-bridged complexes that conform to the Curie–Weiss law[31] exhibit normal moments at room temperature. The magnetic susceptibility of even weakly coupled copper complexes, such as $CuCl_2(2\text{-picoline})_2$ ($-2J = 7.4\ \mathrm{cm}^{-1}$)[6] show distinct antiferromagnetic behavior (Figure 4 and ref 6) but have normal room temperature moments (1.85 μ_B). Therefore, coupling between copper atoms would be readily observed and probably does not occur in the $CuCl_2$–P2VPy complexes.

Given that 22% of Cu^{II} has been reduced to Cu^I, then the oxidized species requires identification. One interpretation, based on infrared results, would indicate that the pyridine rings are oxidized to the pyridinium form. An internal electron-transfer reaction would thus result in the reduction of Cu^{II}. Metal-catalyzed oxidations of aryl rings have been reported.[32] One difficulty with this explanation is that the presence of the bands at 1622 and 1540 cm^{-1} are dependent upon the solvent system. These bands are not observed for the complex isolated from 100% methanol; however, the magnetic moment of this complex (1.59 μ_B) indicates the same concentration of Cu^I as in the compounds prepared in 95% methanol. The IR bands may also be due to vibrations from the water molecule complexed to copper. Water complexed by numerous transition-metal complexes are known to absorb in this region,[15] and the intensity of the bands corresponds to the content of water in the complex. The coincidence of both the position and relative intensity of the water and pyridinium bands, would, however, be unlikely.

Alternatively, the bands at 1622 and 1540 cm^{-1} may be explained by the presence of $\equiv N^+HCl^-$. In aqueous solution, cupric chloride is known to be acidic, so that the equilibrium

$$CuCl_2{\cdot}4H_2O + H_2O \rightleftarrows CuClOH{\cdot}4H_2O + HCl$$

would generate HCl which would be complexed by free pyridine moieties, forming pyridinium bands. The enhanced solubility of these complexes in 95% methanol could also be explained by the presence of the hydrochloride salt.

The Cu^{II} cation could be reduced through the oxidation of methanol. Methanolic solutions of several metal halides including copper,[33] rhodium,[34] and platinum[35] have been reported to undergo redox reactions. In these cases, methanol is oxidized to formaldehyde as a result of the reduction of the metal. Copper(II) chloride has been reported[36] to slowly oxidize methanol in the presence of sunlight, and the oxidation of acetone by $CuCl_2$ has also been reported.[37] In numerous biological systems, copper(II) salts have been reported to oxidize organic substrates.[38] Thus, the reduction of the copper may occur independently of water.

The reduction of Cu^{II} is not limited to the presence of P2VPy. When 2-picoline was used as the ligand and the complex was isolated by removing the solvent under vacuum, a red tar was formed. Similar red tar formation was observed for the redox reaction of alkylamines with $CuCl_2$.[39] The peak at ≈1730 cm^{-1} in the IR spectrum of the red tar (Figure 2) may be indicative of carbonyl vibrations resulting from the oxidation reactions. No tarry products were observed, however, when the complex was prepared in concentrations high enough to precipitate crystals from the solution. In this case both the time the complex was exposed to the solution as well as the heterogeneous nature of the reaction would inhibit redox reactions.

IV.2. Formation of Copper Metal. The first step in the formation of metallic copper from the copper chloride complexes is the complete reduction of Cu^{II} to Cu^{I}. This reaction occurs in the temperature range from 150 to 180 °C, with the loss of water (TGA, DSC, and MS) and reduction of copper (DSC, magnetic susceptibility, XPS). The XPS results confirm that the oxidation state of the copper is +1. The reduction of cupric salts by amines is well-known[39,40] (see also previous section).

As a result of the reduction of the copper, the pyridine rings are oxidized, via internal electron transfer. Pyridinium bands at 1622 and 1540 cm^{-1} are observed for all complexes, regardless of preparation technique. The fact that these bands cannot be attributed to water is evident. A shift in the N–Cu vibrational band from 1610 to 1605 cm^{-1} is also observed, indicating a change in the N–Cu bonding. In addition, intense charge-transfer bands are observed in the UV–visible spectrum of the complex; Cu^{I}, a d^{10} ion, does not absorb in this regime.

The final step in the formation of copper metal occurs during the decomposition of the polymer. The cuprous chloride complex is reduced as the polymer is oxidized. This reaction is the most difficult to characterize due to the numerous, simultaneous reactions which may occur during a relatively short time. Chlorination of the polymer backbone to form HCl, unsaturated carbon–carbon bonds, and copper metal is postulated. A similar mechanism is reported for the chlorination of anthracene by cupric chloride.[41] The formation of metallic copper during polymer decomposition is not limited to the P2VPy system. When a physical mixture of $CuCl_2 \cdot 2H_2O$ and polystyrene was pyrolyzed above 350 °C, copper metal was observed in the carbonaceous char.

The quantitative retention of copper metal in the char contrasts sharply with the results from monomeric analogues. Decomposition of $Cu(pyridine)_2Cl_2$,[42,43] Cu(2-picoline)$_2$Cl$_2$,[4] and Cu(2-ethylpyridine)$_2$Cl$_2$[44] occurs by the release of ligands at relatively low temperatures (120–300 °C) to form $Cu^{II}Cl_2$. Cupric chloride will decompose to form $Cu^{I}Cl$, which sublimes at elevated temperatures to leave no copper residue. In the polymer complex, as the high molecular weight ligand cannot diffuse away from the metal, high-temperature reactions can occur which lead to the oxidation of the polymer and the reduction of the cuprous ion to nonvolatile copper metal.

V. Conclusions

Soluble polymers containing high weight percent copper were prepared through the choice of a mixed-solvent system and by preventing cross-link formation through the use of a sterically hindered polymeric ligand.

Copper in the polymeric complexes is reduced in a stepwise manner to form a chemically stable Cu^{I}–P2VPy complex above 150 °C. The cuprous state is evident based on XPS and magnetic susceptibility results. At higher temperatures, the cuprous complex is reduced to copper metal, as the polymeric ligand is oxidized to form a carbonaceous char. The copper, originally present in the complex, is quantitatively retained in the char.

Registry No. Cu, 7440-50-8; $CuCl_2$(2-picoline), 14493-47-1; $CuCl_2$(2-picoline)$_2$, 42568-67-2.

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Topochemical Photoreactions of Unsymmetrically Substituted Diolefins. 2.[†] Photopolymerization of 4′-(Alkoxycarbonyl)-2,5-distyrylpyrazines

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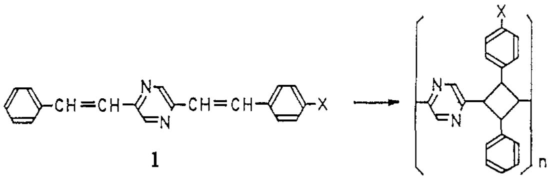
ABSTRACT: Four kinds of crystals, 4′-(alkoxycarbonyl)-2,5-distyrylpyrazines (**1a–d**), showed an extremely high photoreactivity and gave highly crystalline linear polymers (**2a–d**) of high molecular weight ($\eta_{\rm inh}$: 0.8–2.4) having cyclobutane rings in the main chain. The photochemical and thermal behaviors of resulting polymers were similar to those of poly(2,5-distyrylpyrazine) (poly-DSP); these polymers photodepolymerize exclusively into the starting diolefins in solution, whereas in the film state in the air these polymers degrade photooxidatively, accompanied with an unusual deterioration of the pyrazine moiety. Heat treatment of poly(4′-(methoxycarbonyl)-2,5-distyrylpyrazine) (**2a**) under reduced pressure gave 4′-(methoxycarbonyl)-2,5-distyrylpyrazine (**1a**), DSP, and bis(methoxycarbonyl)-2,5-distyrylpyrazine as sublimation products, indicating the competing occurrence of the symmetric and asymmetric thermal cleavages of the cyclobutane ring. X-ray crystal structure analysis showed that the molecules in these crystals of **1a** and **1b** were packed in the hetero α-type (head-to-tail) arrangement. The reactivity of the monomers and the structure of the photoproducts are reasonably explained on the basis of the molecular arrangement in these monomers.

Introduction

[2 + 2] topochemical photopolymerization was first reported on the reaction of 2,5-distyrylpyrazine (DSP) crystal.[1,2] On photoirradiation, an extremely highly crystalline poly-DSP is formed quantitatively from the α-type (head-to-tail) DSP crystal, in which the intermolecular reactive double bonds are arranged in parallel at a distance of 3.939 Å across a center of symmetry.[3] Since then, a great number of highly crystalline linear polymers have been prepared from diolefinic compound crystals by repeating step-by-step [2 + 2] topochemical photocyclodimerization.[4]

Recently we found a number of unsymmetrically substituted photoreactive diolefinic crystals that afford various types of photoproducts, such as a homo- or a heteroadduct types of the polymers and dimers[5–8] or a cyclophane.[9] In the topochemical photoreaction of the α-type unsymmetric diolefinic crystals that results in the heteroadduct type cycloaddition, the photoproduct is expected to be a highly stereoregulated linear polymer having alternating substituents of 1,4-arylene and a cyclobutane ring of the same chirality. Furthermore, in a special case, the monomer arrangement resulted in the formation of a chiral crystal, giving optically pure oligomeric substances on photoirradiation.[10]

In this paper, we report the photoreaction of several kinds of unsymmetrically substituted diolefin crystals having DSP skeleton. These are 4′-(methoxycarbonyl)-, 4′-(ethoxycarbonyl)-, 4′-(propoxycarbonyl)-, 4′-(butoxycarbonyl)-, 4′-cyano-, and 4′-(trifluoromethyl)-2,5-distyrylpyrazines (**1a–f**).



1 → 2 (1)

X: H, 2,5-distyrylpyrazine (DSP)
X: COOR (R: Me (**a**), Et (**b**), Pr (**c**), Bu (**d**))
X: CN (**e**)

Structures and properties of the resulting polymers were investigated by ordinary spectroscopic measurements. Moreover, the crystallographic studies were carried out of two photoreactive crystals, **1a** and **1b**, to correlate the photoreactivity of the monomer and the structure of the photoproduct with the molecular arrangement in the monomer crystal.

Experimental Section

Measurements. Melting points of the monomers were measured by a Laboratory Devices MEL-TEMP and are uncorrected. ^{1}H NMR spectra were measured in trifluoroacetic acid (TFA-d_1) by a JEOL PMX-60SI or a JEOL GX-400 spectrometer with tetramethylsilane (TMS) as an internal standard. Infrared spectra were measured by a JASCO IR-810 infrared spectrophotometer. Thermogravimetric differential scanning calorimetry (TG-DSC) curves were recorded on a Rigaku Thermoflex TG-DSC instru-

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