Polymer Anchored Metal Complexes. IV. X-ray Photoelectron Spectroscopic Analysis of a Polycondensate from Cu(II) 1,10 Phenanthroline and Pyromellitic Dianhydride

INTRODUCTION

Chemical characterization of intractable metal-containing polymers is often limited by the processing difficulties associated with such systems. In this regard, use of X-ray photoelectron spectroscopic (XPS) technique, which is widely applied to study metal–polymer interactions and related problems,[1] may be effective. However, very little experimental information is available to judge the efficiency of this technique in the chemical characterization of intractable systems. Accordingly, in the course of our continuing work[2,3] on metal-containing polymers, we have used XPS techniques for elemental and chemical analysis of an intractable polycondensate. Cu-Phen-Cl$_2$-PMDA, recently prepared by us[3] through polycondensation of Cu(II), 1,10 Phenanthroline dichloride and 1,2,4,5 benzene tetracarboxylic dianhydride (Scheme 1). The results reported herein are encouraging within certain limitations that do not rule out the applicability of this technique for routine chemical analysis in intractable systems.

EXPERIMENTAL

Materials

1,2,4,5 benzene tetracarboxylic dianhydride, (Fluka, PMDA) was vacuum sublimed prior to use. 1,10 phenanthroline monohydrate (Aldrich) was used directly as supplied. All other reagents and solvents were of analytical grade.

Preparation

Cu-Phen-Cl$_2$ was prepared by a published procedure.[3] An intimate mixture of Cu-Phen-Cl$_2$ and PMDA in two different mole ratios, 1 : 2 and 1 : 3, was heated in presence of anhydrous ZnCl$_2$ (threefold excess of reactant feed) at 220°C for 6 h under N$_2$. The mixture was extracted in a Soxhlet for 8 h in water followed by further extractions with tetrahydrofuran, CHCl$_3$, and ethanol. The product was vacuum dried at 80°C for 24 h and subsequently characterized.[3]

Characterization

X-ray photoelectron spectra were recorded with a VG ESCA LAB MK II spectrometer using Al K (14.86.6 eV) on a strip chart recorder. The X-ray source was operated at 12 KV, 20 mA. Analyzer pass energy for all the high-resolution spectra was 40 eV. This gave the instrumental resolution at 0.8 eV. During the measurements, the analyzer chamber pressure was maintained at 10^{-9} torr.

The dry samples taken in the powdery form were pelletized under 5–6 ton pressure. The pellets were kept in vacuum at room temperature for 24 h before being mounted on the stylus and then kept in the preparation chamber for 1 h and subsequently transferred to the analysis chamber. For energy referencing, C is the peak corresponding to the lower position of the binding energy (BE), which was considered to be 285 eV. All the energy positions corresponding to the different photoelectron peaks were with respect to this reference.

Data Analysis

High-resolution X-ray photoelectron core level spectra of C, O, Cl, and N reported here were recorded using a large value of the time constant. For this, no smoothing of the experimental data was necessary prior to peak-fitting the spectra. From a knowledge of component peak positions,[1] and assuming the component distribution to be of Gaussian type, the necessary software developed[4] was used to separate the superimposing peaks. For quantitative estimation, areas under the photoelectron peaks were determined using a linear background subtraction method.[5] Predicted stoichiometry was calculated using published values of the sensitivity factor.[6] Under these conditions, the reported quantitative results are expected to be accurate within 10%.

RESULTS AND DISCUSSION

Cu-Phen-Cl$_2$-PMDA is insoluble in all common solvents. The details of elemental analysis and UV and IR spectral analyses results for Cu-Phen-Cl$_2$-PMDA have been described in a preceding publication.[3] However, one special feature of IR absorption results that is of
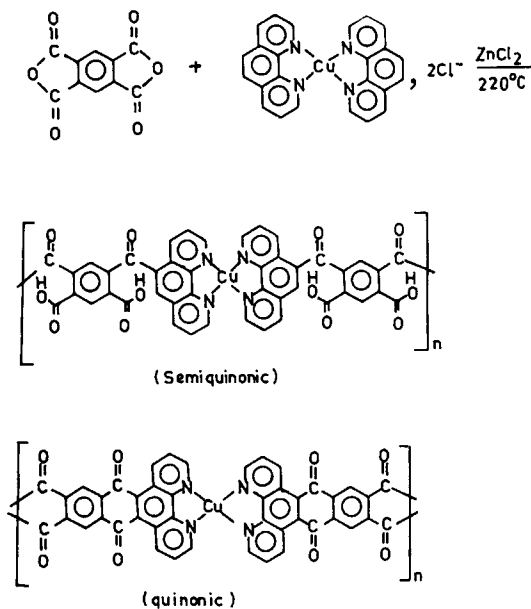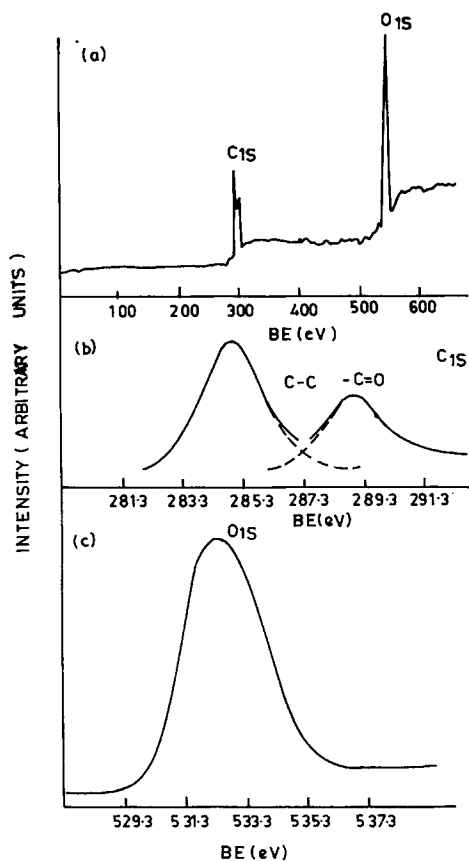
Scheme 1.

Figure 1   Wide-scan XPS of PMDA (a), high-resolution XPS of C 1s (b), and O 1s (c). Energy resolution = 0.8 eV.
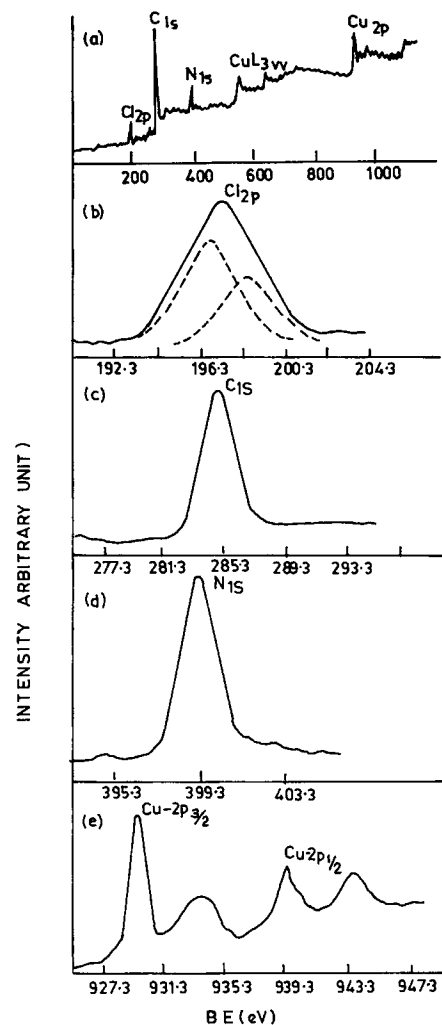

Figure 2   Wide-scan XPS of Cu-Phen-Cl₂ (a); high-resolution XPS of Cl 2p (b) C 1s (c), N 1s (d), and Cu 2p₃/₂ Cu 2p₁/₂ (e).

much relevance in the present context is the appearance of an absorption around 3400 cm⁻¹ in Cu-Phen-Cl₂-PMDA in addition to the strong carboxyl stretching at 1699 cm⁻¹ (semiquinone). The 3400 cm⁻¹ absorption is tentatively ascribed[3] to O — H stretching from any — COOH moiety likely to be formed in Cu-Phen-PMDA through PMDA during condensation.

XPS Analysis

XPS characteristics of the individual reactants, PMDA and Cu-Phen-Cl₂ and of Cu-Phen-Cl₂-PMDA, were evaluated. Figure 1 shows the wide-scan spectrum of PMDA and the high-resolution spectrum of C 1s and O 1s, respectively. Evidently, the C 1s peak may be
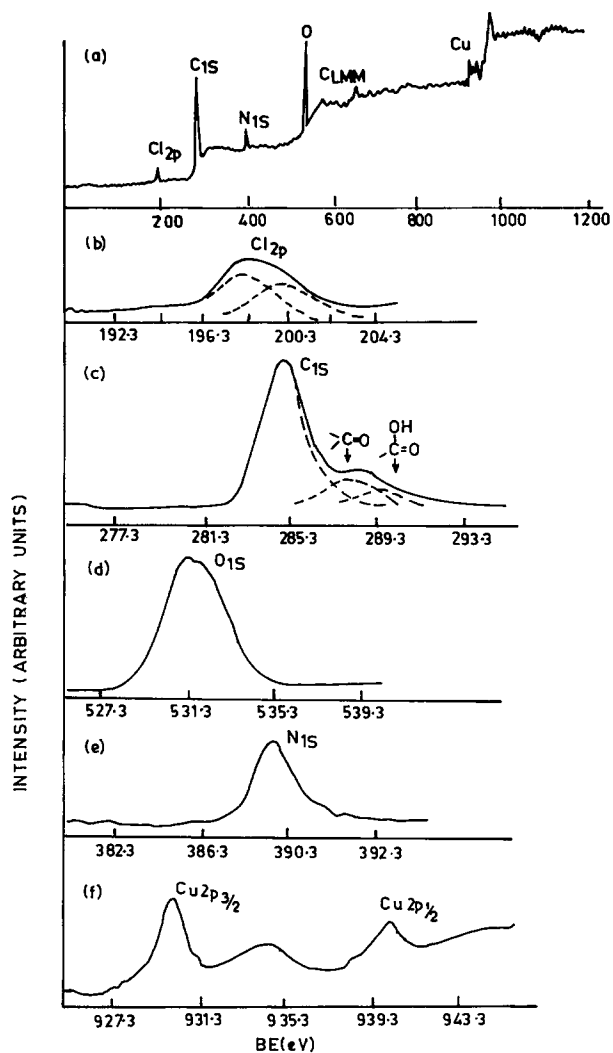
Figure 3 Wide-scan XPS of Cu-Phen(Cl₂) PMDA (a); high-resolution XPS of Cl 2p (b), C 1s (c), O 1s (d), N 1s (e), and Cu 2p₃/₂ and Cu 2p₁/₂ (f).

regarded as a contribution of two different carbons in two different environments. The 285.3 eV peak is due to phenylcarbons,[3] while the other peak at 289.3 eV is generally attributed to —COO—CO— moiety[3] in PMDA.

Figure 2 shows the wide-scan spectrum for Cu-Phen-Cl₂, where the peaks are labeled as showing the presence of Cl 2p, C 1s, N 1s, Cu 2p, and Cu L₃ VV lines. The high-resolution spectrum of C 1s in Cu-Phen-Cl₂ (Figure 2) reveals the presence of a single C 1s peak at 285 eV due to phenylic carbons in the Phen moiety. The presence of Cl and N in Cu-Phen-Cl₂ is endorsed in Figures 2(b) and 2(d). Figure 2(b) also shows the resolved components of Cl 2p peak. With C 1s at 285 eV as the energy reference,

the peak at 196.7 eV is attributed to ionic Cl, while the peak at 198.7 eV is assigned to a bonded Cl. The reported difference in binding energies between these two states is 2 eV.[5] This feature implies that one of the Cl in Cu-Phen-Cl₂ is bonded, while the other exists in ionic form. This will also imply that Cu exists in the Cu-Phen-Cl₂ complex with a coordination number of +5. Conductance measurements by Harris et al.[7] and Barclay et al.[8] also confirm such a notion. However, this conclusion is rendered somewhat uncertain by the fact that the observed spin-orbit splitting of Cl 2p₃/₂-Cl 2p₁/₂ is also around 2 eV.

Figure 2(c) shows the Cu 2p₃/₂ and Cu 2p₁/₂ peaks arising out of Cu in the Cu-Phen complex. The presence of strong shake-up peaks following the photoelectron lines Cu 2p₃/₂ and Cu 2p₁/₂ affirms that Cu is in the +2 oxidation state.[6]

Figure 3 shows the wide-scan spectrum of Cu-Phen-Cl₂-PMDA. The photoelectron lines corresponding to Cl, C, N, O, and Cu are labelled in the diagram. Figure 3(b-e) show the high-resolution spectra of O 1s (531.8 eV), C 1s, Cl 2p, and N 1s (399 eV), respectively. The C 1s peak shown in Figure 3(c) may be resolved into three components. The peak corresponding to lower BE (285 eV) may be attributed to phenylic carbons, while the other two are ascribed to C=O (288.3 eV) and COOH (289 eV), respectively.

The presence of —COOH photoelectron peak also substantiates the tentative proposal (Scheme 1) that Cu-Phen-Cl₂-PMDA may not be completely cyclized and thus may retain some of the free —COOH groups in the structure. Further, the resolved components also indicate that the concentration of >C=O is more compared to that of COOH.

The high-resolution spectrum of Cl [Fig. 3(b)] in Cu-Phen-Cl₂-PMDA also exhibits the same features as in Figure 2(b).
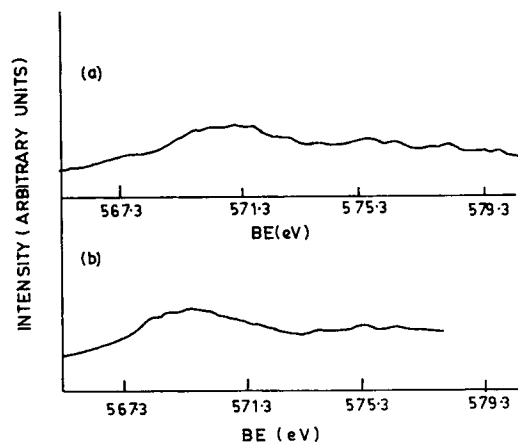

Figure 4 X-ray excited Cu–Auger lines, CuL₃VV, in Cu-Phen(Cl₂)-PMDA (a) and in Cu-Phen-Cl₂ (b).

Table I   Auger Parameter Evaluation Data

Element	Compound	Reference Lines	Auger Parameter $e\nu^{(\alpha)}$
Cu	Cu-Phen-Cl$_2$	L$_3$VV	1850.1 $\pm$ 1
Cu	Cu-Phen-Cl$_2$-PMDA	L$_3$VV	1850.9 $\pm$ 1

Auger Parameter Evaluation

The Auger parameter is defined as α = KE (Auger) + BE (photoelectron), where α is the Auger parameter. KE (Auger) refers to the kinetic energy of the Auger lines, and BE refers to the binding energy of the photoelectron[9] line for a given element in a given spectrum. Table I presents the results for Auger parameter evaluation for Cu in Cu-Phen-Cl$_2$ and Cu-Phen-Cl$_2$-PMDA (Fig. 4). The difference between the Auger parameters (Table I) for Cu in Cu-Phen-Cl$_2$ and Cu-Phen-Cl$_2$-PMDA is 0.8 eV. This difference is quite significant and is comparable to the difference in energy seen for very different Cu-compounds (Al$_2$Cu, CuO, for example). Further, a comparison of Figure 2(f) with Figure 3(f) reveals that Cu 2p envelopes of the two compounds are not exactly similar and the absence of Cu 2p$_{1/2}$ satellite in Cu-Phen-Cl$_2$-PMDA is conspicuous. These features indicate that chemical environment of Cu in Cu-Phen-Cl$_2$ may be different from that in the polycondensate Cu-Phen-Cl$_2$-PMDA. It is not exactly clear at this moment what the reason may be for such difference, and the feature is receiving closer attention.

Quantitative Elemental Analysis by XPS Studies

The procedure applied for estimating atomic percents for the respective elements involved measuring the in-tensities by assuming a linear background. The sensitivity factor used for all elements was taken from standard charts,[10] and the relation used was $C_n = \dfrac{I_n/S_n}{\Sigma I_j S_j}$, where C_n = atomic percent of element n, I_n = intensity of the photoelectron peak of the element, S_n = sensitivity factor of n, and Σ_j taken over all elements present. Table II summarizes the elemental analysis data for Cu-Phen-Cl$_2$-PMDA.

CONCLUSIONS

Application of photoelectron spectroscopic techniques to an intractable metal-containing Cu-Phen-Cl$_2$-PMDA polycondensate may provide useful information on the chemical states of the elements incorporated in the polymer, as well as their chemical compositions.

Table II   Quantitative Elemental Analysis of Cu-Phen(Cl$_2$) PMDA by XPS Analysis

Element	Sensitivity Factor	Element (%) Observed	Element (%) Theoretical
O	0.66	19	14.3
C	0.25	56	58
Cl	0.73	5.9	7.9
N	0.42	5.2	6.2
Cu	6.3	5.7	7.1

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