Electrical Resistivity and ESCA Studies on Neutral Poly(alkylbenzimidazoles), Their Salts, and Complexes

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Synopsis

A series of metal and acid salts having poly(alkylbenzimidazoles) as the parent ligand were synthesized. The room-temperature electrical resistivity of the parent and the salts was measured. Values for the dc electrical resistivity varied from ~1 × 10^{13} ohm·cm for the neutral polymers to ~1 × 10^6 ohm·cm for the acid conjugate formed by reaction with HCl. Unexpectedly, changes in resistivity did not correlate with acid strength as measured by us but could be roughly correlated with the molar volume of the corresponding acid or metal salt. The nature of the complexes was elucidated using the ESCA technique. The electron core levels of nitrogen, chlorine, and the various metals were examined. The observed photoelectron spectra indicated the formation of polybenzimidazole/acid and polybenzimidazole/metal salts. In addition, one was able to conclude that the complexes of Co and Ni were high spin, thus ruling out a planar geometry for the Ni(II) complex.

INTRODUCTION

In an extension to the work of one of the authors,[1-3] two series of alkylbenzimidazole polymers, and several of their salts and complexes were prepared. These were tested to find whether structural changes in the neutral parent polymers affect their electrical resistivity and what effect do various ligands have on the resistivity of the polymeric salts and complexes.

The electron spectroscopy for chemical analysis (ESCA) technique was employed in order to elucidate the nature of some of the salts and complexes. Our observations concerning the electrical resistivity and ESCA results are presented below.

EXPERIMENTAL

The polymers were prepared from various aliphatic diacids and either 3,3'-diaminobenzidine or 1,2,4,5-tetraaminobenzene by polycondensation in hot polyphosphoric acid according to the procedure of Iwakura et al.[4,5]

Salts of the poly(alkylbenzimidazoles) were prepared by either dissolving them in the appropriate acid and subsequently stripping off the excess acid or by mixing solutions of the polymer and acid in DMSO and stripping the solvent off. Colored complexes with metals or triiodide were prepared by titrating DMSO solutions of the particular ligand into a DMSO solution of the polymer until the endpoint, determined by a sudden color change of the polymer solution, is reached. The complexed polymer may precipitate during the titration or may be collected by subsequent precipitation with acetone. In all instances the solid products were heated for several hours under vacuum at temperatures not less

than 20°C above the normal boiling points of the acid in the case of salts, or the DMSO solvent in the case of metal ligands, to remove all excess acid and solvent traces.

Electrical resistivity was measured on films and/or pellets of the materials by means of a General Radio Type 1864 megohmmeter. No significant differences in resisitivity were observed as a function of changes in the test voltage within the range of 10 to 100 V.

X-ray photoelectron spectra were recorded on an AEI ES 200 B spectrometer using Mg $K\alpha$ radiation. The samples were examined as films or as powders brushed onto pressure sensitive cellophane tape. All spectra were run at a temperature of at least −50°C so as to prevent the possibility of radiation damage. As a binding energy standard we used the C(1s) line (285.0 eV) of the hydrocarbon contaminant present on the sample surface.[6]

RESULTS AND DISCUSSION

For the purpose of studying the room-temperature electrical resistivity of alkylbenzimidazole polymers and their salts, a sequence of ten such polymers were condensation polymerized in hot polyphosphoric acid. The polymers were poly(alkylbisbenzimidazole) (I) and poly(alkyldibenzimidazole) (II) with 4, 5, 6, 7, and 8 (CH_2) groups between the aromatic residues:

I

II
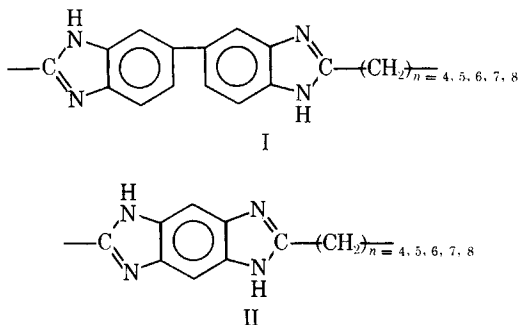
In their neutral form all the polymeric analogs recorded a dc electrical resistivity of about 1×10^{13} $\Omega\cdot$cm. This is slightly higher than the 1×10^{12} $\Omega\cdot$cm previously reported[1] for poly(trimethylene-2,5-benzimidazole), but the difference may be due to the different setups and equipment used in the two studies.

The polymers are soluble, with or without warming, in formic, trifluoroacetic, and phosphoric acid; the viscosity in the latter at 85°C is much smaller than in formic acid at the same temperature. This, plus the dramatic reduction of the viscosity upon the addition of NaCl or KCl to the formic acid solution, indicates the strong polyelectrolyte nature of poly(alkylbenzimidldazole) in formic acid. Lower molecular weight homologs are soluble, with extensive heating, in DMSO.

When the viscosity measurements in formic acid were repeated 24 hr after the initial ones, no significant change in the solution viscosity was noticed. This indicates that within this period no measurable degradation of the polymer in the acidic solvent took place. Similar observations were previously noted in reference 3. Solution viscosity measurements and thermogravimetric studies

of the polymer before and after vacuum drying also failed to reveal any degradation during this treatment.

A proof for the formation of salts was the existence of acid in the resultant product. Using the pH of a $0.01N$ aqueous solutions as a scale, it was found that acetic acid (which just swells the polymers and does not dissolve them)[7] with a pH of $\sim$3.5 is the transition point. Weaker acids such as acrylic (pH $\cong$ 3.8) do not form salts, while stronger acids such as formic (pH $\cong$ 2.8) do. Elemental analyses and thermogravimetric measurements indicate that the acids tend to form 1:1 complexes of one acid residue per benzimidazole ring. Infrared spectroscopy reveals that the acids are present in the system not in their free state but in the ionized form—formate, perfluoroglutarate, etc. At this point we have true salts of the alkylbenzimidazole polymers and the ionized strong acids. In only a few instances was some crystallinity found in the poly(alkylbenzimidazole) salts.[2] In them the acid appears to be an integral part of the crystal structure. The presence of the crystallinity, however, does not seem to affect measurably either the benzimidazole ring/acid ratio or the electrical conductivity of the salt. It should be reemphasized that the crystallinity is associated with the presence of a polymer/acid salt. Because the acids used for the formation of the crystalline salts are themselves fluid, no crystallinity may be associated with the presence of free, excess acid. A more detailed discussion of the formation of crystalline poly(alkylbenzimidazole)/acid salts was presented in reference 2.

Many inorganic metal salts may be easily dissolved in DMSO. Mixing DMSO solutions of salts with solutions of poly(alkylbenzimidazole) may lead to one of three results: (1) precipitation of a complex with fixed stoichiometry from the DMSO [CO(II), Ce(III), Ni(II), Cu(II), Zn(II), Cd(II)], (2) precipitation of a complex upon dilution with acetone where the stoichiometry is not as well defined [Cr(III), Fe(II), Sn(II), Ca(II), Ba(II), Mg(II), W(VI), U(VI)], and (3) no precipitation even after dilution [Al(III), Na(I), K(I)]. In the case of $CoCl_2 \cdot 6H_2O$, for example, each Co(II) ion is complexed with four benzimidazole rings. In Ni(acetate)$_2 \cdot 4H_2O$ and $CrCl_3 \cdot H_2O$, the Ni(II) and Cr(III) are complexed each with one benzimidazole ring. The stability of the complexes seems to be related to their composition: while the Co(II) complex requires a strong acid conditions for its destruction and will not decompose in boiling water, the Cr(III) and the Ni(II) complexes are rather unstable in aqueous environment.

The resistivity values of the alkylbenzimidazole polymers and their salts and complexes are given in Table I. In it, the polymer poly(heptamethylenebisbenzimidazole) is designated by I-7, poly(octamethylenedibenzimidazole) by II-8, poly(trimethylene-2,5-benzimidazole) by 3(2,5)BZ, etc. When the resistivity values of the neutral polymers are compared, one finds that no significant difference exists between the various polymer analogs. In the polymer salt, the resistivity changes with changes in the acid counterion. Unexpectedly, changes in resistivity did not correlate with the acid strength as estimated by us, but could roughly be correlated with the molar volume of the corresponding acid or metal salt. This correlation is shown in Figure 1. It should be emphasized that the resistivity of each salt or complex is associated with the counterion and not with the various poly(alkylbenzimidazole) analogs; changes among the latter do not affect measurably the resultant resistivity. A similar dependence on the counterion was found previously[3] in dielectric constant measurements of neutral 3(2,5)BZ and its salts.
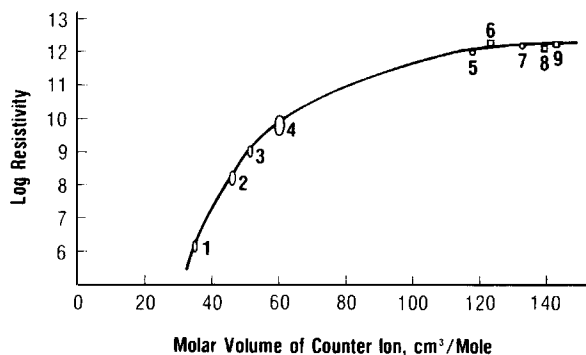
Fig. 1. Resistivity of poly(alkylbenzimidazole) salts of (1) HCl; (2) HCOOH; (3) I_2 (from I_3^-); (4) CF_3COOH; (5) perfluorosuccinic acid; (6) $CoCl_2 \cdot 6H_2O$; (7) perfluoroglutaric acid; (8) $CrCl_3 \cdot 6H_2O$; (9) $Ni(acetate)_2 \cdot 4H_2O$.

TABLE I
Direct Current Resistivities of Alkylbenzimidazole Polymers and Their Salts

Code	Resistivity, ohm·cm	Code	Resistivity, ohm·cm
I-7	1×10^{13}	I-7/Ni(II)	2.2×10^{12}
II-7	1×10^{13}	I-7/Cr(III)	1×10^{12}
I-8	1×10^{13}	I-8/trifluoroacetate	1×10^{10}
II-8	1×10^{13}	I-7/trifluoroacetate	5×10^{9}
3(2,5)BZ	1×10^{12} [a]	I-7/I_3^-	1×10^{9}
I-7/chlorosulfonated PE	6×10^{12}	3(2,5)BZ/formate	3.4×10^{8} [a]
I-5/chlorosulfonated PE	2×10^{12}	I-7/formate	1×10^{8}
I-7/perfluoroglutarate	2.5×10^{12}	II-8/formate	1×10^{8} [b]
I-7/perfluorosuccinate	1×10^{12}	I-7/HCl	2×10^{6}
I-7/Co(II)	3.3×10^{12}	3(2,5)BZ/HCl	1×10^{6} [a]
II-7/Co(II)	2.3×10^{12}		

[a] From reference 1.
[b] From reference 3.

The relationship between intrinsic viscosity and molecular weight for the poly(alkylbenzimidazole) family is not known. The intrinsic viscosities in formic acid of polymers prepared in this study ranged from as low as 0.12 for polymer I-4 to about 7 for I-7. Since no effect of molecular weight on conductivity was noticed, no further attempts to determine molecular weights by other techniques were made.

Complexes of I or II with I_2 could not be attained, the iodine being removed upon heating in vacuum. When KI_3 solutions in DMSO were mixed with solutions of poly(alkylbenzimidazole) in DMSO, a stable complex was obtained. From the fit to the curve in Figure 1, it is assumed that even though I_3^- species exist in the system (with practically no K^+), the conductivity is somehow associated with the presence of I_2 species.

Infrared and Raman spectroscopy failed to reveal the nature of the complexes between the benzimidazole rings and the metal salts or the iodine. To elucidate it, ESCA was found to be a very powerful tool.

In Figure 2, representative N(1s) spectra for (a) the parent poly(bisbenzimidazole), (b) the acid conjugate with perfluoroglutaric acid, (c) the Co(II) de-
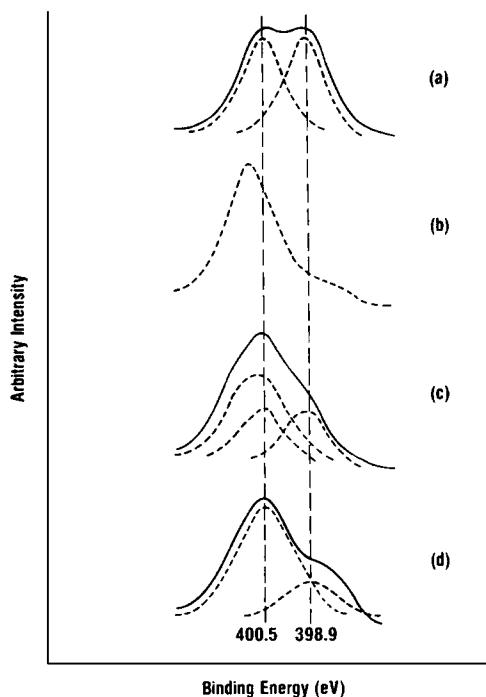
Fig. 2. ESCA N (1s) spectra of (a) poly(alkylbenzimidazole) I-7; (b) I-7/(HO$_2$C-(CF$_2$)$_2$-CO$_2$H); (c) I7/Co(II); and (d) I-7/Cr(III).

rivative, and (d) the Cr(III) derivative are presented. Binding energy data for the various core levels of interest are given in Table II.

For the parent poly(bisbenzimidazole) we observe a doublet separated by 1.5 eV. The higher binding energy N(1s) component at 400.5 eV is associated with the protonated or pyrrole-type nitrogen. The lower binding energy component at 398.9 eV is due to the nonprotonated or aza-type nitrogen. The observed N(1s) spectrum and the N(1s) binding energies agree well with those reported by Niwa et al.[8] for 2-phenylimidazole.

Treatment of the parent poly(bisbenzimidazole) with perfluoroglutaric acid to produce the acid conjugate results in a N(1s) peak at 401 eV. This peak has a binding energy similar to that of the pyrrole-type nitrogen of the free base but shifted to higher binding energy by some 0.5 eV. A similar result is obtained

TABLE II
Binding Energies of the Various Core Levels of Interest in Some Poly(alkylbisbenzimidazole) Complexes

	Poly(alkylbisbenzimidazole)		
	aza 398.9 eV		
	pyrrole 400.5 eV		
	I-7/formate 401.0 eV		
	I-7/perfluoroglutarate 401.0 eV		
I-7/Cr(III)	400.8 eV	Cr(2$p_{3/2}$)	557.2 eV
I-7/Ni(II)	400.6 eV	Ni(2$p_{3/2}$)	857.0 eV
I-7/Co(II)	400.6 eV	Co(2$p_{3/2}$)	787.5 eV

for the acid conjugate resulting from treatment with formic acid. Note that on the low binding energy side of the N(1s) there is additional structure, Figure 2(b). From its location on the binding energy scale it is apparently due to unreacted starting material.

For the metal complexes the situation is slightly more complex. Note from the N(1s) spectra for the Co(II) and Cr(III) derivatives that intense lower binding energy structure is present. In order to deconvolute these spectra, we used the peak shapes for the parent poly(bisbenzimidazole). As a guide we relied on the titration data. For example, the titration data for the Co(II) complex indicate that cobalt complexes four benzimidazole rings. For the Cr(III) and Ni(II) derivatives, the titration data indicated that each of the aforementioned metal ions complexes one benzimidazole ring. Curve fitting the observed spectra based on these data indicates that the nitrogens complexed to the metal ion have binding energies slightly higher than those of the pyrrole-type nitrogens of the parent (Table II). Thus complexation of the parent poly(alkylbisbenzimidazole) with a metal ion causes a positive shift in the N(1s) binding energies. The positive shift is indicative of a decrease in electron density on the nitrogens due to electron donation to the metal. We note that ESCA studies of Co(II) and Ni(II) Schiff base complexes also indicate positive binding energy shifts for nitrogen relative to the free ligand.[9,10]

In Figure 3 we have reproduced the 2p core level spectra for the various metal ions. Note that the Ni(2p) and Co(2p) spectra exhibit additional structure or shake-up satellites[11] adjacent to the $2p_{1/2}$ and $2p_{3/2}$ core level lines. The presence

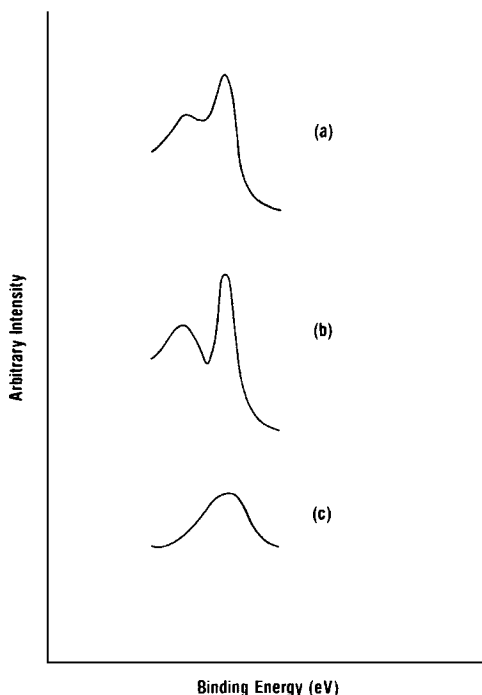Fig. 3. Metal ($2p_{3/2}$) core level spectra for (a) I-7/Co(II); (b) I-7/Ni(II); and (c) I-7/Cr(III). Note the intense satellites associated with the Co(II) and Ni(II) I-7 derivatives. Metal ($2p_{3/2}$) binding energies are tabulated in Table II.

of shake-up satellites associated with the Ni($2p$) and Co($2p$) levels is indicative of high-spin or paramagnetic compounds.[12,13] A paramagnetic complex of Co is indicative of Co(II) since Co(III) is diamagnetic. The oxidation state of the Co is further substantiated by the $2p_{1/2}$–$2p_{3/2}$ separation. For paramagnetic Co(II) complexes, the $2p$ separation is close to 16 eV, while for diamagnetic Co(III) complexes, the same separation is about 15 eV.[13] We measure a $2p$ separation of 15.7 eV which is again indicative of a high spin Co(II) species. It should be noted that low-spin Co(II) complexes behave in a manner similar to that exhibited by Co(III) species.

Similar conclusions regarding the Ni(II) complex can also be reached. Since the Ni($2p$) spectra exhibit shake-up satellites indicative of a paramagnetic Ni(II) species, one can rule out a square planar complex involving Ni(II).[12] This follows since all known square-planar complexes of Ni(II) are diamagnetic. We have measured a Ni($2p_{3/2}$) binding energy of 857 eV for Ni(II)/poly(alkylbenzimidazole) derivative. The Ni($2p_{3/2}$) binding energy is close to that observed for NiCl$_2$. This would indicate that the degree of covalency for the derivative is small, and thus we are dealing with essentially an ionic material although no corrections for Madelung potentials have been considered. Similar conclusions can be reached regarding the Co(II) and Cr(III) derivatives.

Of particular interest is the nature of the chlorine species present in the Cr and Co complexes. The Cr and Co derivatives were prepared from the corresponding metal chlorides and elemental analysis indicates that the ratio of metal ion to chloride ion is for example 1:2 for the case of the Co complex. An examination of the metal($2p$)–chlorine($2p$) binding energies and binding energy separations between the aforementioned $2p$ levels reveals that no discrete CoCl$_2$ or CrCl$_3$ species are detected. The shape of the observed Cl($2p$) spectrum indicates that the chloride species present in these complexes are electronically similar. The measured binding energies of 197.5 eV are indicative of a very reduced type of chloride. For the metal complexes the chloride serves as a counterion imparting overall electrical neutrality to the complex. The Cl($2p$) spectrum lineshape indicates that only a single type of chlorine exists in the system. The binding energies do not allow for the chlorine atoms to be involved in such bridging as N—H- - -Cl or ≡N- - -Cl, because this would reduce the negative charge on Cl and give rise to a more oxidized chlorine.[14] It is most likely, hence, that at least in the case of the cobalt complex the chlorine atoms are positioned equidistantly from the Co(II) atoms above and below the plane defined by the cobalt atom and the four aza nitrogens with which the cobalt atom is complexed.

With respect to the reaction of the bisbenzimidazole with KI$_3$, one observes an I($3d_{3/2}$) binding energy of 619.4 eV which is indicative of a negatively charged I species. We do not observe K$^+$. It should be pointed out that the binding energy of I in CsI$_3$ is 619.6 eV. It is tempting to assign the complexed iodine to I$_3^-$. The perturbation on the N($1s$) spectra is small and one observed a slight increase in the pyrrole-type nitrogen intensity.

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