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Electrical Conductivity of Heat Treated Polyacrylonitrile and Complexes of Polyacrylonitrile with Transition Metal Chlorides

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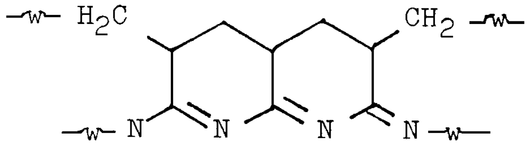
Polymerization of acrylonitrile (AN), without and in the presence of $CuCl_2$, $CoCl_2$, and $NiCl_2$, formed polyacrylonitrile homopolymer (PAN) and polymer complexes of AN–$CuCl_2$, AN–$CoCl_2$ and AN–$NiCl_2$, respectively. These polymer complexes were characterized using spectroscopic techniques. Electrical conductivity and cyclic voltammetry on untreated and heat treated polymers, carried out at different temperatures, showed that the conductivity increased with temperature, presumably due to conjugation and cyclization during heat treatment.

Key words: polyacrylonitrile, transition metal chloride complexes, electrical conductivity

A novel and easily processed conductive polymer was prepared from poly(vinyl alcohol) (PVA) [1]. Metal chelates of PVA film exhibited conductivity around 10^0–10^{-2} Ω^{-1} cm^{-1}. Rickle [2] found that copper(I) chloride, 1,4-diaminoanthraquinone and oxygen react to give a crystalline electrically conducting coordinating oligomer. The free radical polymerizations of polar monomers containing pendant nitrile and carbonyl groups, *e.g.* AN and methyl methacrylate, in the presence of metal halides such as $ZnCl_2$ and $AlCl_3$, are characterized by increased rates of polymerization as well as formation of polymers with considerably higher molecular weights than are formed in the absence of the metal halides [3–5]. This effect has been attributed to the formation of complexes between the polar group of the monomer and the metal halides. The low temperature thermal degradation of PAN is characterized by coloration, which can be accounted for in terms of nitrile group oligomerization, occurring even in pure polymer [6] at temperatures in excess of 150°C. The suggested structure is



The presence of delocalized π-electrons resulting from sp^2 hybridization of the carbon-nitrogen atoms increases the electrical conductivity.

The present work involved preparation and characterization of PAN homopolymer and polymer complexes of AN with $CuCl_2$, $CoCl_2$, and $NiCl_2$. Heat treatment of the homopolymer and complexes was carried out in order to produce a conjugated system. The electrical properties of the untreated and heat treated polymers were measured.

EXPERIMENTAL

Acrylonitrile (AN) (Koch-Light Ltd.) was freed from inhibitor, dried over anhydrous sodium sulphate and twice distilled under vacuum before polymerization. Copper(II), cobalt(II), and nickel(II) chlorides (BDH Chemical Ltd.) were purified by drying under vacuum and stored in a desiccator. 2,2′-Azobisisobutyronitrile (AIBN) (Eastman Kodak) was purified by dissolving in hot ethanol, filtering [7] and cooling. The pure material was collected by filtration and kept under vacuum. All other chemicals and solvents were purified by standard procedures.

Preparation of PAN homopolymer and AN–metal chloride polymer complexes: PAN homopolymer was prepared by refluxing AN monomer with dimethyl formamide (DMF) as solvent using 0.1 w/v % AIBN as initiator. AN–metal chloride polymer complexes were prepared by dissloving the appropriate weight of AIBN in DMF. Equimolar amounts of AN and metal chloride were introduced and the mixture was refluxed. The resulting PAN homopolymer, AN–$CuCl_2$, AN–$CoCl_2$ and AN–$NiCl_2$ polymer complexes were precipitated in a large excess of distilled water, containing hydrochloric acid to remove free metal chloride. PAN and AN–metal chloride polymer complexes were filtered, washed with water and dried in vacuum oven at 40°C for several days.

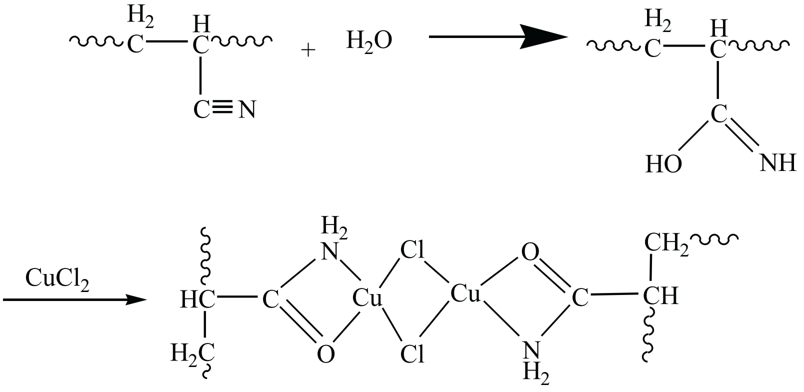
Analytical techniques: *Microanalysis*: Carbon, hydrogen and nitrogen content determinations were performed by standard methods. Metal contents were determined by complexometric titration, after decomposition by aqua-regia, using ethylenediaminetetraacetic acid (EDTA) [8]. IR spectra were recorded on a Perkin-Elmer 883 spectrophotometer with the sample in the form of KBr or CsI discs. Visible-ultraviolet spectra were obtained on samples supported in Nujol mull using a Varian 634 spectrometer. Magnetic susceptibility measurements were obtained on a Johnson-Matthey apparatus with magnetic strength of 1000 Orsted, similar to a previous design [9], using a vacuum semimicrobalance and electromagnet (Nihonkomomitsu model 350). The apparatus was calibrated using Hg[Co(CNS)].

Electrical conductivity measurements were performed with a Keithley 617 programmed electrometer. Polymer samples were dried in a vacuum oven at 40°C for several days, then milled very fine and dried again for one day under the same conditions. They were pressed at 20 ton cm^{-2} forming circular discs of diameter 12 mm and thickness from 1 to a 1.3 mm. Silver coatings were applied to each surface. The samples were inserted in an oven evacuated to a pressure lower than10^{-3} Pa. The temperature was measured better than ~1°C with a Ni-NiCr thermocouple.

Cyclic voltammetry (CV) was carried out on a three compartment electrochemical cell. The working electrode was a platinum wire of 0.5 mm diameter. The surface area of the working electrode, being *ca*. 30 times smaller than that of the coiled counter electrode (a platinum wire). A silver-silver ion in DMF was used as a reference electrode in non-aqueous experiments and was immersed in the bulk solution as working and counter electrode. A potentiostatic wave generator (Oxford Elctrode) and Philip 8043 X–Y recorder were used. The supporting electrolyte was sodium perchlorate and tetrabutylammonium hexaflurophosphate ($TBAPF_6$) in non-aqueous measurements. In aqueous solutions, the supporting electrolyte was sodium nitrite. The measurements were carried out at room temperature and the concentration of the supporting electrolyte (100 mmol) were about ten times higher than the tested solution sample. The scan rate (20–500 mV sec^{-1}) and times of recording were varied.

RESULTS AND DISCUSSION

1) Characterization of PAN homopolymer and AN–transition metal chloride polymer complexes: The IR spectrum of PAN homopolymer exhibits a characteristic stretching band at 2250 cm^{-1}, due to the cyano group C=N [10]. The IR spectrum of the AN–$CuCl_2$ polymer complex shows the disappearance of the cyano group and two new bands appeared at 3430 and 3530 cm^{-1} assigned to –NH_2 and –OH groups, respectively. The IR spectrum and the elemental analysis suggest the addition of water to the triple bond to form the amide group –$CONH_2$ in AN–$CuCl_2$ polymer complex. The observation of new bands at 1720 and 1640 cm^{-1}, assigned to CO and NH_2 vibrations, respectively, can be taken as an evidence for the amide group formation. The following mechanism has been suggested for such reaction:



This bidentate structure was confirmed by its IR spectrum, which shows two bands at 510 and 430 cm^{-1} due to Cu–O and Cu–N bonds, respectively [11].

The electronic spectrum of the AN–$CuCl_2$ polymer complex shows a strong band at 12903 cm^{-1} assigned to $^1B_{1g} \rightarrow {}^2A_{1g}$ transition as reported for a square planar copper(II) geometry [12]. The magnetic moment of the solid copper(II) polymer complex was found to be 1.70 B.M., which lies within the reported range of one unpaired electron [13].

The IR spectra of AN–$CoCl_2$ and AN–$NiCl_2$ polymer complexes show the cyano group at 2230 and 2235 cm^{-1} indicating the involvement of the cyano group in the complexation. There is a weak and broad band in the range 3550 and 3300 cm^{-1} confirming the presence of water molecules in the polymer complexes [14].

These results are similar to those suggested by Diab *et al.* [15] and recently by Summan [16] in the polymerization of AN in the presence transition metal salts.

The electronic spectrum of the AN–$CoCl_2$ polymer complex shows one main strong band at 15260 cm^{-1} attributed to $^2A_{1g}(F) \rightarrow {}^4Tg(P)$ d-d transition in tetrahedral geometry [17]. The electronic spectrum of AN–$NiCl_2$ polymer complex exhibits two well resolved bands at 15830 and 24815 cm^{-1}, which are assigned to $^3A_{2g} \rightarrow {}^3T_{1g}$ (F) (ν_2) and $^3A_{2g} \rightarrow {}^3T_{1g}$ (F) (ν_3) d-d transitions, respectively, in a good agreement with those reported for an octahedral structure [17,18]. The values of the magnetic susceptibilities for AN–$CoCl_2$ and AN–$NiCl_2$ polymer complexes were found to be 3.7 and 2.6 B.M., supporting tetrahedral and octahedral geometries, respectively [19]. From IR, UV-visible spectra and elemental analysis, listed in Table 1, AN reacts with $CoCl_2$ and $NiCl_2$ to form the structure:

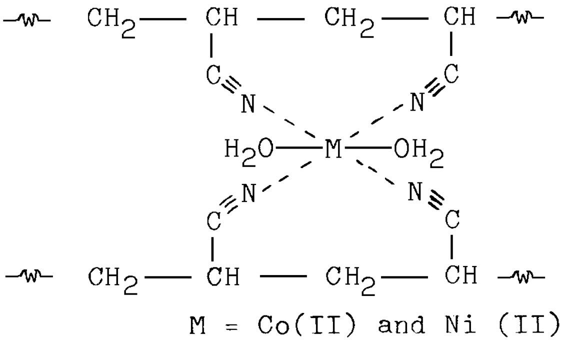


Table 1. Analytical data and magnetic moment PAN homopolymer and AN–metal chloride polymer complexes.

Polymer complex	Microanalysis % $\frac{\text{calc}}{\text{found}}$			$\mu_{\text{eff.}}$ B.M.
	C	H	Metal	
PAN	67.92 67.72	5.84 5.91	–	0.0
AN–$CuCl_2$	21.17 21.27	2.94 2.71	37.35 38.10	1.70
AN–$CoCl_2$	53.49 52.91	4.43 4.40	21.71 21.01	3.70
AN–$NiCl_2$	46.15 45.72	5.10 4.76	19.21 20.03	2.60

2) Electrical properties of PAN and AN–metal chloride polymer complexes: The changes of ln σ as a function of reciprocal temperatures of PAN homopolymer and polymer complexes are shown in Figure 1. The electrical conduction of PAN homopolymer shows two distinct activation energies. The first range shows a slight increase in conductivity with the increase of temperature. The conductivity was 10^{-12} Ω^{-1} cm^{-1} at 30°C, increasing to 10^{-9} Ω^{-1} cm^{-1} at ~ 130°C. The second range starts at 140°C with a conductivity of 10^{-8} Ω^{-1} cm^{-1} and increasing rapidly with temperature to 10^{-4} Ω^{-1} cm^{-1} above 200°C. The conductivity of heat treated PAN homopolymer could be attributed to thermal excitation in the first region and to the conjugation of the carbon–nitrogen system in the macromolecular chain in the second region.

The IR spectrum of the heat-treated PAN homopolymer shows the disappearance of cyano group band at 2240 cm^{-1} and the appearance of a new broad band at 1620 cm^{-1} due to –C=N– group [20]. With increasing temperature there is a reduction of the

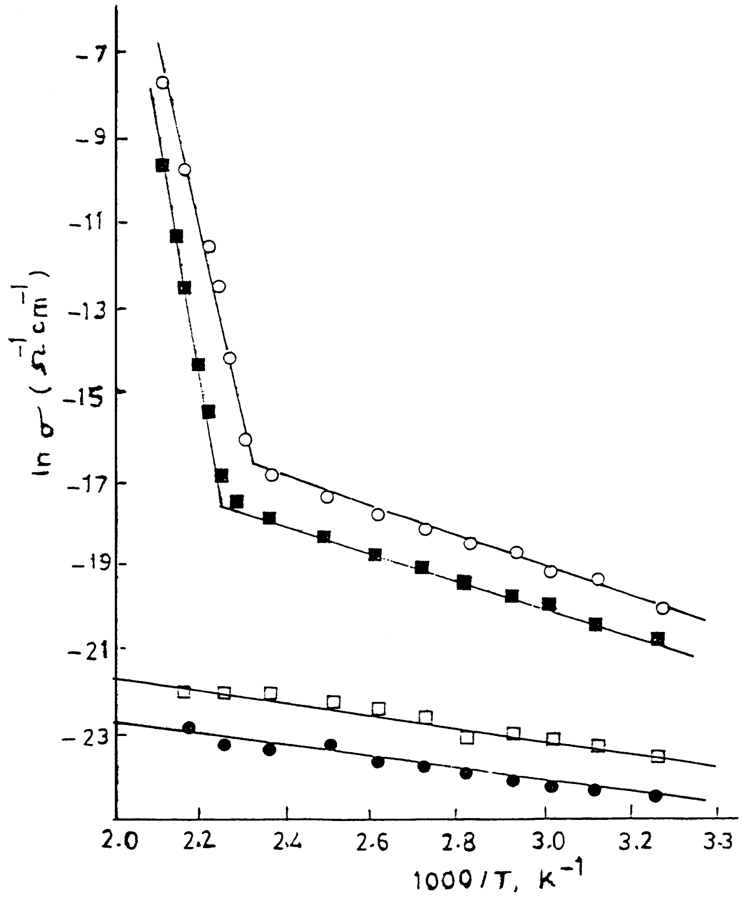
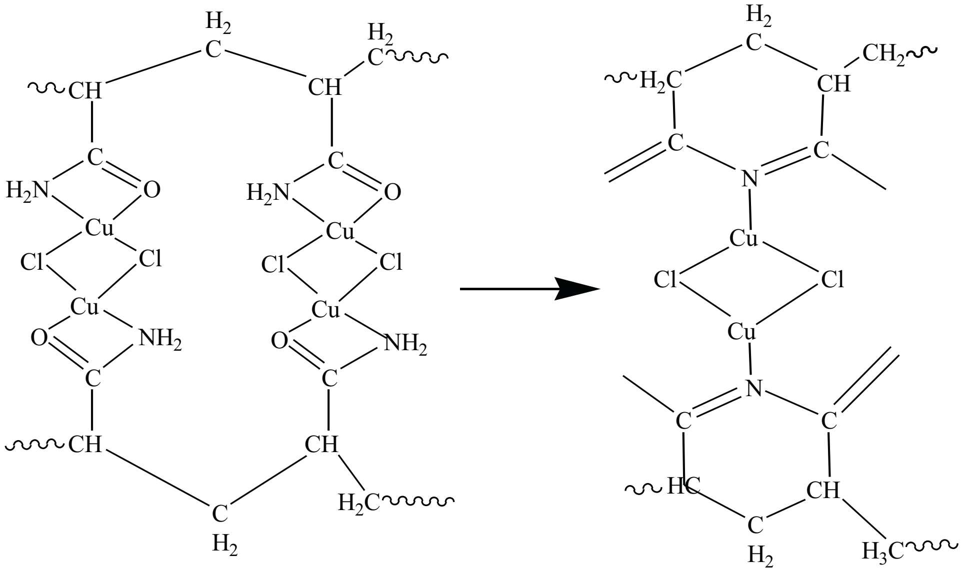


Figure 1. Relation between ln σ and 1/T for PAN homopolymer and AN with $CuCl_2$, $CuCl_2$ and $NiCl_2$ polymer complexes. (■) PAN homopolymer, (o) AN–$CuCl_2$ (❑) AN–$CuCl_2$ and (•) AN–$NiCl_2$ polymer complexes.

nitrile intensity and an increase in the absorption band at 1620 cm^{-1} confirming increasing carbon-nitrogen conjugation.

In the AN–$CuCl_2$ polymer complex, it was found that the electrical conductivity at different temperatures is higher than in the PAN homopolymer, attributed to the presence of chlorine ion as an electron donor [20]. There are two different plateaues. The first range shows a slight increase in conductivity from $\sim 10^{-8}$ to $\sim 3\times 10^{-7}$ Ω^{-1} cm^{-1} from 30 to 135°C due to thermal excitation. The second range starts at ~140°C with conductivity of $\sim 10^{-7}$ Ω^{-1} cm^{-1} and increases with temperature to 10^{-3} Ω^{-1} cm^{-1} at 200°C, attributed to the conjugated –C=N– group. From the structure suggested before, it seems that heating of AN–$CuCl_2$ polymer complex produces a conjugation, which can increase the electrical conductivity of the polymer complex.

Such conjugation increases the electrical conductivity in the second region of the curve. The IR spectra of the heat treated AN–$CuCl_2$ polymer complex at various temperatures show the disappearance of the bands above 3000 cm^{-1} and the appearance



of bands at 430 and 290–340 cm^{-1} due to (Cu–N) and (Cu–Cl) vibrations, respectively [11], supporting the above structure.

There are slight increases in the electrical conductivity of AN–$CoCl_2$ and AN–$NiCl_2$ polymer complexes (Table 2) indicating that carbon–nitrogen conjugation is not possible in these complexes. The IR spectra of the heat treated AN–$CoCl_2$ and AN–$NiCl_2$ polymer complexes show similar spectra as in the untreated polymer complexes except the disappearance of the water band at 3350 cm^{-1}.

Table 2. Electrical conductivity values of PAN and polymer complexes of AN–$CuCl_2$, AN–$CoCl_2$ and AN–$NiCl_2$.

Temp. °C	Electrical conductivity (σ) Ω^{-1} cm^{-1}			
	PAN	AN–$CuCl_2$	AN–$CoCl_2$	AN–$NiCl_2$
30	4.65×10^{-12}	1.01×10^{-8}	6.41×10^{-16}	4.11×10^{-17}
40	3.39×10^{-12}	1.56×10^{-8}	6.11×10^{-16}	3.81×10^{-17}
50	2.81×10^{-12}	3.33×10^{-8}	5.81×10^{-16}	3.51×10^{-17}
60	2.10×10^{-12}	2.49×10^{-8}	4.11×10^{-16}	3.27×10^{-17}
65	1.71×10^{-12}	2.56×10^{-8}	3.81×10^{-16}	3.01×10^{-17}
70	1.01×10^{-12}	6.45×10^{-8}	3.11×10^{-16}	2.86×10^{-17}
75	7.71×10^{-11}	7.41×10^{-8}	2.51×10^{-16}	2.57×10^{-17}
80	4.18×10^{-11}	8.40×10^{-8}	2.08×10^{-16}	2.21×10^{-17}
85	2.14×10^{-11}	9.09×10^{-8}	1.92×10^{-16}	1.90×10^{-17}
90	9.10×10^{-10}	1.28×10^{-7}	1.66×10^{-16}	1.61×10^{-17}
95	7.22×10^{-10}	1.52×10^{-7}	1.47×10^{-16}	1.19×10^{-17}
100	3.91×10^{-11}	1.69×10^{-7}	1.09×10^{-16}	9.11×10^{-16}

Table 2 (continuation)

105	1.02×10^{-11}	1.88×10^{-7}	9.71×10^{-15}	8.71×10^{-16}
110	8.71×10^{-10}	2.38×10^{-7}	8.99×10^{-15}	8.41×10^{-16}
115	6.27×10^{-10}	2.17×10^{-7}	8.41×10^{-15}	8.01×10^{-16}
120	3.29×10^{-10}	2.33×10^{-7}	8.11×10^{-15}	7.66×10^{-16}
125	1.11×10^{-10}	2.50×10^{-7}	7.76×10^{-15}	7.27×10^{-16}
130	8.17×10^{-9}	2.78×10^{-7}	7.30×10^{-15}	6.79×10^{-16}
135	6.66×10^{-9}	3.23×10^{-7}	6.86×10^{-15}	6.21×10^{-16}
140	3.12×10^{-9}	3.45×10^{-7}	6.10×10^{-15}	5.79×10^{-16}
145	8.11×10^{-8}	3.45×10^{-7}	5.56×10^{-15}	5.41×10^{-16}
150	9.67×10^{-7}	3.70×10^{-7}	4.91×10^{-15}	5.11×10^{-16}
160	1.37×10^{-7}	8.13×10^{-7}	4.55×10^{-15}	4.83×10^{-16}
170	9.93×10^{-6}	5.55×10^{-6}	4.01×10^{-15}	4.41×10^{-16}
180	2.14×10^{-5}	3.23×10^{-5}	3.51×10^{-15}	4.01×10^{-16}
190	8.21×10^{-4}	7.67×10^{-4}	3.16×10^{-15}	3.71×10^{-16}
200	4.45×10^{-4}	1.20×10^{-4}	2.71×10^{-15}	3.33×10^{-16}

Table 3 lists the activation energies for the homopolymer and the complexes. The activation energies increase in the sequence AN–$NiCl_2$ > AN–$CoCl_2$ > PAN > AN–$CuCl_2$. It is clear that the activation energies are in the same order as the conductivities [21,22], and may be attributed to the delocalization of the π-electrons in the macrochain. This suggestion can be confirmed by the lower activation energy values obtained.

Table 3. Calculated values of activation energies of PAN homopolymer and polymer complexes of AN with $CuCl_2$, $CoCl_2$ and $NiCl_2$.

Polymer	Activation energy (KJ $mole^{-1}$)
PAN	42.1
AN–$CuCl_2$	35.4
AN–$CoCl_2$	85.9
AN–$NiCl_2$	101.9

The cyclic voltammograms of untreated and heat treated PAN homopolymer were obtained in DMF–$NaClO_4$ and DMF–$TBAPF_6$ at platinum electrode at different scan rates. The results obtained in DMF–$NaClO_4$ were the same as in DMF–$TBAPF_6$. Figure 2 shows the cyclic voltammograms of untreated and heat-treated PAN homopolymer in DMF–$NaClO_4$. The reduction waves observed at –0.72 and –0.42 V *vs.* saturated calomel electrode (SCE) of untreated PAN homopolymer were found to be at –0.70 and –0.26 V *vs.* SCE after heat treatment up to > 200°C for 6 hrs. These differences provide good evidence for increasing conjugation and cyclization of the heat treated PAN homopolymer, where delocalization of the π-electron is possible. The results also prove that the electrogenerated redox species, formed after heat treatment of PAN, are not as easily reduced as those formed before the heat treatment.

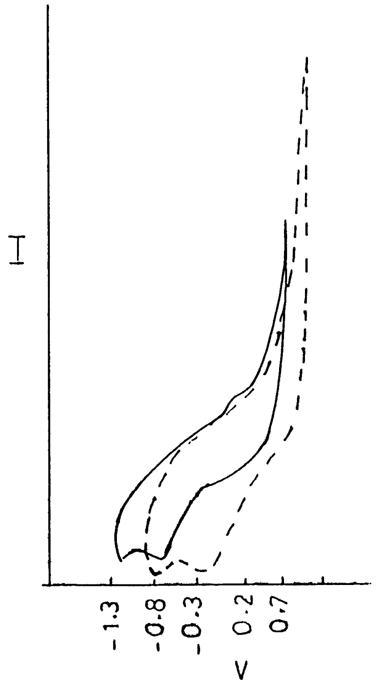


Figure 2. CV for untreated and heat treated PAN homopolymer in DMF–NaClO$_4$ at scan rate of 200 mV sec^{-1} *vs*. SCE. (—) PAN and (- - -) heat treated PAN homopolymer.

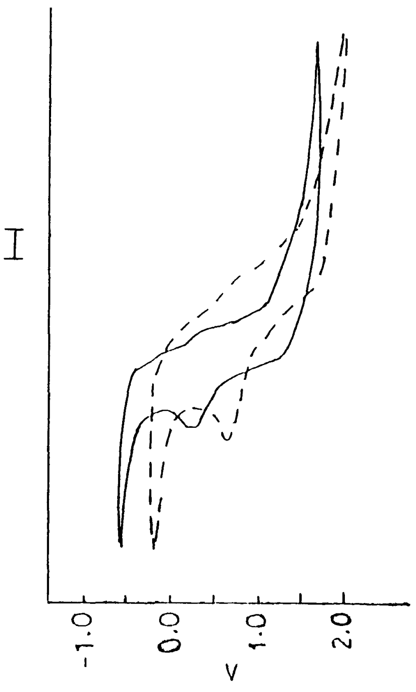


Figure 3. CV for untreated and heat treated AN–CuCl$_2$ polymer complex in DMF–NaClO$_4$ at scan rate of 100 mV sec^{-1} *vs*. SCE. (—) untreated AN–CuCl$_2$ and (- - -) heat treated AN–CuCl$_2$ polymer complexes.

Similar results were obtained in the cyclic voltammetry of AN–CuCl$_2$ polymer complex. The reduction peak of the untreated complex at –0.29 V *vs*. SCE was shifted to a higher value after heat treatment, confirming the increased conjugation of the complex (Figure 3).

In AN–CoCl$_2$ and AN–NiCl$_2$ polymer complexes, no significant changes were observed in the cyclic voltammograms before and after heat treatment, due to the absence of carbon-nitrogen conjugation.

As a result of the above observations, an attempt was made to check the suitability of untreated and heat treated PAN homopolymer and the polymer complexes as working electrodes. Each of the tested polymers was prepared as a disc 1 mm thick and 9 mm diameter. An electrochemical cell was composed, in which SCE served as reference electrode, platinum wire as the auxiliary electrode and a polymer disc was used as the working electrode. 10 mmol of $K_3[Fe(CN)_6]$ solution produces two well defined anodic waves at 0.220 V *vs*. SCE and cathodic wave at 0.160 V *vs*. SCE and the reduction is reversible [22,23]. In Figure 4, the cyclic voltammograms of $K_3[Fe(CN)_6]$, (10 mmol), using untreated PAN homopolymer and AN–CuCl$_2$ complex as working electrodes, showed well defined anodic waves, are coupled with the

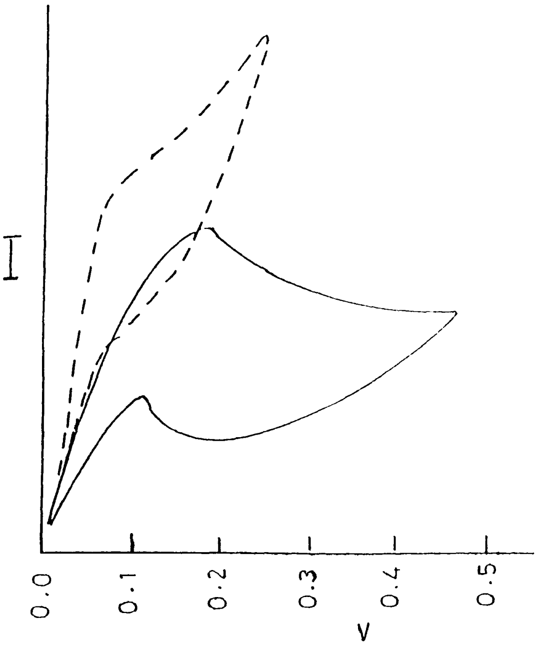


Figure 4. CV of $K_3[Fe(CN)_6]$ in aqueous media using untreated PAN homopolymer and AN–$CuCl_2$ polymer complex as working electrode at scan rate of 500 mV sec^{-1} *vs.* SCE. (—) PAN homopolymer and (- - -) AN–$CuCl_2$ polymer complex.

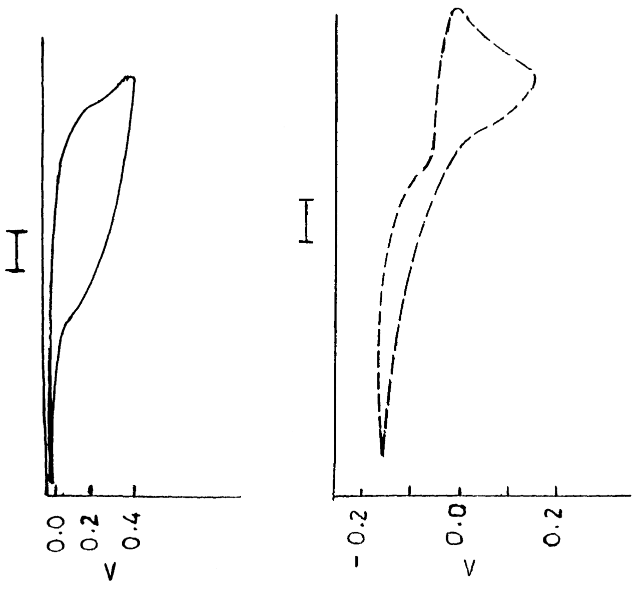


Figure 5. CV of $K_3[Fe(CN)_6]$ in aqueous media using heat treated PAN homopolymer and AN–$CuCl_2$ polymer complex as working electrode at scan rate of 500 mV sec^{-1} *vs.* SCE. (—) PAN homopolymer and (- - -) AN–$CuCl_2$ polymer complex.

cathodic wave at 0.140 and 0.130 V *vs*. SCE for PAN homopolymer and AN–$CuCl_2$ polymer complex, respectively.

On the other hand, the cyclic voltammograms of $K_3[Fe(CN)_6]$, using heat treated PAN homopolymer and AN–$CuCl_2$ polymer complex discs (Figure 5), showed well resolved oxidation waves at 0.132 and 0.115 V *vs*. SCE, respectively. These anodic waves were coupled with cathodic waves at 0.170 V *vs*. SCE for PAN homopolymer and AN–$CuCl_2$ complex, respectively. These data provide reassurance that the heat-treated homopolymer and polymer complexes enhance the conductivity, due to the greater conjugation and cyclization species formed.

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