Electrochemical Polymerization and Analysis of Some Aniline Derivatives

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In this study, conductive homopolymers of o-chloroaniline, p-bromoaniline and N-methylaniline were synthesized electrochemically in perchloric acidic solution and their properties were analyzed. Initially, the maximum oxidation potential values of these monomer solutions were determined by Cyclic Voltammetry (CV). Their conductive polymers were then synthesized under a nitrogen atmosphere using a potentiostat. FTIR spectra were taken in order to analyze the structural properties of the resulting polymers. Thermogravimetric analysis (TGA) was conducted and surface micrographs were taken by a Scanning Electron Microscope (SEM). The conductivity levels of the polymers were determined by the Four Probe technique. Magnetic properties of the samples were analyzed and the conduction mechanisms were examined. Based on the resulting conductivity data, it was concluded that poly(p-bromoaniline) was of polaron structure, whereas poly(o-chloroaniline) and poly(N-methylaniline) were of bipolaron structure.

Thermogravimetric analysis results indicated that poly(N-methylaniline) has the highest maximum decomposition temperature, and conductivity measurements revealed that poly(o-chloroaniline) has the highest conductivity level.

Introduction

Polymeric materials, used in the production of a great percentage of the goods used commonly in our daily lives, have gained considerable importance. Today, the tendency is to conduct studies for the improvement of the properties of existing polymers rather than synthesize novel polymers. Until recently, conductivity properties were the key factor in determining the usage area of the polymers. With the latest improvements in science and technology, the synthesis of conductive polymers from a number of monomers containing double bonds has finally become possible. The very first effort related to this topic involved oxidation of aniline in 1835[1] and the term "aniline black" was given to the resulting polyaniline (PAn). Later, in 1862, Letheby[2] managed to synthesize PAn on a platinum electrode in aqueous sulphuric acid solution by oxidizing aniline electrochemically. Other researchers[3−8] also worked on the synthesis of polyaniline through chemical and electrochemical techniques with various oxidizing agents.

The high conductivity levels of polysulphur nitrites at low temperatures, obtained during studies carried out in 1975, were particularly appealing[9]. The term "conductive polymer" was first used in 1977,

after the synthesis of polyacetylene and the discovery that its conductivity is of metallic structure[10,11].

The synthesis of conductive polymers from monomers containing conjugated double bonds such as pyrrole, thiophene, furan, and their derivatives, has become the subject of many recent studies[12−18]. Furthermore, some researchers have synthesized conducting aniline blends and composites[19−21].

Conductive polymers found a wide variety of application areas in various experimental studies and industry. They are commonly used in rechargeable batteries, chemical transistors, gasometers, electronic display boards, production of indicators and ion-selective electrodes, protection of semi-conductive photoanodes and biochemical analysis[1,22,23].

This study covers electrochemical synthesis of homopolymers of three different derivatives of aniline, namely o-chloroaniline, p-bromoaniline and N-methylaniline. The conductivity levels, thermal properties, surface structures and conducting mechanisms of the resulting polymers were analyzed thoroughly and the observations were discussed.

Experimental

Monomers (Merck) were exposed to certain preparatory operations, such as crystallization and purification, prior to use. Electrochemical polymerization experiments were carried out at constant potentials using Wenking Model Potentiostat-Galvanostat. The electrolysis cell used for the experiments was H-shaped. It consisted of working, counter and reference electrodes. Working and counter cells were separated via a sintered glass disk. Working and counter electrodes were made of platinum plates with a surface area of $2,5$ cm^2. A saturated calomel electrode (Luggin capillary) was used as the reference electrode. Cyclic voltammograms of the monomers were taken in perchloric acid media using Linseis LY-1600 recorder, in order to determine their rodox potentials. Nitrogen gas was purged with solutions of 0.1M monomer concentration and 0.20 M perchloric acid concentrations for 20 minutes. Scannings performed separately for each monomer in the anodic direction at a range of 0 to +1.0 V showed the peak potentials for o-chloroaniline, p-bromoaniline and N-methylaniline to be +0.55 V, +0.75 V and +0.95 V, respectively. Based on the obtained data, poly(o-chloroaniline), POClAn, poly(p-bromoaniline), PPBrAn and poly(N-methylaniline), PNMAn homopolymers were synthesized. The polymers that coated the working electrode were washed using bidistilled water. They were then dried at 75 °C in a vacuum oven for 24 hours. Finally, the polymers were peeled off from the electrode surface. The magnetic properties of the polymer samples were analyzed with Sherwood Scientific MKI Model Gouy Balance to reveal their conduction mechanisms. Magnetic susceptibility measurements of the samples were carried out as follows: finely powdered polymer samples were placed into a glass tube at a height of not less than 2.5 cm. This glass tube was placed into a hole in the magnetic balance, and the magnetic susceptibility of polymer samples was recorded at room temperature.

Results and Discussion

Comparative IR spectra (Mattson-1000 FTIR Spectrometer) of monomers and homopolymers were used for the structural analysis of the synthesized polymers. IR spectra of o-chloroaniline and POClAn are given in Figure 1. The doublet peak belonging to -NH$_2$, at approximately 3422 cm^{-1} turned into a singlet peak in the polymer. This proves that the polymerization occurs through the -NH$_2$ group. Similar peaks were observed on the IR spectra of the other polymers. Conductivity measurements of the polymers were conducted using the Four Probe technique, also known as the van der Pauw technique[1]. The polymer samples were made

into pellets and their conductivity levels were measured. The results obtained from these measurements are given in Table 1. As seen in the table, POClAn had the highest conductivity, with a value of 8.4×10^{-1} Scm^{-1}, whereas PNMAn had the lowest conductivity with a value of 1.8×10^{-4} Scm^{-1}.
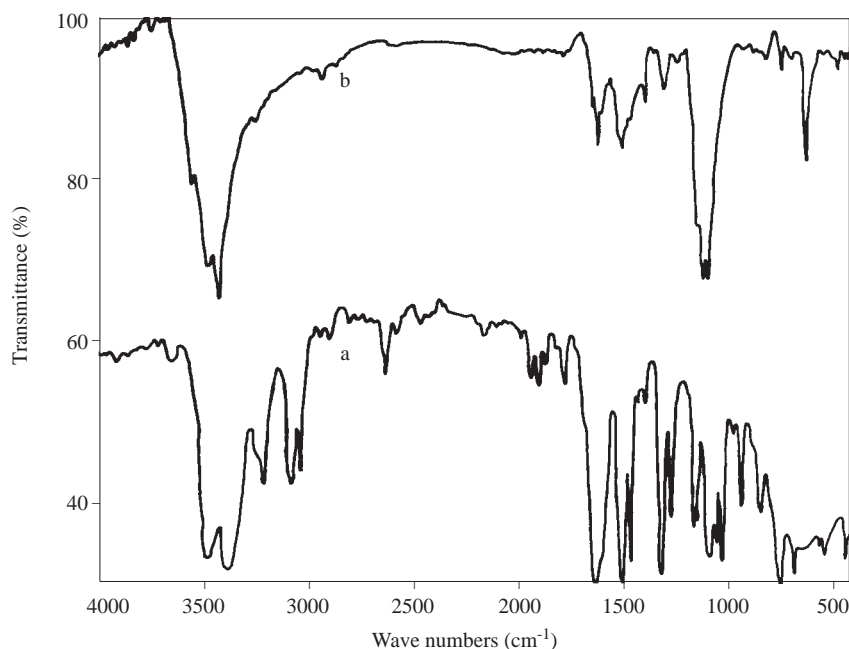
Figure 1. IR spectra of o-chloroaniline and poly(o-chloroaniline). a) Monomer, b) Polymer

Table 1. The conductivities of polymers

Polymer	Medium	Conductivity (Scm^{-1})
POClAn	0.2 M HClO$_4$	8.4×10^{-1}
PPBrAn	0.2 M HClO$_4$	2.7×10^{-1}
PNMAn	0.2 M HClO$_4$	1.8×10^{-4}

The conductivity range for semi-conductive materials is known to be $10^{-7} - 10^2$ Scm^{-1}. Conductivities of most doped conducting polymers lie approximately in this region[24]. Hence, the measured values corresponding to polymers synthesized in this study seem to fall into the latter. This is because the conductivities of conducting polymers are affected by the solvent, method of synthesis, dopant, temperature, concentration, moisture, counter ion, pH and type of monomer used. For example, in a study by Duič et.al.[25], polyaniline was synthesized in H$_2$SO$_4$, HNO$_3$, HCl and HClO$_4$ solutions, with all the conditions kept the same, conductivities were found to be 8.3 Scm^{-1}, 3.4 Scm^{-1}, 10^{-3} Scm^{-1} and 1.3 Scm^{-1}, respectively. On the other hand, the conductivity of PNMAn was lower than the others due to its having the highest polymerization potential, causing it to yield quinone-imine type side products[26]. However, it is essential to consider the effect of the doping level, which was kept constant (0.2 M HClO$_4$) throughout the polymerization of all the three samples, in order to make a healthy comparison of conductivities.

Various studies have already revealed that it is possible to change the conductivity radically by alternating the doping percentage. A striking example of this is a study by J. Guay et.al.[27,28] in which conductive polymers were synthesized from aniline derivatives such as poly(N-phenyl-1-naphthylamine), poly(PNA). Their conductivity was determined to be 10^{-3} Scm^{-1} at a doping rate of 30%, while the conductivity of poly(diphenylamine), poly(DPA), was determined to be 2.0 Scm^{-1} at a doping rate of 53%.

Magnetic susceptibility data of the polymers is shown in Table 2. As seen in the table, the magnetic susceptibility values of POClAn and PNMAn were negative while that of PPBrAn was positive. Negative and positive magnetic susceptibility values reveal diamagnetism and paramagnetism, respectively[29,30]. This analysis indicates that POClAn and PNMAn have diamagnetic properties and their conducting mechanisms are of bipolaron nature. PPBrAn, on the other hand, was concluded to have paramagnetic characteristics and a polaron conducting mechanism[31].

Table 2. Gouy balance measurements of polymers

Polymer	Magnetic Susceptibility Measurements
POClAn	-32
PPBrAn	+237
PNMAn	-23

A Jeol. JEM. 100 CX II Model Scanning Electron Microscope (SEM) was utilized in analyzing the surface structures and properties of the polymers. The resulting micrographs are shown in Figures 2, 3, and 4. When the micrographs of the samples taken from the solution part of all the three polymers are examined, it can be concluded that each has a different morphological structure. The structure of POClAn (Figure 2) is rather fibrous and porous. Duič et.al[25] synthesized PAn in $HClO_4$ medium and found that PAn was fibrous in structure. The same fibrous properties were observed in the SEM micrographs of POClAn. The structure of PPBrAn (Figure 3) is granular and scattered. During the polymerization of p-bromoaniline, three-types of products may form[32], namely, site blocking (a), addition (b) and substitution (c).
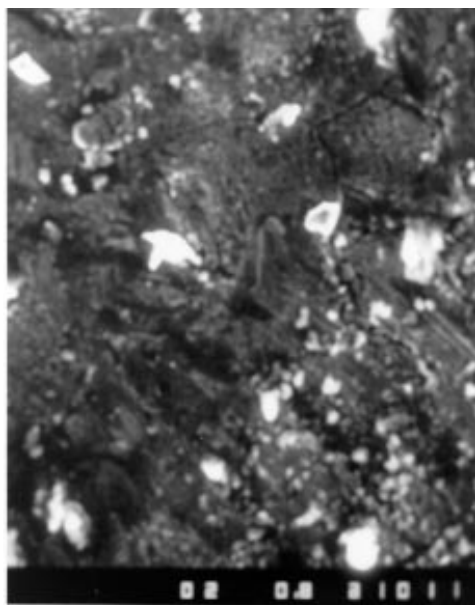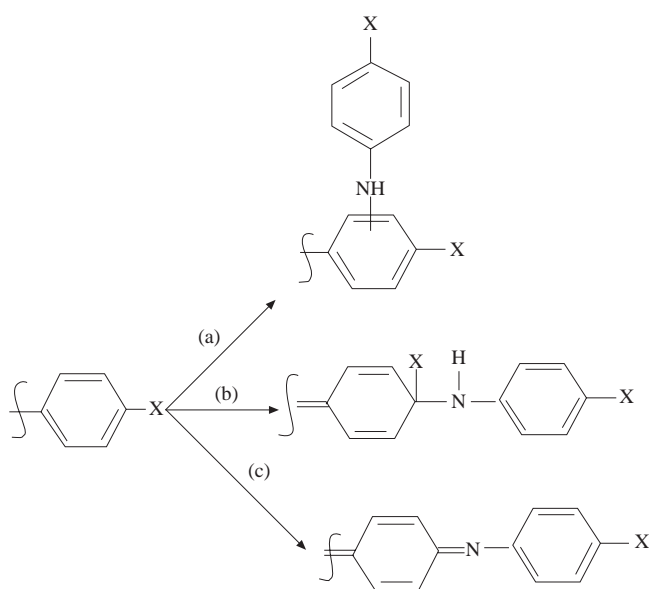

Figure 2. SEM micrograph of poly(o-chloroaniline). (Magnification 800X)

Figure 3. SEM micrograph of poly(p-bromoaniline). (Magnification 800X).

Figure 4. SEM micrograph of poly(N-methylaniline) (Magnification 800X)

Scheme 1

Those three products may also form during the polymerization of PPBrAn, giving rise to the scattered granulated structure of SEM. The structure of PNMAn (Figure 4) is closely stacked, granular, porous and single layered. The morphological structure of PNMAn obtained from SEM was different from those of POClAn and PPBrAn. The polymerization mechanism of N-methylaniline is similar to that of aniline. Polymer chains propagate via nitrogen atom at para position[33]. As a result, PNMAn has a more homogeneous and closely stacked morphology. As these observations demonstrate, different monomers may yield conductive polymers with different morphological structure even when same synthesis method and the same supporting electrolyte are used.

Finally, thermogravimetric analysis of the polymers were carried out using General V2.2A DuPont 9900 Model TGA. Thermograms of the samples were taken under a nitrogen atmosphere at a heating rate of $10\,^{\circ}$C/min and a temperature range of 0-800$\,^{\circ}$C. The results are shown in Table 3, where it can be seen that POClAn had the lowest maximum decomposition temperature, whereas PNMAn had the highest. The losses of mass percentages of polymers were obtained from TGA thermograms and the results are shown in Table 4. Even at 600$\,^{\circ}$C, mass losses of polymers were less than 50%. It can be concluded that their polymers have high thermal stability.

Table 3. The values of TGA analysis results of polymers

Polymer	Maximum Decomposition Temperatures ($^{\circ}$C)
POClAn	304
PPBrAn	311
PNMAn	315

Table 4. Mass losses (%) of polymers at various temperatures

Polymer	Temperatures ($^{\circ}$C)	Mass losses (%)
	200	1.4
POClAn	400	28
	600	41
	200	1.0
PPBrAn	400	26
	600	44
	200	11
PNMAn	400	32
	600	49

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