Electron localization and oxidant/monomer effect in alkoxy polyanilines

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Electrical dc conductivity, magnetic susceptibility and electron spin resonance studies are reported in poly(o-methoxyaniline), poly(o-ethoxyaniline), and equimolar blends of poly(o-methoxyaniline) and polyaniline as a function of oxidant to monomer ratio. It is found that increased oxidant levels generally lead to lower conductivity, lower Pauli-like susceptibility, and a higher number of Curie spins, but essentially the same localization length. These results imply the presence of increased disorder between ordered regions as a function of increasing oxidant/monomer ratio.

The usual procedure for chemically synthesized polyaniline or derivatives of polyaniline involves oxidation of aniline monomers with ammonium peroxodisulfate or other strong oxidizing agents in the presence of HCl. Poly(o-methoxyaniline) (POMA) prepared in this way was found to be soluble in dimethylformamide, acetic acid, sulfuric acid, and trifluoroacetic acid. Its electrical conductivity was in the range $10^{-2}$ - $10^{0}$ S/cm. Due to its relatively high conductivity, this polymer has been studied as a function of the preparation parameters in order to increase its yield and its electrical conductivity. A number of parameters such as catalyst type, solution pH, oxidant/monomer (OM) ratio, and synthesis temperature have a significant effect on the chemical as well as the physical properties of chemically synthesized polyaniline and its derivatives. The inclusion of LiCl during the synthesis also affects the molecular weight and thus the transport and electronic properties.

POMA has been synthesized in the presence of many organic acids in an effort to improve such properties as the solubility, thermal stability and conductivity. Additionally, the dependence of the reaction yield on various parameters including the oxidant/monomer ratio has been investigated.

POMA has been prepared in yields as high as 90% with conductivities of 0.1 S/cm at room temperature when para-toluene sulfonic acid was used. The use of functionalized acids has also been found to increase the thermal stability of the polymer compared to that when HCl is used, with no change in the room temperature electrical conductivity. For POMA-HCl, the use of larger amounts of oxidant (or larger values of OM ratio) leads to increased yield but decreased conductivity. The reason for the reduction in conductivity on increasing the amount of oxidant is believed to be due to the formation of shorter polymer chains, polymer degradation, and increased production of insoluble oligomers effected by larger amounts of the oxidant. Addition of LiCl to the reaction medium was, however, found to increase conductivity of POMA-HCl by a factor of eight or so and the reaction yield by over 10 percent. In a series of papers on emeraldine-base polyaniline (PAN-EB), MacDiarmid, Epstein, and coworkers have proposed an explanation for LiCl leading to higher conductivity. As-synthesized PAN-EB is shown in their work to possess a high degree of aggregation due to interchain H-bonding between amine and imine sites.

While the room temperature electrical conductivity of POMA is known, its electron localization behavior has not been studied in detail. In this communication, the results of a systematic study, using the techniques of dc conductivity, magnetic susceptibility and electron spin resonance (ESR), on the following systems are presented: PTSA (para-toluenesulfonic acid) and HCl doped POMA, HCl doped poly(o-ethoxyaniline) (POEA), and HCl doped blends of POMA and polyaniline (PAN). These systems have been synthesized with various oxidant/monomer ratios.
POMA doped with HCl was synthesized chemically as described in the literature. The as-prepared salt was first converted into the base polymer, and the conducting POMA-ES was then prepared by doping with PTSA or HCl. POEA doped with HCl was also prepared in a similar way. All the polymers were synthesized by slow addition of the oxidant over a period of eight hours. Blends of POMA-PTSA or HCI was also prepared in a similar way. All the polymers were synthesized by slow dropwise addition of precoked oxidant under vigorous stirring in an ice-bath. Powders pressed into round pellets of thickness ~0.05 cm were used for conductivity measurements by the Van der Pauw method. Powdered samples of approximately 25 mg, loaded in a quartz bucket, were used for susceptibility measurements using a “Force Magnetometer”. A computer-controlled X-band Bruker EMX 6/1 spectrometer was used for ESR experiments.

As far as dc electrical conductivity is concerned, most of the polyaniline derivatives have been found to follow the relation

$$\sigma = \sigma_0 \exp \left[-(T/\eta T)^{1/2}\right]$$  \hspace{1cm} (1)

which is characteristic of quasi-one-dimensional variable range hopping between nearest neighbors\(^{10,12}\). Here,

$$\eta_0 = 16/[\alpha^{-1}N(E_F)k_B]$$  \hspace{1cm} (2)

where, \(\alpha\) is the decay length of the localized electron state, \(N(E_F)\) is the density of states at the Fermi level, \(\alpha=4\) is the number of nearest neighbor chains, and \(k_B\) is the Boltzmann constant. A fit of the experimental data to Eq.(1) gives \(\eta_0\). The localization length \(\alpha\) can be determined using values of \(\eta_0\) and \(N(E_F)\). \(N(E_F)\) can be obtained from \(\chi_p\) using Equation (1), which is usually obtained from magnetic susceptibility experiments.

Figure 1 shows the results of dc conductivity \(\sigma(T)\), plotted as \(\log \sigma vs T^{-1/2}\) for (POMA-HCl)\(_{0.5}\) and (POMA-PTSA)\(_{0.5}\) corresponding to two oxidant/monomer molar ratios. It is found that \(\sigma\) for (POMA-HCl)\(_{0.5}\) with an OM of 1.35 and 0.68 and (POMA-PTSA)\(_{0.5}\) with an OM of 0.21 are almost of the same value, while \(\sigma\) for (POMA-PTSA)\(_{0.5}\) with an OM of 1.35 is smaller by about one order of magnitude. The values of \(\eta_0\) obtained from the above plots are, however, different: 12,000 K and 17,000 K for (POMA-PTSA)\(_{0.5}\) corresponding to OM values of 0.21 and 1.35, respectively, and 8,000 K and 10,500 K for (POMA-HCl)\(_{0.5}\) corresponding to OM values of 0.68 and 1.35, respectively. That is, an increased amount of the oxidant leads to higher \(\eta_0\) for both (POMA-HCl)\(_{0.5}\) and (POMA-PTSA)\(_{0.5}\). Since \(\eta_0\) is a measure of the amount of disorder present in the system, increased oxidant/monomer ratio reflects more disorder in the packing of chains in so-called “ordered” as well as “amorphous” regions. Magnetic susceptibility experiments were therefore performed to look separately at the Curie and Pauli-like (\(\chi_p\)) susceptibilities as a function of oxidant/monomer ratio. The Pauli and Curie susceptibilities can be obtained from the linear part of the \(\chi T vs T\) plot because

$$\chi T = \chi_p T + C$$  \hspace{1cm} (3)

where C is Curie constant.

Figure 2 shows susceptibility data, plotted as \(\chi T vs T\), for the above samples. The slope of \(\chi T vs T\) plots yields \(\chi_p\), which can be used to obtain \(N(E_F)\) and hence \(\alpha^{-1}\) using Equation (1). Values of the various quantities such as room temperature conductivity, \(N(E_F)\), \(\alpha^{-1}\), and ESR peak-to-peak linewidth are given in Table I. While \(N(E_F)\) (or \(\chi_p\)) decreases on increasing the oxidant amount, the localization length is found to stay practically unchanged. The number of Curie spins, however, increases on increasing the oxidant level.

There are many implications of these results. First, the increased oxidant level, which leads to reduced \(\chi_p\), can be viewed as arising from smaller ordered regions. This conclusion is obviously based upon the
di so rdered as a result of increa se d oxidant content, electron delocalization in ordered regions. Second, the regions between the ordered regions are more conventional picture, according to which systems like POMA consist of ordered and disordered regions. The Pauli susceptibility is thought to arise from electron delocalization in ordered regions. Second, regions between the ordered regions are more disordered as a result of increased oxidant content, which is reflected through higher values of $T_n$ and increased numbers of Curie spins. This conclusion follows from the fact that increasing the oxidant levels in the reaction mixture usually leads to the generation of a larger number of radical cations, which result in shorter polymer chains. The sample consequently possesses more “disorder”, and protonation with HCl or PTSA will, therefore, lead to more Curie-like polarons. Third, the “ordered” regions show better order because in spite of more disorder and smaller “ordered” regions the average localization length $\alpha^{-1}$ is essentially unchanged. Furthermore, as shown by ESR lineshape as well as linewidth, spins are more localized on chains when the OM ratio is high. The lineshape for POMA-PTSA is more Gaussian-like for the sample with higher OM, whereas the sample with lower OM ratio gives a Lorentzian-like lineshape. This observation is a direct consequence of the existence of more disorder in the amorphous regions.

The results for $\sigma (T)$, plotted as $\log \sigma$ vs $T^{-1/2}$, on as-synthesized POEA-HCl are shown in Figure 3 as a function of the oxidant/monomer molar ratio. The value of $\sigma$ at room temperature is $3.0 \times 10^{-2}$ and $2.9 \times 10^{-4}$ S/cm for OM ratios of 0.68 and 1.35, respectively. The corresponding $T_n$ values are 11,000 K and 14,000 K, respectively. It can be seen that as the OM ratio is decreased, $\sigma$ is increased by nearly two orders of magnitude. The value of room-temperature conductivity for POEA-HCl has been earlier reported as $2.5 \times 10^{-7}$ S/cm with a $T_n$ of 20,000 K.

Figure 4 shows the magnetic susceptibility data, plotted as $\chi' T$ vs $T$, for the above two samples. The values of $n_c$ (in units of per 2-rings) and $N(E_F)$ (in states/eV 2-rings) obtained from magnetic measurements are: 0.027 and 1.3 for the sample with an OM ratio of 0.68, and 0.030 and 1.1 for the sample with an OM ratio of 1.35. Thus, while $T_n$ was found to increase on increasing the OM ratio, $N(E_F)$ is seen to decrease. But, the value of the localization length $\alpha^{-1}$, obtained from the conductivity and the magnetic data, changes only slightly from 30 to 32 Å. These results on POEA-HCl are similar to that for POMA-HCl and POMA-PTSA.

### Table I — Room temperature $\sigma$, $N(E_F)$, $\alpha^{-1}$, and $DH_{pp}(G)$ for POMA-ES as a function of oxidant to monomer ratio

<table>
<thead>
<tr>
<th></th>
<th>PTSA (0.21)</th>
<th>PTSA (1.35)</th>
<th>HCl (0.68)</th>
<th>HCl (1.35)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma$ (10^{-2} S/cm)</td>
<td>$3.6 \times 10^{-2}$</td>
<td>$8.2 \times 10^{-4}$</td>
<td>$4.0 \times 10^{-2}$</td>
<td>$4.4 \times 10^{-2}$</td>
</tr>
<tr>
<td>$N(E_F)$ (states/eV 2-rings)</td>
<td>2.9</td>
<td>1.8</td>
<td>3.4</td>
<td>1.8</td>
</tr>
<tr>
<td>$\alpha^{-1}$ (Å)</td>
<td>$13 \pm 3$</td>
<td>$15 \pm 2$</td>
<td>$18 \pm 2$</td>
<td>$24 \pm 3$</td>
</tr>
<tr>
<td>$DH_{pp}(G)$</td>
<td>1.0</td>
<td>2.6</td>
<td>1.0</td>
<td>1.2</td>
</tr>
</tbody>
</table>

**Figure 2** — Temperature dependence of magnetic susceptibility, plotted as $\chi' T$ vs $T$, of POMA-HCl and POMA-PTSA as a function of oxidant/monomer molar ratio.

**Figure 3** — Temperature dependence of conductivity, plotted as $\log \sigma$ vs $T^{-1/2}$, of POEA-HCl as a function of oxidant/monomer molar ratio.
To investigate whether the above conclusions also hold for more diverse systems, blends of POMA and polyaniline, to be referred to as [(POMA-PAN)-HCl]_{0.5}, were synthesized for various OM values namely, 0.11, 0.43 and 1.35. The log(α) vs \( T^{-1/2} \) plots on these samples were found to be linear. The magnetic susceptibility data plotted as \( \chi T \) also showed a linear dependence on temperature. As with the POMA and POEA samples, the number of Curie spins increases with an increase in the OM ratio, but the localization length stays more or less unchanged around 20 Å.

In summary, increased oxidant to monomer ratio in synthesizing poly(\( o \)-alkoxyanilines) leads to decreased Pauli susceptibility, an increased number of Curie spins, increased ESR linewidth, and increased T_0. But the localization length remains largely the same. These results show clearly that samples prepared with larger amounts of the oxidant exhibit more structural and electronic disorder.

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References