Synthesis and electrical conductivities of some nitrogen- and sulphur-containing polymers

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SUMMARY

We have synthesized poly(p-azophenylene) (PPN), poly(2,4-azotoluene) (PMT), poly(2,6-pyridine) (PPy), poly(2,6-pyridine sulphide) (PPyS) and poly(ethylene vinylene sulphide) (PEVS), doped them with iodine and ferric chloride and measured the electrical conductivities. The doped polymers were also studied with ESR and IR.

INTRODUCTION

In the beginning of the seventies Heleskivi et al. (1) and Löfgren et al. (2) have studied the conductivities of different non-doped aromatic azopolymers. These polymers were synthesized by catalyzed oxidative coupling (3-5):

\[ +O_2, -2H_2O \]
\[ H_2N-Ar-NH_2 \rightarrow \{Ar-N=N\}_x \]
(catalyst)

where Ar is an aromatic, aromatic-heterocyclic or aromatic-aliphatic bivalent radical. The conductivities of these pure polymers were in the range of \( 10^{-10} \) to \( 10^{-12} \) S cm\(^{-1}\), linear polyazophenylene being the most conductive. The authors above did not, however, use doping. In this work we have therefore chosen two of these polymers and doped them with iodine and FeCl\(_3\).

Ikeda et al (6,7) have synthesized poly(vinylene sulphide) (PVS) in two different ways. In the first way they used a pressure reaction vessel, trans-1,2-dichloroethylene and Na\(_2\)S\(\cdot\)9H\(_2\)O as starting substances and N-methyl-2-pyrrolidone as a solvent. In the second way the synthesis was carried out in a reactor equipped with a powerful stirrer under an argon atmosphere.

Boscato et al. (8) have synthesized polyphenylene polysulphur using the following method:

\[ 4Li + S_8 + Cl^- \rightarrow \left\{ \left(\text{Cl}\right) - S_{x} \right\}_n + 2LiCl + S_yLi_2 \]

We have synthesized poly(p-azophenylene) (PPN), poly(2,4-azotoluene) (PMT), poly(2,6-pyridine), poly(2,6-pyridine sulphide) (PPyS) and poly(ethylene vinylene sulphide) (PEVS) (Fig. 1) using this method.

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EXPERIMENTAL

Azopolymers were synthesized by oxidative coupling of the monomers p-phenylenediamine and 2.4-diaminotoluene in CuCl-pyridine-dimethylsulphoxide mixtures. The reaction conditions are in Table 1.

Table 1. Reaction conditions and yields of PPN and PMT.

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Monomer added (g)</th>
<th>DMSO/Py (mL/mL)</th>
<th>Reaction time (min)</th>
<th>Reaction temp. (°C)</th>
<th>Yield (%)</th>
<th>( M_n )</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-phenylenediamine</td>
<td>1.08</td>
<td>40/10</td>
<td>390</td>
<td>50</td>
<td>97</td>
<td>16200</td>
</tr>
<tr>
<td>2.4-diaminotoluene</td>
<td>1.22</td>
<td>40/10</td>
<td>255</td>
<td>50</td>
<td>95</td>
<td>20000</td>
</tr>
</tbody>
</table>

The products were washed twice (4 h) with boiling pyridine-ammonia solution (1:1, 4% NH₃), three times with distilled water (4 h) to remove extra copper which comes from the used catalyst (CuCl) and finally dried under nitrogen at 140 °C.