Synthesis and electronic spectral characterization of conducting benzidine copolymers

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The copolymers benzidine-aniline, benzidine-α-anisidine and benzidine-p-anisidine have been synthesised by chemical method. Their absorption and fluorescence spectra have been analysed. The copolymers are found to have conductivities in the range of semiconductors. In copolymers the longer wavelength absorption band of homopolymer is extended to infrared region.

Copolymerisation is an alternative method for modifying the polymer to meet specific requirement\(^1,2\). The copolymerisation technique is widely used to synthesise commercial polymers and in the study of structure-property relationship\(^3\). Some of the limitations of polyacrylonitrile in the fibre industry due to high melting point, high melt viscosity and poor thermal stability have been overcome by the copolymerisation of acrylonitrile with acrylates and acetates\(^4,6\). A series of polyimides-polyoxyethylene copolymers have been reported to have a reduction in tensile strength and elongation related to homopolymers\(^7\). The copolymer of aniline and toluidine was found to have shorter electrochromic response times for oxidation and reduction when compared to homopolymers polyaniline and polytoluidine\(^8\).

Polyaniline is one of the most illustrious conductive polymers with demonstrated success in diverse applications\(^8,10\). Similarly polyaniline and its doped forms are found to have high thermal stability and conductivity\(^1\). The aim of the present work is to synthesise benzidine copolymers viz. benzidine-aniline (BA), benzidine-α-anisidine (BOA) and benzidine-p-anisidine (BPA) and to analyse their conductivities and electronic spectra.

Materials and Methods

Chemical synthesis

The copolymers were synthesised by the following procedure\(^9\). For the preparation of benzidine-aniline copolymer, 1.84 g benzidine and 0.92 g of aniline were dissolved in 100 ml of 0.1 M HCl. The solution was cooled in an ice-bath. A pre-cooled solution containing 2.7 g of K\(_2\)S\(_2\)O\(_8\) in 100 ml of 0.1 M HCl was added dropwise under vigorous stirring for 4-5 h. The reaction mixture was kept in a freezer overnight and filtered to recover the precipitated copolymer. The copolymer was then dried by keeping it in oven at 80°C for about 4 h. The dried copolymer was weighed. For the preparation of benzidine-α-anisidine and benzidine-p-anisidine copolymers 1.3 g of α-anisidine and 1.23 g of p-anisidine were used in the same procedure.

Electrical conductivity of polymer samples were determined by the two probe method with a digital multimeter HIL 2120 (HCL-Ltd) at room temperature using the following procedure. The polymer powder was pressed to form a pellet by using KBr pellet press. The pellet was placed between two aluminium foils and the resistance was measured. The conductivity was determined from the resistivity of the pellet.

\[
\text{Resistivity} = \frac{ra}{i}; \quad \text{where } r = \text{resistance in ohms; } a = \text{area of cross section of the pellet; and } i = \text{thickness of the pellet.}
\]

The IR spectra of the polymer in KBr were recorded using JASCO 700 IR spectrophotometer. UV-visible spectral measurements were carried out by using JASCO-UVIDEC 650 recording double beam spectrophotometer. The fluorescence spectra were obtained using JASCO-FP 550 spectrofluorimeter.

Results and Discussion

Electrical conductivity

Conducting polymers show conductivity over a wide range\(^12\) (10\(^{-11}\) to 10\(^{2}\) S/cm). All the three copolymers are found to have significant conductivities Table 1. The conductivity of benzidine-α-anisidine is high and the conductivities of the other two polymers...
Table 1—Electrical conductivity of the copolymers

<table>
<thead>
<tr>
<th>Polymers</th>
<th>Resistance (r) mΩ</th>
<th>Thickness (l) mm</th>
<th>Radius (a) cm</th>
<th>Conductivity S/cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzidine-aniline</td>
<td>0.35</td>
<td>0.20</td>
<td>0.69</td>
<td>3.8223×10⁻⁶</td>
</tr>
<tr>
<td>Benzidine-o-anisidine</td>
<td>0.65</td>
<td>0.55</td>
<td>0.66</td>
<td>6.1863×10⁻⁶</td>
</tr>
<tr>
<td>Benzidine-p-anisidine</td>
<td>0.89</td>
<td>0.41</td>
<td>0.67</td>
<td>3.2682×10⁻⁶</td>
</tr>
</tbody>
</table>

Table 2—Characteristic IR frequencies of benzidine copolymers and polyaniline

<table>
<thead>
<tr>
<th>Polymers</th>
<th>N-quinoid cm⁻¹</th>
<th>Benzenoid cm⁻¹</th>
<th>Charge delocalization cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyaniline*</td>
<td>1571</td>
<td>1483</td>
<td>1125</td>
</tr>
<tr>
<td>Benzidine-aniline</td>
<td>1552</td>
<td>1494</td>
<td>1110</td>
</tr>
<tr>
<td>Benzidine-o-anisidine</td>
<td>1554</td>
<td>1496</td>
<td>1112</td>
</tr>
<tr>
<td>Benzidine-p-anisidine</td>
<td>1558</td>
<td>1498</td>
<td>1134</td>
</tr>
</tbody>
</table>

*Ref. 13

are nearly equal. The conductivity of polymers depend on the extent of delocalization and electron availability on the ring. The high value of conductivity of BOA may be due to the more electron releasing nature of-OCH₃ group. The -OCH₃ group increases the electron availability in the ring thereby increasing the conductivity. In the case of benzidine-p-anisidine chain link occurs at ortho to -NH₂ group and meta to -OCH₃ group. There is no resonance effect of OCH₃ group. Moreover, the chain is not linear and so the conduction of BPA is less than BOA and BA. The conductivity values clearly indicate that the copolymers are conducting polymers and the conductivities of these three copolymers are in the range of semiconductors.

Spectral analysis

The IR spectra of the three copolymers have been compared with the known polyaniline system. The bands at 1571 cm⁻¹, 1483 cm⁻¹, and 1125 cm⁻¹ were reported to be the characteristic bands for N-quinoid, benzenoid and charge delocalization bands of polyaniline respectively. In these three copolymers similar strong bands are obtained close to these bands. These three bands confirm the formation of copolymers and reveal that the structure of these copolymers are similar to that of polyaniline system (Table 2).

The UV-visible absorption maxima of the monomers, their homopolymers and the copolymers BA,

Table 3—Absorption maxima of monomers, polymers, and copolymers in methanol

<table>
<thead>
<tr>
<th>Compound</th>
<th>λₘₐₓ nm</th>
<th>Polymer</th>
<th>λₘₐₓ nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aniline</td>
<td>282.8</td>
<td>Polyaniline*</td>
<td>326, 635</td>
</tr>
<tr>
<td>Benzidine-aniline</td>
<td>283.6</td>
<td>Polybenzidine</td>
<td>316, 685</td>
</tr>
<tr>
<td>o-Anisidine</td>
<td>285.2</td>
<td>Benzidine-aniline</td>
<td>286, 395, 863</td>
</tr>
<tr>
<td>p-Anisidine</td>
<td>299</td>
<td>Benzidine-p-anisidine</td>
<td>288, 396, 832</td>
</tr>
</tbody>
</table>

*Ref. 13; **Ref. 8

BOA, BPA are given in the Table 3. The absorption spectra of copolymers in methanol are shown in Fig. 1.

The monomers have absorption maximum only in the UV region. Their homopolymers are coloured and have the maxima both in the UV and visible region. In homopolymers, the absorption maximum in the UV-region is due to π-π* transition and the maximum in the longer wavelength region is due to the band arising by the shift of electron from benzenoid ring to quinoid ring. In the copolymers the longer wavelength band is further red-shifted and it is extended to infrared region. This shows that the copolymerization in the presence of HCl leads to the formation of radical cation or polarns. The polarns are reported to be the dominant species in the conductance process. The presence of longer wavelength maxima of these copolymers also indicate their conductivities.

The fluorescence maxima of the monomer and the three copolymers are given in Table 4 and the fluorescence spectra of polymers in methanol are displayed.
Table 4—Fluorescence maxima of monomers, polymers, and copolymers in methanol

<table>
<thead>
<tr>
<th>Monomers</th>
<th>Compound</th>
<th>( \lambda_{\text{max}} ) ( \text{nm} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzidine</td>
<td>390</td>
<td>Polyamine* 355</td>
</tr>
<tr>
<td>Aniline</td>
<td>335</td>
<td>Polybenzidine 399</td>
</tr>
<tr>
<td>( \alpha )-Anisidine</td>
<td>358</td>
<td>Benzidine-aniline 383</td>
</tr>
<tr>
<td>( \beta )-Anisidine</td>
<td>365</td>
<td>Benzidine-( \beta )-anisidine 385</td>
</tr>
</tbody>
</table>

*Ref. 13

in Fig. 2. The fluorescence is observed only from the \( \pi-\pi^* \) transition. The emission could not be observed for the longer wavelength absorption band. Since the energy gap is very less for this band, the copolymer loses its energy by radiationless process. The fluorescence maxima of copolymers are red-shifted to the monomers. This change is due to the extended conjugation in the copolymers. Based on the results the following structure is suggested for the copolymers.

\[
\text{HOQ}^+ \quad \text{I} \quad \text{NH} \quad \text{Cl}^- \quad R=H, \text{OCH}_3
\]

Fig. 2—Fluorescence spectra of copolymers in methanol (a) Benzidine-aniline; (b) benzidine-\( \alpha \)-anisidine and (c) benzidine-\( \beta \)-anisidine

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The authors are thankful to Dr C Rakkapan, Department of Physics, Annamalai University, for his help in taking conductivity measurements.

References