

## Polyaniline: Synthesis and Characterization of Pernigraniline Base

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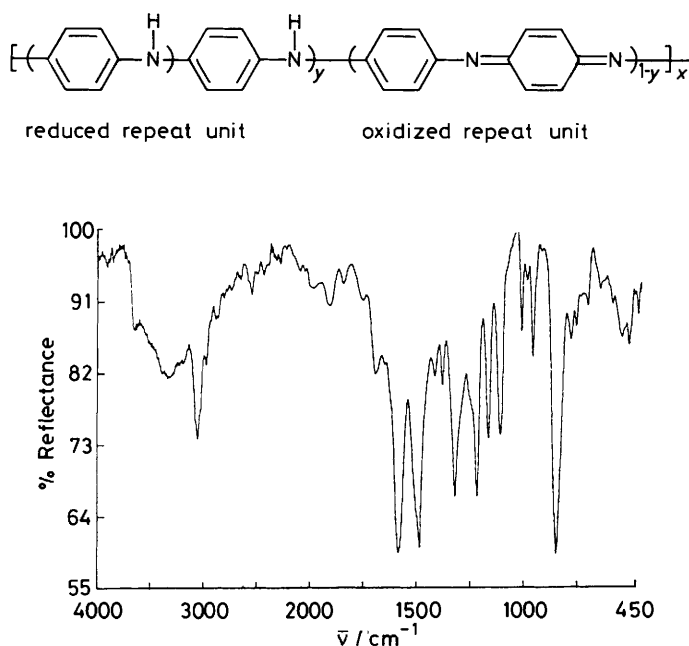
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The synthesis and characterization of free-standing flexible films and powder forms of pernigraniline base, the fully oxidized form of polyaniline, by the oxidation of emeraldine base with *m*-chloroperbenzoic acid is reported.

The base forms of polyaniline are described by a series of polymers having different oxidation states ranging in principle from the completely reduced to the completely oxidized members as represented by the general formula (1).<sup>1</sup> The emeraldine oxidation state ( $y \sim 0.5$ ) which consists principally

of alternating reduced and oxidized repeat units<sup>2,3</sup> has recently aroused considerable interest<sup>1,4,5</sup> since on protonation with aqueous acids such as HCl its conductivity is increased by  $\sim 10$  orders of magnitude (compressed pellet,  $\sigma \sim 5 \text{ S cm}^{-1}$ ;<sup>1,4</sup> stretched-aligned fibres,  $\sigma_{\parallel} \sim 10^2 \text{ S cm}^{-1}$ ) to



**Figure 1.** Diffuse reflectance FTIR spectrum of pernigraniline base powder. The spectrum is essentially a transmittance spectrum, because the specularly reflected component of the radiation is small.

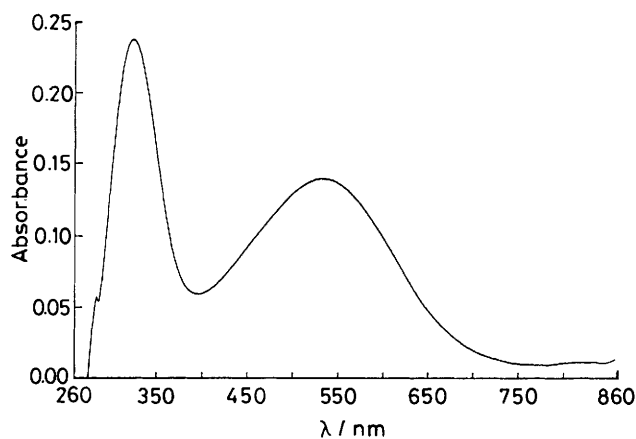
give a polysemiquinone radical cation having a half-filled polaron conduction band.<sup>1,5-7</sup> The completely reduced form of the polymer ( $y = 1$ ), leucoemeraldine base, is formed by reduction of emeraldine base.<sup>8,9</sup> However, it has been reported<sup>8</sup> that the completely oxidized form, pernigraniline ( $y = 0$ ), cannot be isolated and that it decomposes while drying during its attempted synthesis by oxidation of emeraldine base in aqueous acid. We report the first synthesis of pernigraniline base as an analytically pure powder and as free-standing flexible films.

Emeraldine base (~1 g) synthesized as previously described,<sup>4,9</sup> was dissolved in a solution consisting of *N*-methylpyrrolidinone (NMP; 100 ml) glacial acetic acid (5 ml). A glacial acetic acid solution (10 ml) containing purified<sup>10</sup> *m*-chloroperbenzoic acid (0.72 g) was then added in 1 ml portions every 10 min.† A dark violet solution was observed after stirring at room temperature for an additional 15 min. Triethylamine (10 ml) was added to produce a dark purple precipitate, which was filtered on a Buchner funnel. The precipitate was then stirred with acetone (60 ml) for 30 min and filtered. This procedure was repeated and the precipitate was washed on the filter with acetone (200 ml) followed by diethyl ether (200 ml). The analytically pure,‡ partly crystalline pernigraniline was obtained as a brownish-purple powder. A  $\text{TiCl}_3$  volumetric titration<sup>8</sup> of the oxidized repeat units gave a value  $(1 - y)$  of  $0.97 \pm 0.02$ .

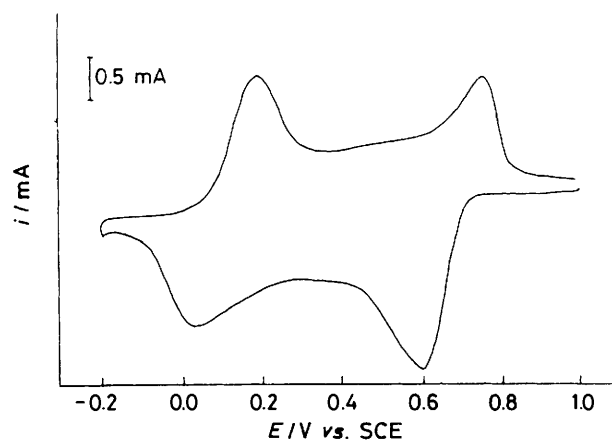
The intensity ratio (1.0:0.9) of the benzenoid (1483  $\text{cm}^{-1}$ ) to quinoid (1581  $\text{cm}^{-1}$ ) peaks in the diffuse reflectance FTIR spectrum (Figure 1) was consistent with its proposed structure, the whole spectrum being very similar to that of the fully

† With some batches of NMP, even after purification, some epoxidation of the aromatic ring appeared to occur as judged by the electronic and FTIR spectra of the product. This could be avoided by adding 10 drops of a 7% (w/w) aqueous  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  solution before addition of the *m*-chloroperbenzoic acid.

‡ Satisfactory elemental analyses (CHN) were obtained for  $\text{C}_6\text{H}_4\text{N}$ .



**Figure 2.** Electronic spectrum of pernigraniline base in DMF solution.



**Figure 3.** Cyclic voltammogram of pernigraniline base in  $\text{HClO}_4$  (1.0 M) aqueous electrolyte. Scan rate:  $50 \text{ mV s}^{-1}$ .

oxidized analogous octamer.<sup>11</sup> The electronic spectrum (Figure 2) in dimethylformamide (DMF) was also essentially identical to that of the fully oxidized octamer in DMF, having  $\lambda_{\text{max}}$  values at 528 and 320 nm corresponding to the values of 525 and 320 nm for the octamer. The cyclic voltammogram (Figure 3) in aqueous  $\text{HClO}_4$  (1.0 M) was, as expected, also essentially identical to that of emeraldine base [ $E_{1/2}$  0.12 V,  $E'_{1/2}$  0.70 V vs. standard calomel electrode (SCE)].<sup>12</sup> It is noteworthy that this voltammogram showed only two sets of peaks ( $E_{1/2}$  0.13 V,  $E'_{1/2} = 0.69$  V vs. SCE); impure samples exhibited in addition a peak intermediate between the two sets.

Free-standing, lustrous, flexible copper-coloured films could be obtained from the violet solution, produced after oxidation but before addition of triethylamine, by evaporating the solvent on a glass plate, removing the film under methanol and washing it by soaking in methanol (100 ml) for 2 h. The washing process was repeated four times.

The molecular weight of the pernigraniline which was synthesised from emeraldine base having a maximum molecular weight of ~325 000 (GPC, monodisperse polystyrene standard)<sup>13</sup> has not yet been measured; however, there is no evidence for any chain scission during its synthesis. This is qualitatively consistent with the flexibility of the free-standing films of the polymer.

The fact that the two extreme members of the polyaniline bases, the completely reduced and the completely oxidized,

have now been synthesized should make it easier to interpret future systematic studies of intermediate members of the series.

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