Polymer Vol. 37 No. 2, pp. 367–369, 1996

0032-3861/96/$15.00+0.00

The formation of polyaniline and the nature of its structures

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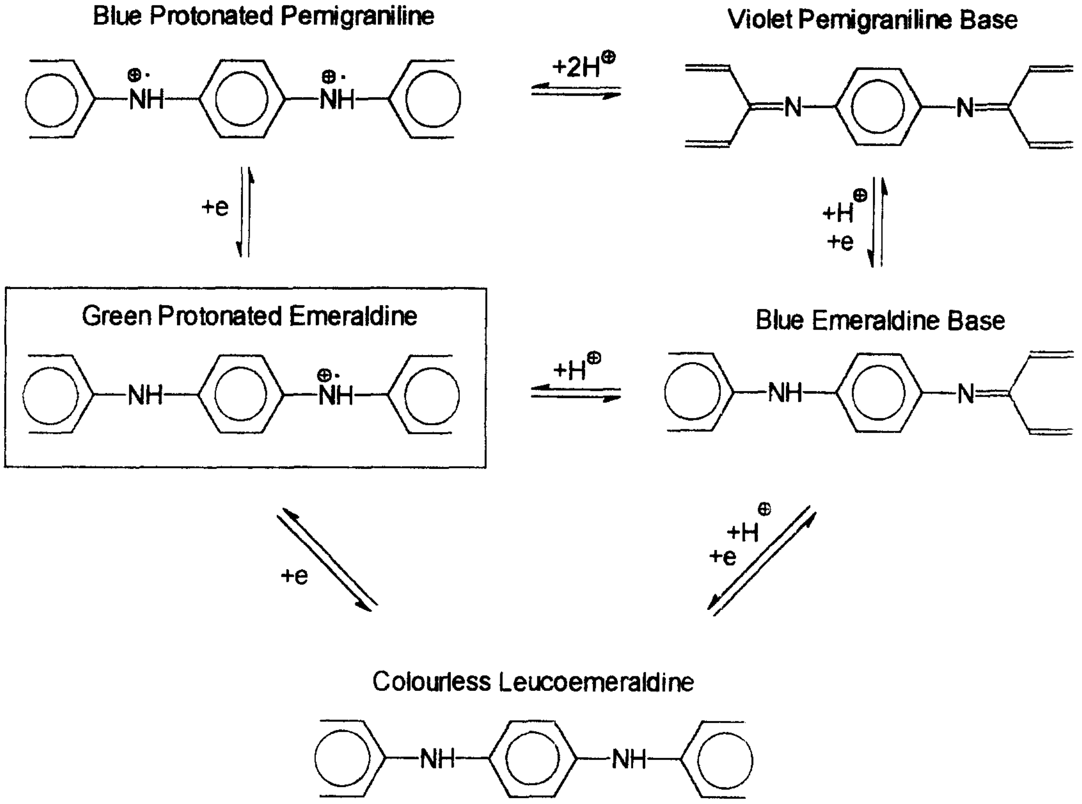
The oxidative polymerization of aniline gives rise to polyaniline which exists in a variety of forms, differing in electrical conductivity and in colour. A scheme of interrelated structures which accounts for all the spectroscopic and conductometric observations, is proposed, together with a set of equations summarizing the chemical transformations involved.

(Keywords: polyaniline; emeraldine; pernigraniline)

In recent years, polyaniline has attracted much attention[1–3] on account of its ability, under certain conditions, to exhibit a high level of electrical conductivity[4]. It is known to exist in a variety of forms[3,5] differing in colour, some of which are not electrically conducting. In order to understand the chemical nature of polyaniline, it is necessary to correlate both the colour and the conductivity with structure in a way that is compatible with the conditions of preparation (oxidative polymerization of aniline) and the circumstances in which interconversion between the various forms takes place. The present state of knowledge of the nature of the various forms of polyaniline and their transformations can be summarized in a simple reaction scheme, which, it is hoped, will provide a useful basis for further development in the understanding of the chemistry of polyaniline (*Scheme 1*).



Scheme 1 Polyaniline forms and their interconversions

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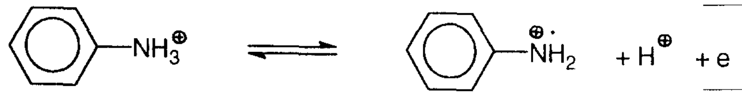
The most important form of polyaniline, protonated emeraldine, is green and electrically conducting; it is produced directly by the oxidative polymerization of aniline, usually as the hydrochloride. If stronger oxidizing conditions are subsequently employed, it can be converted to protonated pernigraniline[6,7], which is blue and may be expected to be conducting, further treatment with alkali results in the pernigraniline base, violet and non-conducting. The acid–base transition[7] occurs at pH 0–1.

On direct treatment with alkali, protonated emeraldine converts to the blue, non-conducting emeraldine base[5], this transition being located[8] at pH 6–7. The two blue forms, protonated pernigraniline and emeraldine base, are of different colour shades[6,7]. Alternatively, emeraldine can be reduced to colourless, non-conducting, leucoemeraldine[5].

The scheme formulated here comprises a set of interrelated structures which require only the exchange of protons or electrons or both to undergo interconversion, and which would be expected to display the visible colours actually observed. As far as we are aware, this scheme is compatible with all the known facts.

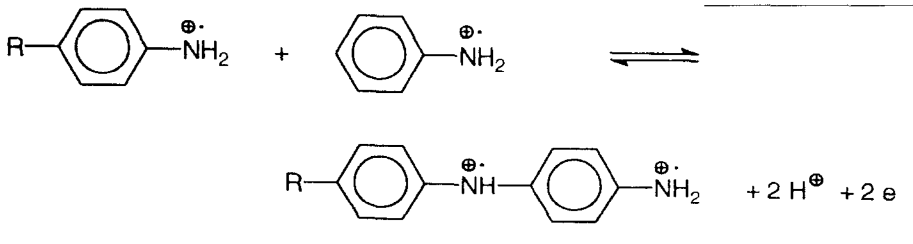
The colours of the individual forms can conveniently be characterized by the visible spectra of polyaniline dispersions[6,8–11]. These are prepared by the polymerization of aniline in the presence of a steric stabilizer, e.g. poly(vinyl alcohol)[8,12–14]. Analysis of the visible spectra recorded during the polymerization of aniline[6,8] indicates that protonated polyaniline structures play an important role in the formation of polyaniline. The following reactions are proposed to account for the fundamentals of polyaniline formation.

In aqueous acidic media, aniline exists predominantly as the anilinium cation; the aniline cation radical is assumed to be the first product of its oxidation[3,15]:



(1)

Aniline cation radicals may recombine into benzidine or *N*-phenyl-*p*-phenylenediamine[15,16] or participate in the growth of polyaniline chains in the pernigraniline form:



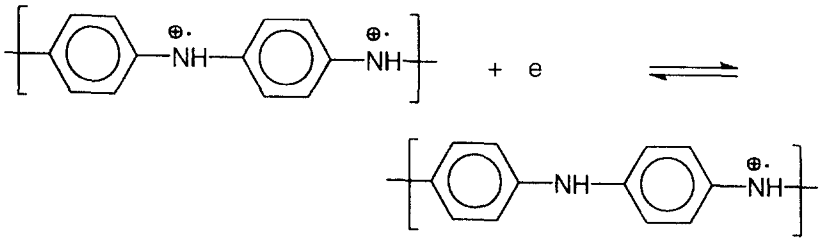
(2)

R = H or pernigraniline chain

The protonated pernigraniline, the repeating unit of which is dication diradical[2,17,18], is responsible for the blue colour of the reaction mixture[6,7] (cf. *Scheme 1*) observed during polymerization. The acidity of the reaction mixture increases during polymerization due to the release of protons[6,9,19]. The electrons abstracted from aniline in the above oxidation processes are used in the reduction of the oxidizing agents, e.g. peroxydisulfate to sulfate:

$$S_2O_8^{2\ominus} + 2\,e \rightleftharpoons 2\,SO_4^{2\ominus} \quad (3)$$

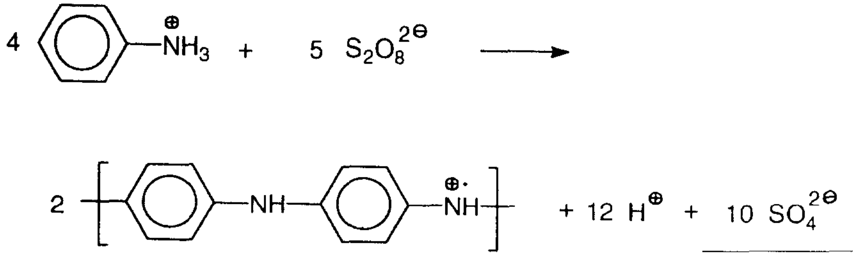
When aniline is still present in the reaction mixture after all the oxidizing agent has been consumed, pernigraniline takes over the role of an oxidant and becomes reduced by aniline[10] to the final product, emeraldine:



(4)

Oxidative polymerization of aniline then proceeds according to equations (1) and (2) until all the pernigraniline has been converted into emeraldine by equation (3). This is reflected by the change of the colour of the reaction mixture to green. The ability of pernigraniline to oxidize aniline is responsible for the autoacceleration effect in the polymerization of aniline[6,20]. Also, the addition of compounds which can form cation radicals upon oxidation, e.g. *p*-phenylenediamine, accelerates the formation of polyaniline[19]. When, on the other hand, oxidizing agent (peroxydisulfate) is present in excess, the pernigraniline decomposes to colourless low-molecular-weight products of the quinone type, and the yield of emeraldine is reduced.

The combination of equations (1)–(4) yields:



(5)

Thus 1.25 mol of ammonium peroxydisulfate are needed[21] for the polymerization of 1 mol of aniline into the emeraldine form of polyaniline, in close agreement with the experimental results[13,21,22].

The facile preparation of polyaniline – the oxidation proceeds with stoichiometric yield in aqueous media at ambient or lowered temperature – and the existence of forms differing in colour and electrical conductivity make this polymer a good candidate for applications in electrochromic devices[23], batteries[24], electronic components[25,26] and imaging[27].

Acknowledgements

The financial support of the Grant Agency of the Czech Republic (203/95/1297) and the Grant Agency of the Academy of Sciences of the Czech Republic (A 4050515) is gratefully acknowledged. Thanks are also due to the Royal Society for the support of scientific contacts between the authors.

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