

Oxidative Polymerization of Phenylene diamines

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After considering and proposing pyrazine synthesis from alpha-amino ketones and making several suggestions for new chemistry, I found what I thought was an even simpler method for their synthesis. My story begins with a 2002 Chem. Rev..

On the other hand, the oxidative polymerization of *p*PD with $K_2S_2O_8$ yields a polyquinoxaline, a material having a ladder structure and fully oxidized state (Scheme 7).⁶²

Scheme 7

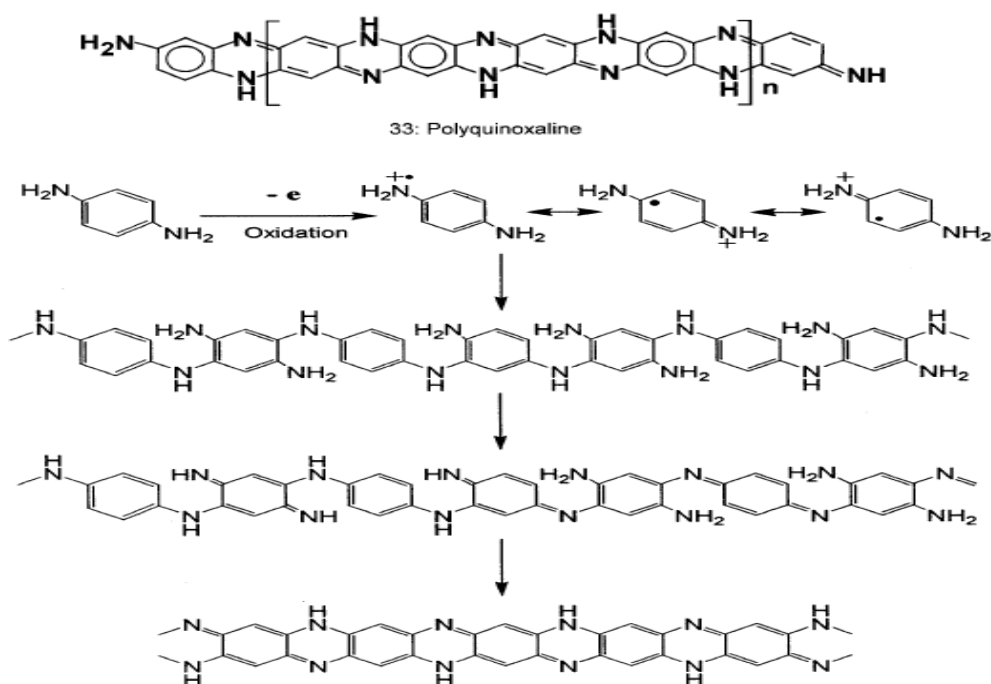
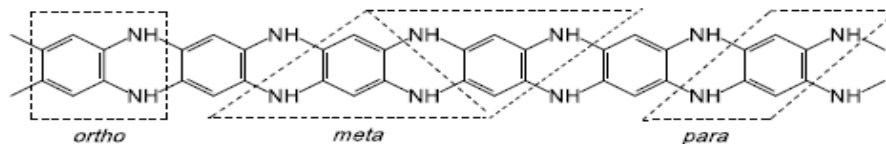


Figure 15. Chemically oxidative polymerization mechanism of *p*-phenylenediamine (*p*PD).⁶²

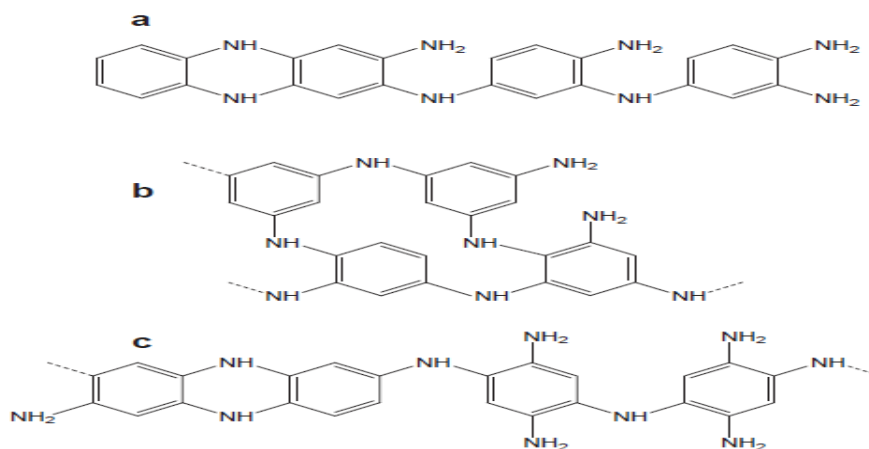
Li, X. G., Huang, M. R., Duan, W., & Yang, Y. L. (2002). Novel multifunctional polymers from aromatic diamines by oxidative polymerizations. *Chemical Reviews*, 102(9), 2925-3030.

Further oxidation would result in pyrazine aromatics now referred to as polyphenazines. Obviously, I was thrilled to see what looked like a rather simple route to these polyphenazines. However, looking further into this polymerization revealed that the products were mostly black poorly soluble polymers. Looking at the literature since the 2002 review proved to be enlightening.



Scheme 2. Polyphenylenediamine ladder-like structure can be, in principle, produced from any phenylenediamine isomer (adapted from Refs. [5,21,24]).

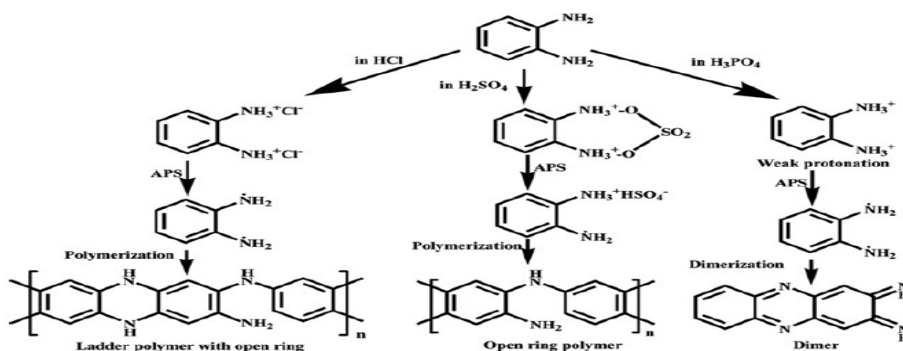
This reference goes on to demonstrate that the actual structures are as follows;



Scheme 3. Possible coupling of phenylenediamine isomers, (a) *ortho*, (b) *meta*, and (c) *para*, complying with the FTIR spectroscopic analysis. Formulae are shown for the simplicity in reduced "leucoemeraldine-like" state but may be oxidized as well as protonated depending on the acidity of reaction medium.

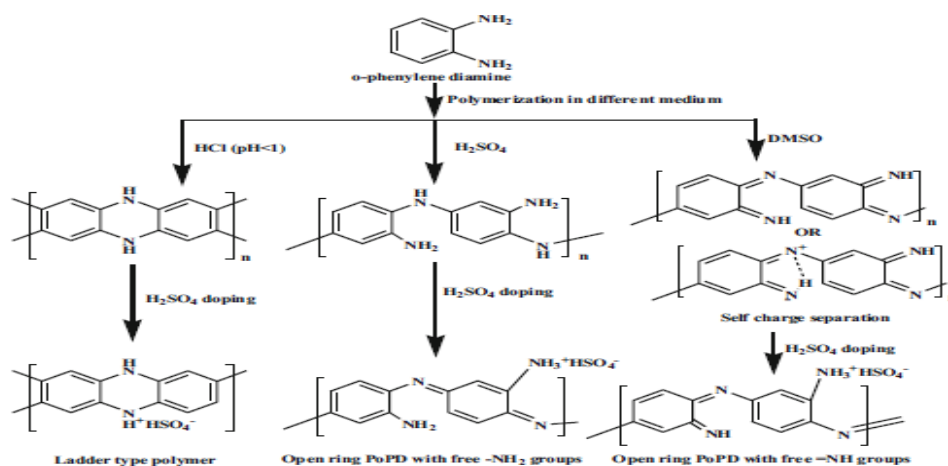
Bláha, M., Trchová, M., Morávková, Z., Humpolíček, P., & Stejskal, J. (2018). Semiconducting materials from oxidative coupling of phenylenediamines under various acidic conditions. *Materials Chemistry and Physics*, 205, 423-435.

Also;



Scheme I. Proposed polymerization mechanism of monomer (oPD) in different inorganic acid medium.

Samanta, S., Roy, P., & Kar, P. (2016). Structure and properties of conducting poly (o-phenylenediamine) synthesized in different inorganic acid medium. *Macromolecular Research*, 24(4), 342-349.



Scheme 1 Proposed doping mechanism of the polymer with ladder structure and open ring structure with free -NH₂ groups and =NH groups

Samanta, S., Roy, P., & Kar, P. (2017). Influence of structure of poly (o-phenylenediamine) on the doping ability and conducting property. *Ionics*, 23(4), 937-947.

The above articles illustrates the variability in the structures of the oxidative synthesis of these polymers.

I want to add this brief review to my web page because I overlooked this chemistry when proposing routes to polyphenazines.

Thank you for your interest in my proposals.
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