

MECHANISM OF POLYMERIZATION OF ANILINE: A REVIEW

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ABSTRACT

Aniline is oxidized to polyaniline by using ammoniumpersulphate as an oxidizing agent. The polymerization is a chain reaction that involves chain initiation, propagation and termination steps. In the initiation step, aniline cation radical or nitrenium ions are formed. In the propagation step, dimeric and trimeric units are formed via the semidine and phenazine intermediate formation. Protonated pernigraniline forms of aniline are produced in the propagation step of polymerization. The chain termination step is taking place by recoupling and reoxidation of terminal cation radicals.

Keywords: polyaniline, polymerization, mechanism

I. INTRODUCTION

The oxidation of aniline to polyaniline is usually presumed to be a chain process which involves various steps: chain initiation step, chain propagation step, and chain termination steps. This topic is well discussed in the literature. The general mechanistic steps may be potted as follows [1]. It is generally assumed that the first product of aniline oxidation is an aniline cation radical. However the formation of aniline cation radicals and nitrenium cations is also documented in literature [2], depending upon the reaction conditions i.e. type of oxidant, anode potential, etc. Semidine, an aniline dimer is the first product of aniline oxidation. It is known from the chemistry of mauveine dye as shown in Fig. 1 that the formation of phenazine heterocycle [3] occurs due to ortho-isomer of semidine and not due to its para-isomer. Formation of aniline trimer via a phenazine intermediate is still open to discuss. It is believed that aniline trimers serve as nucleates/ initiation centres in the morphology formation [3]. Fig. 2 shows the schematic diagram of conversion of aniline into dimeric and trimeric units. Aniline cationic radical is produced in the first step of aniline oxidation and reacts with another terminal cationic radical via coupling. This coupled product is rearranged into another molecular structure which after oxidation produces another terminal cationic radical as shown in Fig. 3. In this way the propagation proceeds in the form of protonated pernigraniline forms of aniline and it is revealed by a blue color of the reaction mixture. The cause for the diversity of the molecular structures is because of the two basic factors: (1) the monomer and (2) the growing chain of polymer. These factors determine the morphologies and properties of products in aniline oxidation [1]. The chain reaction of electrophilic substitution and the coupling of cation-radical centres are two pathways that describe the mechanism of polymerization of aniline. Which way polymerization occurs that depends on the reactants protonation, deprotonation states and hence, the pH of the reaction medium. At pH >2.5, non-protonated forms of the aniline are favoured. Under such circumstances,

polymerization of aniline occurs via the electrophilic substitution reaction. This reaction proceeds at low oxidation potentials. At pH 2.5–4, protonation of aniline is reduced. Thus electrophilic substitution reaction occurs at a slight increase in its oxidation potential. At pH <2.5, The protonated forms of aniline are favoured. The polymerization of aniline occurs via the coupling mode of cation radicals. In this mode, initially cyclic dimer, the phenazine, is formed which converts into chain terminal cationic radical after lengthening at 0.7 V. The cation radical further reacts with another monomeric cationic radical producing a π -complex. It is thought that the transformation of π -complex into para-substituted monomer unit occurs through an intramolecular semidine rearrangement (Fig. 3). The growing chains have regular structure. This is due to the high regioselectivity of the sigmatropic rearrangements and significant energy benefit of protonated polyconjugated chains in the agglomerated state. After monomer expansion, the terminal cation radical is recouped by reoxidation. For further details the reader may go through the literature [4].

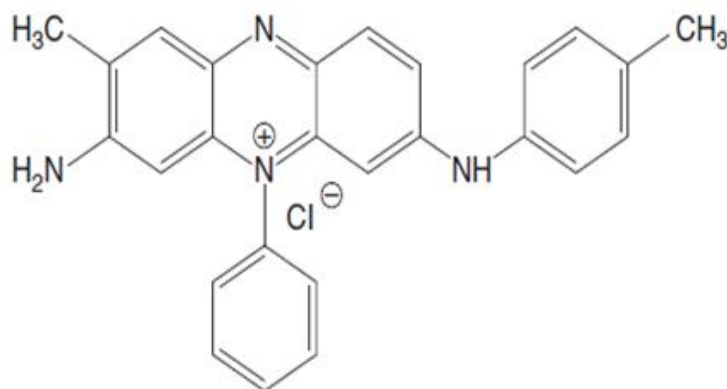


Fig.1. Structure of mauveine dye

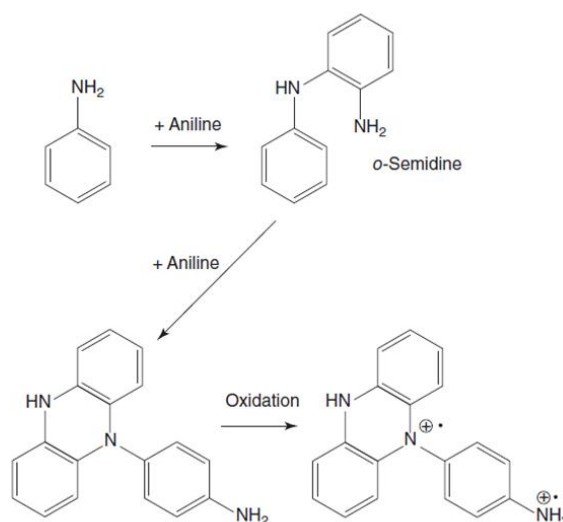


Fig. 2: Oxidation of aniline into dimer, semidine, and subsequently a trimer.

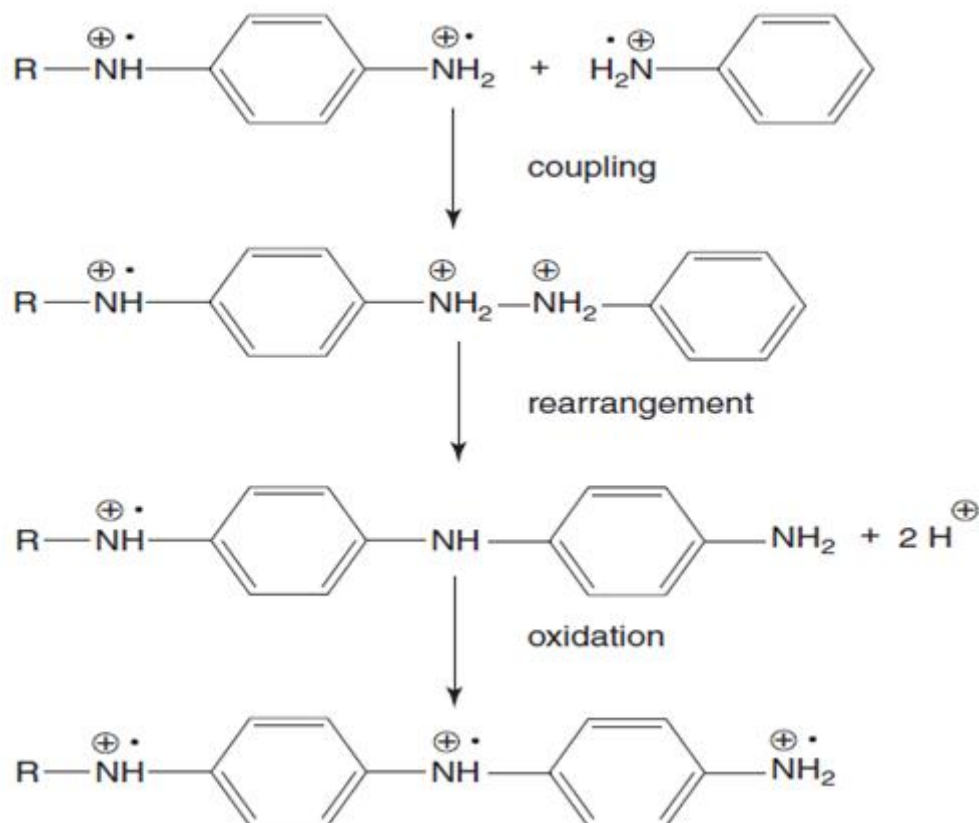


Fig.3: Coupling of aniline cation-radical unit with terminal aniline cation radical by recombination method followed by rearrangement of dimeric unit and reoxidation into another terminal cationic radical.

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