Abstract

This Ph.D. thesis is dealing with catalytic polymerization of aniline (ANI) and partially also of substituted anilines with $FeCl_3/H_2O_2$ catalyst system, in which according to obtained results both active species, Fe^{3+} and $HO^{\bullet}$, participate in the overall polymerization mechanism, creating a synergic system. The Fe^{3+}/H_2O_2 catalyst system, also called Fenton's system can considerably lower contamination of forming neat polyanilines (PANIs) by side-products characteristic of stoichiometric polymerization. However, catalytically prepared PANIs exhibit reduced conductivity related most probably to side reactions involving radicals generated as integral components of the $FeCl_3/H_2O_2$ system. Catalytic polymerization of ANI with $FeCl_3/H_2O_2$ system was found to be the reaction of approx. 2^{nd} order with respect to ANI and gives PANIs of a good quality only when $[H_2O_2]$ in the reaction mixture was kept low, i.e., at under-stoichiometric ratios $[H_2O_2]/[ANI]$. At over-stoichiometric ratio $[H_2O_2]/[ANI]$, PANIs of lowered conductivity, worse spectroscopic characteristics and increased size of PANI nanostructures were obtained; nevertheless, these PANIs were not over-oxidized to pernigraniline state. The reaction-time profiles of the open-circuit potential of reaction mixtures exhibited an inflection related to the H_2O_2 depletion from the system. Total consumption of H_2O_2 exceeded its consumption necessary on ANI polymerization, which proves partial decomposition of H_2O_2 by Fe ions. UV/vis and resonance Raman spectra indicate incomplete deprotonization of PANIs prepared with $FeCl_3/H_2O_2$ system and subsequently treated with aqueous ammonia, which proves partial self-doping of these PANIs. However, IR and NMR spectra indicate rather low extent of self-doping. It has been proposed that self-doping of PANI involves phenolic OH groups originated from side reactions involving radical species formed from H_2O_2. Since change of spectral properties of polyaniline prepared by ammonium peroxodisulfate after its exposure to Fenton's reagent was of the same character, we expect that $HO^{\bullet}$ radicals attack not only growing polymer chains, but also non-active ones to form proposed phenolic groups. Ours idea, that giving hydrogen peroxide into reaction mixture in small consecutive doses can lead to PANIs containing lower amount of structural defects, fulfilled just partially. Comparison of spectral properties of PANIs prepared by ammonium persulfate at room temperature and at 0 °C showed presence of same structural defects in chains of polyaniline prepared at room temperature.

Keywords:

Catalysis, catalytic oxidation, polyanilines, reaction mechanism