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ORIGINAL PAPER

Self-organization of polyaniline during oxidative polymerization: formation of granular structure

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The paper is focused on oxidative polymerization of aniline proceeding in an acid medium with a strong oxidant; formation of polyaniline (PANI) granular structures in different steps of the synthesis was studied. The relationship between the processes of self-organization of the growing polymer into supramolecular structures and the steps of molecular synthesis has been revealed. It was shown that during the induction period (the initial synthesis step), insoluble non-conducting products are formed. They are characterized by the absorption band at 430 nm corresponding to the wavelength of the phenazinium cation radical peak. In the second step, the polymer chain growth, conducting PANI granules with the diameter of 50 nm were obtained. These granules consist of spherical particles with the diameter as small as several nanometers. Then, the granule dimensions increased to 200 nm due to the growth of the spheres; the sphere diameter reached 20 nm. The number of spheres in a granule remained constant. Both precipitate and PANI film consist of common structural elements, polymer spheres, organized into granules and larger structures. Suppression of the polymer chain growth leads to the formation of non-conducting aniline oligomers which are self-organized into large particles with fractal structure. To describe the self-organization processes of a growing polymer chain, the diffusion-limited aggregation mechanism was used.

Keywords: granular polyaniline, conducting polymer, molecular mechanism, self-organization, diffusion-limited aggregation

Introduction

The growing interest in nanostructured forms of conducting polymers is caused by the expanding area of their practical application. Conducting polymers can be used in new electronic devices (organic transistors, displays, sensors, energy storage, and memory cells), materials for electromagnetic irradiation shielding, corrosion inhibition, membrane construction, in catalysis and medicine (Skotheim & Reynolds, 2007). A great number of publications have been devoted to the synthesis and studies of nanostructured polyaniline, since PANI was the first among conducting polymers to find practical application due to its stability and low cost. Nanostructured forms of PANI demonstrate a striking diversity. They can be subdivided into one-dimensional morphologies (nanofibers, nanorods, and nanotubes), two-dimensional objects (ribbons, nanobelts, and nanoplates), and three-dimensional particles (microspheres, nanospheres, and granules). These main architectural elements serve as a basis of more complicated hierarchical formations such as fantastic plants, flowers, corals, complex geometric figures (Tran et al., 2009; Stejskal et al., 2010; Olad et al., 2012; Trchová et al., 2012).

All the above-listed supramolecular PANI structures are formed in the course of oxidative polymerization of aniline. The synthesis includes two associated processes: chain reaction (formation of macromolecules from the monomer) and assembly of growing

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