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ORIGINAL PAPER

Effect of cations on polyaniline morphology

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Nanostructured polyanilines of different morphologies were prepared by chemical polymerization of aniline with ammonium peroxodisulfate in aqueous HCl using various inorganic and organic chlorides as additives with the aim to determine the effect of cations of the added electrolyte on the morphology, spectroscopic characteristics, and conductivity of formed polyanilines. Chlorides of basic metals: NaCl and $CaCl_2$ did not show any significant effect while $AlCl_3$ and organic electrolytes were found to influence the morphology of polyanilines. The effect of organic-electrolyte additives, which actually are ionic liquids, is explained by the organization of their molecules to micellar structures that act as soft templates for emerging polyaniline nanoparticles. The effect of $AlCl_3$ is ascribed to the transformation of its molecules to $[AlCl_4]^-$ anions.

Keywords: polyaniline, nanostructures, ionic liquids, morphology, electrolytes

Introduction

Polyaniline (PANI) is a conductive polymer that degrades before melting and, in addition, it has a low solubility in organic solvents which limits its use. On the other hand, PANIs prepared by chemical polymerization of aniline (ANI) with ammonium peroxodisulfate (APS) exhibit strong tendency to form nanostructures. Thus, these polymers combine properties of organic semiconductors and large surface-area materials, which provides them with a great potential for various applications. Size and shape of PANI nanoparticles can play important role in the applications of PANIs in conducting blends, nanocomposites, catalysis, etc. For example, Mezzenga et al. (2003) reported that the electrical conductivity of blends comprising fibrous PANI nanoparticles is higher than that of blends comprising PANI nanoparticles with spherical morphology. Huang et al. (2012) showed that PANI nanoparticles can be used as a redox catalyst for selective oxidation of cyclohexene with H_2O_2, the activity of which depends on the particle size and redox state of the applied PANI sample.

Morphology of PANI prepared by chemical oxidation strongly depends on the reaction conditions. PANI prepared by the standard oxidation of ANI with APS in an acidic aqueous medium exhibits the morphology of agglomerated granular particles of different sizes. Starting pH of the reaction mixture can significantly influence the morphology as well as the formation of side products as reported by Konyushenko et al. (2006), Stejskal et al. (2008), and Przybyłek and Gaca (2012). When the polymerization is done in a neutral or slightly acidic medium (solution of a weak acid), the main product are PANI nanotubes (Ding et al., 2009; Zhou et al., 2009). If the reaction starts in a basic medium, PANI microspheres are formed. If the starting pH is higher than 4, it is assumed that propagation is drastically slowed down owing to the lack of protons and formation of cyclic oligomers that comprise phenazine-like units prevails. Formation of phenazine units in the early stages of PANI polymer-

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