

The Influence of Phenylenediamine Additions on the Synthesis of Polyaniline

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Polyaniline (PANI) is a conductive polymer and its physical and chemical characteristics depend on the experimental parameters (method of synthesis, potential of synthesis, pH, counter-ion etc). PANI has been proven to be an interesting material for the application in different areas like batteries, catalysis, corrosion protection, electrochromic devices etc. It is, therefore, of a great interest to be able to produce PANI of the most desirable characteristics for the particular application.

It is known from the literature [1] that additions of different derivatives of aniline influence the synthesis of PANI, but also the characteristics of the resulting polymer.

The aim of this work was to establish the influence of *ortho*-*meta*- and *para*-phenylenediamine (OPDA, MPDA, PPDA) additions on the rate of PANI synthesis, as well as on the mechanism of the polymerization, and on the characteristics of the resulting polymer.

The synthesis was carried out by cyclic voltammetry from 0.1M aniline solution in 1.0M HCl, and also with the addition of OPDA, MPDA, PPDA and *ortho*-etoxyaniline (OEA). The working electrode was Pt disc ($A=0.07\text{cm}^2$) and the reference electrode was SCE.

From Fig. 1 it follows that the addition of PPDA, even at 1mM concentration, has dramatic influence on the increase of PANI polymerization rate, while the addition of OPDA, MPDA and OEA at 1mM level does not show any significant influence. However, higher additions (5mM) slow down the PANI polymerization rate. As it is shown in Fig. 2 the monomer oxidation potentials (E_{45°) are considerable lower than of aniline monomer, but it is not in direct correlation with the polymerization rate.

OPDA, showing the lowest value of the oxidation potential, was examined in more detail. Fig. 3 illustrates the polymer charge, Q , corresponding to the quantity of the deposited polymer, vs. number of cycles (N), at the beginning of the polymer layer growth ($N=1-10$) and at prolonged cycling ($N=10-100$). As it is shown, at low N the increase of charge is larger in case of OPDA than in case of PANI, but slows down until the final increase after the 40th cycle. In case of aniline there is sudden increase after the 15th cycle. However, the addition of OPDA, even at low levels, slows down the polymerization rate.

Fig. 4 illustrates the voltammograms obtained for the same systems as in Fig. 3. It is evident that, even at low additions of OPDA, there is no current peak characteristic for PANI. At higher additions of OPDA voltammograms show new current peak at lower potentials. It is assumed that in presence of OPDA there is preferential adsorption of OPDA on the electrode surface, and primarily poly-OPDA is formed for which the ladder structure is assumed [2]. This change in voltammograms reflects also on the morphology of the resulting polymer what is evident from SEM micrographs.

References:

1. K. Chiba, T. Ohsaka, Y. Ohnuki and N. Oyama, J. Electroanal. Chem., **219**, 117 (1987).
2. A. Malinauskas, M. Bron, R. Holze, Synth. Met., **92**, 127 (1998).

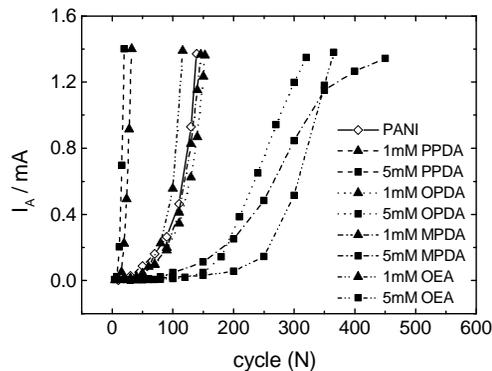


Fig. 1. The increase of anodic current peak (I_A) vs. number of cycles (N) in synthesis of PANI with different additions of monomers.

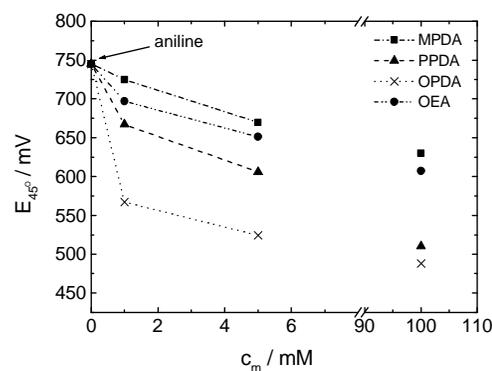


Fig. 2. Oxidation potentials (E_{45°) of systems examined vs. the concentration of monomers (c_m).

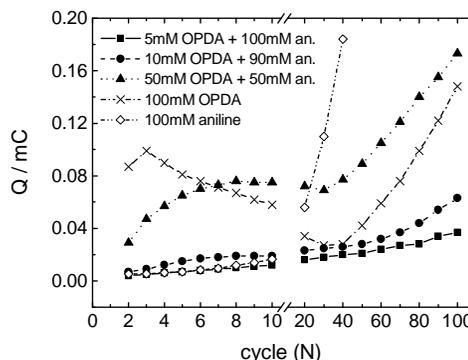


Fig. 3. Deposited polymer charge, (Q) vs. number of cycles (N) in synthesis.

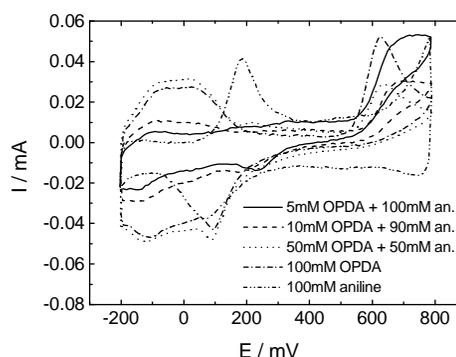


Fig. 4. Voltammograms of the 100th cycle of synthesis (except PANI - 40th cycle) at $v = 50\text{mV/s}$.