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Dielectric behavior of polyaniline synthesized by different techniques

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Abstract

Polyaniline doped with dodecylbenzenesulfonic acid (Pani.DBSA) was synthesized by different procedures: by a dedoping–redoping process, by one step inverted emulsion polymerization and by one step aqueous dispersion polymerization. The effect of these different techniques on the electric properties (dielectric constant, dielectric losses, and complex electric modulus) of the corresponding emeraldine base has been studied by thermal dielectric analyzer (DETA) in the temperature range −130 °C to 200 °C and in frequency range 0.03–10^5 Hz. It was found that the preparation technique has significant influence on the dielectric properties of Pani. The different synthetic routes give rise to polyaniline with different distribution of electric relaxation process, indicating different chain structure. Emeraldine base from Pani.DBSA prepared by one step aqueous dispersion polymerization exhibits one single relaxation peak with narrow distribution whereas that prepared by inverted emulsion polymerization exhibits two relaxation peaks, indicating two-phase structure as indicated by a bimodal distribution of relaxation process. Emeraldine base from Pani.DBSA prepared by dedoping–redoping process presents an intermediary behavior. Percentage crystallinity of Pani.DBSA samples has also been investigated using wide-angle X-ray diffraction analysis. Pani.DBSA prepared by aqueous dispersion exhibited higher crystallinity degree, which agrees with the higher conductivity.

Keywords: Polyaniline; Conductive polymer; Dielectric properties

1. Introduction

Polyaniline (Pani) is an important conducting polymer that has been extensively studied because of its relative easy preparation, good environment stability and high degree of conductivity. It somewhat differs from the other conducting polymers in that the insulating emeraldine form (Pani-EB) can be converted into a conductive form, the emeraldine salt (Pani-ES) through protonation of the polymer [1]. The emeraldine base form is accepted

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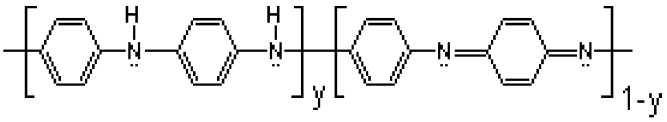
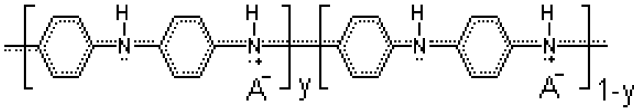
to be an alternating copolymer of reduced (phenylenediamine) and oxidized (quinoid diimine) segments, where $Y \approx 0.5$:



When the imine nitrogens are fully protonated (with around 0.5 mol of protonic acid, $A^- H^+$, per mol of PhN repeated unit of Pani), the alternating copolymer transforms to a polyconjugated polyradical cation salt, which corresponds to the conductive form Pani-ES [2,3].



The nature of the protonating agent is very important to impart solubility to the emeraldine salt form of Pani. Among several organic acids used for this purpose, dodecylbenzenesulfonic acid (DBSA) is particularly interesting because it can act as both protonating and surfactant agent and also act as a processing aid in mechanical blends of Pani with other conventional insulating polymers [4]. Polyaniline doped with DBSA (Pani.DBSA) can be prepared by treating the Pani emeraldine base with DBSA [4,5] or by direct polymerization of aniline in the presence of DBSA [6–8]. These different synthetic routes give rise to Pani.DBSA samples with different morphologies and conductivities. In our recent report, we observed that Pani.DBSA synthesized by one step polymerization in aqueous dispersion exhibited the highest conductivity values, which was attributed to the highest degree of protonation [9].

The protonation process results in an insulator–conductor transition with a concomitant conformation change in the polymer backbone, to accommodate the electronic transformation. It is generally accepted that the conductivity of highly protonated polyaniline ($A^- > 0.3$) is governed by hopping of charge among crystalline regions embedded in an amorphous disordered insulating matrix [10], whereas in slightly protonated form of Pani ($A^- < 0.07$), the charge transport is mainly due to small mobile polarons involving pair-wise hopping of charges between polarons and bipolarons in the unprotonated amorphous portions of the bulk emeraldine base polymer [11].

Besides doping level and redox state, other factors will influence the conductivity values of Pani, such as, humidity of the polymer [12,13], treatment in specific solvent [14–16] and the orientation of polymer chains [17].

Dielectric measurement at radio frequency is a powerful method of studying the charge transfer characteristics and its delocalization within the amorphous region of the polymer. Several authors have been used this method to investigate the mechanism of the electrical conduction in undoped (unprotonated) or weakly doped (protonated) polyaniline [10,11] and the factors that influence its electrical properties such as: water [12,13,18], the inherent disorder presented in alkyl-substituted polyaniline [15,19–21], the crosslinking reactions in Pani [22], the thermal ageing [17], etc.

The aim of this paper is to investigate the effect of the different synthetic routes adopted for the preparation of Pani.DBSA on the dielectric properties of the corresponding emeraldine base. For this purpose, the emeraldine base of Pani.DBSA obtained by redoping process and those obtained by one step inverted emulsion polymerization in toluene or by aqueous dispersion were analyzed. The crystallinity degree of different Pani.DBSA was also determined.

2. Experimental

2.1. Materials

Aniline (Ani) (analytical grade, Merck) was distilled twice under vacuum and stored under nitrogen