Preparation of conductive polyaniline solutions for electronic applications

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Abstract. Electrically conductive processible polyaniline films have been synthesised from the electropolymerization of aniline under non-aqueous conditions. The characterization of the polymer was carried out by spectroscopic methods.

Keywords. Soluble polyaniline; electrochemical polymerization.

1. Introduction

Electrically conductive polymers are attracting considerable attention in order to explore the possibility of using them in rechargeable batteries (Genies *et al* 1985), photovoltaics devices (Noufi *et al* 1982), EMI shielding (Bigg *et al* 1981) and many other applications in the electronics industry. The characterization and processing of conducting polymers are important unsolved problems from the scientific and industrial point of view. The soluble conducting polymers can find applications such as: (i) conducting ink; (ii) conductive adhesives and (iii) EMI shielding. Till now polyaniline has been known only as a green interactable material (Green 1910), the base form of which was assigned the composition,

and termed emeraldine, which contains equal numbers of reduced,

and oxidised units,

Very little effort has been devoted to the solubilization of this polymer. Soluble polyanilines may be interesting in fundamental studies for evolving physicochemical properties, and for commercial applications as a more easily processible material. Recently soluble polyanilines have been reported (Suzhen Li *et al* 1987; Dhawan and Trivedi 1988), where it is observed that when polymerization of aniline is carried out with organic proton acids of large molecular size e.g. *p*-toluene sulphonic acid, a soluble polymer of aniline is obtained. Angelopoulos *et al* (1987) have reported the processible polyaniline from 80% aqueous acetic acid. But if the same polymerization is carried out in mineral acids, the polymer obtained is insoluble and has a much larger chain length.

The electro-activity of polyaniline, and particularly of electrochemically synthesised polyaniline, has been widely explored in aqueous electrolytes (MacDiarmid *et al* 1984). While investigating the behaviour of aniline in non aqueous media it has been observed that mechanism of polymerization and subsequent fragmentation of polymerized products are different from the aqueous media. The aniline polymer so obtained is soluble in organic solvents of higher dielectric constant such as DMSO and DMF.

The identification of the polymer so obtained has been carried out with UV visible and IR spectroscopy.

2. Experimental

The experimental procedure consists of polymerizing 0.1 M of aniline in acetonitrile (containing not more than 10^{-2} mol/l of water) containing 1 mol of either LiClO_4 or $(n\text{C}_4\text{H}_9)_4\text{NBF}_4$ as supporting electrolyte, galvanostatically in an undivided cell using either Pt or ITO electrodes. All electrochemical measurements reported herein are carried out with SCE as a reference electrode. The chemical polymerization of aniline was carried out by the method reported earlier (Dhawan and Trivedi 1988).

3. Results and discussion

Experimental evidence suggests that oxidative polymerization of aniline in non-aqueous media does not stop at the dimerization stage but that further polymerization takes place. The first inflection in the current potential curve at 0.6 V is assigned to the proton extraction and formation of the free radical which occurs at the interface of the electrode, and can be observed as being due to the development of a light yellow colour indicating the formation of a charge transfer complex. The free radicals thus formed dimerize to give a dication which gets further polymerized at the anode to yield a high molecular weight polymer at higher potential (≈ 1.2 V). The possible reaction mechanism may be written as

The slow evaporation of the electrolyte after removing all the insoluble polymer gave a conducting film, the conductivity of which was 1.8×10^{-4} s/cm. In this film the possibility of ionic conduction due to LiClO_4 or TBABF_4 cannot be ruled out. An interesting observation made in the chemical polymerization of aniline in non-aqueous media is that the polymer so obtained is soluble in DMSO and DMF and less soluble in CHCl_3 and CH_3OH . This phenomena of solubility varying with the nature of the solvent may be due to the effective solvation of the polymer matrix by solvent molecules. Further studies are in progress to understand the mechanism of solute-solvent interactions.

On comparing the UV-visible spectra of soluble polyaniline with that of the model for polyaniline proposed by Lu *et al* (1986), interesting observations were made. The phenyl capped octa aniline shows absorption bands in DMF at 332 and 618 nm, whereas fully oxidised perinigraniline, B_3Q_4 has absorption bands in DMF at 320 and 525 nm. In the present studies, the polymer obtained chemically from non-aqueous media had absorption bands at 321,582 nm and 318,571 nm in DMSO and DMF respectively (figure 1). The difference in electronic spectra can be attributed to the lesser degree of conjugated polymer chains obtained in non-aqueous media than in polyaniline synthesised in aqueous media. Preliminary investigations reveal that heptamer formation occurs under these conditions.

The soluble oligomer of aniline in acetonitrile shows absorption bands at 310, 344 and 541 nm which are identical with the values observed for the oligomers of aniline (Yong *et al* 1986), when monomer units are linked at para-positions. Figure 2 shows the IR spectra of electrochemically polymerized aniline in non-aqueous media in the presence of TBABF_4 . The spectra is different than that of the usual spectra of polyaniline synthesized in aqueous media. The peak positions characteristic of benzenoid and quinoid ring vibration bands are shifted to 1605 and 1490 cm^{-1} respectively, approximately 40 and 20 cm^{-1} higher as compared with the usual polyaniline. Major bands observed in the IR spectrum of the

Figure 1. Electronic spectra of soluble polyaniline in DMSO (1 and 3) and DMF (2 and 4).

Figure 2. IR spectra of polyaniline synthesised in (a) a nonaqueous medium and (b) soluble polyaniline.

polymer obtained from non-aqueous media are (bands for the polymer from aqueous media are given in parentheses): 2940 (2917), 2860 (2854), 1605 (1565), 1490 (1470), 1300 (1292) and 1125 (1109) cm^{-1} . An additional sharp absorption band at 1080 cm^{-1} is observed due to BF_4^- ion, which gets doped in the polymer during the course of the polymerization reaction.

Different opinions have been expressed regarding the polymerization of aniline under non-aqueous conditions. One group of workers (Ohsaka *et al* 1984) proposed that the polymerization occurs at the meta-position, while the other group (Volkov *et al* 1980) came to the conclusion that polymerization occurs at the para-position. Both these arguments are based only on the IR data. We are of the opinion that the polymerization occurs at the para-position and that the meta-position is not energetically suitable for the generation of free radicals which are responsible for further polymerization. Degradative analyses of the polymers and preparation of their derivatives suggest that polymerization occurs at the para-position. The IR data also confirms this.

4. Conclusions

The above study reveals that short chain polymers obtained are highly soluble in DMSO and DMF and less soluble in CH_3OH and CHCl_3 . We are of the opinion that ion-pair formation may be one of the factors responsible for the solubility of short chain polymers in these solvents. The data also reveals that the possible polymerization involves the 1,4-positions, as these positions are energetically highly suitable for obtaining stable polymers.

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