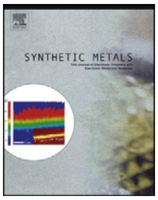
Synthetic Metals 161 (2011) 1813–1819

Contents lists available at ScienceDirect

Synthetic Metals

journal homepage: www.elsevier.com/locate/synmet



Interaction of polyaniline with hydroxyl-ions in N-methylpyrrolidinone

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ARTICLE INFO

Article history:
Received 30 January 2011
Received in revised form 26 May 2011
Accepted 5 June 2011
Available online 28 July 2011

Keywords:
Polyaniline
Tetraalkylammonium hydroxide
Potassium hydroxide
Conductivity
Doping
Degradation

ABSTRACT

Interaction of emeraldine base (EB) of polyaniline (PANI) with tetraalkylammonium hydroxides (TAAHs) has been studied in N-methylpyrrolidinone solutions and complex films. The spectral changes in the solutions at the early stage of the interaction showed features typical of the increased intramolecular conductivity in PANI backbone, which has been assigned to a “pseudo” doping effect upon interaction of EB with TAAHs. Conductivity of films was found to also increase, however, intrinsic electronic conductivity of the films was completely masked by the ionic one. The above effect has been compared with that of the conventional inorganic base KOH in the same medium. It has been found that similar changes in electronic absorption spectra of EB take place within some range of concentrations of KOH in the mixture. The conclusion on strong interaction of EB and the above bases was supported by IR spectra of the complex films, which evidenced in favor of the chemical transformation of the polymer backbone. The final product was found to be unstable and degrades readily. Based on the above results the interaction of PANI and the bases used is discussed. A scheme of the possible PANI transformations is suggested.

1. Introduction

Interactions of emeraldine base (EB) of polyaniline (PANI) with substances which affect physical and chemical properties of the polymer can be obviously reduced to five main cases. The first one is protonic doping of EB through its interaction with protonic acids, leading to conversion of the insulating EB to conducting emeraldine salt and being accompanied with corresponding changes in optical, electrical and paramagnetic properties of the polymer [1]. The second one, called sometimes pseudodoping, concerns interaction of EB with Lewis acids [2] and also results in spectral and conductivity changes of EB, although these changes are much smaller than those observed in the first case. In the third case, PANI interacts with electron acceptors, e.g., such as TCNQ [3], and forms a charge-transfer complex, where the amine nitrogen atoms are affected, although such an interaction is less effective and does not lead to a highly conductive form of PANI. The fourth kind of interactions concerns electrochemical/chemical oxidation or overoxidation of PANI followed by its interaction with nucleophilic agents, e.g., water molecules, which are present in the reaction medium [4]. This kind of interaction is practically irreversible and frequently results in PANI instability and degradation. Mechanistic and kinetic aspects of the electrochemical degradation of PANI are now well investigated [5–8]. Specifically, new products such as p-benzoquinone, p-diphenylamine, quinoneimines are suggested to appear in aqueous media as a consequence of this process, namely, due to hydrolysis of PANI with participation of both protonated charged fully oxidized form, i.e., pernigraniline salt [5] and neutral pernigraniline base form [9,10]. However, the latter route seems to be less plausible because pernigraniline in these systems is formed initially in the charged salt state [11] and its charged backbone is obviously more electrophilic and consequently easier hydrolyses than the neutral basic form. Moreover, it was shown recently that molecular structure of PANI in its EB state does not undergo notable chemical changes not only in the acidic aqueous media [5], but even in much more nucleophilic ones, namely, in strong alkali aqueous solutions (9 M KOH) at 90 °C for 60 days [12].

The fifth case in the above classification includes reactions involving nucleophiles or bases, which are strongly accelerated in polar aprotic solvents as compared with the protic ones [13]. Therefore, the change of protic aqueous media, where PANI is most frequently synthesized and exploited, for a nucleophilic medium can lead to dramatic changes of the polymer itself. These interactions are particularly important when such a medium is used to improve PANI processibility, e.g., when preparing PANI solutions in N-methylpyrrolidinone (NMP) in the presence of some amines or when using amines as solvents for production of spinnable solutions [14] or when producing corrosion resistant epoxy coatings [15]. Thus, it was shown that secondary amines with strong basicity and small molecular size, e.g., azetidine or pyrrolidine, attack both

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doi:10.1016/j.synthmet.2011.06.006

the quinoid rings and the N═C sites in the EB backbone immediately [16,17]. Consequently, in the attacked EB molecule the conjugated structure becomes damaged due to the ring substitution and, moreover, the chains break down through pathways including formation of an intermediate adduct of the strong amine molecules with carbons of the N═C sites along the EB chains followed by their hydrolysis involving moisture always presenting in any solvent [17]. On the other hand, it is well-known that amines with strong basicity interact with water and form organic alkali dissociated to corresponding cations and hydroxyl anions. From our point of view such ability of amines suggests that in the aprotic solvent of NMP the appearance of hydroxyl anions which are additional strong nucleophiles could lead to changes in the EB chains also. This suggestion is consistent with a strong nucleophilic activity of hydroxyl anions and products of their interaction with aprotic solvents, i.e., dimethylformamide and acetonitrile, in respect to other polymers, such as polyvinylchloride, poly(vinylidene fluoride) and polycarbonate, which results in the deep transformation/degradation of these polymers [18]. However, a real influence of hydroxyl anions on PANI properties in aprotic solvents is still unclear.

In our work, we have tried to fill this gap and estimated the changes in emeraldine base of PANI resulted from its interaction with tetraalkylammonium (TAA) and potassium hydroxides in NMP in the presence of small quantities of water.

2. Experimental

2.1. Sample preparations

Polyaniline was synthesized via the oxidative polymerization of aniline with ammonium persulfate in 1 M HC1 similarly to the well known method [19] when keeping molar ratio aniline to the oxidant 1:1.25. The obtained emeraldine salt was converted to EB by treatment with excess of 3 wt.% ammonia water solution for 10 h, followed by filtration and washing at the filter by distilled water until the washing water became neutral and did not contain livings of aniline oligomers and other byproducts under UV–Vis control. The base powder was dried in dynamic vacuum at 70 °C up to the constant weight.

Two organic bases, namely tetrabutylammonium hydroxide (TBAH, $(C_4H_9)_4NOH$) (30 wt.% aqueous solution) and tetraethylammonium hydroxide (TEAH, $(C_2H_5)_4NOH$) (10 wt.% aqueous solution), as well as inorganic base potassium hydroxide KOH were dissolved in N-methylpyrrolidinone (NMP) or distilled water, respectively, to prepare 0.1 M solutions. Tetraalkylammonium salts (TAAS: $(C_4H_9)_4NBr$, $(CH_3)_4NBr$, $(CH_3)_4NClO_4$) were dissolved in NMP to prepare 0.1 M solutions. EB powder was dissolved in NMP (10 mg/ml) under ultrasonication, followed by filtering of the solution. The obtained mother liquor was used as a stock EB solution for further dilution to the necessary PANI concentrations. Final concentrations of the EB solutions (calculated per a tetramer unit of the polymer) were determined by monitoring intensity of the electronic absorption band at ~640 nm in the polymer solution by UV–Vis spectroscopy, using the known approach [20] as well as from our calibration procedures data on the molar absorption for the tetramer unit to be 22,000 L/(mol cm). Liquid mixtures of KOH or TAAH or TAAS and EB were prepared by the addition of the fixed amounts of the alkali or salt solutions to the EB/NMP one. For UV–Vis measurements of films, the liquid mixtures were drop-cast onto a glass plate. For IR measurements, complex films were cast onto a Ge plate and dried in vacuum or, otherwise, EB–TAAH complex films have been dried at ~110° C, scrapped off the substrate and mixed with the KBr powder to prepare pellets from the mixture. For conductivity measurements the complex films were drop-cast onto the glass plate and dried under ambient conditions or annealed at ~150° C. It should be noted that drying under ambient conditions resulted in the gel-like form of the film. Thickness of the obtained films was normally in the range of 5–10 μm.

2.2. Measurements

Electronic absorption spectra were measured using a dual-beam spectrophotometer SPECORD-M40 and an AvaSpec-2048 spectrometer, with pure NMP as a reference sample. The measurements of the sample solutions were conducted using the same cuvette. IR absorption spectra of the samples have been measured using a SPECORD-M80 spectrophotometer.

The electrical in-plane conductivity of the films was measured using a standard four-probe technique. During the measurement, an appropriate constant current, J, in the range of 0.1–10 μA was maintained on two outer probes, and the voltage drop, V, was measured across two inner probes, using a UNI-T M890C$^+$ electrometer. The resulting conductivity, σ, was found according to the formula $\sigma = \ln 2(J/\pi dV)$, where d is the film thickness.

3. Results

3.1. Effect of organic bases on EB solutions

Addition of small and medium amounts of the solutions of the organic alkalis TAAHs (either $(C_4H_9)_4NOH$ or $(C_2H_5)_4NOH$) with molar ratios of [TAAH]:[EB] up to about 10:1 practically did not affect the electronic absorption spectrum of the EB/NMP solution (Fig. 1a). A further significant increase of this ratio up to 627:1 (Fig. 1b), with the EB concentration being constant, resulted in gradual changes in the spectra. The first significant effect was the suppression of the benzenoid-to-quinoid electronic transition at 630 nm and an appearance of the near-IR absorption tail above 700 nm. These changes are accompanied with the presence of isosbestic points which evidence on transformation between two forms of PANI. It is very surprising, but the above changes are similar to changes which are typical of changes upon protonation of the EB [21]. A small amount of water (up to ~5 wt.%) present in the solution (due to the hydrated form of TAAH) can also contribute to the hypochromic shift of the absorption bands [22], however, this effect is negligible in our case.

When $[(C_4H_9)_4NOH]$:[EB] molar ratio increases up to 68:1 (Fig. 1a), two isosbestic points at ~380 and 430 nm are clearly seen, and there is also the third one at ~735 nm which is less contrast. These points indicate obviously that there are two forms of PANI present in the solution which gradually transform to each other with changing concentration of the TAAH. At the same time, a polaronic absorption band at ~440 nm originating from the intrachain charge transfer between $NH^{+\bullet}$ radical-cations and benzenoid rings [23] and which is normally appears upon doping of EB by protonic acids [21,22], is not clearly seen in the spectra. Moreover, at higher [TAAH]:[EB] molar ratios one can see dithering of the isosbestic points that suggests some more deep changes of the EB (Fig. 1b, shown on the example of $(C_2H_5)_4NOH$). This suggestion is consistent with the fact that the relative intensity ratio of the long wave (Q) band height to the short wave (B) one, which is known as the quinoid to benzenoid (Q/B) ratio, decreases from 0.74 to 0.65 that testifies in turn to the decrease of amount of the quinoid units in the EB affected by the alkali comparatively with the initial EB [16]. The decrease of the Q/B ratio is synchronous to the growth of the near IR absorption tail (Fig. 1) that testifies that these chemical changes in EB can cause an appearance of free charge carriers in the system.

In order to clarify the role of hydroxyl-anions in the above effects, TAAHs have been replaced with TAAS. The addition of TAASs to the EB solution in analogous concentrations did not result