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Oxidation State and Proton Doping Level in Copolymers of 2-Aminobenzoic Acid and 2-Methoxyaniline

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Summary: UV-vis spectra of homopolymers and copolymers of 2-aminobenzoic acid (OAB) and 2-methoxyaniline (OMA) were analyzed in order to obtain information about the oxidation state and proton doping level of these polymers. Dimethyl sulfoxide (DMSO) was used as a solvent in which protonated forms of polyanilines are preserved and a mixture of *N*-methyl-2-pyrrolidone and triethylamine (0.5 %) as a solvent (NMP/TEA) in which polyanilines are assumed to be non-protonated. Polymers were prepared in the emeraldine salt form, externally doped with HCl. It was found that only external doping is eliminated in NMP/TEA while internal doping by carboxylate groups bound in OAB units remains operative. Since doped quinoid units do not contribute to the quinoid band (Q-band at 630 nm), the intensity ratio of the Q-band and benzenoid band (B-band at 320 nm) cannot be simply correlated with the oxidation state of poly(OMA-*co*-OAB) copolymers in contrast to poly(OMA) and polyaniline. Spectra of copolymers with less than 60 % of OMA units as well as those of poly(OAB) in DMSO and NMP/TEA are almost identical due to internal doping, which is proposed to lead to structures in which main-chain protons are coulombically bound with immobile carboxylate anions. In the spectra of copolymers with less than 60 % of OMA units, a well-resolved band occurs at 500 nm, which can be ascribed to alternating or close-to-alternating sequences of OMA and OAB units.

Keywords: conducting polymers; UV-vis spectroscopy

Introduction

Functional properties of synthetic metals, including polyanilines (PANI), are closely related to their doped states, in which the number of electrons associated with the macromolecule backbone is either decreased (p-doping) or increased (n-doping) as compared with their number associated with the backbone of the parent nonmetallic polymer molecule [1]. This doping is achieved by chemical or electrochemical redox processes involving parent

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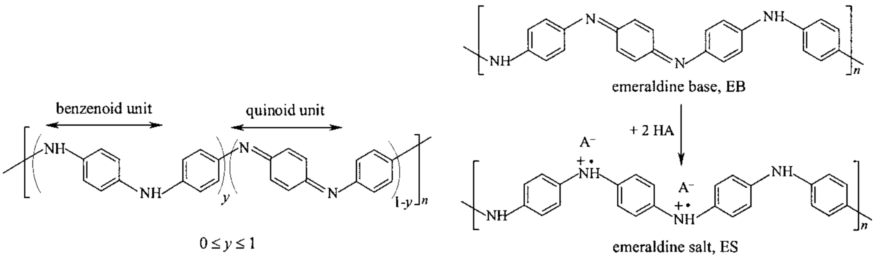
polymers. Unlike other conducting polymers, PANIs also exhibit proton doping consisting in proton exchanges between PANI main chains and proton acid molecules (or acid groups), HA, in which the number of π-electrons associated with a PANI molecule is conserved. As a result, functional properties of PANIs depend on the extent of both oxidation and protonation of their macromolecules.

Oxidation states of PANI are described [2] by the general formula shown in Scheme 1a, where y is the mole fraction of benzenoid units in PANI chains. If $y = 1$, PANI is fully reduced (leucoemeraldine form, here leucoemeraldine base, LB); if $y = 0.5$, it is half-oxidized (emeraldine form, here emeraldine base, EB), and if $y = 0$, PANI is fully oxidized (pernigraniline form, here pernigraniline base, PB). In other words, the quantity $(1 - y)$ is the degree of oxidation of a PANI chain.



(a) General formula of PANI base forms (b) Proton doping of PANI emeraldine base

Scheme 1.

The oxidized PANI base forms easily undergo proton-exchange reactions with HA (Scheme 1b), in which they are transformed to corresponding emeraldine (ES) and pernigraniline salts (PS). These salts are synthetic metals because their main chains comprise mobile electrons, the formation of which is closely related to the presence of quinoid units in PANI chains (Scheme 1b). The ES form is the most important form of PANIs since it shows not only high electrical conductivity but also high stability in air as well as under working conditions [2], which is not the case of PS.

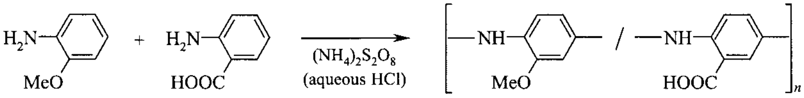
For obtaining high-quality PANI samples, it is essential to achieve a precise control of the polymer oxidation state and level of proton doping. PANIs are generally prepared by diverse synthetic procedures using various reaction conditions and modes of crude PANI post-treatment, which makes the prediction of y value on the basis of synthetic path practically impossible. Typically, the oxidation state of as-prepared PANI ranges from emeraldine to pernigraniline form [3] and the true value of y must be determined by an independent method. The UV-vis spectroscopy of PANI solutions in *N*-methyl-2-pyrrolidone (NMP) was shown [4] to be a suitable and sufficiently accurate method for the determination of y values of PANI samples.

Since PANI is only sparingly soluble, more soluble polymers of substituted anilines have become a subject of scientific interest. Among substituted PANIs, those with acid pendent groups such as SO_3H [5-10] and COOH [11] are of special interest, because these groups also act as internal proton dopants. Although the conductivity of ES forms of these self-doped PANIs is lower than that of unsubstituted PANI, it is pH-independent at $pH \leq 4$, which is advantageous from the application point of view. However, the substitution of PANI brings about some drawbacks. First, attached acid groups affect not only the proton-doping level but also the degree of oxidation of PANI chains as it was shown, e.g., for copolymers of aniline-3-sulfonic acid with aniline [9] or 2-methoxyaniline (OMA) [10]. Second, preparation of self-doped PANIs by homopolymerization of corresponding aniline acids (ANIA) meets with difficulties since this reaction usually does not take place under mild conditions. Therefore, self-doped PANIs are typically prepared by copolymerization of ANIA with aniline (ANI) or a reactive substituted aniline bearing alkyl or alkoxy groups [5-10]. Apart from chemical, also electrochemical copolymerization was utilized in preparation of self-doped PANIs, e. g., electrolytic copolymerization of *N*-(3-sulfopropyl)aniline with *N*-methylaniline [12] and aniline-2-sulfonic acid with 3-methylaniline and 3-ethylaniline [13].

We have recently reported [14-16] on a chemical copolymerization of OMA with anilinesulfonic acids and aminobenzoic acids. We determined the monomer reactivity ratios by '*in situ*' ^1H NMR measurements and characterized the composition of copolymers and oxidation level of emeraldine and leucoemeraldine forms of poly(OMA-*co*-aniline-3-sulfonic acid) also by NMR spectroscopy [10]. In the present paper, we report on the oxidation state and proton doping of as-prepared poly(OMA-*co*-OAB) (OAB stands for 2-aminobenzoic acid) as a function of the copolymer composition. OMA is used as the main comonomer because methoxy groups on benzene rings considerably increase copolymer solubility compared to that of analogous copolymers with unsubstituted aniline. OAB is advantageous because it undergoes homopolymerization under mild conditions unlike other aniline acids.

Experimental

Chemicals. 2-Methoxyaniline (OMA, Aldrich), 2-aminobenzoic acid (OAB, Fluka), ammonium peroxodisulfate ($(NH_4)_2S_2O_8$, Fluka), hydrochloric acid (HCl, Merck), *N*-methyl-2-pyrrolidone (NMP, Aldrich), triethylamine (TEA, Aldrich), methanol (MeOH, Aldrich), dimethyl sulfoxide (DMSO, Aldrich) and DMSO-d_6 (Aldrich) all of AR grade were used as supplied.



Scheme 2.

Synthesis of copolymers (Scheme 2*)*. A solution of $(NH_4)_2S_2O_8$ (0.1 mol) in aqueous HCl (1M, 100 mL) was added to a constantly stirred aqueous HCl solution (1M, 700 ml) of a mixture of OMA and OAB (sum of both monomers0.1 mol) and the mixture was allowed to react for a given time up to 20 h. After ca 10 – 15 min, the color of the reaction mixture changed from light yellow-red to dark purple and, finally, a continuous precipitation of a dark green polymer occurred. After a chosen reaction time, the polymer precipitate was filtered off, extensively washed with aqueous HCl (1M, 1 L) until a colorless filtrate was obtained, in order to remove soluble oligomers and residual monomers, then with methanol (250 mL) and, finally, the purified polymer was dried in vacuum at 40 °C for 48 h. The feed mole fraction of OMA in the monomer mixture, f_1, varied from 0 to 1 and other reaction conditions were set as follows: oxidant-to-monomer mole ratio Ox/mon = 1, $[HCl]_0$ = 1M, T = 20 °C and t = 20 h.

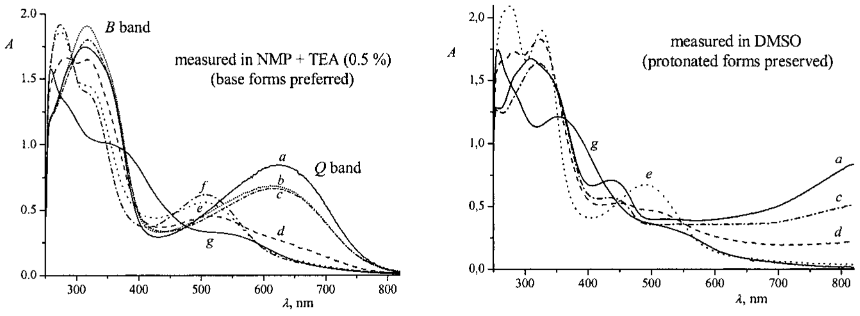
Analyses, measurements. Nitrogen content was determined on a CE440 LeemanLabs (CHN) analyzer. Mole fraction of OMA units in a copolymer, F_1, was determined from integral intensities of ^{1}H NMR signals of aromatic (around 7 ppm) and methoxy protons (around 3.7 ppm), respectively. NMR spectra were recorded on a Varian VXR 300 MHz spectrometer using a 4.5 degree pulse, a relaxation delay of 3 s, an acquisition time of 4 s and 500 repetitions (1 h). For NMR measurements, copolymers were dissolved in a mixture of NMP, TEA and DMSO-d_6 (70:10:20); solutions of concentration 10 % w/v were used. TEA was added to increase the solubility of copolymers by transforming them from the ES into the EB form. The ^{1}H NMR spectra were referenced to tetramethylsilane internal standard and the ^{13}C spectra to the DMSO-d_6 signal at 39.5 ppm. UV-vis absorption spectra of PANI solutions

(0.02 %) were recorded on a Hewlett Packard 8452 diode-array instrument using quartz cuvettes of optical path of 0.2 cm. A mixture of NMP and TEA (0.5 %) was used as the solvent in which PANIs are in the unprotonated state, whereas DMSO was used as a solvent in which protonated forms of PANIs are preserved [17]. The spectra were measured using as-prepared samples, which were not subjected to any modification so that their oxidation state corresponds to that one resulting from synthetic procedure.

Results and Discussion

Optical spectra of dissolved PANI EB forms consist of two bands of different origin [4,18, 19]. The first band with maximum at about 320 nm, which is the only band of LB form, is due to intrachain $\pi \rightarrow \pi^*$ transition within benzenoid units and, therefore, it is called B-band. The second band with maximum at about 630 nm is due to electron transitions from the benzenoid HOMO to quinoid LUMO states (Q-band of exciton origin). It is contributed to by intrachain as well as interchain processes and its absorption coefficient is in general concentration-dependent, but concentration-independent in dilute solutions ($c < 0.1$ %). The Q/B band intensity ratio is closely correlated with the degree of oxidation of PANI chains as it was shown for unsubstituted as well as for partly and fully ring-substituted PANIs [4,9,19,20]. If EB is oxidized to the PB form, the Q band is replaced by another band with maximum at about 550 nm, which is attributed to a Peierl's gap typical of fully conjugated systems [4]. The Q band is not present in UV-vis spectra of PANI ES forms, in which new bands occur in the regions from 400 to 450 nm and from ca 700 nm to the NIR region. These bands are ascribed to the polaron transitions associated with charged conjugated chains [5,21].

UV-vis spectra of as-prepared (i.e., protonated by HCl) samples of poly(OMA-*co*-OAB) obtained using various feed ratios f_1, poly(OMA), and poly(OAB) dissolved in NMP/TEA mixture and in DMSO are shown in Fig. 1. The spectrum of poly(OMA) in NMP/TEA (Fig. 1a, curve *a*) is practically identical with that of the poly(OMA) EB form dissolved in neat NMP [4,18], which proves that the as-prepared poly(OMA) undergoes effective deprotonation in NMP/TEA. The B/Q band intensity ratio of 2 indicates that the poly(OMA) sample is slightly under-oxidized ($1 - y = 0.47$) as compared to the ideal EB state (see, e.g., Fig. 5 in Ref. [4]), which corresponds to a slightly lower than stoichiometric amount of oxidant used in the sample preparation (we used Ox/mon = 1 and reached an OMA conversion of 84 % while the ideal Ox/mon ratio is 1.25 for total monomer conversion [3]). The spectrum of protonated poly(OMA) (Fig. 1b, curve *a*) contains two polaron transition bands at 450 nm and 820 nm, but an unresolved Q band, as expected.



a

b

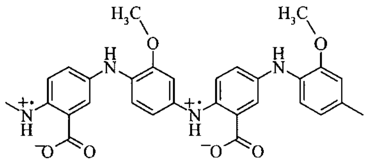
Figure 1. UV/vis spectra of poly(OMA-*co*-OAB) and corresponding homopolymers dissolved in NMP/TEA, in which base forms are preferred, and in DMSO, in which protonated forms are preserved, as a function of the mole fraction of OMA, f_1, in the starting mixture of monomers as well as mole fraction of OMA units, F_1, in the formed copolymer. Polymerization conditions: $[OMA]_0 + [OAB]_0 = 0.1$ M, $T = 20$ °C, reaction time $t = 20$ h, $[HCl]_0 = 1$M, Ox/mon = 1, f_1 (F_1): *a* 1 (1), *b* 0.80 (0.86), *c* 0.66 (0.76), *d* 0.5 (0.65), *e* 0.33 (0.54), *f* 0.20 (0.45), *g* 0 (0).

The second homopolymer, poly(OAB), exhibits substantially different spectroscopic behavior. First, a distinct Q band is not observed in the spectrum of as-prepared (externally doped with HCl) poly(OAB) in basic NMP/TEA solution (Fig. 1a, curve g). The spectrum can be described as a broad band decreasing in intensity continuously from the region of $\pi - \pi^*$ transitions below 300 nm to ca 800 nm, on which two shoulders corresponding to maxima at ca 400 and 550 nm occur. Second, the spectrum of DMSO solution of poly(OAB) is very similar to that obtained with NMP/TEA, showing only slightly stronger absorption at 400 nm. This indicates that (i) the band at 400 nm is partly associated with external doping, which disappears in NMP/TEA, and (ii) the internal doping with COOH groups is reduced almost negligibly. Accordingly, bands occurring at 400 and 550 nm should be ascribed to transitions in the doped poly(OAB). In general [22-24], these transitions are associated with polarons and/or bipolarons (PANI chain distortions associated with a quinoid unit in which one (in polaron) or both (in bipolaron) nitrogens are protonated, see Scheme 1b). Theoretical calculations for externally doped PANIs suggest the co-existence of polarons and bipolarons in short chains and predominance of polarons in long chains [24]. However, in a self-doped polymer such as poly(OAB), a high population of bipolarons can be expected due to attractive Coulombic interactions between main-chain cations and immobile COO^- counter-anions linked directly to main-chain benzene rings, which makes the dissociation of a bipolaron to two independent polarons difficult. Nevertheless, the question whether the bands observed in poly(OAB) spectra are associated with polarons or bipolarons or both cannot be solved on the basis of the results available and it needs further experimental and theoretical investigation.

Spectra of OMA-rich ($F_1 \geq 0.75$) poly(OMA-*co*-OAB) copolymers (Fig. 1a, curves *b* and *c*, and Fig. 1b, curve *c*) resemble those of poly(OMA), from which they differ mainly by lowered intensity of both Q (in NMP/TEA) and polaron (in DMSO) bands. The B/Q band intensity ratio evaluated according to Fig. 6 in Ref. [4] provides a value of $(1 - y) \cong 0.4$ for both above-mentioned OMA-rich copolymers containing about 80 % of OMA units, which indicates a close correlation between $(1 - y)$ and F_1 values in OMA-rich copolymers. This is in agreement with block arrangement of OMA units in these copolymers, which is supported by a large difference in reactivity ratios found for the OMA/OAB copolymerization system (21.8 for OMA and 0.064 for OAB [14]). Thus, it can be concluded that an experimental value of the B/Q band intensity ratio provides information on the oxidation state of OMA unit blocks in a given OMA-rich poly(OMA-*co*-OAB) copolymer only, but not information concerning the entire copolymer molecules. The Q band of OAB units is not observed in UV spectra of NMP/TEA solutions of these copolymers because, as it was shown above, the internal doping does not vanish in this solvent and protonated segments do not exhibit the Q band absorption.

A dramatic change occurs in UV-vis spectra when the OMA unit fraction F_1 decreases to 0.65 or to a lower value (Figs 1a and 1b, curves *d*, *e* and *f*). The Q band (Fig. 1a) as well as polaron bands (Fig. 1b), typical of poly(OMA), are strongly reduced ($F_1 = 0.65$, curve *d*) or practically disappear ($F_1 < 0.55$, curves *e*, *f*) and new distinct bands with maxima at 500 nm and 275 nm appear in the spectra. It is notable that UV spectra measured in both the solvents used become almost identical, similarly to the case of poly(OAB). On the other hand, distinct bands at 500 nm and 275 nm are not present in the poly(OAB) spectra (Fig 1, curve *g*), which clearly indicates that these bands are not associated with long sequences of OAB units.

We also considered the possibility of the EB form oxidation to the PB form. However, UV band of PB occurs at 530 nm for PANI [25] and at 560 nm for poly(OMA) [4] and the oxidation of EB to PB is accompanied by only a small decrease in the Q band intensity, whereas we observe band at 500 nm and disappearance of the Q band. Neither NMR nor IR spectra of copolymers provide an evidence for the copolymer oxidation to the pernigraniline state. The observed differences can be explained by changes in the proton doping extent of copolymers of diverse composition. These observations suggest that bands at 500 nm and 275 nm are closely associated with self-doped copolymers, in which alternating or close-to-alternating hetero-unit sequences of OMA and OAB units are present in high concentrations.



Scheme 3. Self-doped alternating sequences.

The decreased mobility of cations due to Coulomb interactions with immobile COO$^-$ anions is expected to take place in these self-doped sequences (Scheme 3), which provides an explanation for a rather low intensity of the corresponding absorption bands.

Acknowledgements

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