Aggregation and Conformational Changes of Undoped and Protonated Doped Polyanine in Binary Solutions

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Abstract. Aggregation and conformational changes of undoped and protonated doped forms of polyaniline in the emeraldine oxidation state were studied in binary solutions of dimethylformamide/water by optical absorption spectroscopy. It was found that undoped macromolecules tend to aggregate in binary solution, while protonated species undergo conformational changes. The effect of memory in aggregated macromolecules is considered.

Key words: polyaniline, aggregation, conformational change, electronic spectrum

1. Introduction

Polyaniline (PANI) is a promising material for the sensing and recognition of various agents from the environment. Exposure to water [1], organic solvents and acid vapours [2], aliphatic and aromatic hydrocarbons [3] or some electron-accepting agents [4] all cause changes in conductivity and electronic absorption spectra of the polymer films. Two factors, the interaction of macromolecules with each other and their conformational state, strongly affect these processes, and it is therefore important to study them.

The present work studies aggregation and conformational changes of PANI in binary solutions, where 'good' and 'poor' solvents are used as the components of the solution. The binary solution causes aggregation of small organic molecules (for example, polymethines [5], phthalocyanines [6], etc.), and can be used as a model system to study molecular interactions. However, in addition to inter-molecular aggregation the polymer macromolecules undergo intra-molecular conformational changes. Due to the significant molar absorbance of PANI and its sensitivity to various conditions both molecular interactions and conformational changes are studied here by optical absorption spectroscopy.

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2. Experimental

The emeraldine oxidation state (emeraldine base, EB) of PANI was synthesized at the Institute of Molecular Biology and Genetics (Kiev) by chemical polymerization of aniline as described elsewhere [7].

Dimethylformamide (DMF) and doubly distilled water were used as components of the binary mixture. PANI dissolves readily in DMF and does not dissolve in water, while both liquids mix well to give a homogeneous solution. Nitric acid was used as a protonating dopant. This acid dissolves well in both DMF and water and protonates the polymer without yielding an insoluble precipitate, in contrast to other inorganic acids, such as HCl and H_2SO_4. Both DMF and HNO_3 were reagent grade.

To prepare a stock solution, the EB powder (1 mg/mL) was placed in DMF for two days. The resulting dark blue solution was then filtered through a 1.00 μm Milipore filter unit. Nitric acid was dissolved in water to give a concentration of 4 $\times 10^{-2}$ M.

Binary solutions of EB for optical measurements were prepared by gradually adding fixed amounts of water to a cuvette containing the EB stock solution. While the ratio of the solvents was varied, the concentration of the EB was maintained constant.

Protonation of the EB solutions was performed in three ways:

(a) Gradually adding a small amount of 4×10^{-2} M aqueous solution of nitric acid to a cuvette containing 2 mL of 4.5×10^{-5} M solution of EB in DMF
(b) The same addition of nitric acid to a cuvette with 0.2 mL of 4.5×10^{-4} M solution of EB in DMF, followed by addition of 1.8 mL of water to give a 4.5 $\times 10^{-5}$ M solution of protonated EB in a binary DMF/water mixture.
(c) The same addition of nitric acid to a cuvette with 4.5×10^{-5} M concentration of EB in a binary mixture consisting of 0.2 mL DMF and 1.8 mL water.

A reference cuvette contained only solvents in the same ratio. Measurements of UV-VIS absorption spectra were carried out in the region of DMF transparency, using a SPECORD M-40 dual-beam spectrometer.

Optical absorption measurements were used to monitor conformational changes of the polymer as a function of: (i) increasing water content of the mixed solution containing water and DMF between 0% and 90% water for unprotonated EB; (ii) increasing the protonation level of EB by adding different amounts of aqueous nitric acid solution to the EB solution in DMF as described in point (a) above, and to binary solutions of EB in DMF/H_2O as described in points (b) and (c).

3. Results and Discussion

3.1. EFFECT OF WATER ADDITION ON AGGREGATION AND CONFORMATIONAL CHANGES OF THE EB

Figure 1a demonstrates spectral changes of the undoped EB at constant concentration (10^{-4} M), with increasing water content in the binary solution of DMF/H_2O. The higher the relative concentration of water in the solution, the more the intensity decreased, with broadening of the absorption peaks centered at 323 and 620 nm, respectively. Only two extreme points of our experiments are shown in Figure 1a, corresponding to 100% DMF and to 10% DMF in the DMF : H_2O mixture.

The maximum intensity was found to decrease by approximately the same factor for both peaks. No shifts of the absorption maxima were found. Thus, addition of water causes a hypochromic effect in the undoped EB.

Spectral changes of the protonated doped EB are shown in Figure 1b. Upon addition of water to the solution of the protonated EB, a shift of the maximum absorption in the near-IR to shorter wavelengths is observed.

It can be concluded from Figure 1 that addition of water causes a variety of effects on undoped and protonated doped EB. Two macromolecular processes are possible upon addition of water to the EB solution: inter-molecular aggregation and intra-molecular conformational changes. Both processes are driven by a tendency of the hydrophobic species to reduce their hydrodynamic volume. The hypochromic effect revealed in the undoped EB is quite similar to that observed in polynucleotides [8] and can be explained by a dispersion force interaction between chromophores of the polymer backbone [9]. Such an interaction may occur via hydrogen bonding between amine and imine nitrogen sites in the EB as a result of aggregation of macromolecules in the solution. Therefore, aggregation is responsible for the spectral changes in the undoped EB.

It should be noted, however, that we cannot distinguish here inter-molecular aggregation and interaction of different parts of the same macromolecule which has a coil-like structure in a solution.

Changes in the near-IR absorption of the protonated EB occur simultaneously with conformational changes of the macromolecules. As shown previously [11], an absorption tail extending from ∼500 nm to the IR region corresponds to the expanded-coil conformation, while a single peak at ∼800 nm corresponds to the compact-coil conformation of the polymer. Therefore, according to the spectra in Figure 1b, addition of water to the protonated EB solution causes conformational changes of the backbone from a more expanded-coil to a more compact-coil. It is easy to understand that aggregation of the protonated species could not occur because no imine sites are present in the completely protonated backbone, so that conformational changes occur to reduce the hydrodynamic volume of the protonated EB. Thus, the addition of water causes aggregation of undoped EB macromolecules and conformational changes of the doped protonated EB.
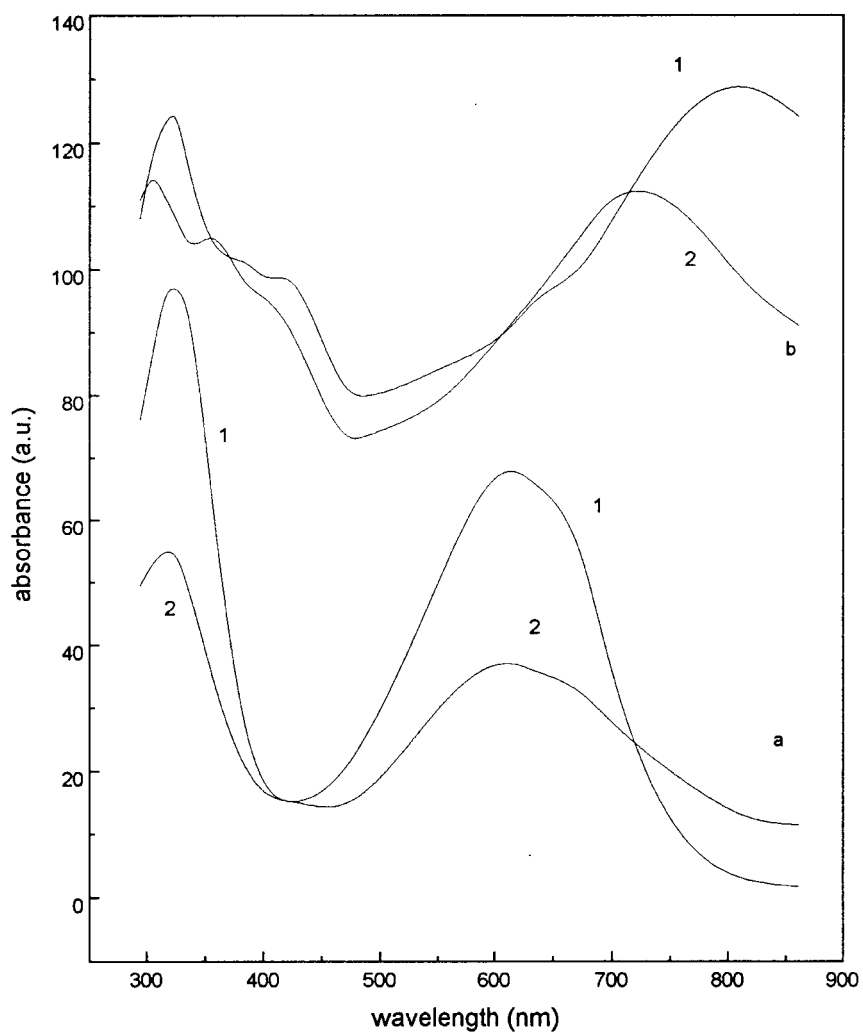
Figure 1. Effect of water addition on absorption spectra of (a) undoped and (b) protonated doped EB. (1) no water; (2) 90% water in solution.

3.2. EFFECT OF WATER ON THE PROTONATION OF THE EB

Spectral changes of the EB upon protonation are shown in Figure 2. Addition of acid to the EB solution in DMF (Figure 2a) leads to a gradual increase of the protonation level of the polymer from the undoped (curve 1) to the completely protonated form (curve 6). Isosbestic points at 350 nm and 450 nm indicate that transformation of the EB to the EB salt occurs without any intermediate forms of the polymer.
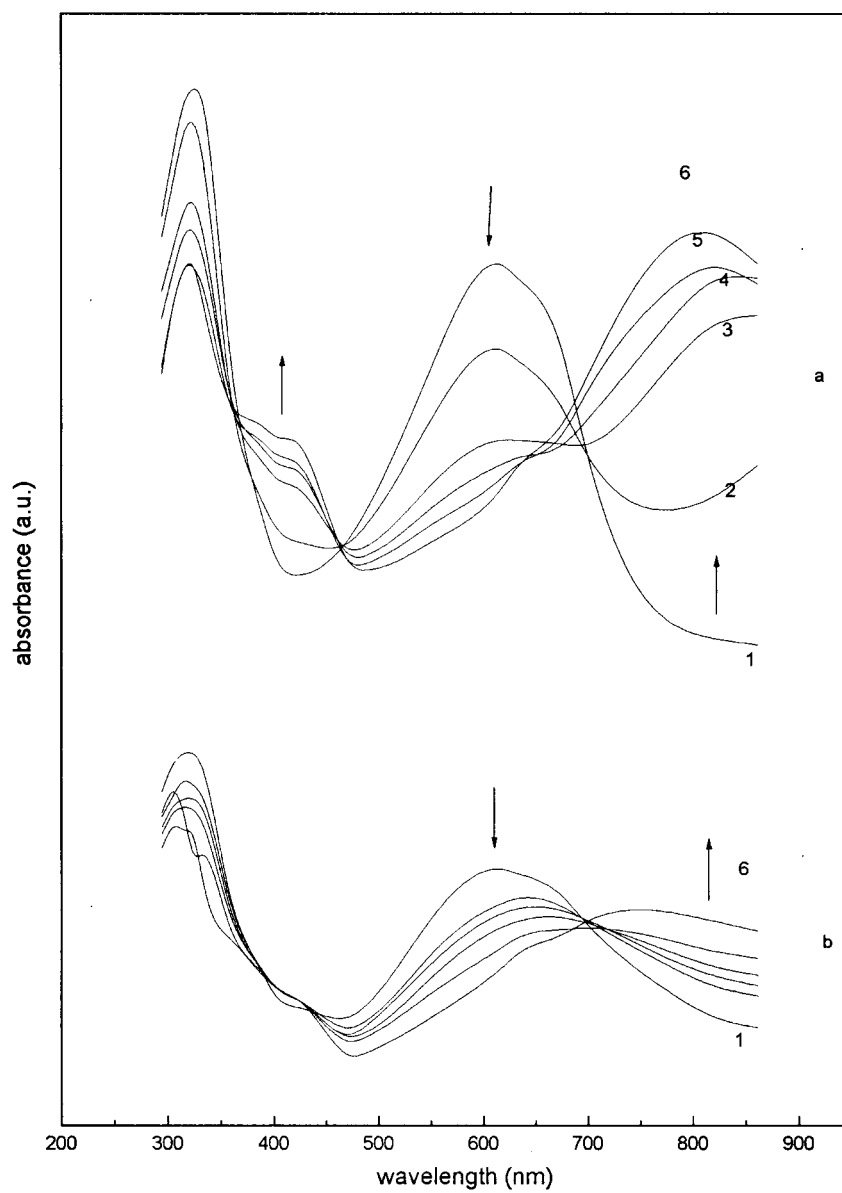
Figure 2. Changes in absorption spectra upon protonation of the EB in DMF (a) and in a binary solution of DMF/water (b). Protonation level increases successively from curve 1 to curve 6. Concentrations of the protonated EB is constant: Arrows indicate spectral changes due to the increased protonation level.
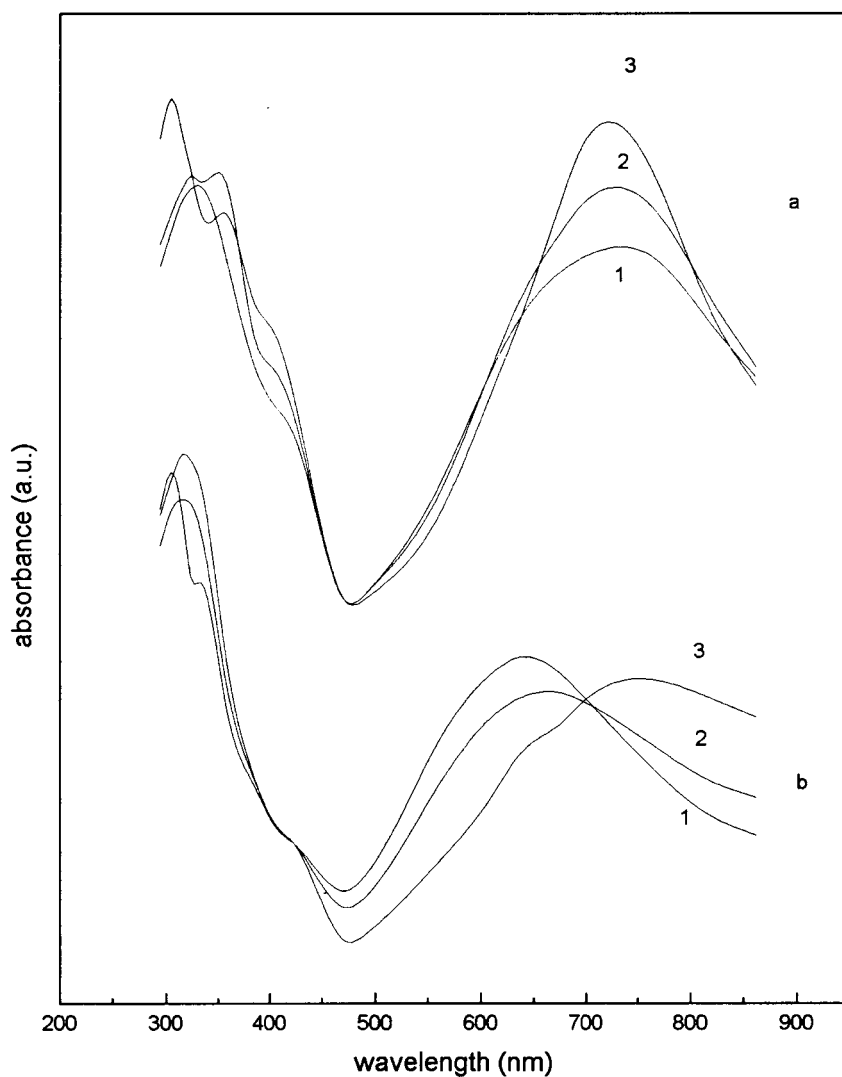
Figure 3. Effect of the preparation history of solutions with the same components on the resulting absorption spectra of the EB: (a) Protonation followed by water addition; (b) Addition of water followed by protonation. Curves with same numbers correspond to equal protonation levels of the solutions.

The addition of acid to the EB solution in a binary DMF/H_2O mixture causes similar spectral changes (Figure 2b). However, the changes in spectra are suppressed and smoothed as compared to the EB protonation in pure DMF.

Although the spectral changes of the EB in DMF and in DMF/H_2O solutions occur in a similar way the hypochromic effect in the latter case leads us to conclude that aggregation of macromolecules persists.

3.3. EFFECT OF THE PREPARATION HISTORY OF A SOLUTION

Preparing the protonated EB in the binary solution in two ways, as described in points (b) and (c) of the experimental section above, we found that spectral changes of the solutions with the same components content depend on the preparation mode of the solution. This effect is demonstrated in Figure 3.

As discussed, protonation of the EB in DMF, followed by addition of water causes conformational changes of the protonated molecules, while addition of water followed by protonation yields protonation of aggregates without further conformational changes. The latter is a rather unexpected effect, because all the imine sites should be removed upon full protonation of the backbone, so that hydrogen bonding between macromolecules could not occur.

Conservation of the aggregates upon removal of hydrogen bonds between macromolecules can be related to a memory effect in polymer liquids [12]. To explain this effect in greater detail it is necessary to take a solvate envelope into account. The solvent molecules are tightly coupled to the EB, so that they remain in polymer films which are cast from a solution [2]. It is reasonable to assume that the solvent plays a significant role in forming the aggregates in the solution. We suggest that solvent–solvent and solvent–polymer interactions form a net of intermolecular bonds around the aggregate, so that this net is responsible for conservation of the aggregate structure.

4. Conclusions

Based on optical absorption data, we have found a rather complex behavior of EB in binary solutions. If water is added first to the EB solution in DMF, the macromolecules tend to aggregate and subsequent addition of acid then protonates the aggregated species. If water is added after protonation, the protonated macromolecules prefer conformational changes. Aggregation and conformational changes, therefore, have no commuting properties under the given conditions.

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