



Time resolved excitation dynamics in emeraldine base



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ABSTRACT

Using femtosecond pump–probe transient absorption spectroscopy (wavelengths 330–800 nm), we observed and explained excited state, charge transfer and polaron state dynamics in emeraldine base form of polyaniline in dimethyl sulfoxide solution. The excited state created by a pump pulse (700 nm) in the quinoid absorption *Q*-band loses its initial symmetry by subsequent energy transition to a charge transfer state within 50 fs. The hot charge transfer state either recombines non-radiatively into the ground state with decay time constant 0.55 ps or transfers into a relaxed state corresponding to the relaxed phenyl geometry during ca 2.1 ps. This relaxed state shows a prolonged lifetime of about 6.5 ps before its recombination to the ground state. However, a small amount of long-lived polarons with lifetime of about 2 ns in air and with lifetime longer than 6 ns in the solution bubbled with dry N₂ was detected.

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1. Introduction

Polyaniline (PANI) is a π -conjugated polymer heavily investigated for various applications, like electromagnetic shielding, anti-static coating, electrodes, batteries and sensors [1]. Its relatively flexible backbone influences the dynamics of excited electronic states [2] and thus the optoelectronic functionality of PANI. It is known, that the undoped forms of polyaniline support extremely long-lived photoexcitations [3]. Their exceptionally long stability was explained by a model suggested by Ginder and Epstein [4], according to which the ring torsion angle of the polymer chain and its coupling to electronic energy states plays the key role in the excited state dynamics. In the case of emeraldine base (EB, Fig. 1) the authors assumed the formation of photo-generated charge-transfer exciton upon excitation, which has the negative charge centered on the quinoid group and the positive charge distributed on the phenyl ring on either side of the quinoid. Shortly after photoexcitation (within ca 50 fs), long-living metastable charge transfer states are created, which are stabilized by metastable ring conformations. Those conformations are characterized by the rotation angle of the phenyl ring plane out of the plane defined by the nitrogen atoms (see Fig. 1). In the ground state the quinoid ring is rotated by 8°, the adjacent benzenoid rings are both rotated by –43° and the remaining benzenoid ring is rotated by 16°, cf. Ref. [5].

In this article we report on a time-resolved optical absorption study of the time evolution of charge transfer states in the emeraldine base form of polyaniline after the photoexcitation into its *Q*-band.

The article is organized as follows: In Section 2 the preparation of the EB powder and its solution in dimethyl sulfoxide, as well as the characteristics of the pump–probe transient absorption spectrometer set-up used in our experiment are described. In Section 3 (*Experimental results*) time-resolved differential absorption spectra in the time scale from 50 fs up to 6 ns are presented for the spectral range 340–800 nm. Here, on the basis of a qualitative estimate of the experimental results the physical model describing the deexcitation pathway is suggested. In the following Section 4 (*Theoretical modeling*) the physical model of the time-resolved kinetics of excited, intermediate, charge transfer and polaron states is reformulated using a set of differential equations, which describe the dynamics of the population of respective states within the excited state manifold after photoexcitation. In Section 5 the model is applied to the set of experimental data and it is shown that the suggested kinetic model can simultaneously explain the observed time evolution of the optical absorption for all probe wavelengths with the same internal parameters of the model. Finally, conclusion is drawn in Section 6.

2. Materials and methods

Emeraldine base (EB) (cf. Fig. 1) was prepared according to the procedure outlined in Ref. [6], namely by the reaction of 1.30 g of aniline hydrochloride (Sigma-Aldrich) with 2.86 g of ammonium

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peroxodisulfate in 50 ml of distilled water at room temperature. After 2 h reaction the resulting green precipitate was separated by filtration and washed repeatedly with 0.2 M aqueous HCl and acetone. The obtained emeraldine hydrochloride was converted to the EB form of PANI by washing with distilled water, vacuum drying and dispersing in 25 ml of 5% aqueous ammonia for about 5 min. The obtained EB was separated by filtration and washed repeatedly with deionized water and finally with acetone. The obtained dark blue powder was dried under dynamic vacuum until constant weight.

For the photoinduced transient optical absorption measurements, the EB was dissolved in dimethyl sulfoxide (DMSO) (A.C.S. spectroscopic grade) at concentration 22 ppm. The diluted solution was vigorously bubbled for about 3 h with dry nitrogen just prior to the experiment in order to reduce the amount of O₂ and H₂O.

The transient optical absorption (TA) spectroscopy was measured using pump-probe technique. The detailed description of the experimental apparatus is given in [7]. The excitation pulse (pump pulse duration <50 fs, mean energy 3.8 μJ/pulse) was tuned to the wavelength 700 nm with the spectral width 50 nm (FWHM, cf. Fig. 2) falling within the long-wavelength tail of the optical absorption spectrum of the polymer. CaF₂ crystal was employed to generate broadband white-light continuum used as a probe pulse. A custom-made spectroscopic glass flow-cell was used with very thin glass windows (0.14 mm) and 0.14 mm active optical path, in order to reduce the cell-induced group velocity dispersion over the spectral range of the broadband probe pulse (chirp). Typical sample flow rate was 20 ml/h, yielding the average flow speed in the channel of about 10 mm/s. At this flow rate, every pump pulse (repetition rate 500 Hz) reached the fresh sample (not yet exposed to previous pulses), enabling an effective pseudo single-shot experiment. This allowed avoiding artifacts caused by the sample degradation and problems with extremely long living excited states. TA of the pure solvent in the same flow-cell was measured after each measurement at the same experimental conditions for obtaining reference data for the measurements of the PANI solutions.

3. Experimental results

The steady-state UV-vis optical absorption spectrum of the EB shows two maxima (cf. Fig. 2), which can be attributed to two chromophore units: The short wavelength maximum at 330 nm corresponds to the $\pi-\pi^*$ transition of the phenyl rings (B-band); the broad absorption band centered at 623 nm corresponds to an intramolecular charge transfer within the quinoid ring and surrounding benzenoid rings (Q-band) [8].

The differential time-resolved TA spectra reveal two regions with negative differential absorbance and two regions with positive differential absorbance (cf. Fig. 3). The decrease of the absorbance around the wavelength 650 nm and in the spectral region below 370 nm, corresponding to the Q and B band transitions, respectively, is obviously due to the ground state bleaching (GSB) caused by the depletion of the ground state concentration upon photoexcitation.

There are two spectral regions with positive differential absorbance observed in the TA spectra: The first one occurs within 100 fs after the pump pulse excitation in the long-wavelength region above 750 nm. It was attributed to the optical absorption of the

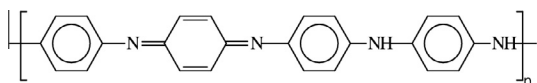


Fig. 1. Chemical structure of polyaniline in emeraldine base form.

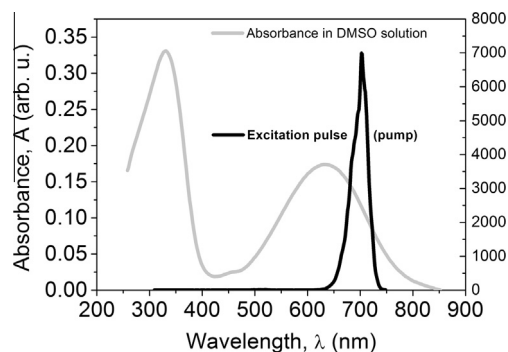


Fig. 2. Steady state UV-vis optical absorption spectrum of emeraldine base (gray curve). Spectrum of a laser excitation pulse (black curve).

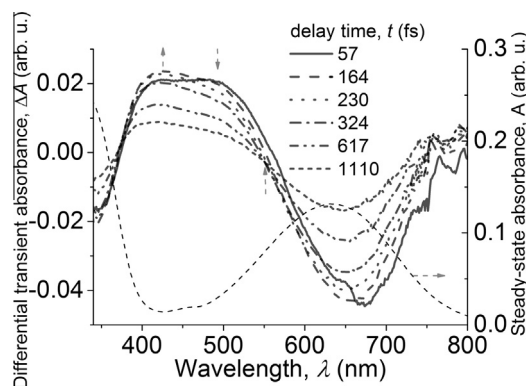


Fig. 3. Photoinduced time-resolved differential and steady-state optical absorbance spectra of emeraldine base in DMSO solution. Concentration 22 ppm. For the sake of clarity, the curves were smoothed to remove random noise and some parts of spectra around 700 nm (the excitation wavelength region) were corrected for light scattering.

photoexcited charge transfer and polaron states (cf. Ref. [8]). The second one located in the wavelength region between 370 and 550 nm was assigned to the excited state absorption band (ESA). The evolution of the latter ESA spectrum is interesting, since it consists of two absorption bands with different temporal behavior and reveals the process of excited state relaxation. At very short time the spectrum of ESA shows a dominant maximum at 490 nm. This maximum decreases continuously with the increasing time delay whereas the second maximum located at 420 nm increases at the same time, becoming dominant at about 150 fs after photoexcitation (indicated by gray dashed vertical arrows in Fig. 3). At longer times both absorption maxima decay simultaneously. This behavior of the transient absorption suggests a presence of an *intermediate* excited state, which is formed from Franck-Condon *hot* excited state initially created by the pump pulse. There is also a small shoulder of ESA absorption around 552 nm with a lifetime of about 150 fs, similar to the period of the increase of the differential absorbance at 420 nm (see Fig. 3).

The analysis of the time-resolved spectra showed no detectable negative contribution that could correspond to the stimulated emission. It was also independently supported by the fact that no detectable emission was found in our photoluminescence measurements when the sample was excited at the wavelength 700 nm.

The transient spectra recorded in the time interval 260–1100 fs show an isosbestic point at 552 nm, which suggests a formation of the *intermediate state* for times shorter than 260 fs. This *intermediate state* is responsible for the early positive peak in the transient absorption signal recorded at probe wavelength $\lambda = 552$ nm. We

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