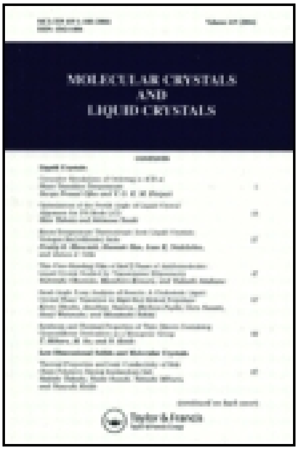

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Optical and Structural Properties of Electrodeposited Polybithiophene Films During the Film Growth as a Function of the Redox Potential

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OPTICAL AND STRUCTURAL PROPERTIES OF ELECTRODEPOSITED POLYBITHIOPHENE FILMS DURING THE FILM GROWTH AS A FUNCTION OF THE REDOX POTENTIAL

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Abstract The optical properties of p-doped polybithiophene films were investigated during the polymerization and discharging process using in situ spectroscopy, while the fluorescence and absorption spectra of the undoped films were ex situ monitored as functions of the film thickness and temperature. The in situ absorption spectra of polybithiophene were observed to depend significantly on the film thickness showing that both the mean effective conjugation length of the polymer chains and the morphology of the films changes during the polymerization. The absorption maximum at 692 nm is assigned to bicationic segments. The similarly structureless absorption spectrum of undoped polybithiophene exhibits a maximum at 480 nm which corresponds to a conjugation length of 7 thiophene units, whereas the red-shifted fluorescence spectrum shows a well-resolved vibrational structure and is attributed to the longest-conjugation length segments (ca. 11 thiophene units) in the film.

INTRODUCTION

Polythiophene, representing a prototype of π-conjugated polymers with a nondegenerate ground state, has been the object of numerous theoretical and experimental studies because of its high electric conductivity and good environmental stability with regard to oxidation.[1-4] It shows a variety of structural defects (stereoirregularities) such as linkage defects, conformational disorder as well as polydispersity of the chain lengths. The degree and type of disorder are largely determined by the mechanism of the polymerization reaction and in particular by the growth processes of electrochemically prepared polymer films. Under optimized conditions electrochemical polymerization is well suited for the reproducible preparation of polythiophene films with well defined optical and structural properties.

In this work we have investigated the spectroscopic properties of electrodeposited polybithiophene films in the course of the oxidative anodic polymerization using in situ and ex situ spectroscopic techniques. These measurements were performed as a function of the redox potential and the temperature.

EXPERIMENTAL

p-Doped polybithiophene films were galvanostatically prepared on In-Sn oxide conducting glass substrates by electrochemical anodic oxidation of 0.01 mol/l dithiophene in acetonitril/0.1 mol/l $LiClO_4$ at a current density of 200 $\mu A/cm^2$. Subsequent cathodic reduction at a potential of -0.2 V vs SHE produces undoped polybithiophene films. The in situ spectroscopy experiments were performed in a quartz electrochemical cell containing the polybithiophene film on the ITO glass electrode and a gold counter electrode which are plunged in the acetonitril/0.1 mol $LiClO_4$ electrolyte. The transmission and reflectance spectra were recorded using a deuterium lamp (Hamamatsu L1905) combined with a tungsten-halogen white light source covering the spectral range from 200 to 800 nm. The transmitted and reflected light was dispersed using a home-built spectrograph consisting of a 1200 lines/mm grating (Jobin Yvon) and a 1024 diodes array (EG&G Reticon RL 1024 SB). The ex situ fluorescence was excited at 472.7 nm with an argon ion laser (Coherent Innova 20) and were recorded using a 0.64 m monochromator (Jobin Yvon HR640) and a photomultiplier (Hamamatsu R928). The polybithiophene films on ITO glass substrates were mounted in a temperature-variable helium flow cryostat (Oxford Instruments OX2 ODX)

RESULTS AND DISCUSSION

A. Ex situ absorption and fluorescence spectra

The absorption spectra of undoped polybithiophene films on ITO glass substrates were recorded as a function of the film thickness at room temperature. Fig.1 depicts the absorption spectra of polybithiophene films with thicknesses between 17 and 150 nm. The broad absorption band is considered to arise from a superposition of S_0-S_1 (π-π^*) transitions of polybithiophene segments with different effective conjugation lengths, so that the absorption maximum corresponds to the mean effective conjugation length. To estimate the latter, the energy of the absorption maximum is compared with the absorption spectra of oligothiophenes in solid films at 80 K.[5] The energy of the absorption maximum of the oligothiophenes linearly depends on the inverse number of linked thiophene units. Extrapolation to 480 nm gives a mean effective conjugation length of ca. 7 thiophene units.

The fluorescence spectra of polybithiophene films were recorded as a function of the temperature and film thickness. Fig.2.a presents the temperature dependence of the fluorescence spectrum of polybithiophene seeds grown on the ITO glass substrate during a polymerization time of 4 s (initial nucleation). For a 120 nm thick polybithiophene film the temperature dependence of the fluorescence spectrum is depicted in Fig.2.b. The fluorescence spectra at 4.2 K show a well-resolved pure electronic and first vibronic band at 620 nm and 682 nm (Fig.2.a), 630 nm and 682 nm (Fig.2.b), respectively. The energy of the vibration responsible for the vibronic transition is determined from the spacing between the pure electronic and vibronic band in the seed spectrum, which is 1466 cm^{-1}, and is assigned to the totally symmetric C=C stretching vibration of polythiophene.[6] Lowering the temperature from room temperature to 4.2 K improves the vibrational resolution and increases the fluorescence quantum yield. The better vibrational resolution at 4.2 K is due to the higher conformational order, and the larger fluorescence quantum yield at this temperature arises from the smaller internal conversion rate. The correlation of the pure electronic fluorescence transition of polybithiophene with that of oligothiophenes in solid films[5] gives a mean effective conjugation length of 11 thiophene units. This value is significantly larger than the mean conjugation length obtained from the absorption spectrum of polybithiophene. The observation of the large Stokes shift of the polybithiophene fluorescence spectrum is explained by excitation energy transfer from the initially excited polybithiophene segments to the longest-conjugation-length segments. The good vibrational resolution of the spectrum as being better than this of oligothiophene film spectra[7,8] supports this hypothesis. An additional indication of efficient energy transfer via neighbored polythiophene segments is given by the rather small fluorescence quantum yield estimated to be smaller than 0.001%. This very small quantum yield resembling that of oligothiophene aggregates in films is

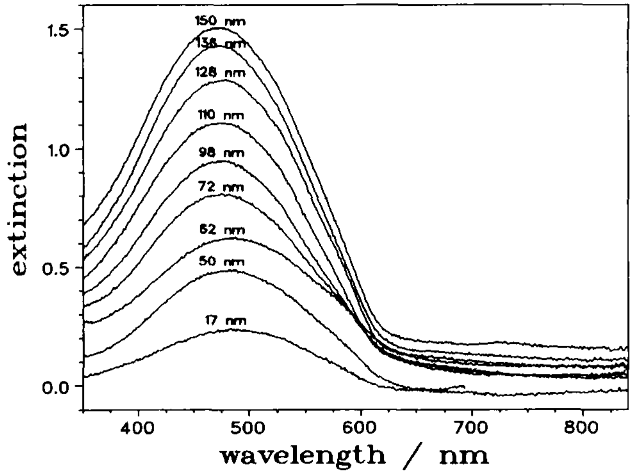

FIGURE 1 Absorption spectra of undoped polybithiophene films.

explained by strong exciton coupling between parallel polymer chains, where the fluorescence transition to or from the low exciton band edge is completely forbidden.[7]

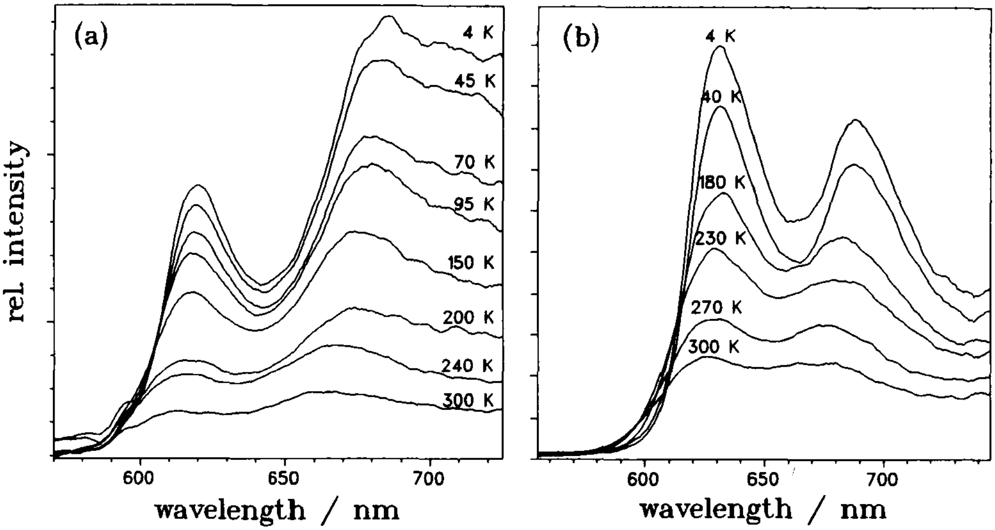

FIGURE 2 Fluorescence spectra of undoped polybithiophene seeds (a) and a 120 nm thick film (b).

B. In situ characterization of the film growing process

Since anodic polymerization of bithiophene occurs via double oxidation, the as-grown p-doped polybithiophene films contain bicationic segments. These bicationic species are expected to change the optical absorption and the reflectivity of the polymer film.

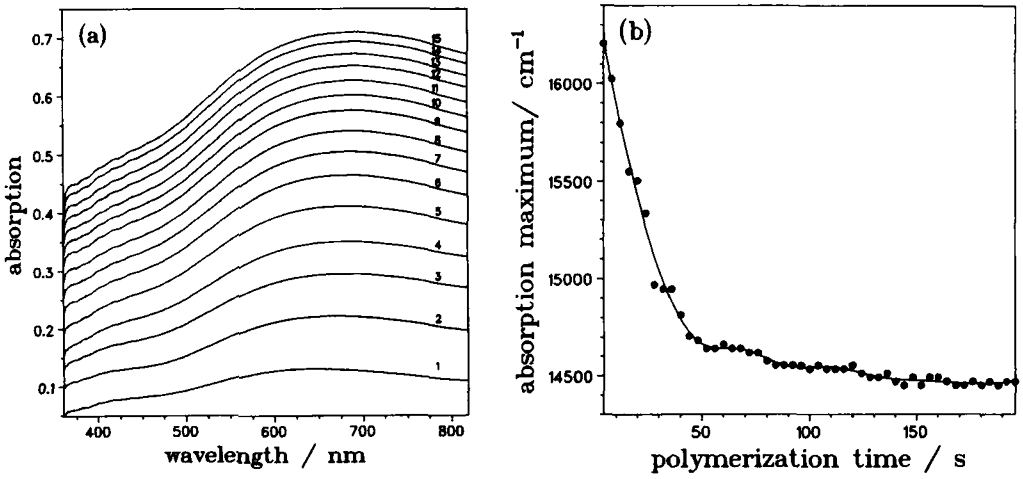

FIGURE 3 In situ absorption spectra of p-doped polybithiophene films as function of polymerization time (a); absorption maximum energy vs polymerization time (b).

Therefore, the in situ absorption spectra of the p-doped films were determined from transmission spectra corrected for the wavelength-dependent reflectivity losses. Fig.3.a shows the in situ absorption spectra of polybithiophene films as a function of the polymerization time recorded at t= (n-1)x12 s + 4 s with n= 1,2,...,15 (n labels the spectrum). The absorption maximum in spectrum 1 at 620 nm is red-shifted with rising polymerization time and reaches 692 nm in spectrum 15. The dependence of the absorption maximum energy on the polymerization time is depicted in Fig.3.b. The plot shows a steep decrease within the first 50 s corresponding to a film thickness of 25 nm. At longer polymerization times a slow decay follows converging to 692 nm. The steep decrease for film thicknesses of up to 25 nm indicates a fast increase of the mean effective conjugation length, while the ensued slow decay is explained to arise from a steady increase of linkage defects and conformational disorder, which limit the mean effective conjugation length to a near constant value.

C. In situ characterization of the redox processes

To monitor the electrochemical reduction process of p-doped polybithiophene in situ absorption spectra were recorded during the potential scan from 0.00 to 1.10 V/SHE (see Fig.4). These absorption spectra illustrate the successive transition from spectral features of fully p-doped polybithiophene to that of undoped polybithiophene (see Figs.3.a and 1). For the undoping and doping parts of the potential isobestic points appear at 590 nm and 525 nm, respectively. These isobestic points characterize equilibrium redox states proving the reversibility of the redox process.

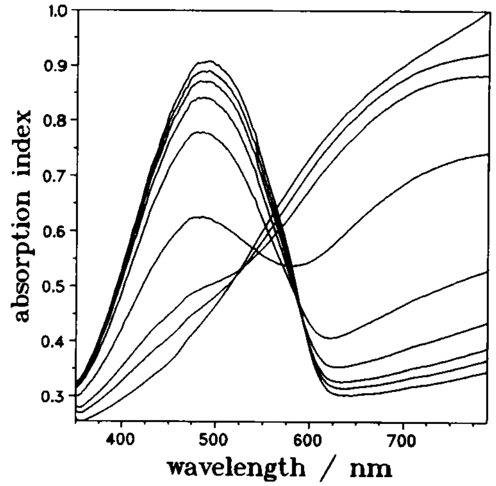

FIGURE 4 Absorption spectra of polybithiophene films during the potential scan.

CONCLUSIONS AND SUMMARY

Optimizing the reaction conditions of anodic oxidative polymerization polybithiophene films with reproducible structural, redox and optical properties could be obtained. The ex situ absorption spectra of undoped polybithiophene reflect the distribution of effective conjugation lengths in the film with an estimated mean conjugation length of ca. 7 thiophene units. The fluorescence of the undoped polymer was assigned to the longest-conjugation-length segments (ca. 11 thiophene units). This difference in the effective conjugation lengths of absorbing and fluoresceing polybithiophene segments was explained by excitation energy transfer from the initially excited segments of a broad distribution of effective conjugation lengths to those with an effective conjugation length of ca. 11 units. The rather small quantum yield observed to be more than 4 orders of magnitude smaller than that of isolated oligothiophene molecules indicates to quasi-excitonic states which predominantly decay nonradiatively. The features of the in situ absorption spectra were observed to strongly depend on the initial film growth process as well as on the redox potential. The significant dependence on the film thickness indicates to changes of the structure and the morphology of the polybithiophene films during the growth process, while the absorption spectra of the successively undoped or p-doped polymer manifest the reversibility of the redox process.

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