In Situ Attenuated Total Reflection FTIR Spectroelectrochemistry Of Polybenzimidazobenzophenanthroline (BBL)

Teketel Yohannes[1], H. Neugebauer[1], Niyazi S. Sariciftci[1], S. Yi[2] and Samson A. Jenekhe[2]

[1]Physical Chemistry, Johannes Kepler University Linz, Altenbergestraße 69, A-4040 Linz, Austria

[2]Department of Chemical Engineering, University of Rochester, Rochester, NY 14627-0166, USA

ABSTRACT

Fourier transform infrared (FTIR) spectroscopy is a powerful method to determine the doping induced structural changes and electronic band structure modifications of conjugated polymer films. Here, we report *in situ* attenuated total reflection (ATR) FTIR spectroelectrochemical results of reduction reactions (*n*-doping) of the conjugated ladder polymer polybenzimidazophenanthroline, BBL. The ATR-FTIR spectra are recorded *in situ* during continuous potential cycling of a BBL coated germanium reflection element in a three electrode spectroelectrochemical cell. The spectra and the structural changes during the reduction (*n*-doping) of the polymer film at different electrode potentials are presented. In contrast to most of the other conjugated polymers, this polymer shows four reversible redox reactions during *n*-doping, corresponding to various forms of BBL with different conductivities.

INTRODUCTION

The combination of electrochemical and spectroscopic techniques has been used successfully to study doping induced reactions in conjugated polymers [1-7]. Among these is FTIR spectroelectrochemistry, which is a fast and sensitive technique used to probe doping induced structural changes and electronic band modifications. BBL (see inset in figure 1) is a member of a class of materials called ladder polymers, which are double-stranded, highly conjugated macromolecules with rigid chain structure. In this work we present *in situ* spectroelectrochemical evidence for the presence of four clearly distinct reactions with various forms of BBL having different conductivities during electrochemical reduction. As such this is the only conjugated polymer known with four consecutive redox reactions on the main chain.

EXPERIMENT

Tetrabutylammonium perchlorate, Bu_4NClO_4, (Fluka) was dried under vacuum at 130^0C for 2 hours before use. Water free acetonitrile (Merck) was stored over molecular

sieve prior to measurement. Great precaution was taken in order to protect the electrolyte from atmospheric oxygen and water throughout the experiments. The chemical synthesis of BBL was reported elsewhere [8]. Thin films were prepared by spin coating from a solution of 0.8% BBL in gallium chloride/nitromethane onto glass substrates in laboratory atmosphere. The resulting polymer/Lewis acid complex film was washed with deionized water several times and subsequently placed in fresh deionized water overnight to remove the Lewis acid completely. Using a pair of tweezers the film was peeled off while still wet yielding a film floating on the water surface. The free standing film was then transferred onto a germanium reflection element covered with thin layer of evaporated platinum. The resulting solid film was dried in a vacuum oven for 6 hours at 80^0C.

The *in situ* ATR-FTIR spectroelectrochemical measurements were carried out in a three-electrode spectroelectrochemical cell (figure 1) with a germanium working electrode, a platinum foil counter electrode, and a silver wire coated with silver chloride reference electrode. The electrolyte for the *in situ* spectroelectrochemical experiments was 0.1 M Bu_4NClO_4 in acetonitrile. The spectroelectrochemical cell was sealed with paraffin to prevent leakage of the electrolyte solution. The cell was placed in the FTIR cell compartment and the instrument was purged with nitrogen continuously throughout the experiment. A continuous flow system for the electrolyte was used where the electrolyte (placed in an external container where it was blanketed with argon after purging for few minutes) flows in and out of the electrochemical cell using teflon plastic tubes. To obtain *n*-doping, a potential scan between 0.6 V and -2.0 V with a scan rate of 5 mV s^{-1} using a sweep generator Prodis 1/14 I and a potentiostat Jaissle Model 1002 T-NC was applied to the film. The cyclic voltammogram was recorded on an x-y recorder. During the scan, *in situ* FTIR spectra were recorded with a resolution of 4 cm^{-1} using Bruker IFS 66S spectrometer with an MCT detector. To obtain specific spectral changes during individual electrochemical reaction processes a spectrum just before the considered reaction was chosen as a reference spectrum. The subsequent spectra were related to the spectrum, showing only the spectral differences to this reference state. The spectra are plotted as $\Delta(-\log(T_{ATR}))$, where T_{ATR} is transmission in ATR geometry. For each spectrum 32 interferograms were coadded covering a range of about 90 mV in the cyclic voltammogram. The potential values given for each reference spectrum in this paper corresponds to the mean value of this range.
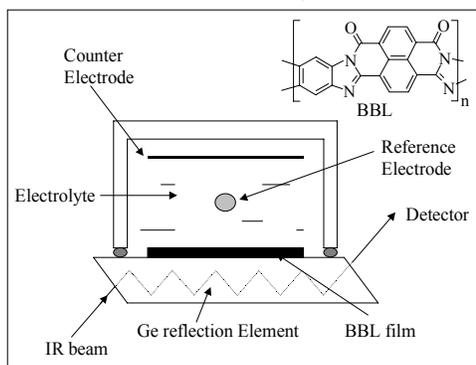
Figure 1. *In situ* ATR-FTIR spectroelectrochemical cell. Inset: BBL chemical structure.

RESULTS AND DISCUSSION

The cyclic voltammetric response (CV) for the reduction (*n*-doping) and reoxidation (undoping) processes of BBL film is shown in figure 2. From the CV four
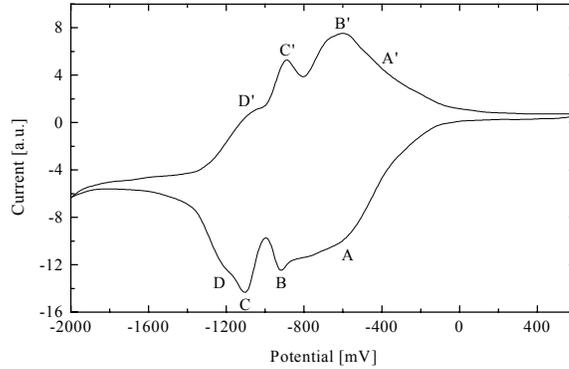
Figure 2. CV for *n*-doping (reduction) processes of BBL.

distinct reduction waves were obtained at ≈ -0.6 V (A, shoulder), ≈ -0.9 V (B, peak), ≈ -1.1 V (C, peak), and ≈ -1.2 V (D, shoulder). During reoxidation, the corresponding waves were found at ≈ -1.0 V (D', shoulder), ≈ -0.89 V (C', peak), ≈ -0.61 V (B', peak), and ≈ -0.38 V (A', shoulder).
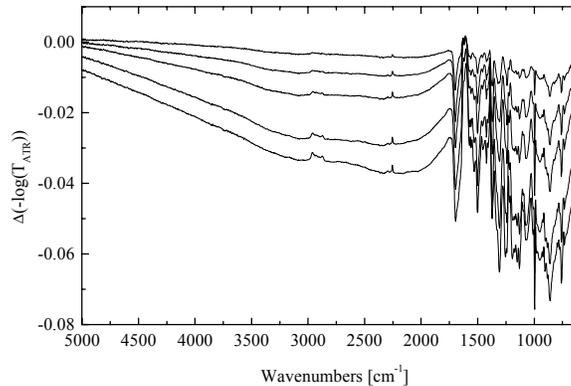
Figure 3 shows the difference *in situ* FTIR absorption spectra of BBL during the
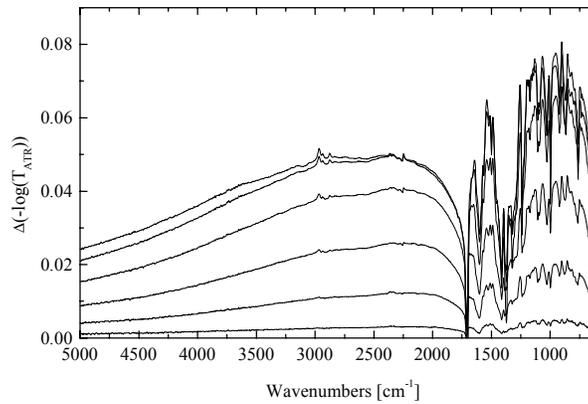
Figure 3. Difference *in situ* ATR-FTIR absorption spectra during reduction process A for potentials from -95 mV to -618 mV. Reference spectrum taken around –48 mV.

first reduction process (wave A). A broad absorption band with absorption maximum above 2000 cm^{-1} appears. This broad absorption comes from an electronic transition of the polaronic or bipolaronic states [9] and is correlated with the increase in the conductivity where the neutral insulating polymer (substance I) is transformed to an electrically conducting polymer (substance II). Usually, vibrational spectra of conjugated polymers show strong unusual effects during doping (redox) processes due to strong electron-phonon coupling within these quasi one dimensional solids [9]. Upon doping the infrared spectrum is dominated by new very strong doping induced infrared bands called infrared active vibration (IRAV) bands. IRAV bands similar to other conjugated polymers are seen in the vibrational part of the spectra. These growing IRAV bands indicate the formation of a new substance II.

Figure 4 shows the difference *in situ* spectra during the second reduction process (wave B). The broad negative band at high energy indicates the formation of a new substance III with decrease in conductivity. Further decrease in the intensities of substance I and II together with an increase in sharper vibrational bands of substance II are observed (formation of substance III).
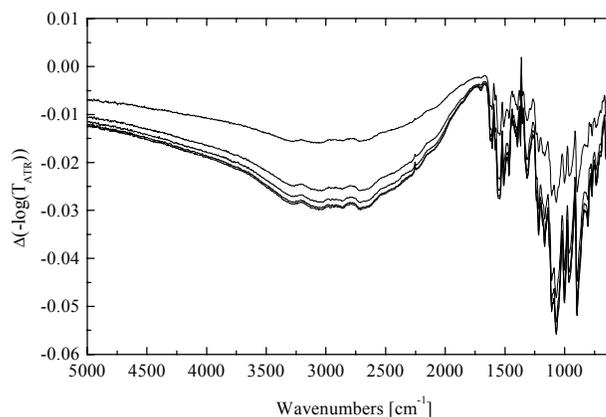

Figure 4. Difference *in situ* ATR-FTIR absorption spectra during reduction process B for potentials from -618 mV to –1039 mV. Reference spectrum taken around –572 mV.

Figure 5 depicts the difference *in situ* FTIR spectra during the third reduction process (wave C). Increase in the broad band above 2000 cm^{-1} (but smaller than in the first reduction process A) was noticed with increase in applied reduction potential indicating again the increase in conductivity of the film. Decrease of bands of substance III and increase of IRAV bands of substance IV are observed. The IRAV bands in the third reduction process C show lower intensities compared to the IRAV bands in the first reduction process A. In addition, the bands are sharper than in process A. The lower intensities and the sharper IRAV bands of substance IV indicate that the delocalization of the positive charges on the chain is rather low compared to substance II.
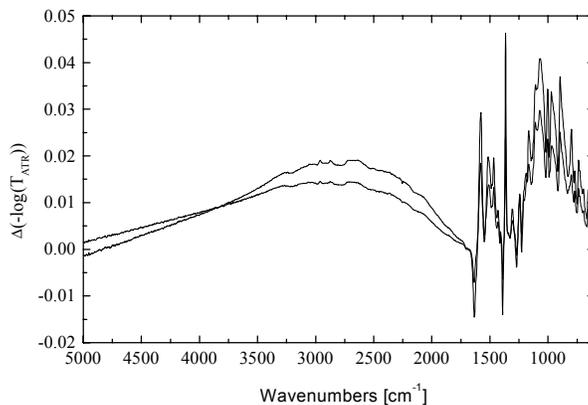
Figure 5. Difference *in situ* ATR-FTIR absorption spectra during reduction process C for potential from -1039 mV to –1206 mV. Reference spectrum taken around –996 mV.

In figure 6 the spectra for the fourth reduction process (wave D) are shown. A decrease in the electronic band at high energy is observed with increasing in doping level. This is again an indication of the decrease in the conductivity of the film with increase in the reduction potential. Decrease in the vibrational bands of substance IV and increase in few sharp bands are observed for substance V.

Figure 6. Difference *in situ* ATR-FTIR absorption spectra during reduction process D for potential from -1206 mV to -1634 mV. Reference spectrum taken around –1164 mV.

From the *in situ* FTIR measurements one can clearly see that transitions between different states from insulator→conductor→insulator→conductor→insulator occur when

going in the direction from positive to negative potentials. Exactly reverse processes are found when going back from negative to positive potentials where the difference spectra obtained during the reoxidation processes (waves D' - A') reverse the spectra of the corresponding reduction processes (waves A – D).

CONCLUSIONS

Four spectroelectrochemically well resolved reversible redox processes were found during electrochemical reduction of BBL. To our knowledge, there are no such reports on conjugated polymers with four consecutive redox reactions on the main chain during *n*-doping resulting in five different forms of BBL.

ACKNOWLEDGMENTS

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