

Electrochemically induced IRAV modes of BeCHA-PPV studied with *in situ* FTIR-ATR Spectroscopy

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Abstract

We present the results of *in situ* spectroelectrochemical studies on poly(bis-2,5-*epi*-cholestanoxo-1,4-phenylene vinylene) (BeCHA-PPV). A broad IR absorption band centered at about 0.5 eV is observed during the oxidation process. The spectra are characterized by strongly enhanced infrared active vibrational (IRAV) modes in the wavenumber region below 1600 cm^{-1} . No distinct reduction current was observed in the investigated potential range, unlike the results on similar systems.

Keywords: *In situ electrochemical spectroscopy, Poly(phenylene vinylene) and derivatives, Spectroelectrochemistry, FTIR-ATR Spectroscopy, Doping induced IRAV modes*

Introduction

Among the many organic polymers showing electrical conductivity upon doping as well as interesting optical properties, poly(*p*-phenylene vinylene) (PPV), has attracted the interest of many researchers¹⁻⁴. Recently soluble PPV derivatives, poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene vinylene] (MEH-PPV) and poly(bis-2,5-*epi*cholestanoxo-1,4-phenylene vinylene) (BeCHA-PPV) have been prepared⁵, which can be cast as films from solution. Photoinduced absorption studies⁶ have shown MEH-PPV and BeCHA-PPV to be efficient electron donors upon photoexcitation which makes them promising candidates for use in photonic devices.

Vibrational spectra of polyconjugated materials in the undoped (insulating), doped (conducting) and photoexcited states show features which can be related to the existence of strong electron-phonon coupling. In this paper we present the results of *in situ* spectroelectrochemical studies on BeCHA-PPV using the FTIR-ATR technique⁷. The infrared spectra are obtained *in situ*, during cyclic voltammetric sweep experiments, which allow to observe structural and electronic changes in the polymer as the electrochemical reaction proceeds.

Experimental

The experimental setup for the *in situ* FTIR-ATR technique has been described in an earlier report⁷. A thin film of BeCHA-PPV was drop cast on a germanium reflection element from a dilute chloroform solution and dried under argon. The polymer coated reflection element, a Pt foil, and a saturated calomel electrode (SCE) were used as working electrode, counter electrode and reference electrode, respectively. The electrolyte used was a solution of 0.1M LiClO_4 in acetonitrile. The potential of the

polymer was cycled at a rate of 10 mV/s in the range 0 to 1.5 V with simultaneous collection of FTIR data. The electrochemical equipment consisted of a potentiostat (Jaisle 1001 T-NC) and a PC-controlled system (SCADA) for data acquisition and potential control. The spectra were recorded on a Nicolet 60 SX FTIR spectrometer. The spectra were obtained by coaddition of 32 interferograms for each spectrum with a resolution of 8 cm^{-1} . Each spectrum covers a range of about 80 mV in the cyclic voltammogram and the spectrum around 400 mV (before the oxidation process) was taken as the reference spectrum. In this way, only spectral changes occurring during the electrochemical oxidation process are shown.

Results and Discussion

The cyclic voltammogram obtained for BeCHA-PPV is shown in Figure 1. The anodic peak current occurs at 1.2 V.

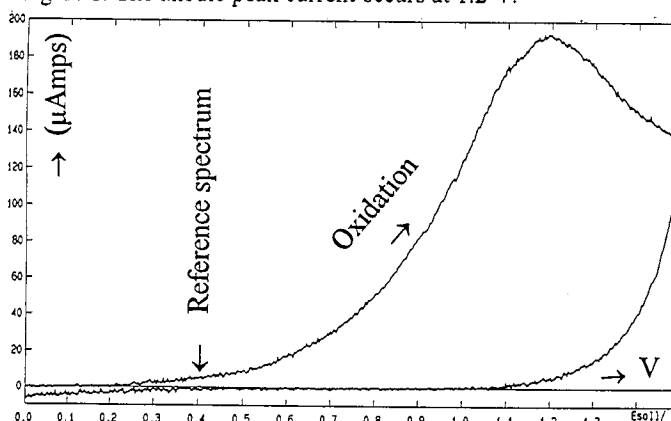


Fig. 1: Cyclic voltammogram of a BeCHA-PPV film on a Ge reflection element using SCE as a reference electrode in 0.1 M $\text{LiClO}_4/\text{CH}_3\text{CN}$ at a sweep rate of 10 mV/s.

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No distinct reduction current was observed in the investigated

potential range. This result is quite unlike the results obtained on unsubstituted and other substituted PPVs by other authors^{2,8}. The difference spectra recorded during the oxidation process are presented in Figure 2.

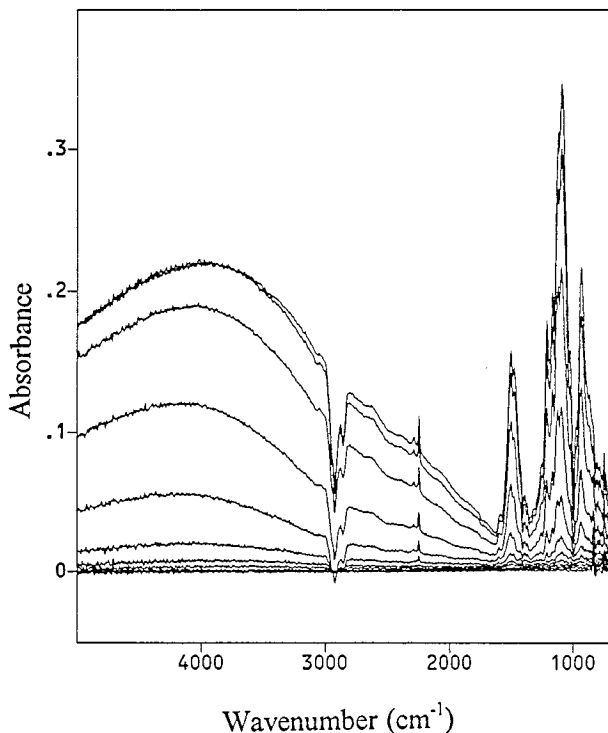


Fig. 2: *In situ* difference spectra during the oxidation of BeCHA-PPV. (Reference spectrum: potential range covering 350-430 mV)

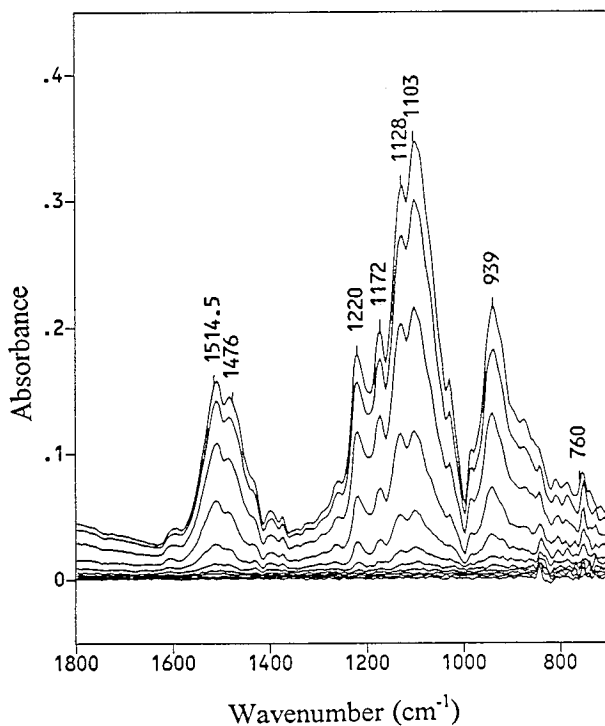


Fig. 3: Section of Figure 2 in an enlarged scale.

The evolution of a broad absorption band (Figure 2) around 4000 cm^{-1} (~ 0.5 eV) during the oxidation process is clearly discernable. This absorption belongs to a sub-gap electronic transition due to the formation of polaronic or bipolaronic charged defects on the polymer chain⁸. The negative bands at 2934 and 2868 cm^{-1} are connected with the loss of absorption of the CH stretching vibrations of the cholestanoxo group.

In Figure 3, the IR spectral absorption features in the vibrational range are shown in an enlarged scale. The spectral features below 1800 cm^{-1} show remarkable correspondence with those observed for photoinduced absorption obtained with a BeCHA-PPV/ C_{60} ⁹ mixture (photo-oxidation with electron transfer to C_{60})

These results indicate that the nature of charged carriers (polarons or bipolarons) generated during both, the photo-oxidation of a C_{60} containing sample and the electrochemical oxidation process are the same. The strongly enhanced infrared active vibrational (IRAV) modes are typical of polyconjugated systems and can be explained in detail by the amplitude mode formalism¹⁰, or by the effective conjugation coordinate theory¹¹.

However, the absorption maximum related to the sub-gap electronic transition occurs at lower energy in the case of photo-oxidation (0.43 eV) as compared to the electrochemical oxidation (0.5 eV). Localization effects due to the incorporated counterions in the polymer or the influence of polymer history on the effective conjugation length may be responsible for this effect.

Further spectroelectrochemical investigations also on unsubstituted PPV are in progress which are expected to explain the effects in more detail.

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