

Vibrational spectroscopic study of a push-pull substituted fluorinated poly(*p*-phenylenevinylene) copolymer

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Abstract

In situ attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroelectrochemistry during oxidation (p-doping) and reduction (n-doping) as well as photoinduced infrared spectroscopy of a random copolymer of 2,3,5,6-tetrafluoro-1,4-phenylenevinylene and 2,5-dioctyloxy-1,4-phenylenevinylene [co(TFPV-DOPV)] is presented. The infrared active vibration (IRAV) patterns obtained during electrochemical oxidation (p-doping) and reduction (n-doping) are different. The copolymer shows photoinduced IRAV bands that are similar to those obtained during electrochemical reduction (n-doping) in contrast to most of the other conjugated polymers which show similarities with oxidation (p-doping) IRAV bands. To our knowledge this is the only p- and n-dopable polymer with different IRAV patterns of charge carriers of both signs, and a similarity between n-doping and photodoping IRAV bands.

Keywords: Electrochemical doping, infrared spectroscopy, in situ electrochemical spectroscopy, photoinduced absorption spectroscopy, Poly(phenylene vinylene) and derivatives

1. Introduction

Doping of conjugated polymers can be performed either by chemical or electrochemical oxidation (p-doping) and reduction (n-doping) or by photoexcitation (photodoping). A number of spectroelectrochemical techniques has been developed to study these reactions [1–9]. Infrared spectroelectrochemistry is one of the most powerful methods to get detailed insight in the electronic and vibrational properties of conjugated polymers, which is necessary for the basic understanding of their physical behaviour. Conjugated polymers in their conductive (doped) states are characterized by intense infrared active vibration (IRAV) bands. These IRAV bands are correlated with a strong electron-phonon coupling which is the basis for the existence of charged quasi-particles such as solitons or polarons on the polymer chain. IRAV bands are related to molecular vibrations and, therefore, contain information on the molecular structure. Usually, these IRAV bands are accompanied by electronic absorption bands, providing also information on electronic properties.

Among conjugated polymers, poly(*p*-phenylenevinylene)s (PPVs) received great attention because of the various methodologies available for their synthesis, ease of processing and good chemical stability. Among the number of synthetic approaches, various organometallic protocols have been developed for the preparation of soluble functionalized PPV derivatives, achieving a good structural control of the properties of the resulting materials [10]. By a proper choice of the side groups it is possible to substantially improve some of the properties such as third order nonlinear optical coefficients [11–14] and photo- and electroluminescence efficiencies [15,16].

The possibility of tuning the linear and nonlinear optical properties of soluble PPV derivatives based on the effect of the simultaneous presence of electron-acceptor and electron-donor substituted aromatic rings in the conjugated backbone has been demonstrated for a series of random copolymers containing variable ratios of electron-deficient tetrafluorophenylenevinylene (TFPV) and electron-rich dioctyloxyphenylenevinylene (DOPV) repeating units [12,13]. These random copolymers, namely copoly(2,3,5,6-tetrafluoro-1,4-phenylenevinylene-2,5-dioctyloxy-1,4-phenylenevinylene)s [co(TFPV-DOPV)s],

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were synthesized via the Stille cross-coupling reaction, that is a classical organometallic protocol [12,17]. The feed ratio of the two aromatic monomers could be varied in order to tune their percentage in the resulting polymers.

Here, we present results of a spectroscopic study of the copolymer co(TFPV-DOPV) with a molar ratio of fluorine-to dioctyloxy-substituted aromatic rings of about 6:4. The chemical structure of the copolymer used is shown in Figure 1. It has a good solubility in chlorinated solvents such as chloroform and dichloromethane [17]. It is transparent in the IR region of the electromagnetic spectrum and exhibit a main absorption band in the visible with a shoulder in the UV [17].

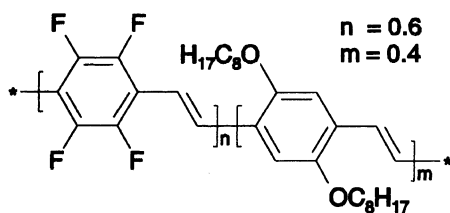


Fig. 1: The chemical structure of co(TFPV-DOPV).

IRAV spectra obtained with in situ ATR-FTIR spectroelectrochemical technique during electrochemical oxidation (p-doping) and reduction (n-doping) are compared with photoinduced IR absorption. In contrast to most of the other conjugated polymers, the photoinduced IRAV pattern looks similar the IRAV pattern obtained during electrochemical reduction (n-doping).

2. Experimental

The synthesis of co(TFPV-DOPV) was performed via the Stille cross-coupling reaction, as described in the literature [12,17]. The supporting electrolyte used for the spectroelectrochemical measurements was 0.1 M tetrabutylammonium hexafluorophosphate, Bu_4NPF_6 (Aldrich), which was dried under vacuum at 180°C before use and dissolved in HPLC grade water-free acetonitrile (Aldrich).

Cyclic voltammetric experiments were carried out with a platinum foil working electrode with a dip coated polymer film from chloroform solution (5 mg/ml). As counter electrode a platinum foil and as quasi-reference electrode a silver wire coated with AgCl were used. The electrolyte solution was kept under argon flow to exclude moisture and oxygen during the electrochemical processes.

For the spectroelectrochemical studies thin films of co(TFPV-DOPV) were drop cast from chloroform solution (5 mg/ml) onto a germanium reflection element covered with a thin layer of evaporated platinum. The ATR-FTIR spectroelectrochemical measurements were carried out in a three-electrode spectroelectrochemical cell with the described germanium working electrode, a platinum foil counter electrode, and a silver wire/silver chloride quasi-

reference electrode. The spectroelectrochemical cell setup is shown schematically in Figure 2.

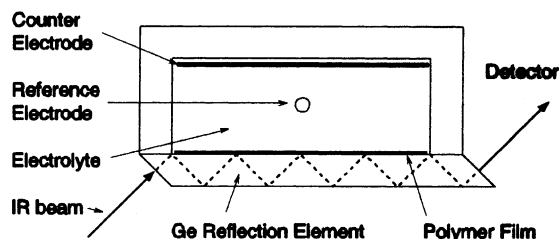


Fig. 2: Experimental setup for the in situ attenuated total reflection Fourier transform spectroelectrochemistry.

The cell was placed in the FTIR compartment and the instrument was purged with nitrogen continuously throughout the experiment. The electrolyte solution for the in situ spectroelectrochemical experiments was 0.1 M Bu_4NPF_6 in acetonitrile. A continuous flow system for the electrolyte solution was used where the solution (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.

The electrochemical equipment consisted of a potentiostat Jaissle 1002 T-NC, a sweep generator Prodis 1/14 I and a x-y recorder. A Bruker IFS66S spectrometer with a mercury-cadmium-telluride (MCT) detector cooled with liquid nitrogen was used. The spectra were measured with a spectral resolution of 4 cm^{-1} .

Spectral changes were recorded consecutively during slow potential sweeps (5 mV/s). To obtain specific spectral changes during individual electrochemical reaction processes, a spectrum just before the considered reaction is chosen as the reference spectrum. The subsequent spectra are related to this reference spectrum, showing only the spectral changes during the process. The spectra are plotted as $\Delta[-\log(T_{\text{ATR}})]$, where T_{ATR} is the transmission in ATR geometry. For each spectrum, 32 interferograms were coadded covering a range of about 85 mV in the cyclic voltammogram.

To study the nature of species that are generated upon photoexcitation, photoinduced absorption (PIA) infrared spectra were recorded. For measuring PIA infrared spectra, the film was drop cast from chloroform solution (5 mg/ml) onto a ZnSe substrate which was mounted in a cryostat and cooled with liquid nitrogen. The vacuum during this measurements was better than 10^{-5} mbar. The sample was illuminated in 45° geometry through a quartz window of the cryostat by an Ar^+ laser (476 nm, 30 mW/cm^2). The PIA infrared spectrum was obtained by measuring 10 single-beam spectra under illumination followed by 10 single-beam spectra taken in the dark. For a better signal-to-noise ratio, 300 repetitions of the measuring sequence were accumulated. The PIA spectra were recorded with the same FTIR spectrometer as used for spectroelectrochemistry. The setup for PIA measurement is depicted in Figure 3.

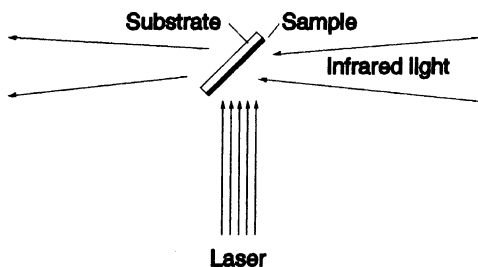


Fig. 3: Experimental setup for infrared photoinduced absorption.

3. Results and Discussion

The cyclic voltammogram of $\text{co}(\text{TFPV-DOPV})$ in 0.1 M Bu_4NPF_6 -acetonitrile solution, recorded during potential cycling between -2 V and 2 V versus Ag/AgCl quasi reference electrode, is depicted in Figure 4. It can be seen that the material can be both oxidized and reduced with a p-doping/dedoping onset potential at about 0.9 V and a n-doping/dedoping onset potential at about -1.0 V versus the Ag/AgCl quasi-reference electrode.

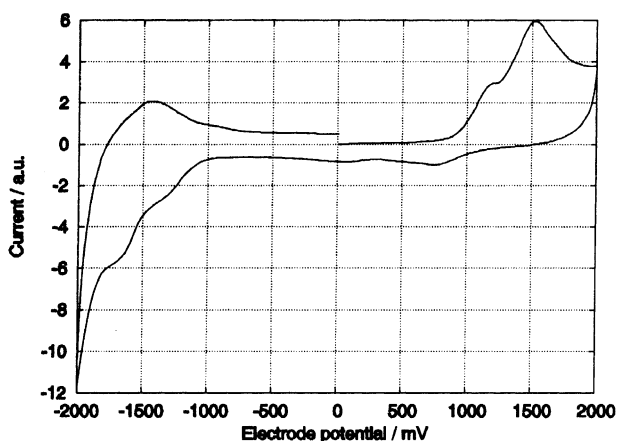


Fig. 4: Cyclic voltammogram of a $\text{co}(\text{TFPV-DOPV})$ film dip coated on Pt foil working electrode. Pt foil counter electrode, Ag/AgCl quasi-reference electrode and 0.1 M Bu_4NPF_6 -acetonitrile electrolyte solution. Scan rate is 100 mV s^{-1} .

The changes of FTIR absorption of $\text{co}(\text{TFPV-DOPV})$ in the IRAV range during the oxidation process from 864 mV to 1379 mV are depicted in Figure 5. The spectrum obtained around 740 mV was taken as a reference. In addition to the increase of the IRAV bands shown in Figure 5, a broad, not well defined absorption band at higher energy was found (not shown), which is related with an electronic transition of the polaronic or bipolaronic type quasi particles in connection with the increasing conductivity of the polymer.

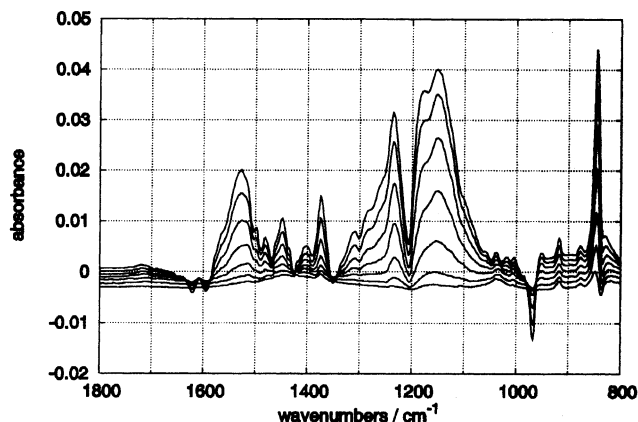


Fig. 5: Spectral changes during electrochemical oxidation of $\text{co}(\text{TFPV-DOPV})$ during a potential sweep from 864 mV to 1379 mV. The spectrum obtained around 740 mV was taken as reference.

Figure 6 shows the changes in FTIR absorption in the IRAV range during the reduction process at various potentials from -1338 mV to -1945 mV. The spectrum obtained around -1210 mV was used as reference. Again, an increase of a broad absorption band at higher energies (not shown) is correlated with the increase in the conductivity where the neutral insulating polymer is transformed to an electrically conducting form.

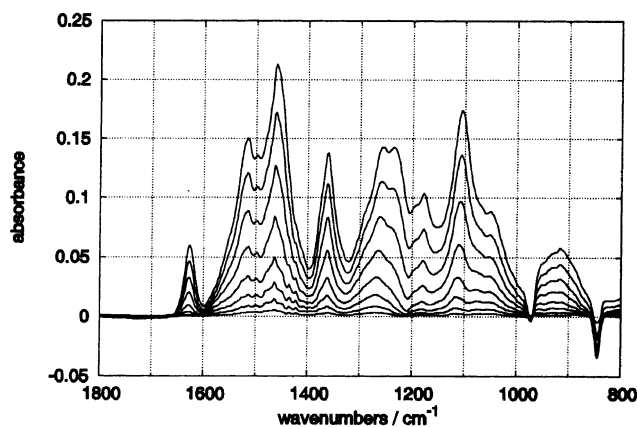


Fig. 6: Spectral changes during electrochemical reduction of $\text{co}(\text{TFPV-DOPV})$ during a potential sweep from -1338 mV to -1945 mV. The spectrum obtained around -1210 mV was taken as reference.

The spectral signatures of the charge carriers obtained during electrochemical oxidation and reduction processes of $\text{co}(\text{TFPV-DOPV})$ are not similar, indicating a different structure and delocalization of the charge carriers of both signs.

To compare the nature of photogenerated species with the electrochemical doping induced charge carriers, photoinduced absorption spectroscopy (PIA) studies were carried out. The photoinduced FTIR spectrum for $\text{co}(\text{TFPV-DOPV})$ is depicted in Figure 7. Broad, not well defined absorption features arise at lower energies (below 1000 cm^{-1}), in addition to a distinctive infrared active vibra-

tion pattern, indicating photoinduced charge carrier formation.

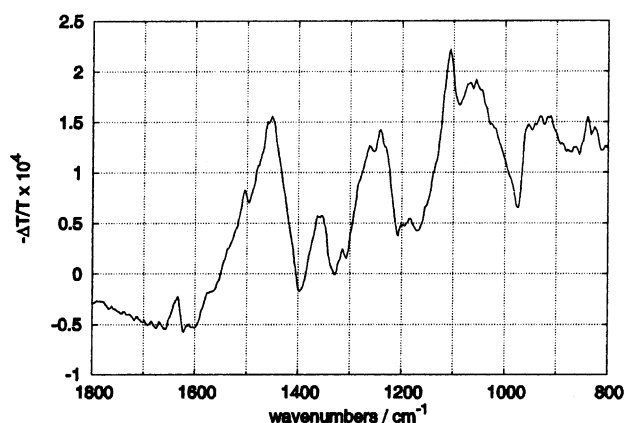


Fig. 7: Photoinduced infrared absorption spectrum of co(TFPV-DOPV).

The photoinduced IRAV pattern corresponds to the IRAV pattern obtained during electrochemical reduction (n-doping) of the material. The high similarity suggests that the nature of the charge carriers that are generated during n-doping and photoexcitation are similar. Therefore, negative polarons are mainly produced by photodoping. These results are in contrast to the usual observation of similarities between IRAV band patterns obtained during electrochemical oxidation (p-doping) and photoinduced IRAV band patterns in most conjugated polymers [18–20]. In our previous study [21] of a ladder polymer known as BBL, where a similarity of photoinduced IRAV bands similar to IRAV bands obtained during electrochemical reduction (n-doping) was found, BBL turned out to be only reduceable, not oxidizable.

To our knowledge, co(TFPV-DOPV) is the only conjugated polymer described until now, which is electrochemically both p- and n-dopable and has photoinduced IRAV bands similar to the electrochemically reduced (n-doped) FTIR IRAV bands.

5. Conclusion

In this work, we performed electrochemical and photoinduced spectroelectrochemical studies of a PPV based copolymer co(TFPV-DOPV). The material was electrochemically oxidized (p-doping) and reduced (n-doping) and also photodoped. The IRAV patterns found for the electrochemical p- and n-doped co(TFPV-DOPV) are different indicating the existence of different structures of positive and a negative charge carriers during electrochemical doping. The PIA IRAV patterns were found to be

similar to the IRAV band patterns obtained during electrochemical reduction (n-doping) and differ from that of electrochemical oxidation (p-doping). The results may have high importance for the construction of optoelectronic devices, where photogeneration of negative charge carriers is important.

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