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Charge Carrier Transport and Optical Properties of Poly[*N*-methyl(aniline)]

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Simultaneous electron spin resonance (ESR) and UV−vis−NIR measurements have been carried out during oxidation of a poly[*N*-methyl(aniline)] (PNMA) film, which was prepared electrochemically in aqueous solutions containing 1 M trifluoroacetic acid. In situ conductance measurements were also performed during the electrochemical doping of PNMA. The combination of the different experimental techniques allows a simultaneous elucidation of optical and electrochemical properties of the conducting polymer film. Although there are a lot of predictions and discussions on the free charge carriers of poly(aniline) (PANI) and its derivatives, there is no direct evidence of the correlation between polarons and conductance for PANI and its derivatives during doping. This article provides the correlation between the spin and spinless species and the conductance of PNMA during the electrochemical doping in acidic aqueous solutions. PNMA differs from other conjugated polymers (e.g. polypyrrole) in that the results from ESR and in situ conductance are consistent. At higher doping (oxidation) levels, the conductance decreases with the decrease in the ESR signal, indicating that there is no spinless bipolaronic conducting state in PNMA. Polaron pairs are supposed to be responsible for these decreases.

1. Introduction

PANI is one of the most studied conducting polymers due to its high stability and wide range of conductivity. It has been widely used in different organic electronics such as transistors, solar cells, light emitting diodes, and sensors.[1−5] New organic electronics can be designed by functionalizing PANI at the nitrogen atom by grafting. Copolymers with N-substituted PANIs were reported to be both electrochemically active and electrochromic during redox switchings.[6] The effect of doping on rectification and photovoltaic characteristics for PNMA Schottky barrier has been reported.[7] Electrochemically deposited PNMA has also been studied as a cathode active material in aqueous rechargeable batteries.[8] In addition, the substituted PANI derivatives provide solubility and processability,[9] which are very important for their use in printable electronics. In comparison with the applications, rather few fundamental studies concerning the intrinsic physicochemical properties of PNMA have been reported.

The most important physicochemical property of conjugated polymers is their ability to switch between the insulating state and the conducting state upon doping. In situ ESR spectroscopy is a very powerful tool and has been widely used to study conduction in disordered semiconducting polymers. Although there are some reports concerning the in situ ESR studies on PANI,[10−14] no paper has reported the in situ ESR investigation on PNMA during the electrochemical doping. The electrical transport mechanism in PNMA remains a central problem in the understanding of this material. The conduction mechanism of PNMA was explained by Lian et al. as variable-range hopping (VRH) of the charge carriers based on their study of different poly[*N*-alkyl(aniline)s].[15] However, the nature of the charge carriers, whether the bipolarons or polarons are responsible for the electronic conduction, is still under debate.[16] In this article, both conductance and ESR/UV−vis−NIR measurements were performed simultaneously during the electrochemical doping, and the relationship between conductance and optical properties is thoroughly studied.

2. Experimental Section

2.1. Chemicals and Preparation of PNMA. *N*-Methylaniline (NMA) (98.0%) was bought from Fluka, and trifluoroacetic acid (CF_3COOH) (99%) was from Aldrich. All chemicals were used as received. Solutions were prepared from deionized water purified through a Maxima ultrapure water system (ELGA, 18.2 MΩ cm). All solutions were purged with nitrogen prior to use.

The electropolymerization was carried out in aqueous solution containing 0.5 M NMA and 1.0 M CF_3COOH in a three-electrode cell. Ag/AgCl was used as reference electrode (RE), and a Pt wire was used as the counter electrode (CE). Pt microarray and Au mesh electrode were used as working electrode (WE) for in situ conductance and ESR measurement individually. The polymerization potential range was set between −0.3 and 0.6 V by an Autolab (PGSTAT 20) potentiostat with a scan rate of 20 mV/s. The obtained PNMA film was then washed in a monomer-free aqueous solution containing 1.0 M CF_3COOH. Afterward, in situ conductance measurement and in situ ESR/UV−vis−NIR spectroscopy were recorded individually during the simultaneous doping in the potential range of −0.3 to 0.5 V (one cycle) in the acidic monomer-free aqueous solution.

2.2. In Situ Conductance Measurement. A comb-shape microarray Pt WE, the design of which has been reported

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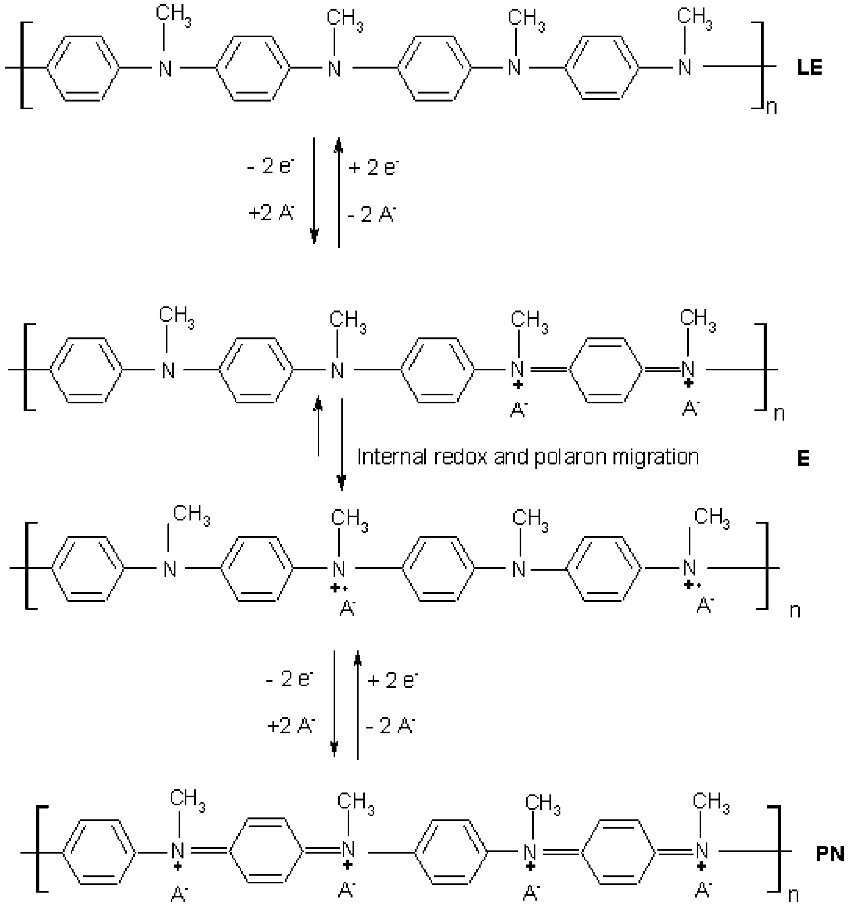
SCHEME 1: Transitions between the Three Basic States of PNMA: LE, Leucoemeraldine; E, Emeraldine; PE, Pernigraniline



earlier,[17] was used for in situ conductance measurements of electrochemically synthesized PNMA. The microarray WE consists of two interlaced platinum electrodes with a gap distance of 5 μm, separated from the potentiostat by two 1 kΩ resistors. The conductance (S) can only be measured when the conducting polymer covers the gaps between the strips of the comb electrodes. Because the current flowing from one part of the comb to the other part can be measured, the conductance of the PNMA film on the microarray electrode was obtained by using Ohm's law. This method has been introduced by Heinze et al.[18,19] The PNMA film was electropolymerized by cyclic voltammetry for 40 cycles, and after the film was washed with acidic monomer-free solutions, the conductance was monitored simultaneously during the redox doping.

2.3. In Situ ESR/UV−Vis−NIR Spectroscopy. The in situ ESR−UV−vis spectrocyclovoltammetric measurements were performed by using a TIDAS diode array spectrometer with Scan2017 software (J&M Analytische Mess- und Regeltechnik GmbH, Aalen). The electrochemical measurements were done with a PG285 potentiostat (HEKA-Elektronik, Lambrecht, Germany) and an ESR spectrometer ELEXSYS (Bruker, Karlsruhe, Germany) The UV−vis spectrometer was used in the kinetic mode with external trigger using an integration time of 80 ms. A deuterium lamp and a halogen lamp served as a light source, and the spectrometer was connected by optical wave guides to the modified optical ESR cavity (ER 4104 Bruker, Karlsruhe, Germany) with its special adapters for this application. A silver chloride-coated silver wire in the same electrolyte as used for the spectroelectrochemical measurement was used as reference electrode and was fixed in a thin flexible Teflon tube with outer diameter less than 300 mm. One end of the tube was located close to the active electrode surface of the laminated Au mesh inside the flat cell.[20] A rectangular black mask with a hole smaller than the active electrode surface of the laminated Au mesh was fixed on the flat cell. Thus, the replacement of the electrode and the repositioning to the same position without changing the baseline of the UV−vis spectrum can be done. The deposition of the PNMA film is possible to make outside the cell under standard conditions as used in earlier investigations.[21,22]

The preparation of the laminated Au mesh working electrode was described elsewhere.[20] PNMA film was electrodeposited on a transparent Au mesh electrode by cyclic voltammetry for 10 cycles outside the ESR cavity in a standard electrochemical cell. A thin PNMA film was made to let the light pass through.

3. Results and Discussion

3.1. In Situ Conductance Measurement. The charge transport in PANI has been described as quasi-one-dimensional conductor with three-dimensional "metallic" states.[23] The significant charge-interchain-transfer rate inside the crystalline region is supposed to result in the "metallic" bundles. Between the bundles are the amorphous (less-ordered) regions in which charge hopping dominates the macroscopic conductivity. The classic metallic transport data have been obtained from conducting PANI samples.[24] By means of low and high field ESR measurements, it has further been proved that the conducting properties of PANI and PNMA are predominantly caused by a three-dimensional charge hopping between different polymeric chains rather than by one-dimensional solitary conducting chains.[25] However, the intrinsic property of the charge carrier is still under debate.

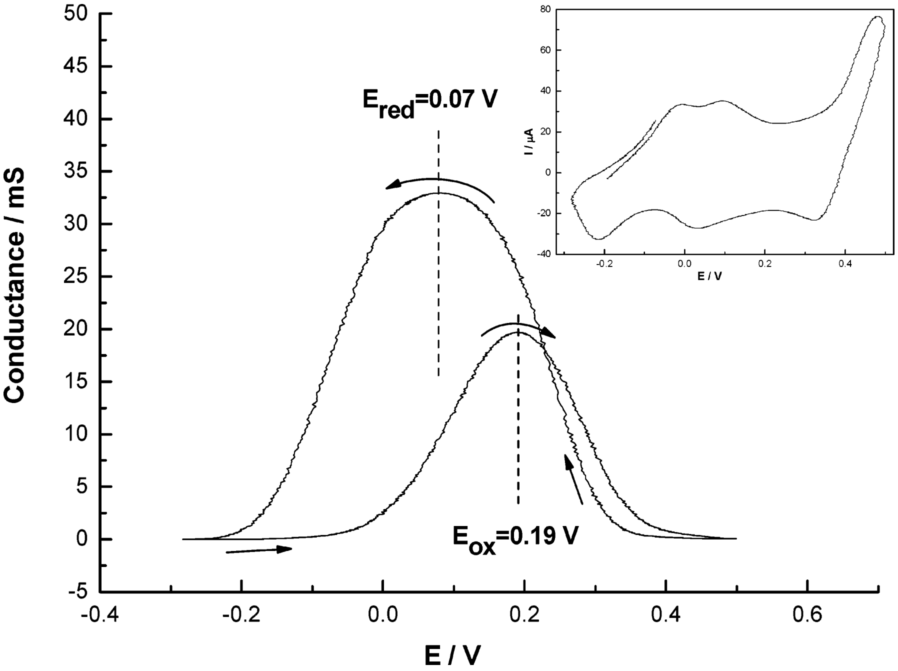


Figure 1. In situ conductance measurement during doping of PNMA film in 1 M CF_3COOH aqueous solutions by cyclic voltammetry at a scan rate 10 mV/s, −0.3 to 0.5 V, one cycle.

PNMA film was obtained by electropolymerization via cyclic voltammetry for 40 cycles. As we have discussed in a previous paper,[17] PNMA is considered to exist in three redox states, among which the emeraldine (E) form is the only conducting form. Neither the fully reduced leucoemeraldine (LE) form nor the fully oxidized pernigraniline (PN) form is conducting. The relationship between these three states is shown in Scheme 1.

The change in conductance during the redox doping of PNMA is shown in Figure 1. Conductance measurement was taken simultaneously during the doping of PNMA with a scan rate of 10 mV/s in the monomer-free aqueous solution containing 1 M trifluoroacetic acid. The highest conductance value during p-doping appears at ca. 190 mV. It decreases when the potential sweeps further in the anodic direction, while PNMA is transformed from its E state to the insulating fully oxidized PN state. However, the conductance will increase again during the reverse scan, and the potential for the highest conductance shifts to a less positive value (ca. 70 mV). This hysteresis in the conductance may be due to the time-dependent charge distribution and rearrangement of the conjugated backbones. Change of spins and optical properties in the similar condition where in situ conductance measurement was carried out may help to study the intrinsic charge carriers that are responsible for the conductance.

3.2. In Situ ESR/UV−Vis−NIR Spectroscopy. The PNMA film was deposited on a transparent Au mesh electrode by electropolymerization. After that, the electrode was fixed in the spectroelectrochemical cell, and a cyclic voltammogram was taken with the scan rate of 5 mV/s, during which 21 UV−vis−NIR and ESR spectra were recorded simultaneously. The electrolyte used for electrochemical doping is the same as that in the conductance measurements. In situ ESR spectra are shown in Figure 2.

During the forward cycle in the anodic direction in Figure 2, the ESR intensity first increases, reaching a maximum at 180 mV, and then decreases to a minimum again at 500 mV. During the reverse cycle to the cathodic direction, the ESR signal reaches a maximum at 20 mV and then decreases. The potential values where the maximum number of spins appears match quite well with the potential values of the highest conductance (E_{ox} = 190 mV, E_{red} = 70 mV in Figure 1). This experiment shows that the spin concentrations correlate with the electronic conductance of the PNMA film. Monkman et al. reported the evidence of polaron formation during oxidation of PANI at the potential of ca. 190 mV.[26] For further oxidations exceeding 200 mV during the p-doping, both the conductance and the ESR signal decrease.

Polarons are supposed to be the predominant charge carriers in nondegenerate polymers such as polypyrrole and PANI. Formation of polarons stabilizes the charge associated with the electron removal/addition from/to the conducting polymer structure, which causes a local distortion. The distortion in the ground state causes shift of HOMO upward and LUMO downward. Polarons usually exhibit two strong electronic absorption transitions in the UV-vis-NIR regions, and these two bands originate from dipole-allowed transitions as shown in Scheme 2.

At higher doping levels, bipolarons, which are double-charged spinless segments, are assumed to be formed and give rise to the high conductivity as observed in many conducting polymers concomitant with the absence of unpaired spins in electron spin resonance (ESR) spectroscopy measurements. Conducting polymers, such as polypyrrole, are known for these spinless conducting states.[27−31] The absence of paramagnetism in the metallic conducting state of polypyrrole was assigned to the formation of bipolarons.[27] Both polarons and bipolarons are considered to contribute to the conduction of polypyrrole. This is clearly distinctive to PNMA, which becomes insulating at spinless states as shown in our experimental results (Figures 1 and 2). PANI and its derivatives are different from polypyrrole in that the nitrogen atoms participate in conjugation and they do not have the bipolaronic spinless conducting state.

The support of the generation of bipolarons is only provided by the loss of ESR signal at higher doping levels. However, the direct formation of bipolarons via binding of a pair of polarons is reported to be suppressed by the Coulombic repulsion.[32] Paasch et al.[33] have theoretically studied the formation of different complexes of polarons and bipolarons

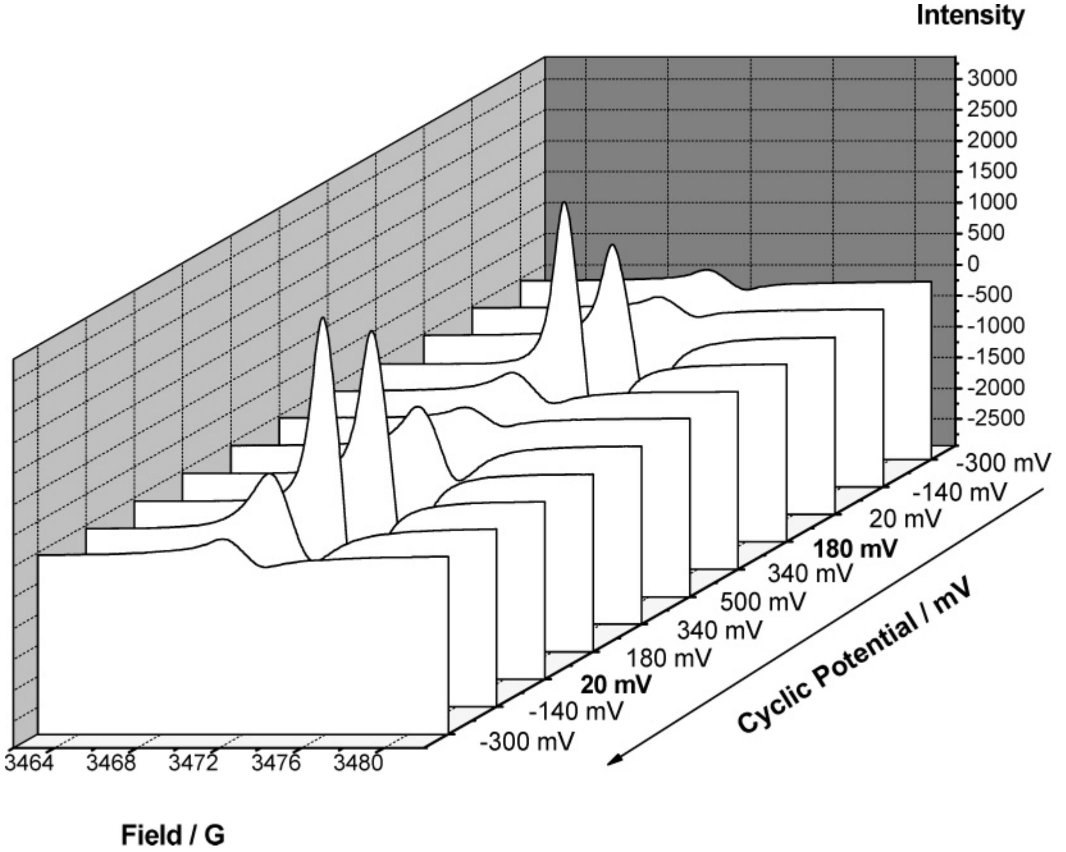
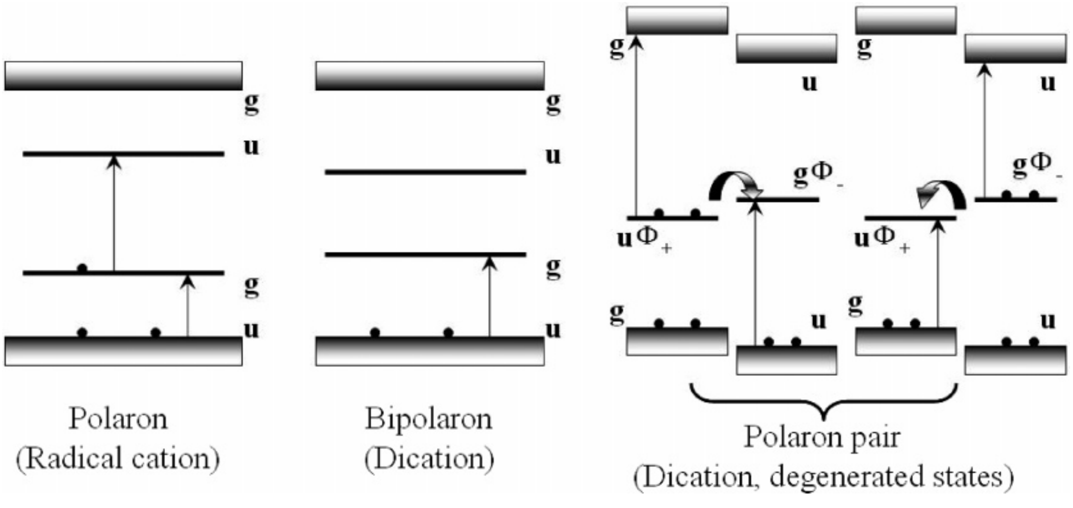


Figure 2. In situ ESR spectra during doping of PNMA film in 1 M CF_3COOH aqueous solutions by cyclic voltammetry at a scan rate 5 mV/s, −0.3 to 0.5 V, one cycle.

SCHEME 2: Scheme for the Energy Levels of the Positive Polaron, Bipolaron, and Polaron Pair[a]



[a] The arrows indicate the dipole-allowed optical transitions. The parities of the levels are indicated by u for ungerade (odd) and g for gerade (even). Φ_+ and Φ_- represent different spatial symmetry in polaron pairs.[34]

with the counterions in conducting polymers and proved this assertion. The theoretical predictions for the electronic spectra of bipolarons do not always match the experimental results.[34] In addition, the conductivity of some conjugated polymers will decrease drastically at high doping levels instead of becoming bipolaronic spinless conducting.[35] Van Haare et al.[34] studied the redox states of oligothiophenes with different lengths. In their report, polarons and bipolarons have been characterized for short-chain oligomers. The electronic structure of long oligomers is not in accordance with the expected features of a bipolaron, but proved to be “two polarons on a single chain”. π-Dimers have also been observed in radical cations of oligothiophenes.[36] π-Dimer is considered as a face-to-face complex of two radical cations interacting through their π-orbitals. In the view of equilibrium and kinetics, the π-dimer and “two polarons on a single chain” are basically equivalent and always denoted as polaron pair, which is neither ESR active.[37] The schematic representations of the positive polaron, bipolaron, and polaron pair are illustrated in Scheme 2. The most appropriate experimental evidence for the existence of mid-gap states in these doping induced quasi-particles is derived from spectroscopy. Paasch et al.[37] also reported that the polaron pair model is in accordance with the optical spectra of some conducting polymers. Although bipolarons and polaron pairs

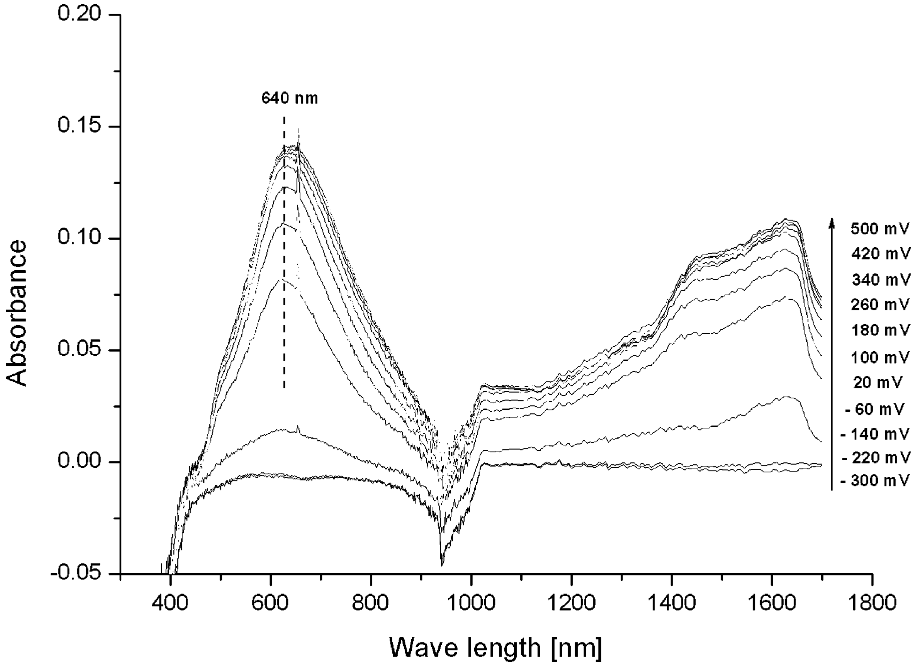


Figure 3. In situ UV−vis−NIR spectra during doping of PNMA film in 1 M CF_3COOH aqueous solutions by cyclic voltammetry at a scan rate 5 mV/s, −0.3 to 0.5 V (the anodic direction), one cycle.

are both double-charged ESR silent species, the crucial difference between them in optical properties is that bipolaron has one absorption band from dipole-allowed transition in the UV−vis−NIR spectrum while polaron pair has two absorption bands ($u\Phi_+ \rightarrow g$ and $u \rightarrow g\Phi_-$) as shown in Scheme 2. The double-charged polaron pairs are supposed not to be conducting, because the hopping probability of two charges in a single chain simultaneously is too small.

The optical properties of conducting polymers are important to understand the electronic structure of these materials at higher doping levels.[38] UV−vis−NIR spectra were recorded in situ when a cyclic voltammetry sweep was taken simultaneously with a scan rate of 5 mV/s. In situ UV−vis−NIR spectra in the forward cycle to the anodic direction (from −300 to 500 mV) during doping are shown in Figure 3.

During the whole oxidation, two bands in the UV-vis-NIR region (640 and 1600 nm) increase, whereas the spins show a maximum concentration at medium potentials. This pair of absorptions may be from the spinless polaron pairs, because bipolaron will only give one absorption band from dipole-allowed transition in the UV−vis−NIR spectrum.[34] The two expected absorptions of the formed polarons might be hidden by the absorption of the polaron pairs.

Formation of polaron pairs causes the localization of polarons, and this may be responsible for the disappearance of spin and decrease in conductance at high doping levels in PNMA.

4. Conclusions

At the early stage of the oxidation process, the repeating units in the PNMA backbone are oxidized to form polarons. Polarons are correlated to the conductance of the film. Upon further oxidations, PNMA does not show the bipolaronic spinless conducting characteristics; instead, it becomes insulating and spinless. Optical methods such as UV−vis−NIR were coupled with cyclic voltammetry to study the different oxidation states of PNMA film during the electrochemical doping. For further oxidations, polaron pairs that are evidenced by the two absorptions in the in situ UV−vis−NIR spectra will appear. Polaron pairs do not have paramagnetic susceptibility and thus do not contribute to ESR signal. The results from ESR studies and in situ conductance are consistent, and this phenomenon was also observed for highly sulfonated poly(aniline).[40] Because the hopping probability of two polarons on a single chain is too small, polaron pairs do not contribute to conductance. The charge carriers that are responsible for the conductance of PNMA are most probably polarons.

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