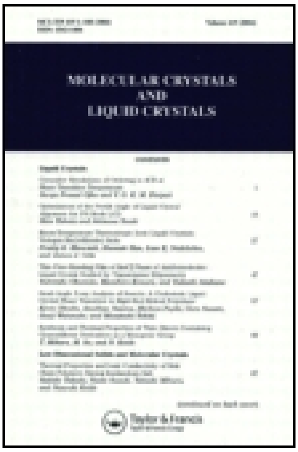

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl18

In Situ Spectroelectrochemical Investigation of the Solvent Effect on Polyaniline and Polypyrrole

Jürgen Lippe [a] & Rudolf Holze [a]
[a] Universität Oldenburg, Fachbereich Chemie, Carl-von-Ossietzky-Strasse 9-11, W-2900, Oldenburg, F.R.G.

To cite this article: Jürgen Lippe & Rudolf Holze (1991): In Situ Spectroelectrochemical Investigation of the Solvent Effect on Polyaniline and Polypyrrole, Molecular Crystals and Liquid Crystals, 208:1, 99-108

To link to this article: http://dx.doi.org/10.1080/00268949108233947

Mol. Cryst. Liq. Cryst., 1991, Vol. 208, pp. 99–108
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

In Situ Spectroelectrochemical Investigation of the Solvent Effect on Polyaniline and Polypyrrole

JÜRGEN LIPPE and RUDOLF HOLZE*

Universität Oldenburg, Fachbereich Chemie, Carl-von-Ossietzky-Strasse 9-11,
W-2900 Oldenburg (F.R.G.)

(Received February 11, 1991; in final form April 15, 1991)

A combination of in situ conductivity, ESR and UV-vis measurements as a function of the electrode potential is applied to study in detail the pH-influence of aqueous solutions containing sulfate anions and the effect of nonaqueous solution with $LiClO_4$ on polyaniline (PANI) and polypyrrole (PPy). Upon electrochemically oxidizing both polymer films in acidic solution, the conductivity increases by a factor of 10^4–10^5. Changing pH from 0.8 to 7 lowers the conductivity values and the anodic potential limit, to which the polymers can be taken without irreversible degradation. Even at pH = 7 considerable conductivity changes are detected.

According to ESR measurements, maximum spin density is found during the transition of the polymers between the insulating and the fully conducting state. With UV-vis spectroscopy only in the case of PANI in acidic solution an optical absorption located at 430 nm can clearly be ascribed to the spin state, but at pH = 7 this characteristic absorption band disappears.

On the basis of the polaron-bipolaron model, the results strongly favor a bipolaronic conduction model for PANI and PPy. The observed pH-effect can be explained with a diminished chemical stability of bipolarons in aqueous solution of higher pH.

Keywords: electrochemistry, spectroelectrochemistry, conductivity, polaron-bipolaron model, pH-effect

INTRODUCTION

Polyaniline (PANI) and polypyrrole (PPy) have aroused considerable interest, because of their potential application in a variety of areas, e.g., batteries, sensors, optical and electronic devices. Due to the subtle interplay of the different properties of conducting polymers, such as color, morphology and electrical behavior, fundamental research is necessary in order to understand and take better advantage of these unique material properties. For this purpose the combination of electrochemical techniques and a variety of spectroscopic methods has proven to be a powerful approach, termed spectroelectrochemistry. While keeping the polymer under potential control corresponding to a specific dopant concentration, FTIR,

---

*Author to whom correspondence should be sent.

ESR, UV-vis spectroscopy and the electrochemical impedance technique have repeatedly been employed to study the concurrent molecule changes taking place in the polymer network upon doping and undoping. In consequence, the polaron-bipolaron model has been developed to account for most spectroscopic results. However, in the literature controversial predictions are made concerning the participation of polarons and bipolarons in the mechanism of conductivity.

Concluding from the narrow linewidth of the obtained ESR signals in PANI some authors[1,2] assume polarons as highly delocalized charge states implying that a polaron lattice is responsible for conductivity in fully oxidized PANI.[3-6] On the other hand, Kaya *et al.*[7] find no direct correlation between the electron spins detected by ESR and the electric conductivity of PANI. For PPy, most reports favor a bipolaronic conduction model. Kaufmann *et al.*,[8] for instance, give UV-vis evidence for the evolution of polarons states into bipolarons in oxidized PPy. Nevertheless, Olmedo *et al.*[9] conclude from four-point-conductivity measurements after comparison with ESR results measured elsewhere[10] that most of the conductivity is due to polarons.

When comparing experimental results, it is important to check the experimental conditions applied during polymer preparation and measurements. The selected preparation technique, for instance, determines the morphological structure of the polymer films and has a strong influence on the resulting chemical and physical properties.[11] Thus, taking the vast amount of different experimental handling performed in the various laboratories into account, caution must be exercised in contemplating previous interpretations.

Fortunately, newly devised electrodes, such as the microelectrode array[12] and the two-band-gap electrode[13,14] have made it possible to monitor in situ the conductivity of polymers as a function of the electrochemical potential. Recent experiments[15-17] show that this new technique allows reliable comparison of conductivity data with spectroscopic results (i.e. at each dopant concentration) and should consequently enable a better characterization of the charge carriers in conducting polymers, in contrast to the confusion in the literature mentioned above. This is the objective of our work.

In this paper we report the results of in situ conductivity, ESR and UV-vis measurements of PANI and PPy as a function of the electrochemical potential in aqueous and nonaqueous solution. The impact of pH-changes on the ESR and UV-vis measurements is studied and compared with the conductivity data of the polymer under the same experimental conditions. For this reason, film preparation and experimental measurements are performed in identical electrochemical potential intervals. The anions incorporated in the polymer films due to charge compensation are sulfate and perchlorate in aqueous and nonaqueous solutions respectively.

EXPERIMENT

Chemicals

All chemicals used in this study are reagent grade and used without further purification unless stated elsewhere. Aniline and pyrrole (Merck) are distilled and stored under argon in a refrigerator. Spectrophotometric grade acetonitrile (Janssen) is used as received and $LiClO_4$ is dried at 100°C under vacuum. Experimental studies are carried out in the following solvents at 25°C: 0.1 M $LiClO_4$/acetonitrile, 1 M and 0.5 M H_2SO_4, 0.1 M $NaHSO_4$, 0.05 M $NaHSO_4$ and 0.1 M Na_2SO_4. According to Karl-Fischer-titration the 0.1 M $LiCLO_4$/acetonitrile solution contains 0.04% water. In the case of aqueous solutions, the pH-value is always determined after each measurement series, in order to take possible pH-deviations during measurements into account.

Electrochemical Cells and Apparatus

A two band-gap electrode is employed for in situ conductivity measurement and comprises of two gold strips spaced approximately 20 μm apart. It is used as the working electrode in a conventional three-electrode-cell with a platinum counter electrode and a saturated calomel electrode (SCE) as a reference. Details of the electrode and conductivity measurement circuit along with the procedure of measurement can be found elsewhere.[14] Polymer films are deposited on both gold strips with a thickness of approximately 15 μm, in order to bridge the interband gap.

ESR measurements are carried out with a coaxial cell containing two helical gold wires as working and counter electrode, and a silver/silver chlorid electrode (Ag/AgCl) as reference electrode in a Bruker ER 200 D ESR spectrometer.[18]

For UV-vis measurements in aqueous solution the polymers are deposited on indium-tin-oxide (ITO) coated glass sheets (ca. 85% transmittance, ca. 300 ohm/cm resistance, Balzers, Liechtenstein), which are carefully washed with trichloroethylene and dried prior to use. Because of optical changes of ITO in 0.1 M $LiClO_4$/acetonitrile at low potentials (Li-insertion and possible interference of water), a glass slide sputtered with gold (ca. 35% transmittance, ca. 5 ohm/cm resistance, Schott, F.R.G.) is taken for measurements in acetonitrile. A gold wire is used as a counter electrode and a silver/silver chlorid electrode (Ag/AgCl) is connected through a salt bridge as reference. The UV-vis spectra are recorded with an Uvikon 810 spectrometer (Kontron) interfaced to a MAC 80A data processing system (Spectradata, Oldenburg). The reference channel of the spectrometer is always occupied by the working electrode without polymer immersed in the same solvent.

A Bank potentiostat (POS 73) is used and all potentials are reported vs. SCE.

Polymer Deposition

PANI is deposited by potentiodynamic cycling in 0.1 M aniline/1 M H_2SO_4. During the preparation the anodic voltage limit is gradually reduced to E_{SCE} = 700 mV in order to exclude possible degradation.[19] For UV-vis measurements, however, PANI is deposited potentiostatically at E_{SCE} = 750 mV in 0.1 M aniline/0.1 M $NaHSO_4$ and after 30 sec. the potential is reduced to E_{SCE} = 700 mV. PPy films are obtained from acetonitrile containing 0.1 M $LiClO_4$, 0.1 M pyrrole and 1% water at constant current (1 mA/cm^2). PANI and PPy films are rinsed with water and acetonitrile respectively.

Measurement Procedure

Except for cyclic voltammetric recordings, all measurements are performed under steady-state conditions at negligible current after holding potentials for 2–5 minutes. The anodic potential limits are adjusted adequately in order to maintain complete reversibility of the switching reaction.

In situ conductivity measurements are carried out after applying appropriate electrode potentials to both metal strips, which are contacted together as the working electrode. The two-band-gap electrode is then connected with the conductivity measurement circuit imposing 10 mV d.c. across the metal strips. The resulting current I_x stabilizes quickly and can be related to the electrical resistance R_x of the studied polymer film according to $R_x = 0.01/I_x$. The obtained resistance data are not corrected with respect to specific resistance and are discussed below in terms of the reciprocal conductivity values.

For in situ UV-vis measurements, optical spectra are run between 290 and 900 nm.

RESULTS

In Situ Conductivity of PANI and PPy

Figures 1 and 2 present the resistance behavior of PANI and PPy samples in different solvents upon reversible electrochemical doping. Similar to PPy, the conducitivity of PANI in aqueous solution increases by a factor of 10^4–10^5 at pH < 1 in agreement with Paul *et al.*[12] However electrochemical potentials of PANI films may not exceed $E_{SCE} = 550$ mV in order to prevent simultaneous degradation. At higher pH, the conductivity of oxidized PANI and PPy decreases and, in fact, the

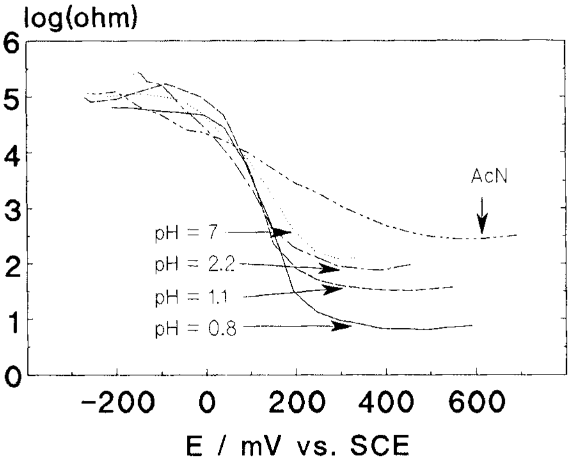

FIGURE 1 Resistivity vs. electrode potential plots of a PANI sample during the anodic electrode potential scan performed in 0.1 M $LiClO_4$/acetonitrile (AcN), 0.1 M Na_2SO_4 (pH = 7), 0.05 M $NaHSO_4$ (pH = 2.2), 0.5 M H_2SO_4 (pH = 1.1) and 1 M H_2SO_4 (pH = 0.8) are shown. Measurements are made in 50 mV steps.

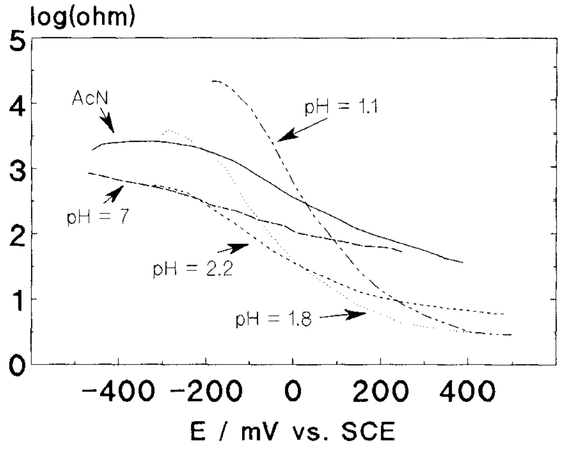

FIGURE 2 Resistivity vs. electrode potential plots of a PPy sample during the anodic electrode potential scan performed in 0.1 M $LiClO_4$/acetonitrile (AcN), 0.1 M Na_2SO_4 (pH = 7), 0.05 M $NaHSO_4$ (pH = 2.2), 0.1 M $HaHSO_4$ (pH = 1.8) and 1 N H_2SO_4 (pH = 1.1) are shown. Measurements are made in 50 mV steps.

anodic potential limit is shifted to lower values. It is noteworthy that in neutral solution, pH = 7, PANI exhibits a reversible conductivity change of 10^3 at potentials below E_{SCE} = 350 mV. Furthermore, the resistance values of PANI in the potential range of E_{SCE} = 0–150 mV seem to decline vs. potential with a similar slope in aqueous solution regardless of pH. For PPy, the resistance vs. potential curve becomes flatter at higher pH.

In acetonitrile, the conductivity change between reduced and oxidized PANI and PPy is not higher than that obtained in aqueous solution at pH = 7. For PANI, the anodic potential limit can be extended to E_{SCE} = 700 mV.

In Figure 3 the pronounced hysteresis of conductivity observed in the course of the anodic and cathodic scan is illustrated for PPy immersed in 1 M H_2SO_4.

In Situ Spin Density of PANI and PPy

The ESR signals found in PANI and PPy exhibit a linewidth of 0.5 G and 0.4 G (peak-to-peak) respectively which notably remains independent of radical concentration. The ESR signals of PANI are symmetric and have a Gaussian form at low radical concentrations and a Lorentzian form at high radical concentrations, in accordance with ESR results reported elsewhere.[5] For PPy the signals show a Dysonian form.[20] By means of double integration the corresponding relative spin density, and thus the relative polaron concentration, are evaluated.

The potential dependent changes of spin density detected for both polymers in the various solutions are shown in Figures 4–5. Starting with reduced PANI at E_{SCE} = −300 mV, radicals are detected above E_{SCE} = 0 mV. Their concentration reaches a maximum and decreases significantly at higher potentials. In acidic solutions the potential interval of maximum spin density is narrow and located at E_{SCE} = 150 mV. At higher pH, this region becomes slightly broader towards positive potentials. Upon undoping oxidized PANI the behavior is reversed exhibiting a hysteresis of E_{SCE} = −100 mV.

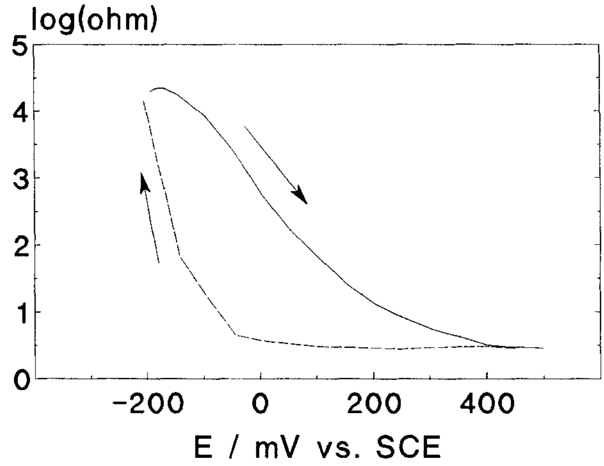

FIGURE 3 The potential dependent resistivity behavior of PPy immersed in 1 N H_2SO_4 (pH = 1.1) during anodic and cathodic electrode potential scan with 50 mV steps.

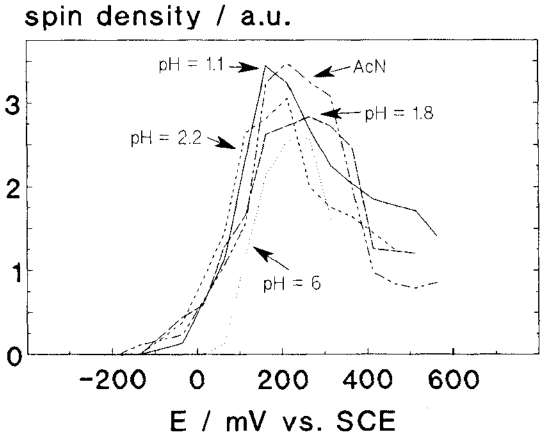

FIGURE 4 Plots of the relative spin density vs. electrode potential of PANI during the anodic electrode potential scan with 50 mV steps. The solvents used are 0.1 M $LiClO_4$/acetonitrile (AcN), 0.1 M Na_2SO_4 (pH = 6), 0.05 M $NaHSO_4$ (pH = 2.2), 0.1 M $HaHSO_4$ (pH = 1.8) and 1 N H_2SO_4 (pH = 1.1).

In the case of PPy, the electrode potentials corresponding to the generation of radicals at their highest concentration are significantly shifted to higher values, as the polymer is transferred from acetonitrile to acidic aqueous solution. In the fully conducting state the spin density diminishes nearly to zero and exhibits a strong hysteresis of ca. 150 mV in the course of reversible doping and undoping.

In Situ UV-vis spectra of PANI and PPy

The optical spectra of PANI in acidic solution exhibit three potential dependent absorption bands at 330, 430 and 800 nm, whereas at pH = 5.5 − 7 only two potential dependent bands at 330 and ca. 620 nm are observed. Figure 6 shows the

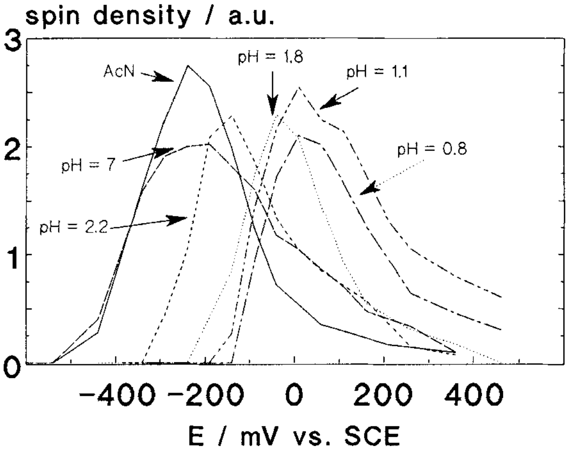

FIGURE 5 Plots of the relative spin density vs. electrode potential of PPy during the anodic electrode potential scan with 50 mV steps. The solvents used are 0.1 M $LiClO_4$/acetonitrile (AcN), 0.1 M Na_2SO_4 (pH = 7), 0.05 M $NaHSO_4$ (pH = 2.2), 0.1 M $HaHSO_4$ (pH = 1.8), 1 N H_2SO_4 (pH = 1.1) and 1 M H_2SO_4 (pH = 0.8).

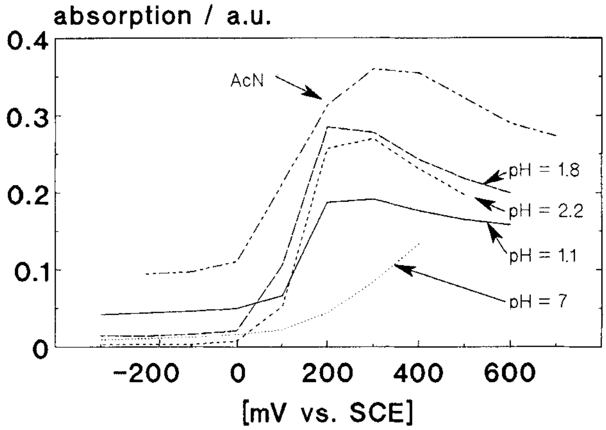

FIGURE 6 Relative absorption changes of PANI at 430 nm during the anodic electrode potential scan with 100 mV steps. The solvents used are 0.1 M $LiClO_4$/acetonitrile (AcN), 0.1 M Na_2SO_4 (pH = 7), 0.05 M $NaHSO_4$ (pH = 2.2), 0.1 M $HaHSO_4$ (pH = 1.8) and 1 N H_2SO_4 (pH = 1.1).

relative absorption changes in PANI at 430 nm as a function of the electrode potential in various aqueous solutions. In the course of doping PANI in acidic solution, the absorption of 430 nm starts to increase at E_{SCE} = 100 mV sharply and declines after a maximum at ca. E_{SCE} = 150 mV. This matches with the potential dependence of the corresponding spin density and confirms previous results of PANI in nonaqueous solution.[21] However, at pH = 7 the absorption at 430 nm vanishes even though spin density its detectable. This is probably due to the fact that the radical concentration evidenced by ESR in neutral aqueous medium is too low in order to induce a characteristic absorption band.

For PPy, we have difficulty in finding an optical absorption band which shows the same potential dependence as the spin density data and which can thus be clearly ascribed to the occurrence of polarons. This result seems puzzling in view of the fact that Kaufmann *et al.*[8] and Zotti *et al.*[21] report polaron induced absorption bands—*at 1.18 eV (ca. 1050 nm) and 530 nm respectively*—. This controversy stems to a certain extent from the altered experimental conditions applied in the various laboratories. However, in all cases no corresponding ESR results are shown which evidence the direct correlation between these absorption bands and the polaron concentration.

Nevertheless, as in the case of PANI, the absorption band of PPy at 800 nm exhibits a similar potential dependence as conductivity values.

DISCUSSION

According to Figures 1 and 2 the pH of aqueous solution has a strong impact on the conductivity behavior of both investigated polymers. Increasing pH not only lowers the conductivity jump between insulating and conducting samples, but also induces polymer degradation at lower potential values. This is in agreement with ex situ conductivity measurements by McManus *et al.*[4]

It is particularly interesting to note the conductivity change of PANI at $pH = 7$ by a factor of 10^3. In contrast, previous reports of cyclic voltammogrammic and infra-red spectroscopic recordings[22–24] are explained with the absence of a conducting state at $pH > 4$. With respect to the fact that protons are involved in the charge transfer reaction of PANI and taking our results into account, we assume that even at $pH = 7$ the amount of protons in the solvent and the polymer film is sufficient for a limited conductivity change. Due to the restricted concentration of charge carriers, it is reasonable that the corresponding potentiodynamic and optical behavior of PANI under these conditions are not the same as in acidic solutions.

In addition to the decreased conductivity values at higher pH, the anodic potential limit has to be shifted in cathodic direction in order to maintain reversible switching. An explanation for this behavior can be proposed by taking the ESR results obtained under the same experimental conditions into account. On the basis of the polaron-bipolaron model, the spin states evidenced by ESR are ascribed to radical ion states in the polymer chain, termed polarons. The loss of spin density at higher electrode potentials is explained by assuming a recombination of polarons into bipolarons.

In the literature numerous experimental reports have led to different mechanistics theories concerning the electrical conduction and assuming the existence of polarons and bipolarons in PANI and PPy. The obtained experimental results have turned out to be highly dependent upon the conditions of polymer deposition and the experimental methods employed, i.e. pH, solvent, type of anion and electrode potential. Hence, whenever discussing the theoretical models proposed by various research groups based on conclusion from their results, the details of the experiment should be kept in mind.

Extensive ESR results of PANI prepared and studied with electrochemical techniques were presented by Genies *et al.*[1,25] who electrochemically prepared and studied the polymer in highly acidic solution such as $NH_4F \times 2.3$ HF and aqueous 35% HBF_4. The ESR measurement recorded during cyclic voltammetry revealed an impressive correlation between the maximum of spin density and the first current wave of oxidation and reduction which seems to be valid for PANI in acidic solution in general. The evaluation of the ESR signals at different potentials showed that the signal width decreased from $H = 1.8$ G at low polaron concentration to $H = 0.5$ G at maximum polaron concentration.[1] Referring to the studies of Epstein *et al.*[26,27] of chemically prepared and acid doped polyemeraldine, the narrow ESR signals were ascribed to polarons with a high degree of delocalization along the polymer chain in the potential interval of their maximum concentration. This specific state assumed in PANI has been termed polaron lattice. In the opinion of Genies *et al.* this polaron lattice leads to the aggregation of high conductivity metal-like islands bearing very delocalized electrons comparable to those in metallic orbitals, which should consequently be responsible for electronic conduction in PANI. This implies that the degree of conductivity should be directly dependent upon the polaron concentration and thus the observed ESR absorption in the polymer.

Unfortunately, extensive in situ conductivity measurements in the same solvents are missing and those performed parallel to ESR studies by other research groups have delivered no unambiguous evidence for the polaron-conducting theory. In fact, the results obtained by Paul *et al.*[12] of PANI in aqueous sulphuric acid (0.5 M $NaHSO_4$) show that highest conductivity values are obtained at potentials beyond the first oxidation wave. In this potential region, however, the polaron concentration declines sharply which is indicated by the decreasing ESR absorption (see e.g. Figure 4). This discrepancy in the spin-conductivity correlation was already noticed by Kaya *et al.*[7] and contradicts the polaron-conduction theory outlined above.

As compared to the different experimental conditions applied by the different authors our studies offer the advantage of examining the course of spin density and electrical conductivity in situ as a function of the electrode potential under the same conditions. In this context we must stress that our results and proposed interpretation account for the behavior of PANI in aqueous sulphate solution of various pH and in nonaqueous solution with perchlorate anions.

According to our experimental results with both PANI and PPy, maximum polaron concentration is always found during the transition of the polymers between the insulating and the fully conducting state, whereas in the state of highest conductivity only a small concentration of polarons is detectable. In consequence, bipolarons are apparently the primary charge carriers for electronic conductivity. The pH-influence on the anodic potential limit, to which the polymers can be taken without irreversible degradation, can be explained with the lower chemical stability of bipolarons in aqueous solution of higher pH. Due to their positive charge, bipolarons are more prone to nucleophilic attack of the solvent, e.g. the OH^- ions. At higher pH, the concentration of OH^- ions is increased and favors an irreversible chemical reaction of OH^- ions and bipolarons already at lower bipolaron concentrations. Thus, in order to avoid polymer degradation, the bipolaron concentration has to be restricted by means of a lower anodic potential limit.

Acknowledgments

The authors gratefully acknowledge financial support from the Fonds der Chemischen Industrie; gold-coated sheets were supplied by Schott.

References

1. M. Lapkowski and E. M. Geniès, *J. Electroanal. Chem.*, **279**, 157 (1990).
2. S. M. Yang and T. S. Lin, *Synth. Met.*, **29**, E227 (1989).
3. K. Tanaka, S. Wang and T. Yamabe, *Synth. Met.*, **36**, 129 (1990).
4. P. McManus, R. J. Cushman and S. C. Yang, *J. Phys. Chem.*, **91**, 744 (1987).
5. T. Ohsawa, T. Kabata and O. Kimura, *Synth. Met.*, **29**, E203 (1989).
6. N. S. Sariciftci, M. Bartonek, H. Kuzamany, H. Neugebauer and A. Neckel, *Synth. Met.*, **29**, E193 (1989).
7. M. Kaya, A. Kitani and K. Sasaki, *Chem. Soc. Jpn.*, 147 (1986).
8. J. H. Kaufman, N. Colaneri, J. C. Scott and G. B. Street, *Phys. Rev. Let.*, **53**, 1005 (1984).
9. L. Olmedo, I. Chanteloube, A. Germain and M. Petit, *Synth. Met.*, **30**, 159 (1989).
10. M. Nechtschein, F. Devreux, F. Genoud, E. Vieil, J. M. Pernaut and E. Genies, *Synth. Met.*, **15**, 59 (1986).
11. D. Bloor, A. P. Monkman, G. C. Stevens, K. M. Cheung and S. Pugh, *Mol. Cryst. Liq. Cryst.*, **187**, 231 (1990).
12. E. W. Paul, A. J. Ricco and M. S. Wrighton, *J. Phys. Chem.*, **89**, 1447 (1985).
13. G. Schiavon, S. Sitran and G. Zotte, *Synth. Met.*, **32**, 209 (1990).
14. R. Holze and J. Lippe, *Synth. Met.*, **38**, 99 (1990).
15. G. P. Kittlesen, H. S. White, M. S. Wrighton, *J. Am. Chem. Soc.*, **106**, 7389 (1984).
16. J. W. Thackeray, H. S. White and M. S. Wrighton, *J. Phys. Chem.*, **89**, 5133 (1985).
17. D. Ofer, R. M. Crooks and M. S. Wrighton, *J. Am. Chem. Soc.*, **112**, 7869 (1990).
18. A. Heinzel, R. Holze, C. H. Hamann and J. K. Blum, *Z. Phys. Chem.*, **160**, 11 (1989).
19. J.-C. LaCroix and A. F. Diaz, *J. Electrochem. Soc.*, **135**, 1457 (1988).
20. S. Dong, J. Ding and R. Zhan, *J. Chem. Soc. Faraday Trans. 1*, **85**(7), 1599 (1989).
21. G. Zotti and G. Schiavon, *Synth. Met.*, **30**, 151 (1989).
22. A. Kitani, J. Izumi, J. Yano, Y. Hiromoto and K. Sasaki, *Bul. Chem. Soc. Jpn.*, **57**, 2254 (1984).
23. W. E. Rudinski, L. Lozano and M. Walker, *J. Electrochem. Soc.*, **137**, 3132 (1990).
24. H. Neugebauer, A. Neckel, N. S. Sariciftci and H. Kuzmany, *Synth. Met.*, **29**(1), E185 (1989).
25. E. M. Genies and M. Lapkowski, *J. Electroanal. Chem.*, **236**, 199 (1987).
26. A. J. Epstein and A. G. MacDiarmid, *Mol. Cryst. Liq. Cryst.*, **160**, 165 (1988).
27. A. J. Epstein, J. M. Ginder, F. Zuo, H. S. Woo, D. B. Tanner, A. F. Richter, M. Angelopoulos, W. S. Huang and A. G. MacDiarmid, *Synth. Met.*, **21**, 63 (1987).