Photoexcited spectroscopy and in situ electrochemical spectroscopy in conjugated polymers: a comparative study

H. Neugebauer[*], C. Kvarnström[1], A. Cravino, T. Yohannes[2], N.S. Sariciftci

Physical Chemistry, Johannes Kepler University Linz, Altenbergerstraße 69, A-4040 Linz, Austria

Abstract

A comparison of doping and photoinduced IRAV spectra of conjugated polymers with more complex structures is presented. Differences in behavior regarding the comparison of p- and n-doped states of different materials were observed. In contrast, a comparison between doped and photoinduced IRAV spectra often show a similar band pattern. Our results do not agree with the predictions given by theoretical descriptions, which were developed for simpler structures. From these theories, the same IRAV pattern for p- and n-doping, but differences to photoinduced IRAV should be expected. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: IRAV bands; Conjugated polymers; Chemical doping; Photodoping; Spectroelectrochemistry

1. Introduction

Vibrational spectroscopy is a powerful technique to investigate conjugated polymers since a strong coupling between vibrational and electronic excitations exists in this class of materials. Much work has been done, both from theoretical and experimental point of view, for understanding the vibrational spectra of simple conjugated polymers in their pristine and doped forms [1]. However, mostly due to theoretical difficulties, detailed studies on the vibrational structure of more complex systems are rather rare.

The infrared spectra of conjugated polymers exhibit upon doping very intense infrared active vibration (IRAV) bands correlated to a strong electron–phonon coupling, which is an extraordinary behavior of these quasi one-dimensional systems. These bands are of great importance, because they provide an unambiguous proof for the existence of charged excitations ("quasi-particles") like charged solitons or polarons on the polymer chain. Since IRAV bands are related to molecular vibrations, they contain information on the structure, but also, due to the electron phonon coupling, they provide information on the electronic properties. Usually,

IRAV bands are accompanied by broad electronic absorptions with maxima at higher energies (mostly between about 0.2 and 0.6 eV, corresponding to 1500 and 5000 cm^{-1}), due to electronic transitions involving new quasi particle states in the band gap.

Several theoretical descriptions to explain these unusual spectroscopic properties have been presented. The Horovitz theory [2–4] considers the charge density wave which exists in the dimerized form of trans-polyacetylene with the fact that π-electrons are coupled to the motion of the polymer backbone. The "pinning parameter" is used as a measure of localization. Zerbi and coworkers showed the correlation of the IRAV bands with the infrared activation of totally symmetric modes which contain a contribution by the "effective conjugation coordinate" [5,6]. This coordinate basically describes the changes of geometry from the ground state to the excited electronic state of the polymer. The smaller the value of the "effective conjugation force constant" the larger the "effective conjugation" of the polymer backbone. Recently Ehrenfreund and Vardeny established a link between the doping induced electronic states within the semiconducting $\pi \rightarrow \pi^*$ energy gap and the IRAV bands of the doping induced infrared spectrum [7]. Their model is based on a linear response theory by Soos and coworkers [8]. Furthermore, there are theoretical descriptions unifying these models [9–11].

Most of the models propose that the IRAV patterns obtained either by p- or by n-doping are similar. In addition, photoinduced IRAV bands (photoinduced absorption, PIA) should occur usually at lower energies than doping induced

---

[*] Corresponding author. Tel.: +43-732-2468-8766; fax: +43-732-2468-8770.

E-mail address: helmut.neugebauer@jk.uni-linz.ac.at (H. Neugebauer).

[1] Present address. Åbo Akademi University, Process Chemistry Group, c/o Laboratory of Analytical Chemistry, FIN-20500 Åbo-Turku Finland.

[2] Present address. Chemistry Department, Addis Ababa University, Addis Ababa, Ethiopia.

bands, since the pinning in the absence of counterions should be lower. With conjugated polymers with relatively simple stuctures (e.g. polyacetylene, polythiophene), these predictions have been confirmed experimentally in many studies. On the other hand, some complex systems are promising candidates for applications, since they combine processability with low electronic band gaps and unusual optical properties [12,13]. A detailed description of the vibrational properties of these materials is necessary for a basic understanding of their behavior.

Doping can be performed chemically by oxidation or reduction processes, or by photodoping. A preferential way of chemical doping is by electrochemical doping, where the oxidation or reduction reactions are initiated by the electrode potential. In this way, an easy control on the doping processes by controlling electrochemical parameters like electrode potential or electrochemical charge can be obtained. Using special techniques (e.g. in situ Fourier transform infrared attenuated total reflection spectroscopy, FTIR-ATR spectroscopy), a direct observation of the infrared spectral changes during electrochemical reactions is possible [14–16]. In this work, a comparison between electrochemically p- and n-doped conjugated polymers, and between doping induced and photoinduced IRAV spectra of conjugated polymers with complex structures is presented.

2. Experimental

In situ FTIR-ATR spectrocopy has been described in previous publications [17–19]. In principle, the working electrode consists of a germanium reflection element covered with a film of the conjugated polymer, in contact with the electrolyte solution (Fig. 1).

During electrochemical reactions of the polymer film, FTIR spectra are recorded by the ATR method. By relating the spectra to a reference spectrum recorded just before the electrochemical process, difference spectra showing only the spectral changes during p- or n-doping are obtained. For measuring PIA infrared spectra, a polymer covered IR transparent substrate was mounted in a cryostat with ZnSe
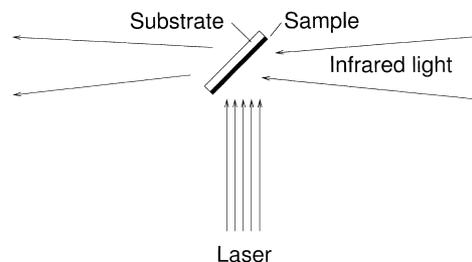

Fig. 2. Setup for infrared photoinduced absorption (PIA).

windows and cooled with liquid nitrogen. The sample was illuminated in 45° geometry through a quartz window of the cryostat by an Ar^+ laser (488 nm, 30 mW/cm^2). The PIA setup is shown in Fig. 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.

3. Results and discussion

3.1. PEDOT

Conducting poly(3,4-ethylenedioxythiophene), PEDOT (structure shown in the inset of Fig. 4), has properties like high stability [20,21], high electrical conductivity [22,23] and a low optical band gap of approximately 1.6 eV [24], making this material a candidate for many industrial applications. Among electrically conducting polymers, PEDOT has been shown to have one of the lowest redox potentials for p-doping. The material is one of the very few examples within the conjugated conducting polymer family which is both p- and n-dopable. In situ FTIR-ATR spectroscopy was performed during both signs of electrochemical doping [25–27]. The results are compared in the vibrational part of the spectra in Fig. 3 and in an extended scale (including the broad electronic transition) in Fig. 4.

Since the amount of n-doping in our experiments was much less than during p-doping, the spectrum of the n-doped
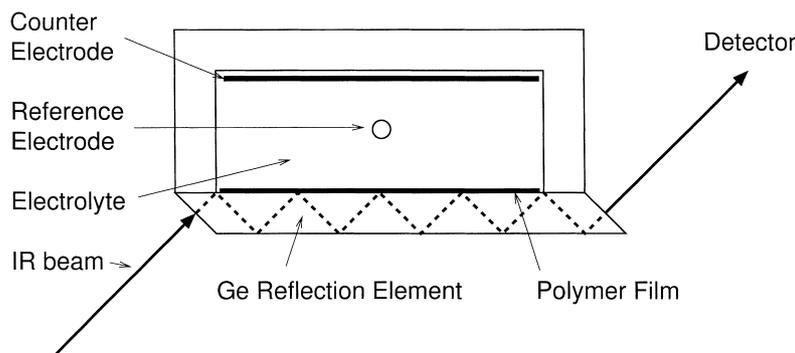

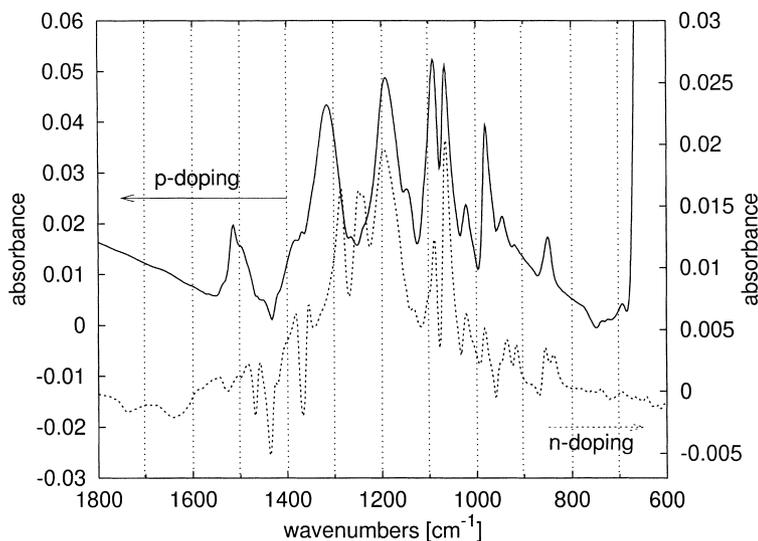Fig. 1. Setup for in situ FTIR-ATR spectroelectrochemistry.

Fig. 3. Comparison of difference spectra obtained during electrochemical oxidation (p-doping) and reduction (n-doping) of PEDOT with the same doping degree of about 2.5% per repeating unit.

form is compared with the spectrum of a p-doped form of similar doping level. The doping level was around 2.5% estimated from the electrochemical charge ratio to fully p-doped PEDOT, which is assumed to be 25% as usually found in thiophene based conjugated polymers [28]. As can be seen, differences in the p- and n-doped form are observed: (1) the band at 1513 cm^{-1} is missing in the n-doped form; (2) instead of the band at 1315 cm^{-1} in p-doping two new bands at 1285 and 1245 cm^{-1} are seen in n-doping; (3) the maximum of the electronic absorbance is found at just above 4000 cm^{-1} for n-doping instead of around 3000 cm^{-1} for p-doping; (4) the relative intensities of the bands are different in the two differently charged forms; (5) the intensities of the bands in n-doping are generally lower than the intensities of fully p-doped material.

A direct correlation to the calculated force field of polythiophene could not be obtained. Obviously, the nature of the charge carriers for both signs of doping are not the same. The lower intensities of the IRAV bands together with the maximum of the electronic absorption at higher energies indicate a higher localization of the doping induced charge carriers and a smaller effective conjugation in n-doped PEDOT.

3.2. pDTT3

Poly(dithieno[3,4-b:2′,3′-d]thiophene) (pDTT3, structure shown in the inset of Fig. 6), belongs to the group of the so-called "low band gap" polymers, with a "polythiophene-like" chain, where an aromatic moiety is fused to each
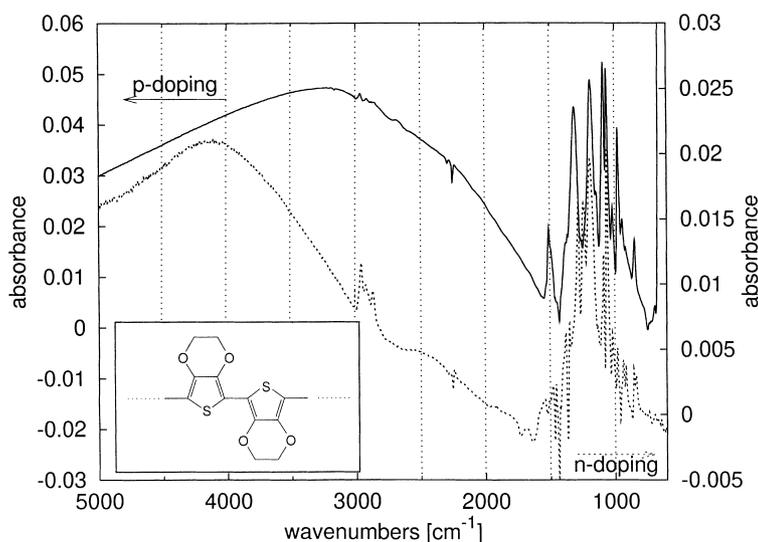

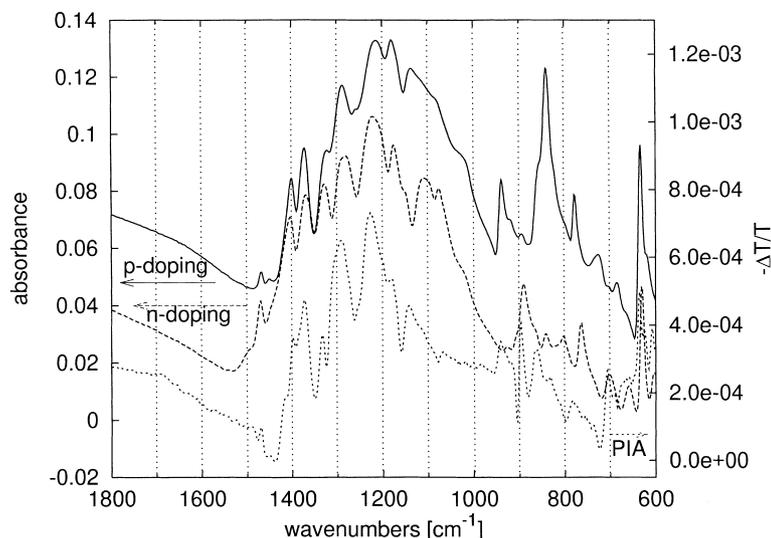Fig. 4. Spectra of Fig. 3 in extended scale. The inset shows the structure of PEDOT.

Fig. 5. Comparison of difference spectra obtained during electrochemical oxidation (p-doping) and reduction (n-doping) of pDTT3, with the PIA spectrum.

thiophene ring. The π-electron delocalization along this "polythiophene-like" chain is deeply affected by π-electrons within the other two rings of the monomer. The energy gap is about 1.05 eV, which is among the lowest values reported until now [13]. This property associated with the fact that the polymer undergoes both p- and n-type electrochemical doping in organic electrolytes, makes the material highly interesting for various applications such as redox capacitors, or electrochromics and photovoltaic devices.

The development of IRAV bands, related to charge carriers injected onto the polymer chain, is observed upon both p- and n-doping [29] and compared to photoinduced IRAV bands in Figs. 5 and 6 for the IRAV range and the extended spectral range, respectively.

With all doping methods, a complicated band pattern appears. The narrow band at 842 cm^{-1} is due to the incor-

poration of hexafluorophosphate counterions, which balance the positive charge on the polymer formed during p-doping. The IRAV bands arising during n-doping give a spectrum similar to the spectrum of the p-doped material. Besides slight differences in the relative intensities, especially above 1000 cm^{-1} all the spectral features are present in both spectra of p- and n-doped pDTT3. In contrast to PEDOT, also the intensities are similar. The most striking difference is the missing hexafluorophosphate band at 842 cm^{-1} in the n-doped polymer. Moreover, except a different maximum of the electronic absorption at higher energy, the photoinduced FTIR spectrum of pDTT3 is highly similar to the electrochemically induced IR spectra. The presence of two derivative-shaped features at about 900 and 710 cm^{-1} is probably due to the heating-induced shift of the corresponding bands observed in the absorption spectrum of the neutral
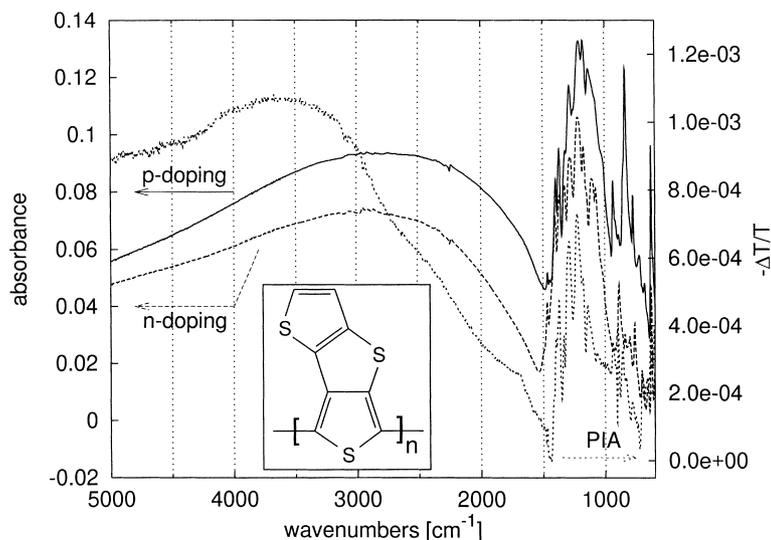

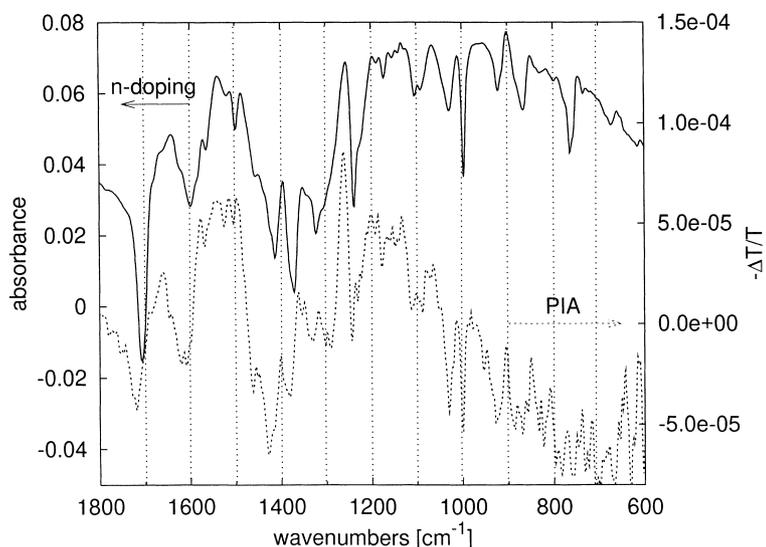Fig. 6. Spectra of Fig. 5 in extended scale. The inset shows the structure of pDTT3.

Fig. 7. Comparison of difference spectra obtained during electrochemical reduction (n-doping) of BBL in the first reduction process, with the PIA spectrum.

form of the polymer. The high similarity between the spectral signatures suggests that the nature of the photo-induced charge carriers and the doping induced charge carriers of both signs is very similar.

3.3. BBL

For applications in optoelectronic devices, such as photo-detectors, organic solar cells, light emitting diodes, organic thin film transistors, or chemical sensors, n-dopable polymers, which show reversible chemical or electrochemical reduction reactions, are of great importance. The conjugated polymer poly[(7-oxo-7, 10-benz[de]-imidazo[4′,5′:5,6] ben-zimidazo[2,1-a] isoquinoline-3, 4:10, 11-tetrayl)-10-carbo-

nyl], abbreviated as BBL (structure shown in the inset of Fig. 8) is a member of a class of materials called ladder polymers, which are double-stranded, highly conjugated macromolecules with rigid chain structure. BBL is n-dopable and has one of the highest electron affinity values among known semiconducting polymers [30–32].

Experimental and theoretical studies on structural changes and redox mechanisms of BBL during reduction have been discussed in the literature [30,33]. It was found, that the reduction of BBL occurs in several steps. Wilbourn and Murray reported that BBL shows two main redox waves during reduction in the cyclic voltammogram using tetrabutylammonium as a cation [30]. In another paper, Wilbourn and Murray studied how the conductivity varies
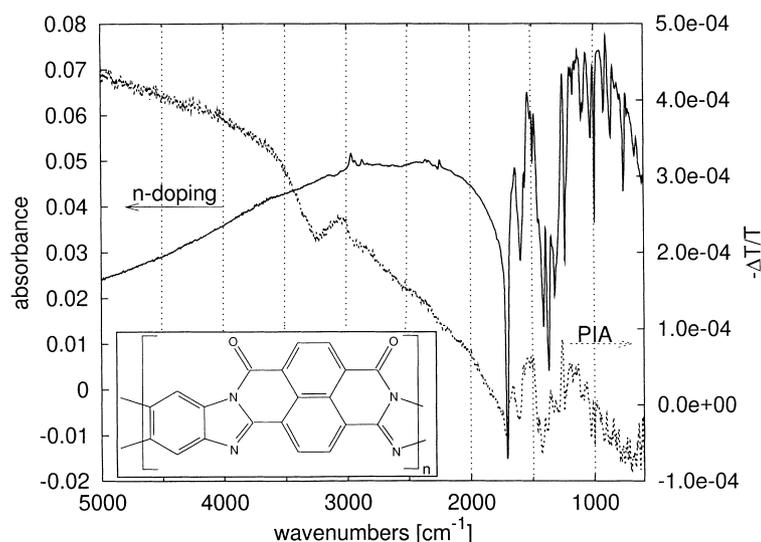

Fig. 8. Spectra of Fig. 8 in extended scale. The inset shows the structure of BBL.

with potential during electrochemical reduction of the film. They reported that the BBL conductivity depends on the electrode potential and displays two maxima that differ by about 10 times in conductivity [31]. The two consecutive insulator → metal transitions cannot be explained by just two electrochemical reactions.

Using in situ FTIR-ATR spectroscopy during electrochemical reduction, we proved the existence of four clearly distinct and spectroscopically well resolved reactions during electrochemical reduction of solid BBL films with different reduction states [34]. As such this is the only conjugated polymer known with four consecutive redox reactions on the main chain: from insulator → conductor → insulator → conductor → insulator, in agreement with the conductivity measurements [31].

A comparison of the PIA spectrum of BBL with doping induced IRAV obtained during the first reduction process (first reduction from insulator → conductor) is shown in Fig. 7 for the vibrational range of the spectrum, and in Fig. 8 for the extended spectral range.

As can be seen, the photoinduced IRAV band positions are very similar to the IRAV bands obtained at low electrochemical n-doping (first reduction process). Only the maximum of the electronic absorption at higher enery is different. In order to clarify the change in the chemical structures during the reduction processes more structural studies are needed due to the complex nature of the molecule. However, it is possible to compare our data with the reaction scheme previously proposed for BBL in acetonitrile [30]. This scheme suggests the formation of quinodimethane resonance structures at very high doping level. Our data indicate the presence of this type of resonance structure even at low doping levels [34].

4. Conclusion

As has been shown in the previous examples, the doping and photoinduced IRAV spectra of complex conjugated polymers often do not show the behavior predicted from theories developed for simpler structures (mostly for polyacetylene). For p- and n-doping, the spectral signature of the charge carriers can be different, indicating a different nature of the charge carriers of both signs. In addition, the predicted shift of photoinduced IRAV bands to lower wavenumbers compared to doping induced IRAV bands is frequently not observed with complex polymers. In this case, some kind of pinning must be taken into account, although counterions are absent. One possible explanation requires the formation of deeply trapped charged states: due to their long lifetime, PIA absorption gives a quasi-steady-state picture. A further investigation by time-resolved photoinduced infrared absorption might be useful to achieve a better description of this behavior. Progress in theoretical descriptions may also improve the understanding of the materials. Finally, the study of the vibrational behavior of doped conjugated

polymers is a valuable source of information regarding structure and electronic properties in this highly interesting class of materials.

References

[1] T.A. Skotheim, R.L. Elsenbaumer, J.R. Reynolds (Eds.), Handbook of Conducting Polymers, Marcel Dekker, New York, 1998; Synth. Met. 84–86 (Proceedings ICSM'96); Synth. Met. 101–103 (Proceedings ICSM'98).
[2] B. Horovitz, Solid State Commun. 41 (1982) 729.
[3] Z. Vardeny, E. Ehrenfreund, O. Brafman, B. Horovitz, Phys. Rev. Lett. 51 (1983) 2326.
[4] E. Ehrenfreund, Z. Vardeny, O. Brafman, B. Horovitz, Phys. Rev. B. 36 (1987) 1535.
[5] G. Zerbi, M. Gussoni, C. Castiglioni, in: J.L. Brédas, R. Silbey (Eds.), Conjugated Polymers, Kluwer Academic Publishers, Dordrecht, 1991, p. 435.
[6] M. Gussoni, C. Castiglioni, G. Zerbi, in: R.J.H. Clark, R.E. Hester (Eds.), Spectroscopy of Advanced Materials, Wiley, New York, 1991, p. 251.
[7] E. Ehrenfreund, Z.V. Vardeny, J. Inter. Opt. Eng. (SPIE) 3145 (1997) 324.
[8] A. Girlando, A. Painelli, Z.G. Soos, J. Chem. Phys. 98 (1993) 7459.
[9] J. Kürti, H. Kuzmany, Phys. Rev. B 44 (1991) 597.
[10] J. Kürti, H. Kuzmany, in: H. Kuzmany, M. Mehring, S. Roth (Eds.), Electronic Properties of Polymers, Springer Series in Solid State Sciences, Vol. 107, Springer, Berlin, 1992, p. 144.
[11] J. Geisselbrecht, J. Kürti, H. Kuzmany, Synth. Met. 55–57 (1993) 4266.
[12] F. Wudl, M. Kobayashi, A.J. Heeger, J. Org. Chem. 49 (1984) 3382.
[13] J. Roncali, Chem. Rev. 97 (1997) 173.
[14] H. Neugebauer, G. Nauer, A. Neckel, G. Tourillon, F. Garnier, P. Lang, J. Phys. Chem. 88 (1984) 652.
[15] H. Neugebauer, A. Moser, P. Strecha, A. Neckel, J. Electrochem. Soc. 137 (1990) 1472.
[16] A. Moser, H. Neugebauer, K. Maurer, J. Theiner, A. Neckel, in: H. Kuzmany, M. Mehring, S. Roth (Eds.), Electronic Propecties of Polymers, Springer Series in Solid-State Sci., Springer-Verlag, Berlin, Heidelberg, 1992, p. 276.
[17] H. Neugebauer, N.S. Sariciftci, in: R.M. Metzger, P. Day, G.C. Papavassiliou (Eds.), Lower Dimensional Systems and Molecular Electronics, Vol. 248, Nato ASI Series, Series B: Physics, Plenum Press, New York, 1991, p. 401.
[18] H. Neugebauer, Macromol. Symp. 94 (1995) 61.
[19] H. Neugebauer, Z. Ping, Mikrochim. Acta (Suppl.) 14 (1997) 125.
[20] M. Dietrich, J. Heinze, G. Heywang, F. Jonas, J. Electroanal. Chem. 369 (1994) 87.
[21] G. Heywang, F. Jonas, Adv. Mater. 4 (1992) 116.
[22] Q. Pei, G. Zuccarello, M. Ahlskog, O. Inganäs, Polymer 35 (1994) 1347.

[23] M.C. Morvant, J.R. Reynolds, Synth. Met. 92 (1998) 57.

[24] C. Gustafsson, B. Liedberg, O. Inganäs, Solid State Ionics 69 (1994) 145.

[25] C. Kvarnström, H. Neugebauer, S. Blomquist, H.J. Ahonen, J. Kankare, A. Ivaska, N.S. Sariciftci, Synth. Met. 101 (1999) 66.

[26] C. Kvarnström, H. Neugebauer, S. Blomquist, H.J. Ahonen, J. Kankare, A. Ivaska, Electrochim. Acta 44 (1999) 2739.

[27] C. Kvarnström, H. Neugebauer, A. Ivaska, N.S. Sariciftci, J. Mol. Struct. 521 (2000) 271.

[28] M. Schärli, H. Kiess, G. Harbeke, W. Berlinger, K.W. Blazey, K.A. Müller, in: H. Kuzmany, M. Mehring, S. Roth (Eds.), Electronic Properties of Conjugated Polymers, Springer Series in Solid State Sciences, Vol. 76, Springer, Berlin, 1987, p. 277.

[29] A. Cravino, H. Neugebauer, S. Luzzati, M. Catellani, N.S. Sariciftci, J. Phys. Chem. B, in press.

[30] K. Wilbourn, R.W. Murray, Macromolecules 21 (1988) 89.

[31] K. Wilbourn, R.W. Murray, J. Phys. Chem. 92 (1988) 3642.

[32] S.A. Jenekhe, Polym. Mater. Sci. Eng. 60 (1989) 419.

[33] S.Y. Hong, M. Kertesz, Y.S. Lee, O.-K. Kim, Macromolecules 25 (1992) 5424.

[34] T. Yohannes, H. Neugebauer, S. Luzzati, M. Catellani, S.A. Jenekhe, N.S. Sariciftci, J. Phys. Chem. B., in press.