

Electronic structure of pyrrole-based conducting polymers: An electron-energy-loss-spectroscopy study

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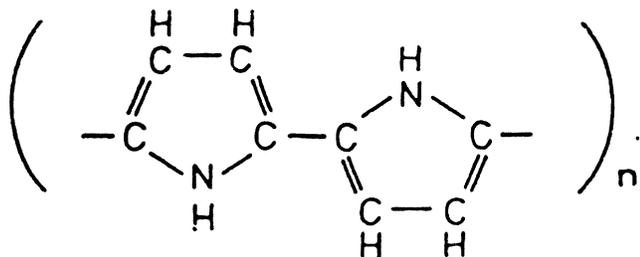
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Pyrrole-based conducting polymers have been investigated by high-resolution electron-energy-loss spectroscopy and by electron diffraction. The evolution of the π -electron band structure as a function of the oxidation can be explained in terms of a bipolaron model. Strongly oxidized polypyrrole is not a metal, but has two narrow bands in the gap which can be assigned to bipolaron bands. The dielectric functions of electrochemically reduced polypyrrole films are well described by a linear-combination-of-atomic-orbitals—complete-neglect-of-differential-overlap calculation on oligomers. The treatment of as-grown oxidized polypyrrole films by alkali metals leads to almost neutralized and not to *n*-type doped films. A reaction of the alkali-metal atoms with the nitrogen atoms is observed. The treatment of oxidized polypyrrole with NaOH does not change the π -electron band structure on the carbon atoms but leads again to a reaction on the nitrogen atoms.

I. INTRODUCTION

The emerging class of conducting organic polymers has attracted considerable interest during the last years. This interest originates from the discovery that a large number of conjugated polymers can be "doped" with either acceptors or donors to yield highly electrically conducting materials. Doped *trans*-polyacetylene (*trans*-PA) exhibiting the highest conductivity has been the focus of most of the experimental and theoretical work.¹ Oxidized polypyrrole (PPY), on the other hand, has received attention because of its attractive physical properties, particularly its stability under ambient conditions. PPY has been synthesized and studied mainly by scientists at the IBM San Jose Research Laboratory. The electrochemical preparation conditions for oxidized PPY films were worked out by Diaz and Kanazawa *et al.*²⁻⁴ It can be readily obtained by oxidative electrochemical polymerization of the pyrrole monomer doped with various anions. It is believed that the monomers are mainly linked by the two α -carbon atoms adjacent to the nitrogen atoms, while the hydrogen on the β -carbon atoms is largely retained. The monomer structure is



The structure of PPY films is reviewed by Street *et al.*⁵ Electron-diffraction patterns⁶ and x-ray diffraction⁷ indicate a kind of layered structure with poor crystalline order. Compared to other conducting polymers like *trans*-PA or polyparaphenylene (PPP) the structure of PPY films is still rather unknown.

The transport mechanism in conducting PPY is even under more active discussion. A coherent description in a conventional picture is not possible at present.⁸ Recently, it turned out that polarons and, more especially, bipolarons, are the defect states created during oxidation or reduction of most of the conducting polymers. These defect states were originally proposed in theoretical studies.^{9,10} In a chemical language, these two defects can also be described as radical cation and as dication.¹¹ The first experimental evidence for their existence was worked out for PPP doped with AsF₅.¹² For PPY, ESR measurements¹³ and optical spectroscopy¹⁴ supported the theoretical predictions that spinless bipolarons are connected with the high conductivity of PPY. Already in an earlier electron-energy-loss—spectroscopy (EELS) investigation,¹⁵ it was found that the conductivity of as-grown PPY must be connected with narrow bands in the gap having a width of less than 0.5 eV.

In the present EELS investigation, we have studied the electronic structure of various pyrrole-based conducting polymers in order to obtain information which can help one to understand the mechanism of the high conductivity. In particular, we have tried to explore the development of the π band structure of oxidized PPY upon electrochemical reduction and upon chemical reduction by Li and K. These studies gave insight into the nature of de-

fect states produced in the doping process. In addition, we have investigated PPY with various side groups to study the influence of the side groups on the π -electron band structure. Moreover, possible changes of the π band structure of oxidized PPY due to different counterions were studied. In previous studies^{16–18} it turned out that treatments of PPY by bases and acids led to a more stable conducting polymer. In order to understand these changes, we have also performed measurements on NaOH-treated PPY samples.

EELS is well suited for investigations of the π and σ band structure of polymers as this kind of spectroscopy offers the possibility of studying interband transitions over a wide energy scale (0.1–40 eV). Moreover, by variation of the momentum transfer, nonvertical transitions can be studied in EELS, which is not possible in optical spectroscopy. Thus, also qualitative information on the width of π bands and on bands related to defects can be obtained.

In addition, EELS offers the possibility of high-resolution core-level spectroscopy (up to 2000 eV) on the K shell of light elements like carbon and nitrogen, as well as on the outer shells of heavier elements. Such measurements continue earlier x-ray-induced-photoemission (XPS) studies^{16,17,19,20} of the charge on the various atoms in the conducting polymer. Finally, we have used our EELS spectrometer to perform elastic electron scattering on PPY to obtain more information on the structure of these compounds. In some cases we have also done XPS measurements to complete our EELS core-level investigations.

II. EXPERIMENTAL DETAILS

A. Sample preparation

Thin PPY films with various counterions having a thickness between 500 and 900 Å were prepared on Sn-In-oxide electrodes in a galvanostatic mode using current densities between 0.1 and 1 mA/cm². Afterwards, the films were rinsed with triple distilled water and methanol

and removed from the electrode by dipping in water. Then the films were mounted on standard electron-microscope grids. Thicker PPY films for conductivity measurements and elemental analysis were grown on platinum electrodes in a similar way. The synthesis of PPY films containing ClO₄[−] and PF₆[−] counterions (PPY-ClO₄, PPY-PF₆) was carried out in an acetonitrile solution containing 0.3 mol/l of the corresponding tetrabutylammonium salts, 2 vol % pyrrole, and 1 vol % water. Poly(N-phenylpyrrole) (PNPPY-ClO₄), poly(bispyrrolylphenylene) (BPYP-ClO₄), poly(N-methylpyrrole) (PPYDM-ClO₄), poly(β,β' -dichloropyrrole) (PPYDCI-ClO₄), and poly(β,β' -dimethylpyrrole) (PPYDM-PF₆) were prepared by the procedure described above but under exclusion of water. PPY films “doped” with anionic ten-sides were synthesized in a deoxygenated aqueous solution containing 0.1 mol/l of the corresponding sodium salts and 2 vol % of pyrrole. In the series of the alkylsulfonates [H—(CH₂)_n—SO₃[−]], films were prepared in the presence of butanesulfonate (PPY-BS), octanesulfonate (PPY-OS), and decanesulfonate (PPY-DS). Moreover, polypyrrole and poly(β,β' -dimethylpyrrole) samples containing dodecylsulfate (PPY-SDS, PPYDM-SDS) as well as 1,10-decanedisulfonate (PPY-DSS) were synthesized. PPY film “doped” with NO₃[−] counterions were prepared by oxidative polymerization of pyrrole vapor on the surface of an Fe(NO₃)₃ (0.1 mol/l) aqueous solution. These films were quite brittle and elemental analysis showed a high oxygen content (C₄H_{2.75}N_{1.2}O_{1.29}) but conductivities up to 30 (Ω cm)^{−1}. By fitting the elemental analytical data to theoretical degrees of oxidation, every fourth to fifth pyrrole ring carries a charge and about every second pyrrole ring contains an additional oxygen atom.

Details on the sample preparation of the PPY films used in this investigation are described elsewhere.^{7,21,22} All samples used in this work are listed in Table I, together with typical anion concentrations and typical conductivities, measured by the van der Pauw method.²³ In addition, other experimental techniques, e.g., electrochemistry and x-ray diffraction, were used to yield well-characterized samples.

TABLE I. Polypyrrole-based samples used in this work with typical anion concentration per monomer c_A and typical conductivities σ .

Polymer	Anions	Abbreviation	c_A (%)	σ [(Ω cm) ^{−1}]
polypyrrole	ClO ₄ [−]	PPY-ClO ₄	33	150
polypyrrole	PF ₆ [−]	PPY-PF ₆	25	100
polypyrrole	H—(CH ₂) ₄ —SO ₃ [−]	PPY-BS	30	10
polypyrrole	H—(CH ₂) ₈ —SO ₃ [−]	PPY-OS	33	~160
polypyrrole	H—(CH ₂) ₁₀ —SO ₃ [−]	PPY-DS	33	~40
polypyrrole	H—(CH ₂) ₁₂ —OSO ₃ [−]	PPY-SDS	30	10
polypyrrole	SO ₃ [−] —(CH ₂) ₁₀ —SO ₃ [−]	PPY-DSS	12.5	20
polypyrrole	NO ₃ [−]	PPY-NO ₃	22	30
poly(β,β' -dimethylpyrrole)	PF ₆ [−]	PPYDM-PF ₆	30	4
poly(β,β' -dimethylpyrrole)	H—(CH ₂) ₁₂ —OSO ₃ [−]	PPYDM-SDS	25	1
poly(β,β' -dichloropyrrole)	ClO ₄ [−]	PPYDCI-ClO ₄	30	10 ^{−3}
poly(N-phenylpyrrole)	ClO ₄ [−]	PNPPY-ClO ₄	20	10 ^{−5}
poly(bispyrrolylphenylene)	ClO ₄ [−]	BPYP-ClO ₄	20	10 ^{−5}
poly(<i>n</i> -methylpyrrole)	ClO ₄ [−]	PPYDM-ClO ₄	25	2 × 10 ^{−3}

Electrochemical reduction of as-grown PPY films was carried out under dry-box conditions in highly purified propionitril solution containing tetrabutylammonium hexafluorophosphate in a concentration of 0.1 mol/l. A cathodic current of $20 \mu\text{A}/\text{cm}^2$ was applied to the pyrrole film until the cell voltage reached 3 V. The measured charge was a little more than what was calculated from the charge used for synthesis and the degree of oxidation. Then the films were rinsed with deoxygenated methanol and transferred to the EELS spectrometer under argon atmosphere. Chemical reduction by Li metal was achieved by evaporating appropriate amounts of Li onto the PPY films under ultrahigh-vacuum (UHV) conditions in the EELS spectrometer. Within several hours the Li had diffused into the polymer films and no further changes in EELS spectra were detected. Chemical reduction by K was performed by treatment of the films in a solution of K-naphthalide in tetrahydrofuran for 40 h. The alkali treatment of polypyrrole was performed by dipping the PPY films into 2M NaOH for several minutes. Treatment with acids was done by soaking the sample in 6M HCl.

B. EELS and XPS measurements

Transmission EELS spectra²⁴⁻²⁶ were taken with a high-resolution, 170-keV spectrometer.²⁷ All valence-band excitations as well as elastic diffraction spectra were taken with an energy resolution $\Delta E=0.13$ eV, a momentum resolution $\Delta q=0.04 \text{ \AA}^{-1}$, and a dose rate $d \sim 10^{-6} \text{ A}/\text{cm}^2$ on the sample. Core-level excitations with high scattering cross sections like the carbon *K*-edge were measured with $\Delta E=0.18$ eV, $\Delta q=0.1 \text{ \AA}^{-1}$, and $d \sim 10^{-5} \text{ A}/\text{cm}^2$. For excitations of core levels with lower scattering cross sections like the nitrogen *K* edge, $\Delta E=0.6$ eV and $\Delta q=0.2 \text{ \AA}^{-1}$ was chosen, leading to a higher dose rate of $5 \times 10^{-4} \text{ A}/\text{cm}^2$ on the sample. XPS measurements were performed on a modified AEIES200 spectrometer providing a resolution of 1.5 eV and a vacuum of 10^{-9} Torr.

III. RESULTS AND DISCUSSION

A. Electron diffraction

From all samples investigated by EELS, we have taken in our EELS spectrometer elastic-electron-diffraction spectra in the momentum-transfer range 0.15–3.5 (or 5.5) \AA^{-1} parallel to the film plane. First, this is a kind of additional characterization of our samples. Second, these spectra give some qualitative information on the crystalline order of the PPY films. In some cases also more detailed information on the structure of pyrrole-based conducting polymers can be obtained.

A representative selection of those spectra for $q=0.15$ to 3.5 \AA^{-1} is shown in Fig. 1. Nearly in all cases broad maxima as compared to the momentum-transfer resolution ($\Delta q=0.04 \text{ \AA}^{-1}$) were observed, indicating the not-well-ordered structure of PPY films. In the momentum-transfer range $3.5\text{--}5.5 \text{ \AA}^{-1}$ (not shown), the spectra of all samples are almost identical. In Table II we have listed

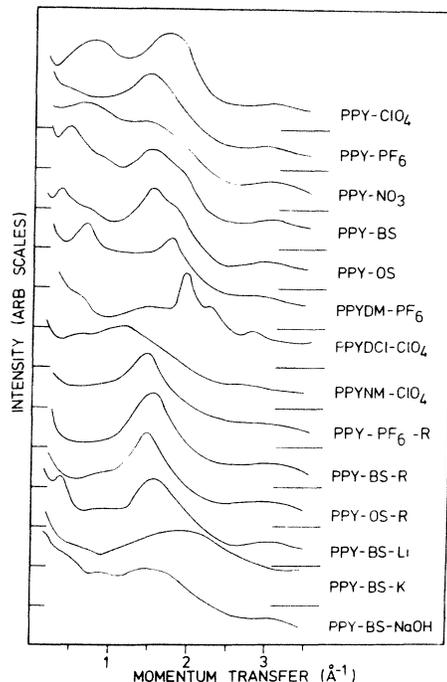


FIG. 1. Electron-diffraction patterns of pyrrole-based films. The curves are labeled according to their counterions and substituents as explained in Table I. The label PPY-BS-R denotes polypyrrole with butanesulfonate anions, electrochemically reduced. The labels Li, K, and NaOH denote treated samples as described in the experimental section.

the d values corresponding to maxima at certain values of q ($d=2\pi/q$). As the diffuse patterns are thought to originate from very small crystalline regions consisting of highly disturbed polymer chains, the d values calculated from the position of maxima in the diffraction spectra correspond to real d values between lattice planes.

Geiss *et al.*⁶ have explained their electron-scattering data on PPY films on the basis of a graphite-like structure with planes built up from planar polymer chains. The structure proposed has a monoclinic unit cell with the lattice constants $a=8.2 \text{ \AA}$, $b=7.35 \text{ \AA}$, $c=6.82 \text{ \AA}$, $\alpha=\beta=90^\circ$, and $\gamma=117^\circ$. While at first view the spectra shown in Fig. 1 appear rather different, most of the diffraction maxima can be explained in this model. For example, peaks *A*, *B*, *C*, and *D* may be assigned to the reflections 006 ($d=1.12 \text{ \AA}$), 004 ($d=1.69 \text{ \AA}$), 030 ($d=2.18 \text{ \AA}$), and 002 ($d=3.41 \text{ \AA}$), respectively. As these peaks were observed almost in all spectra on PPY films (see Table II), this indicates that the proposed layered structure appears in all PPY samples studied independent of the size of the counterions and on the degree of chemical or electrochemical reduction. This would imply that the dopant does not intercalate between the basal planes, as might be expected, but rather appears to intercalate between the chains at empty places within the planes. These results are in agreement with those reported by Geiss *et al.*⁶ on polypyrrole perchlorate.

Peaks *F* and *G* are probably correlated with the distances of pyrrole chains in the planes. This was worked

TABLE II. d values (in Å) for various polypyrrole-based films as derived from electron-diffraction patterns. NO denotes not observed and NM denotes not measured.

	<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>	<i>E</i>	<i>F</i>	<i>G</i>
PPY-ClO ₄	1.13	1.69	2.12	3.36	4.25	9.20	NO
PPY-PF ₆	1.14	1.68	2.12	NO	4.31	NO	NO
PPY-NO ₃	1.14	1.68	2.12	3.55	4.31	9.10	NO
PPY-BS	1.12	1.68	2.12	3.36	4.38	NO	15.8
PPY-OS	1.13	1.71	2.11	3.36	4.25	7.67	18.2
PPYDM-PF ₆	1.13	1.71	2.15	3.36	NO	9.1	NO
PPYDCl-ClO ₄	1.14	1.68	2.24	2.82 and 3.29	4.31	9.8	NO
PPYNM-ClO ₄	NM	NM	2.22	3.21	5.02	10.1	NO
PPY-PF ₆ -R	NM	NM	2.20	NO	4.25	10.1	NO
PPY-BS-R	1.13	1.69	2.15	NO	4.23	NO	NO
PPY-OS-R	NM	NM	2.13	NO	4.22	NO	NO
PPY-BS-Li	NM	NM	2.13	3.62	4.32	NO	15.8
PPY-BS-K	NM	NM	NO	2.5–4.3	NO	NO	NO
PPY-BS-NaOH	NM	NM	2.12	3.5	4.4	7.4	~15

out in more detail in a previous x-ray study on PPY tensides.⁷ There, the d values of peak G were interpreted in terms of distances correlated to the alkyl chain length of the tensides. In general, our electron-diffraction data are in good agreement with these investigations.

Upon electrochemical reduction of PPY tenside films, there is not much change in the diffraction peaks at higher momentum transfer ($q > 2 \text{ \AA}^{-1}$). However, peaks G , which were explained by the distance of PPY chains separated by the tensides, were considerably broadened or have disappeared completely. This indicates that a considerable part of the tensides are removed upon electrochemical reduction and a collapse of the lattice in the basal plane. Chemical reduction of a PPY-BS sample with elemental Li did not change the diffraction spectrum; in particular, the low-momentum peak at 0.4 \AA^{-1} remained. This can be explained just by a neutralization of the counterions without change of structure. The reason for the strong broadening of diffraction peaks upon chemical reduction with K is not clear at present. The treatment of oxidized films with NaOH leads to an additional broadening of the maxima, indicating a further reduction of crystallinity. In particular, peak G is strongly broadened.

In order to eliminate α - β linkages, we have investigated PPY with both β positions of pyrrole rings blocked by methyl groups and by Cl atoms. In both cases narrower diffraction peaks were found, indicating an increased crystalline order. This is in line with electron diffraction on poly(β , β' -dimethylpyrrole) perchlorate reported by Geiss *et al.*⁶ However, also in these cases, it was not possible to resolve completely the crystal structure of the samples due to the limited number of diffraction peaks. Further systematic investigations on preferentially oriented samples with much less disorder over a large momentum-transfer range by neutron scattering, x-ray scattering, or electron diffraction are necessary to resolve definitely the structure of PPY films.

B. Valence-band excitations

The intensity determined in inelastic-electron-scattering spectra is proportional to the loss function $\text{Im}[-1/\epsilon(\omega, q)]$, where ϵ is the complex dielectric constant depending on the energy loss $\hbar\omega$ and the momentum transfer $\hbar q$.²⁴ In Fig. 2 we show the loss function for PPY-ClO₄ in the energy range 0–40 eV. In order to avoid contributions from surface losses and radiation losses, the spectrum was measured at a momentum transfer of 0.1 \AA^{-1} . The elastic line as well as contributions from double scattering are subtracted. The spectrum is typical for all low-energy spectra taken on PPY samples. From previous EELS studies on conducting polymers, it is well known that the maxima in the loss function below 8 eV are related to transitions from the occupied π bands to the unoccupied π^* bands. At the lowest energies (below ~ 3 eV) also transitions from the highest π band into empty defect levels in the gap appear. Maxima between ~ 8 and 20 eV can be ascribed to $\sigma \rightarrow \sigma^*$ transitions. The collective oscillation of all valence elec-

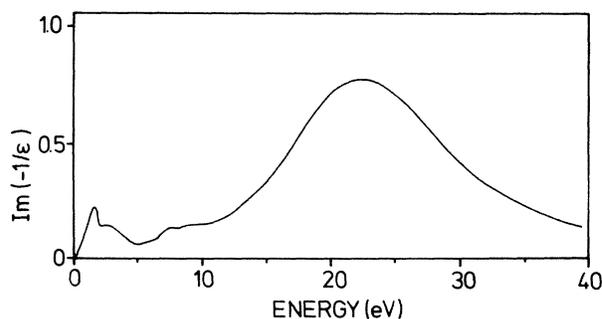


FIG. 2. Loss function $\text{Im}(-1/\epsilon)$ for PPY-ClO₄ in the energy range 0–40 eV, measured for $q=0.1 \text{ \AA}^{-1}$. The elastic line as well as contributions from double scattering are already removed.

trons leads to a $\sigma + \pi$ plasmon close to 22 eV, depending on the density of the valence electrons. The energy position of maxima in the loss function do not necessarily correspond to the exact energy of interband transitions. For a quantitative comparison with band-structure calculations or calculations of the oscillator strength, we have evaluated in some cases the dielectric functions by a Kramers-Kronig analysis of the loss function, following closely the procedure described by Daniels *et al.*²⁵ The absolute value of the loss function was obtained by adjusting the value in such a way that the measured optical-absorption coefficients on similar PPY samples^{4,28-30} in the energy range 3–6 eV are reproduced.

Changes at the spectrum shown in Fig. 2 due to different counterions or due to electrochemical reduction of the sample occur only at energies below 8 eV. The maximum near 1.5 eV, which is not seen in neutral PPY samples, is attributed to excitations of electrons from the highest occupied molecular orbital (HOMO) to defect states in the gap. To illustrate the variation of the π -band-related excitations as a function of counterions, we show in Fig. 3(a) the loss spectra of various as-grown samples in the energy range 0–10 eV. In Fig. 3(b) we show loss spectra of β, β' - and of *N*-substituted PPY in the energy range 0–10 eV. For the β, β' -substituted PPY, we observe spectra that are qualitatively similar to those

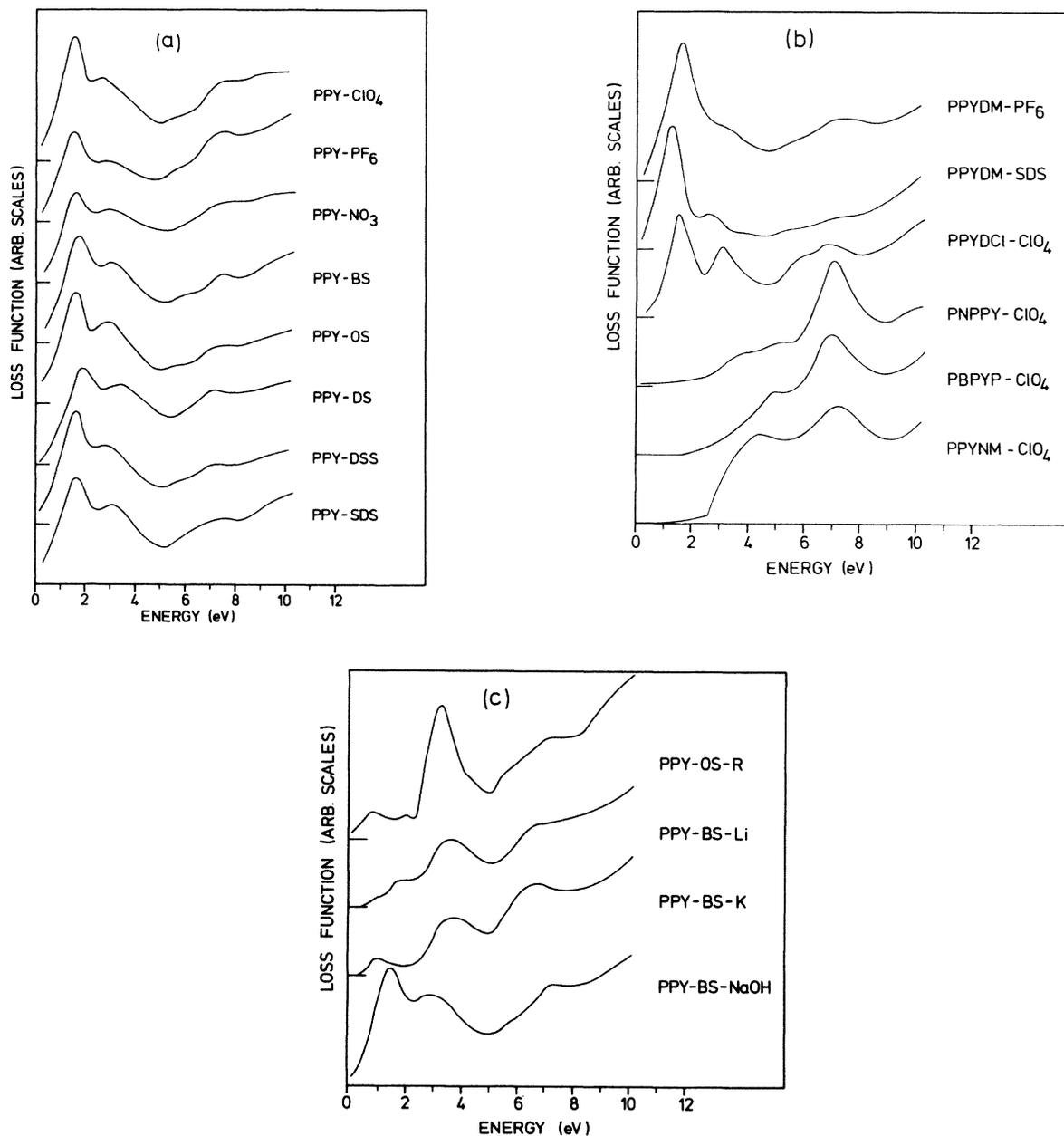


FIG. 3. Loss spectra in the energy range 0–10 eV, measured for $q=0.1 \text{ \AA}^{-1}$. The elastic line is already removed. (a) as-grown oxidized nonsubstituted samples. (b) as-grown substituted samples. (c) Electrochemically reduced sample PPY-OS-R and chemically reduced samples PPY-BS-Li and PPY-BS-K, as well as NaOH-treated sample PPY-BS-NaOH.

from unsubstituted PPY. For the poly(β,β' -dimethylpyrrole) samples, the intensity of the first peak is much stronger than in the unsubstituted PPY films. For poly(β,β' -dichloropyrrole) perchlorate, the first peak is smaller and well separated. For the low conducting N-substituted PPY samples, contrary to the other samples, a gap of 2.5–2.8 eV is observed. In Fig. 3(c) we show loss spectra of samples, which were electrochemically reduced, chemically reduced by alkali metals, or treated by NaOH. For the electrochemically reduced sample PPY-OS-R, and for PPY-BS-Li and PPY-BS-K, a considerable reduction of intensity in the gap of 2.5 eV is observed. For the NaOH-treated sample only a small energy shift of the two lower excitations is found.

In order to gain more information on the nature of the observed transitions, we have measured the momentum dependence of the loss function for various PPY samples. This is illustrated in Fig. 4 for the sample PPY-BS. For the other samples similar spectra were observed. The first maximum near 1.8 eV as well as the shoulders at 6 and 7 eV show almost no dispersion. The second maximum near 3 eV consists of two transitions, one showing a large dispersion, as expected for the lowest $\pi \rightarrow \pi^*$ transition, and another showing no dispersion.

In Fig. 5 we show the momentum dependence of the loss function of the nearly reduced film PPY-OS-R. The low-energy transitions in the gap are removed for clarity. The lowest $\pi \rightarrow \pi^*$ transition near 3.2 eV shows a strong dispersion, whereas a higher $\pi \rightarrow \pi^*$ transition appears independent of q near 7 eV. The shoulders at 4.5 and at 5.5 eV disappear at higher momentum transfer.

In Fig. 6 we show loss spectra of electrochemically re-

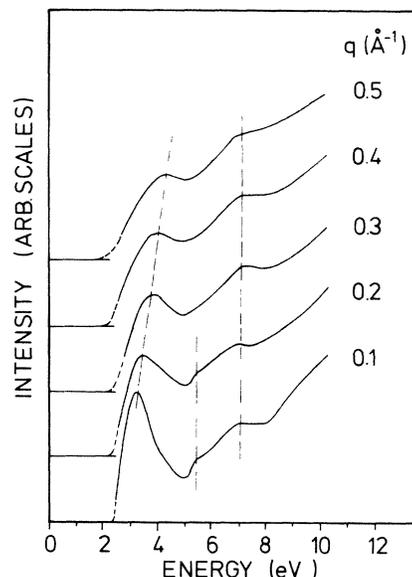


FIG. 5. Momentum dependence of the loss function of electrochemically reduced sample PPY-OS-R. The low-energy transitions are removed for clarity.

duced PPY-OS for various reduction times. Upon reduction, the intensity of the first maximum decreases and the energy position is also changed. The first $\pi \rightarrow \pi^*$ transition near 3 eV moves to higher energies. Upon further reduction, a second maximum near 2.2 eV emerges in the gap. At the lowest oxidation states, a gap of 2.5 eV is clearly seen and two transitions in the gap at 0.8 and at

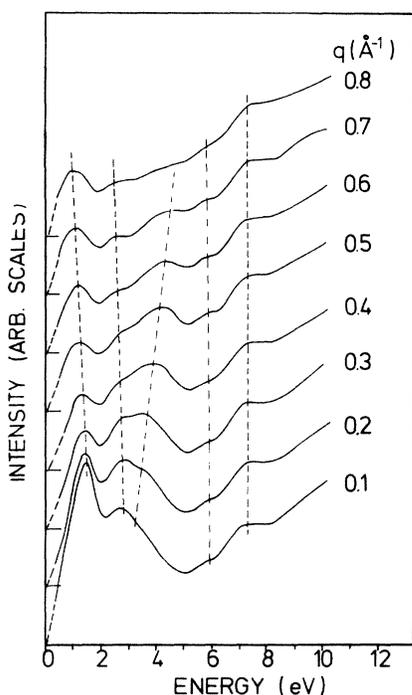


FIG. 4. Momentum dependence of the loss function of PPY-BS. The elastic line is already removed. The curves are labeled according to the momentum transfer.

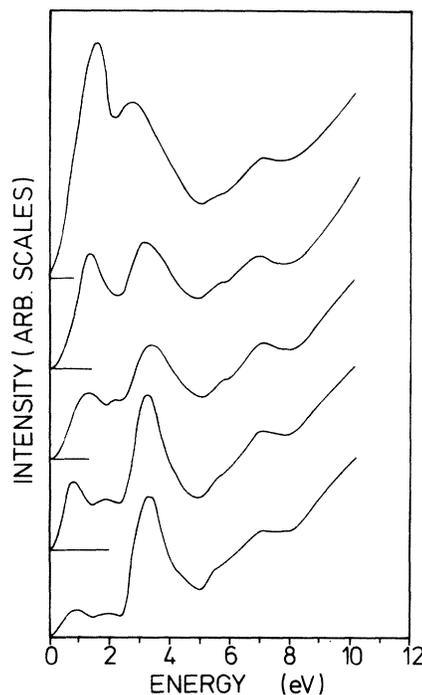


FIG. 6. Loss function, taken at $q = 0.1 \text{ \AA}^{-1}$, for PPY-OS for various reduction rates. Uppermost curve: oxidized sample as-grown. Lower curves: after increasing electrochemical reduction. Lowest curve: almost neutral PPY.

2.2 eV are realized. The other $\pi \rightarrow \pi^*$ transitions in the energy range 4–8 eV remain at the same energy position but are more pronounced. Similar spectra on electrochemically reduced samples were obtained for PPY-PF₆, PPY-BS, and PPY-SDS. In all cases it was not possible to get completely neutral PPY films, i.e., there remained always transitions in the gap.

In Fig. 7 we show the imaginary part of ϵ , i.e., ϵ_2 for PPY-ClO₄, PPYDM-PF₆, and the nearly neutral film PPY-OS-R. In the gap of 2.5 eV, transitions into defect states are observed. Between 2.5 and ~8 eV, $\pi \rightarrow \pi^*$ transitions, and around 14 eV a broad hump of $\sigma \rightarrow \sigma^*$ transitions, are realized.

We start the discussion of the valence-band excitations with the band structure of nearly neutral PPY following the imaginary part of the dielectric function, ϵ_2 , and the momentum dependence of the loss function for PPY-OS-R shown in Figs. 5 and 7, respectively. The sample PPY-OS-R, electrochemically reduced, was the sample where the highest reduction grade could be achieved. An estimate of the number of counterions per pyrrole ring in this film, made by comparing the oscillator strength in the gap with that of as-grown films and assuming that this oscillator strength is proportional to the oxidation, results in an anion concentration of about 1 mol % per monomer. In the gap with a band edge of 2.4 eV, two transitions were observed (see Fig. 7), which will be discussed later. As the intensity of these transitions is proportional to the reduction grade, these transitions certainly originate from

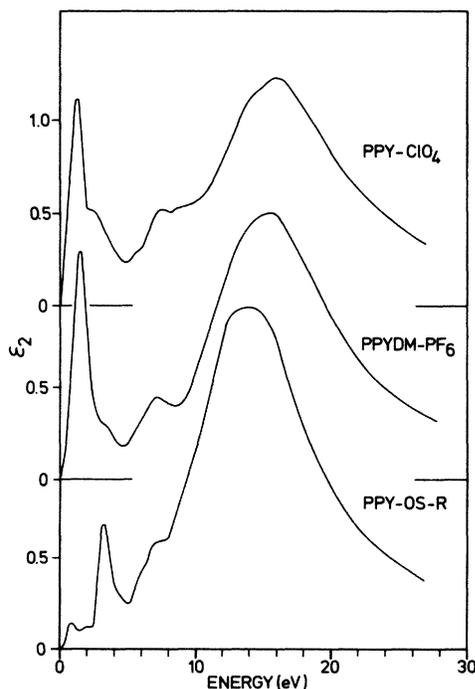


FIG. 7. Imaginary part of the dielectric function, ϵ_2 , as derived from a Kramers-Kronig analysis of the loss function of PPY-ClO₄, PPYDM-PF₆, and PPY-OS-R (electrochemically reduced).

the fact that the polymer was not completely neutralized. The first strong transition near 3.3 eV in the loss function and at 3.2 eV in ϵ_2 is the transition across the fundamental gap, i.e., the transition from the highest occupied π band to the lowest unoccupied π^* band. It is not surprising that the maximum of the loss function is close to the maximum in ϵ_2 . In the energy range of consideration we have an almost constant positive value of ϵ_1 of about 2.5 mainly due to the $\sigma \rightarrow \sigma^*$ excitations at higher energies. If we now assume an additional $\pi \rightarrow \pi^*$ oscillator with small damping superimposed on the σ dielectric function, we get a zero crossing of ϵ_1 and thus a maximum in the loss function $\text{Im}(-1/\epsilon) = \epsilon_2/\epsilon_1^2 + \epsilon_2^2$ very close to the oscillator frequency. This maximum is then called an interband plasmon or π plasmon. The assignment is confirmed by comparison with band-structure calculations on polypyrrole.^{31,32}

These calculations give energy values for the gap between 2.5 and 3.6 eV. The first $\pi \rightarrow \pi^*$ transition was also found in optical studies of electrochemically reduced polypyrrole^{14,28,33,34} and poly(β, β' -dimethylpyrrole) (Ref. 29) films. The band-structure calculations for PPY (Refs. 31 and 32) show that the highest occupied band is composed of π electrons delocalized over several pyrrole rings and having a large amplitude of the wave function at the α -carbon atoms. The width of this π band is about 4 eV. The width of the lowest unoccupied π band is given to be about 2 eV. Starting from this band structure, the lowest $\pi \rightarrow \pi^*$ transitions and thus also the π plasmon should show a strong dispersion in momentum transfer. This is really observed, as shown in Fig. 5. The momentum dependence of the lowest $\pi \rightarrow \pi^*$ transition can be well described by

$$E = E_0 + \frac{\hbar^2}{2m} \alpha q^2,$$

with $E_0 = 3.25$ eV and $\alpha = 1.10$. Similar values for α were reported for other conducting polymers.^{35,36}

For the identification of the higher valence band excitations we have derived the oscillator strength for the $\pi \rightarrow \pi^*$ transitions by a linear-combination-of-atomic-orbitals, self-consistent-field, complete-neglect-of-differential-overlap (LCAO-SCF-CNDO) calculation³⁷ for the monomer, the trimer, and the pentamer of pyrrole. For the geometry of the molecules, standard bond lengths and bond angles have been used. The results, broadened by a Lorentzian of 1 eV full width at half maximum (FWHM) are compared in Fig. 8 with the experimental oscillator strength $\omega\epsilon_2$. Excellent agreement is found for the lowest-energy transition with the calculation for the pentamer. In agreement with previous band-structure calculations,^{31,32} our calculations, taking full account of correlations between the electrons within the oligomers, predict the first transition to be a HOMO-LUMO (lowest unoccupied molecular orbital) transition on the pyrrole ring, the energy of which is shifted from ~5 eV in the monomer to ~3.3 eV in the pentamer through α -carbon- α' -carbon interaction. The shoulders between 4.5 and 5.5 eV appearing both in the experiment and in the calculation are due to excitations from a second occupied π state below the Fermi level to the LUMO and from the HOMO to the second-lowest unoccupied level. The same holds for the

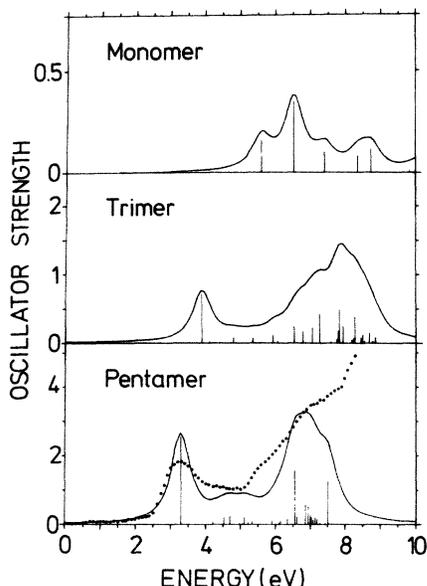


FIG. 8. LCAO-CNDO calculations of the π -electron oscillator strength of the monomer, trimer, and pentamer of pyrrole (solid curve). Points give the oscillator strength $\omega\epsilon_2$ measured on the chemically reduced sample PPY-OS in arbitrary units.

transition near 8 eV. The second occupied π band below the Fermi level is built up from π electrons whose wave functions have nodes on the α -carbon atom. Hence, these π electrons are localized in the pyrrole rings or, in terms of band-structure calculations, we have a flat π band. As the 4.5-, 5.5-, and 7-eV transitions are predominantly related to this narrow π band, no dispersion in momentum transfer should be observed, which is in agreement with the experimental data shown in Fig. 5. The differences at higher energies between calculated and experimental oscillator strength are mainly caused by the fact that oscillator strength of $\sigma \rightarrow \sigma^*$ transitions have not been included, although their influence on the transition energies of the spectrum has been taken into account. Most of these $\sigma \rightarrow \sigma^*$ transitions appear near 14 eV, as shown in the ϵ_2 curve for PPY-OS-R in Fig. 7.

In summary, the comparison of the theoretical and experimental oscillator strength of nearly neutral polypyrrole indicates that the pyrrole rings remain preserved in the electrochemical polymerization process and during the electrochemical reduction. Also, the proposed structure of alternating pyrrole rings coupled via the α atoms is confirmed. However, from this comparison, we can only conclude that undisturbed segments exist in the chain with a minimum length of about five rings. Longer undisturbed chains or segments in the chain would show almost the same spectrum, since band-structure calculations on various oligomers³⁸ indicate that oligomers of about five rings already show most of the characteristic features of the band structure of the polymer. This result was also obtained by a comparison of calculated oscillator strength with ϵ_2 derived from EELS measurements on PPP oligomers.³⁹

After the discussion of the band structure of nearly neutral PPY, we try to understand the π band structure of

as-grown oxidized PPY films as well as the evolution of the band structure upon reduction of the films. In all oxidized unsubstituted PPY films again the maxima near 5.5 and 7 eV typical of neutral polypyrrole are found in the loss function [see Fig. 3(a)] as well as in ϵ_2 as shown in Fig. 7 for PPY-ClO₄. This indicates that pyrrole rings also exist in oxidized PPY. The lowest $\pi \rightarrow \pi^*$ peak observed at 3.2 eV in neutral PPY is also observed, but shows a considerable scattering in the energy between 2.5 and 3.4 eV depending on the sample preparation and on the counterions.

The lowest peak shows also a strong variation in intensity and in energy position (1.5–2.0 eV). No significant excitations due to the counterions were observed in the energy range under consideration. Originally, oxidized PPY was thought to be a metal and the lowest transition was associated with a free-carrier absorption.⁴ The analysis of reflection data on PPY-BF₄ films by a Drude model led to a free-carrier plasmon at 2.15 eV and the free-carrier concentration was estimated to be 5% of the total π electrons.⁴⁰ By looking at the momentum dependence of the lowest transition near 1.5 eV by EELS it was clearly shown that this transition is not connected with a free-carrier absorption.¹⁵ A free-carrier plasmon should show a strong positive dispersion, whereas the 1.5-eV peak showed a small negative dispersion, indicating the transition to be related to narrow bands with a maximum width of 0.5 eV. Our present EELS data on thinner samples yielding better statistics especially at high momentum transfer lead to the same result (see Fig. 4) for this 1.5-eV transition. Moreover, these data reveal that the second peak near 3 eV is composed of two peaks, one showing also a small negative dispersion and another one being the $\pi \rightarrow \pi^*$ transition with a strong positive dispersion. Due to the overlapping peaks, it is difficult to analyze the dispersion coefficient of the $\pi \rightarrow \pi^*$ transition in oxidized PPY. A rough estimate leads to the result that the dispersion constant has nearly the same value in neutral and in oxidized PPY, indicating that there is not a strong change of π -band width upon oxidation. Extrapolating the momentum dependence of the $\pi \rightarrow \pi^*$ transition in oxidized PPY to zero momentum transfer leads to a $\pi \rightarrow \pi^*$ transition energy of 3.5 eV, which is slightly higher than the value for neutral PPY (3.25 eV). There remains the problem of assigning the lowest two transitions having a small negative dispersion. Recently, it has been pointed out that in the conjugated polymers having a nondegenerate ground state, polarons and, more especially, bipolarons, are the defect states created during doping.^{9,10} The nondegenerate ground-state polymers like PPP, PPY, or polythiophene (PT) are polymers, where a reversal of single and double bonds do not lead to the same ground-state energy as in PA. Thus single defects like the solitons proposed for PA (Refs. 41 and 41) with a midgap state cannot exist in the nondegenerate polymers. For these polymers the polarons and bipolarons lead to two defect states in the gap. The theory was later worked out by band-structure calculations as a function of doping concentration¹⁰ for the conjugated polymers PPP, PPY, and PT. In the framework of this model, the two lowest transitions can be assigned to transitions from the valence band into

the two empty bipolaron bands in the gap. Theoretical calculations of the oscillator strength for these transitions have predicted⁴³ that the lower one should be much stronger in intensity than the higher one. This is in line with our experimental data. The evolution of the bipolaron states as a function of the oxidation is well seen in the spectra on PPY-OS as shown in Fig. 6. At low, oxidation, two transitions are seen in the loss function as well as in ϵ_2 (see Fig. 7) at 0.8 and 1.9 eV. Theory predicts two bipolaron states 0.75 eV away from the band edges.¹⁰ Thus transitions at 0.75 and 1.65 eV should appear, which is very close to our experimental findings. At higher oxidation the bipolaron transitions increase in intensity and move to higher energy. The shift in energy comes from the fact that the gap is enlarged due to the removal of states by the formation of the bipolaron bands. This is in line with the above-mentioned increase in energy of the lowest $\pi \rightarrow \pi^*$ transition upon oxidation. Moreover, our spectra clearly reveal that in as-grown PPY films there is no overlap of the bipolaron bands with the valence and conduction bands, which is proposed for strongly doped conjugated nondegenerate ground-state polymers by the theory,¹⁰ leading to a partially filled valence band and thus to a metallic state. While this is observed in *n*-doped PPP leading to *one* maximum in the loss function,⁴⁴ the metallic state is not reached in *p*-doped PPY [and in *p*-doped PPP (Ref. 12)]. The fact that as-grown oxidized PPY is not a metal can be also seen from ϵ_2 evaluated for PPY-ClO₄ shown in Fig. 7. From EELS measurements we get a loss function which is proportional to $\text{Im}(-1/\epsilon)$. To obtain the absolute value of the loss function, an adjustment to optical data has to be done. As mentioned above, we have adjusted our data to optical data on oxidized PPY between 3 and 6 eV which are rather insensitive on the oxidation grade of the samples. This adjustment can never be achieved by using Drude-like behavior at low energies. ϵ_1 has to be near 2.5 for low energy (0.1 eV), which is typical for a polymer but not for a metal. In this way, our ϵ_2 shows not a Drude-like decay at low energies as in metals, but it increases at low energies.

Comparing our results with recent optical data of Yakushi and co-workers,^{14,28,29} we obtain rather good agreement. The transitions to bipolaron states were found at nearly the same energy. The enlargement of the gap upon oxidation is in good agreement with our EELS data. Also, the nonexistence of a metallic state was derived. The only difference is that we have not observed a third transition in the gap near 1.4 eV for nearly neutral PPY, which was explained by the existence of polarons at a low doping level.^{14,34} The reason why we do not see polarons in our nearly neutral PPY may be the following. As our samples were electrochemically reduced outside the spectrometer, it took about 2 h to start the measurements. During this time, the polarons have presumably recombined into bipolarons, as was described by Kaufmann *et al.*³⁴

From the Kramers-Kronig analysis of our loss function, we can also derive the absorption constant over a wide energy range and we can compare it with optical data. Our absorption constant is in good agreement with that derived from optical spectroscopy.²⁸ For the PPY-

ClO₄ sample, the absorption is 30% less for the first peak near 1.5 eV. If we assume that the oscillator strength of this first transition is proportional to the doping concentration, the difference may be explained in terms of a lower oxidation of our samples. The comparison of our loss function for PPY-ClO₄ with that derived from optical data gives good agreement concerning the shape of the function. However, the absolute value of the loss function in the low-energy range is 7 times larger in the optical study compared to our EELS data. This may be caused by the rather small energy range used for the Kramers-Kronig analysis of the optical data. This is then also the reason for the large discrepancy of our ϵ_2 values from those derived by Yakushi *et al.*²⁸ In this context, we mention that we have obtained much better agreement for our dielectric functions with those derived by spectroscopic ellipsometry on PPY-BF₄ films.³⁰

Next, we discuss the variation of the loss spectra with the counterions and with the substitution of hydrogen atoms at the pyrrole rings. As mentioned above, there is a considerable scattering of the energy positions and the intensity ratio of the first two transitions. The change in intensity is presumably caused by different concentrations of counterions. Thus, for example, PPY-ClO₄ contains 33% counterions per monomer, whereas PPY-PF₆ contains only 25%. Consequently, the intensity of the lower $\pi \rightarrow B$ ($\pi \rightarrow$ bipolaron state) transition compared to the second transition ($\pi \rightarrow B^*$ and $\pi \rightarrow \pi^*$) is larger for the PPY-ClO₄ sample than for the PPY-PF₆ sample, as shown in Fig. 3(a). The energy shift can be explained by different damping constants of the oscillators. Higher damping shifts the maximum of the loss function to higher energies, although the energy of the oscillator is not changed. Different damping constants may be caused by different order in the chains.

In the poly(β, β' -dimethylpyrrole) films, the lowest $\pi \rightarrow B$ transition is considerably stronger compared to the unsubstituted samples, indicating a stronger oxidation. As the highest concentration of counterions is about the same, a higher oxidation rate per anion is realized in these films. This has also been observed in the optical study on poly(β, β' -dimethylpyrrole) perchlorate samples.²⁹ The lower conductivity of these compounds may be related to a nonplanar structure of the poly(β, β' -dimethylpyrrole) chain, where the overlap of π bonding between monomers is reduced. On the other hand, from the diffraction spectra there is no evidence of a nonplanar geometry as the peaks which are related to the interplanar spacing of pyrrole planes are very close to those found in the unsubstituted PPY samples. For poly(β, β' -dimethylpyrrole) dodecylsulfate, the $\pi \rightarrow \pi^*$ transition has almost disappeared. However, also for this film the lowest peak cannot be assigned to a free-carrier plasmon as in *n*-doped PPP (Ref. 44) or PT (Ref. 45). Looking at the momentum dependence of the excitations, the peak near 1.2 and 2.6 eV show a small negative dispersion, whereas a free-carrier plasmon should show a strong positive dispersion. At higher momentum transfer, a dispersive peak near 3.5 eV emerges from the background, which may be connected with the lowest $\pi \rightarrow \pi^*$ transitions, having a small oscillator strength.

In the Cl-substituted film poly(β, β' -dichloropyrrole) perchlorate a very sharp $\pi \rightarrow B$ transition is observed. This low damping may be connected with the high crystalline order of the sample, as indicated in the narrow reflections of the diffraction pattern shown in Fig. 1. There is probably again an overlap of the $\pi \rightarrow B^*$ and the $\pi \rightarrow \pi^*$ transitions. In the N-substituted PPY films no defect states in the gap are observed and the spectra are close to those of neutral PPY films. This result is in line with the observation that N-substituted films changed the color from black to yellow-brown when they were removed from the electrochemical cell. The instability of the oxidized form of N-substituted films and the transformation to the neutral form was already recognized in previous optical studies.^{30,46} The details of this transformation were not studied up to now. Finally, we point out that the large width of the lowest $\pi \rightarrow \pi^*$ transition indicates short conjugation length. This result may be an explanation for the low conductivity of these films, already observed in previous investigations.⁴⁷ The strong transition near 7 eV observed in the phenyl-substituted PPY films, also observed in PPP,³⁵ is due to the $^1A_{1g} \rightarrow ^1E_{1u}$ transition of the benzene ring.

To conclude the discussion of π -electron band structure we come to the attempts to neutralize or to reduce oxidized as-grown PPY films by chemical treatment. The treatment with Li and K-naphthalide led to a reduction of transitions in the gap. However, we never achieved a complete emptying of the gap. As shown in Fig. 3(c) in PPY-BS-Li, two shoulders near 1.2 and 1.8 eV remained, whereas in PPY-BS-K a peak near 1.2 eV is observed. Thus these films are either still slightly oxidized or already slightly reduced. A stronger reduction (n doping) could not be achieved by doping with alkaline metals. There is also a shift and a broadening of the $\pi \rightarrow \pi^*$ transitions: the 3.2-eV transition is shifted to higher energies, whereas the 7-eV transition is shifted to lower energies. The origin of this change of the π band structure will be clarified later by looking at the core excitations. Treatment of oxidized PPY by NaOH leads to strong reduction of the conductivity by 3–4 orders of magnitude as reported before.^{16–18} However, the π band structure is nearly preserved, as can be seen in Fig. 3(c) in the spectrum labeled PPY-SDS-NaOH. Compared with the untreated film, there is only a small shift to higher energy for the $\pi \rightarrow B$ transition. The change in conductivity may be connected with these small shifts or with chemical changes on the nitrogen atoms which will be discussed in the next section.

C. Core-level excitations

Before coming to our results obtained by core-level spectroscopy, some general remarks on this technique applied to conducting polymers are necessary. In core-level spectroscopy, we observe transitions from deep and narrow core levels into the unoccupied states. In principle, we should observe the density of unoccupied states weighted by matrix elements related to transitions from the core level into the various unoccupied states. However, this simple picture only works on sp metals having

rather extended unoccupied states. The core hole, created in the absorption process, is well screened and changes of the single-particle transition probability appear only in the first 100 meV above the absorption edge.⁴⁸ On the other hand, in insulators, the core hole is much less screened and there is a strong interaction of the unoccupied states with the core hole. Thus, the single-particle transition probability is strongly changed. An excitonic transition is observed which is no more related to the density of states of the unoccupied states. Even in graphite, which is a semimetal, the $1s \rightarrow \pi^*$ transition does not reproduce the density of the unoccupied π^* states, as shown by a comparison of the $1s$ absorption EELS spectrum of graphite with theoretical calculations.⁴⁹ The electronic relaxation near the core hole strongly enhances the transition probability at the bottom of the π^* band, leading to a core-exciton line at 285.4 eV.

In undoped polymers like PPP, polyparaphenylene sulfide, and polyparaphenylene oxide,³⁵ and other aromatic compounds,⁵⁰ even narrower lines related to the $1s \rightarrow \pi^*$ transitions were observed. In these cases the changes of the $1s \rightarrow \pi^*$ transition energies are mainly related to changes in the binding energy E_B of the $1s$ core level. From XPS investigations,⁵¹ it is well known that the chemical shift of the binding energy E_B depends on the charge of the valence electrons, q_i , and on the charge of the neighboring atoms, q_j , at distance R_{ij} ,

$$\Delta E_B = Kq_i + e^2 \sum_{j (\neq i)} \frac{q_j}{R_{ij}}. \quad (1)$$

K is a constant which is about 22 eV/electron for C and N. The first term is partially compensated by the second term, which is 14.4 eV Å/electron. For a given structure, the charges on the atoms can be deduced from measurements of E_B . For a large class of organic compounds, the simpler relation⁵¹

$$\Delta E_B = K'q_i \quad (2)$$

holds with $K' \sim 6$ eV/electron for C and N. Equation (2) describes well the chemical shifts of substituted organic compounds like for example fluoromethanes.⁵¹ For the chemical shifts of the $1s$ level of carbon in conducting polymers, Eq. (1) is probably more adequate. In this case, the transferred charges from the counterion to the polymer may be spread over several rings. Thus, the first term in Eq. (1) may be smaller and the second term due to the potential energy of the counterions becomes more important.

Due to the interaction with the core hole, only a very local part of the π^* density of states is sampled in the $1s \rightarrow \pi^*$ transition. Thus, in a first approximation, the $1s \rightarrow \pi^*$ transition energy does not depend on the detailed band structure of the π^* electrons. However, in materials with higher dielectric constants, like heavily doped polymers, intercalated graphite, or even metals, the transition energy will also depend on the final-state energy as well as on the screening of the core hole. As this is a rather complex interplay of various mechanisms, the understanding of the core-level spectra is not straightforward with the present theoretical support. Nevertheless, we think that

valuable information can be obtained by use of this kind of spectroscopy.

Core-level excitations are much weaker than valence-band excitations and therefore require longer exposure times. The carbon 1s core excitation is easily measured on thin polymer films, whereas measurements of the nitrogen 1s core excitation and other low-cross-section core-level excitations are seriously restrained by radiation damage produced by the electron beam.

We first show in Fig. 9 some representative data on carbon 1s excitations in PPY-based films in the energy range 280–300 eV. The lower part of these absorption edges between 283 and 288 eV is identified as excitations from the carbon 1s states into antibonding π^* transitions, whereas above 292 eV the final states have mainly σ^* character. In addition, small loss structures above the $1s \rightarrow \pi^*$ transi-

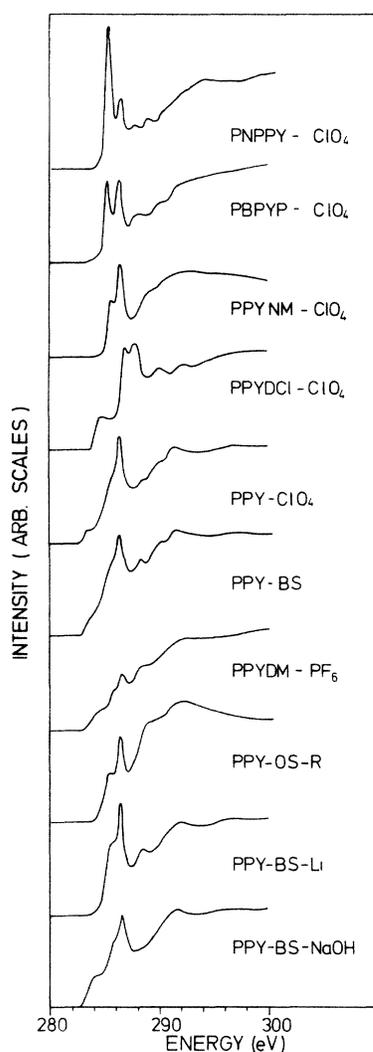


FIG. 9. Carbon 1s core-level excitation spectra in the energy range 200–300 eV for various pyrrole-based polymers. The curves are labeled with abbreviations explained in Table I. The labels R, Li, and NaOH denote electrochemically reduced samples, samples chemically reduced with Li, and NaOH-treated samples, respectively.

tions (at 287.8 and 288.8 eV) are observed which may be explained by satellites also observed in XPS spectra on such polymers, i.e., a combined $1s \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ excitation or by a $1s$ excitation into higher π^* bands. Similar spectra have been observed by x-ray-absorption spectroscopy and by EELS on conjugated molecules,^{52,53} as well as on graphite⁴⁹ and on conjugated polymers.^{35,54}

We start the discussion of carbon K -shell absorption spectra with the $1s \rightarrow \pi^*$ transitions in almost neutral PPY films having only a few defect states in the gap. For poly(*N*-phenylpyrrole) perchlorate (PNPPY-ClO₄) two prominent peaks at 285.1 and near 286.2 eV are observed which can be assigned to the $1s \rightarrow \pi^*$ transitions of two different carbon atoms having different 1s binding energies. Those carbon atoms which are bonded to a nitrogen atom have less charge because nitrogen is more electronegative than carbon. Less charge leads to a decrease in screening of the nuclear charge and thus to a higher binding energy. The other carbon atoms, neighboring only carbon and hydrogen atoms with almost the same electronegativity, have a larger charge and thus a lower binding energy. Counting the carbon atoms in the pyrrole ring and in the benzene ring, the ratio of carbon atoms with lower binding energy not adjacent to nitrogen atoms to those having a higher binding energy adjacent to nitrogen atoms should be 7 to 3. This intensity ratio is found in the experiment for the two $1s \rightarrow \pi^*$ transitions. XPS measurements of the difference of the binding energy of the 1s level of α - and β -carbon atoms in pyrrole⁵⁵ give a value of 1 eV, which is somewhat smaller than the separation of the two observed $1s \rightarrow \pi^*$ transitions found in our EELS spectra. This difference can be understood, as in PPY the α -carbon atoms are adjacent to α' -carbon atoms, from which charge is removed due to a neighboring nitrogen atom, whereas in the monomer there is a hydrogen atom at the α -carbon atom, which has almost the same electronegativity. Using Eq. (2) the charge difference of the two carbon atoms is about $0.2e$. In the LCAO-CNDO calculations we obtain—in the oligomers—a value of $0.24e$. In the carbon 1s spectrum of poly(bispyrrolylphenylene) perchlorate (PBPYP-ClO₄) the ratio of the two carbon $1s \rightarrow \pi^*$ transitions should be 8:6, as we have two pyrrole rings coupled by a benzene ring. The estimated intensity ratio is in good agreement with the observed intensity ratio, assuming an increasing background below the $1s \rightarrow \pi^*$ transitions. The energy difference of the two peaks is again 1.1 eV. For poly(*N*-methylpyrrole) perchlorate (PPYNM-ClO₄), the ratio of the two $1s \rightarrow \pi^*$ transitions should be 1:1, as there are the two α - and the two β -carbon atoms per monomer having an sp^2 configuration. These intensities are again well reproduced in the experiment when we assume an increasing background below the $1s \rightarrow \pi^*$ transitions. The same arguments should hold for the almost neutral films PPY-OS-R and PPY-BS-Li. In fact, a 1:1 intensity ratio for the two $1s \rightarrow \pi^*$ transitions is observed in the spectra shown in Fig. 9.

For the oxidized PPY films, the explanation of the 1s transitions is more complicated. In poly(β, β' -dichloropyrrole) perchlorate (PPYDCl-ClO₄) considerable charge is extracted from the β -carbon atoms due to the

electronegative chlorine atoms. Assigning the peak at 287.6 eV to the $1s \rightarrow \pi^*$ transition of β -carbon atoms, a chemical shift of 2.5 eV is obtained. The same chemical shift is found comparing C_6H_6 and C_6Cl_6 ,⁵⁶ which confirms our assignment. The peak corresponding to the α -carbon atoms has also moved to higher binding energies. The small shift of 0.6 eV can be readily understood when looking at the chemical shifts on the different carbon atoms in C_6H_5Cl .⁵⁶ The chemical shift of the $1s \rightarrow \pi^*$ transitions can be explained just by the removal of 0.4 electron from the β -carbons and 0.1 electron from the α -carbons by the chlorine atoms bounded by the β -carbon atoms. Thus, these peaks are related to carbon atoms not influenced by the ClO_4^- counterions. Carbon atoms still more oxidized by ClO_4^- have probably a distribution of binding energies, depending on the charge on the carbon atoms and the position of the counterions [see Eq. (1)], and may explain the onset at 284 eV.

Next, we discuss the $1s$ core-level excitation spectrum of PPY- ClO_4 and PPY-BS. Nearly identical spectra were obtained on the samples PPY- NO_3 , PPY- PF_6 , PPY-OS, PPY-DS, PPY-SDS, PPY-DSS, for samples electrochemically reduced and reoxidized in air, and for samples treated by NaOH and by HCl (not shown in Fig. 9). Moreover, we mention that a previous unpublished measurement of the carbon K absorption edge on a PPY- BF_4 sample used in Ref. 15 resulted in $1s \rightarrow \pi^*$ transitions almost identical to those of PPY- ClO_4 or PPY-BS.

A strong peak near 286.4 eV is observed which we attribute to the $1s \rightarrow \pi^*$ transition of α -carbon atoms. There is only a small chemical shift of ≤ 0.2 eV compared to the neutral PPY films. Thus the spectrum reveals the existence of almost undisturbed α -carbon atoms in as-grown PPY- ClO_4 films. If the β -carbon atoms are likewise undisturbed, a second peak with the same intensity at lower energy should appear. However, only a smooth shoulder at 285.4 eV is observed. This can be explained by a stronger charge extraction from the β atoms, leading to a broadening and shift to higher energies. It may also be explained by a stronger influence of the second term in Eq. (1) due to counterions close to β -carbon atoms.

In this case, oscillator strength related to β -carbon atoms should appear at lower energies. This may be the reason why a shoulder with an intensity roughly proportional to the oxidation grade is observed near 283.5 eV. Assuming that the counterions are positioned in the layers between polypyrrole chains, the second term of Eq. (1) will give a distribution of energy shifts for the $1s \rightarrow \pi^*$ transition up to $\Delta E = -6$ eV. On the other hand, according to the calculations of Bredas *et al.*,¹⁰ changes of charges on the α - and β -carbon atoms up to ~ 0.2 eV are expected, which should result in a shift of ΔE up to ~ 3 eV. This was calculated, however, for the counterions on top of the pyrrole rings, while the present and previous investigations of the structure of PPY films indicate that the counterions are in the planes between the chains. Another explanation for the intensity at lower energy (283.5 eV) may be transitions from the $1s$ state into the empty bands in the gap, the bipolaron bands. At present we do not know the oscillator strength of such transitions. A similar investigation of oxidized PT films did not show

such transitions. Therefore, the second explanation for the low-energy transition at 283.5 eV is very unlikely. When we look at the methyl-substituted films (see PPYDM- PF_6 in Fig. 9), the peak related to undisturbed α -carbon atoms and that related to undisturbed β -carbon atoms are strongly reduced by almost the same amount. The reason for that may be that in this case the β -carbon atoms are blocked by the methyl groups, so the counterions may be at positions which lead for both the α - and β -carbon atoms to a larger second term in Eq. (1) and thus to a reduction in intensity of the undisturbed α - and β -carbon lines.

The carbon $1s$ spectra on NaOH-treated samples do not show strong changes compared to as-grown PPY. Only a small increase in intensity near 284 eV is observed. An explanation for this cannot be given at present.

To conclude the discussion of the carbon $1s \rightarrow \pi^*$ transitions, we mention that a detailed quantitative analysis of the spectra on oxidized PPY films is at present not possible. When the knowledge of the structure and especially of the position of the counterions has improved, these spectra may yield, with the help of Eq. (1), information on the charges on carbon atoms.

In Fig. 10 we show some representative spectra of the nitrogen $1s$ core-level excitation spectra on pyrrole-based materials. All as-grown pyrrole-based films (e.g., PPY- ClO_4) show a narrow peak at 401.2 eV which can be assigned to the core-exitonic $1s \rightarrow \pi^*$ transition as in similar studies of molecules containing π -bonded nitrogen

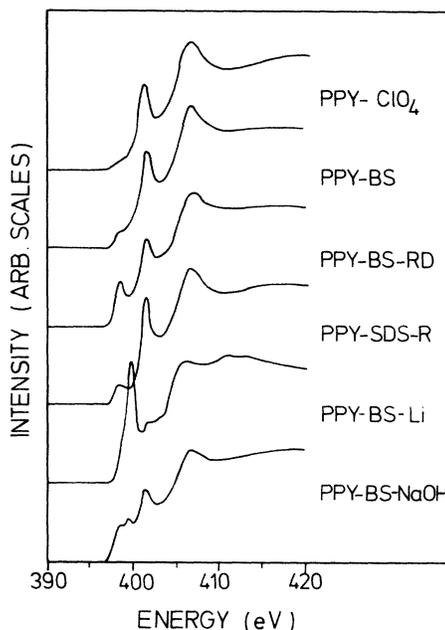


FIG. 10. Nitrogen $1s$ core-level excitation spectra in the energy range 390–420 eV for various pyrrole-based polymers. The curves are labeled with abbreviations explained in Table I. The label RD denotes after prolonged radiation damage in the electron beam. The labels R, Li, and NaOH denote electrochemically reduced samples, samples chemically reduced with Li, and NaOH-treated samples, respectively.

atoms.⁵⁷ A second broader peak at 406.2 eV can be assigned to the $1s \rightarrow \sigma^*$ transition. There appears a peak near 398.5 eV for most of the PPY samples whose intensity depends on the radiation damage. This is shown in Fig. 10 for the sample polypyrrole butanesulfonate. While the spectrum labeled PPY-BS was measured in 5 min with negligible radiation damage, the spectrum labeled PPY-BS-RD was exposed for 30 min to the electron beam, before taking the spectrum. It is well known from electron-microscopy studies of organic materials under electron bombardment⁵⁸ as well as from irradiation of PA (Ref. 59) that hydrogen is emitted from these materials. Thus, we assume that this peak is connected with the dehydrogenation of nitrogen atoms, which may increase the charge on the nitrogen atoms by one electron. Using Eq. (2) the decrease in $1s$ -level binding energy should be 6 eV. On the other hand, part of the charge is distributed in the pyrrole ring. From the chemical shift of the $1s \rightarrow \pi^*$ transition by 3 eV, an additional charge of 0.5 electron on the nitrogen atoms can be deduced. It is remarkable that irradiated as-grown PPY samples already exhibiting a large peak near 398.5 eV show only minor changes in the valence excitation spectra and in the carbon $1s$ -level spectra. Mainly the transitions from the valence band into the states in the gap are reduced. After even longer irradiation time, the π band structure is destroyed. The details on the variation of the conducting polymer upon radiation damage are not clear until now. Furthermore, we do not know why this lower $1s \rightarrow \pi^*$ transition at 398.5 eV does not appear even after prolonged irradiation in samples like PPY-ClO₄ or HCl-treated samples containing chlorine.

Upon electrochemical reduction of as-grown PPY samples, there is *no* change of the nitrogen $1s$ core-level excitation spectra. The two $1s \rightarrow \pi^*$ transitions and the $1s \rightarrow \sigma^*$ transitions remain within ± 0.1 eV at the same position. The intensity of the lower $1s \rightarrow \pi^*$ transition depends again on the time the sample is exposed to the electron beam. The fact that the energy of the $1s \rightarrow \pi^*$ and $1s \rightarrow \sigma^*$ transition is not changed can be explained by a charge on the nitrogen atoms which is not changed upon electrochemical reduction. Other explanations are an accidental compensation of the two terms of Eq. (1) or a strong shift to higher binding energies accompanied by a strong broadening in oxidized PPY films.

The chemical reduction by Li and K leads to a shift both for the $1s \rightarrow \pi^*$ transition and for the $1s \rightarrow \sigma^*$ transition to lower energies. The $1s \rightarrow \pi^*$ transition occurs for Li doping at 399.9 eV and for the more electropositive K doping at 399.5 eV, corresponding to an additional charge of 0.22 and 0.3 electrons, respectively, using Eq. (2). Thus, these measurements show that not only are the counterions neutralized by alkali metals, as indicated in the valence excitation spectra, but that there is an additional reaction of alkali metal with the nitrogen atoms but not with the carbon atoms. A possible reaction may be the replacement of the hydrogen atoms by alkali metals. This reaction may be also the reason for the observation of intensity in the gap of Li- and K-treated samples and for the broadening of the $\pi \rightarrow \pi^*$ transitions.

The treatment of as-grown films with NaOH leads to two additional $1s \rightarrow \pi^*$ transitions at 398.5 and 399.6 eV.

Following the above-mentioned arguments, the line at 399.6 eV may be caused by nitrogen atoms, where the H atoms are replaced by Na, while the line at 398.5 eV may be caused by deprotonized nitrogen atoms. A treatment by NaOH and a following treatment by HCl leads to a spectrum as in untreated PPY-ClO₄ samples, indicating that the reaction on the nitrogen atom is reversible. This fact and the deprotonization has been already shown in previous XPS studies.^{16,17}

We have also tried to measure the absorption edges of atoms in the anion molecules. However, the intensity of these absorption edges was rather low due to the lower concentration of the atoms and due to the small cross section of the excitation. Thus longer measuring times were necessary and we are not sure whether these spectra are strongly influenced by radiation damage. In the sample poly(β, β' -dichloropyrrole) perchlorate two Cl $L_{2,3}$ doublets are observed at 201.5 and 203.2 eV, as well as near 207 and 208.8 eV. By comparison with other chemical shifts of similar molecules,⁵⁶ the lower doublet is due to the chlorine atoms on the pyrrole ring, whereas the second doublet can be assigned to the ClO₄⁻ anion. In SO₃⁻-containing PPY films, the sulfur $L_{2,3}$ absorption edge was observed near 169.5 eV. For PF₆⁻ the threshold appeared at 135 eV. Similar binding energies for such anions were also found in XPS spectroscopy in the literature.⁵⁶ For the PPY-OS sample we have taken XPS spectra for samples as-grown and for samples electrochemically reduced and reoxidized in air. The carbon $1s$ spectrum does not change upon reduction and reoxidation, whereas in the nitrogen $1s$ spectrum an additional shoulder near 397 eV develops. Both spectra are in agreement with spectra given in the literature.^{17,19} Upon cycling the sample, the sulfur $2p$ line at ~ 168 eV shows a reduction in intensity. The reduction of the $L_{2,3}$ line upon neutralization of SO₃⁻-containing PPY samples was also observed in EELS measurements. This indicates a loss of counterions upon neutralization, in agreement with the above-mentioned electron-diffraction results.

Concluding the section on core-level excitations, we mention that many discrepancies are realized when we compare our results on carbon and nitrogen atoms with those of previous XPS studies.^{16,17,19,20} First, we point out that there are also strong discrepancies among the various XPS studies which may be explained by a different analysis of the spectra and by different surface contamination, which strongly influences these measurements. On the other hand, EELS mainly probes bulk properties and is thus not a surface-sensitive technique. Finally, we note that our energy resolution is a factor of 8 better for the carbon $1s$ level and a factor of 3 better for the nitrogen $1s$ level compared to the previous XPS studies on PPY. Therefore, we resign at this point to give a detailed comparison of previous XPS and present EELS results.

IV. CONCLUSION

We have investigated electrochemically and chemically prepared oxidized polypyrrole films with various counterions, electrochemically and chemically reduced poly-

pyrrole films, and NaOH-treated as-grown polypyrrole by high-resolution electron-energy-loss spectroscopy and by electron diffraction. The investigations of the structure of electrochemically prepared polypyrrole films indicate a poorly crystalline, layered structure independent of the counterions and on the oxidation grade. The same structure was also observed for the chemically prepared polypyrrole nitrate. For the β, β' -substituted samples a better crystalline order appeared, while for the N-substituted films the same poorly crystalline order as in nonsubstituted samples was observed. The momentum-dependent dielectric functions of almost neutral polypyrrole can be well described by a calculated π band-structure or by a LCAO-CNDO calculation of the oscillator strength of oligomers. This supports the present understanding of polypyrrole as a polymer composed of pyrrole rings dominantly linked by α -carbon atoms. The evolution of the π band structure as a function of oxidation can be well described in terms of a bipolaron model recently developed for conducting polymers with a nondegenerate ground state. The dielectric functions of oxidized as-grown polypyrrole cannot be described by a Drude model, i.e., no free-carrier plasmon was observed. The momentum-dependent valence excitation spectra clearly reveal the existence of two narrow bands in the gap which

can be assigned to the theoretically proposed bipolaron bands. The electronic structure of the π bands is almost the same for neutralized and for oxidized polypyrrole.

Thus, oxidized polypyrrole films are not metals, contrary to conclusions derived from transport measurements. For N-substituted polypyrrole films, we have confirmed previous studies on the instability of these films and the transformation to the neutral state.

Treatment of oxidized polypyrrole films with alkali metals leads to almost neutral polypyrrole and n doping of polypyrrole could not be achieved. Core-level spectroscopy reveals that there is a reaction of the alkali metal with the nitrogen atom of the pyrrole ring. Treatment of as-grown polypyrrole films with NaOH does not change the π -electron structure on the carbon atoms. There is a reaction at the nitrogen atom, presumably a deprotonization and a replacement of the H atom by a Na atom. The strong reduction of conductivity due to NaOH treatment cannot be explained by the present experiments.

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