

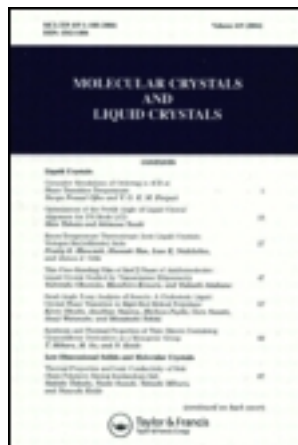
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ELECTRONIC STRUCTURE OF DOPED POLYPARAPHENYLENE

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Abstract Electron energy-loss spectroscopy has been used to investigate the electronic structure of n- and p-doped polyparaphenylene. For low doping concentration evidence is found for the formation of bipolaron states in the gap. For Li doping at the highest doping level, the gap between bonding and anti-bonding π -electrons is closed and a metallic state is observed.

INTRODUCTION

So far, among the conducting polymers polyacetylene (PA) has been the focus of most experimental and theoretical work. Trans PA is unique in possessing a degenerate ground state and this degeneracy led to the prediction of soliton excitations and the soliton-based model for the insulator-metal transition. On the other hand, all other conducting polymers as polyparaphenylene (PPP), polypyrrole or polythiophene do not possess a degenerate groundstate. Therefore, single defects like solitons cannot exist and other defects should be related with the high conductivity of these materials. Recent theoretical calculations¹ on doped polymers with nondegenerate groundstate indicate the formation of bipolarons, i.e. doubly charged defects having no spin. A first indication of the existence of spinless charge carriers in p-doped polyparaphenylene was obtained by ESR and susceptibility measurements.² Evidence for the existence of bipolaron states in the gap has been observed for the first time in a previous electron energy loss study of p-doped PPP.³ As the calculations were performed for n-doped polymers, the experimental verification of the model on n-doped PPP is of parti-

cular interest. In this contribution we present the investigation of the electronic structure of Li-doped PPP as a function of dopant concentration by electron energy loss spectroscopy. We also show for comparison first data on K-doped PPP and new results on AsF₅ doped PPP.

EXPERIMENTAL

Partially oriented undoped PPP films with a thickness $\leq 1000 \text{ \AA}$ were prepared by the method of Kovacic⁴ using a stirring system for shear flow polymerization in a thin slit zone.⁵ All films were heat treated at 420°C for 24h in a vacuum of $< 10^{-9}$ Torr to increase the crystallinity. Li-doping was achieved by evaporating various amounts of Li onto the PPP-film under UHV-conditions. Within several hours the Li had diffused into the polymer films. The concentrations were estimated from the relative intensities of the Li and C K-absorption edges measured by ELS. K-doped films were obtained by treatment of the films in a solution of K-naphtalide in THF. AsF₅-doping was achieved by exposing the films to AsF₅ gas (1200 mbar). Electron energy loss experiments were performed using an UHV spectrometer with a primary electron energy of 170 KeV and an energy and momentum resolution chosen to be 0.15 eV and $0.04\text{--}0.1 \text{ \AA}^{-1}$, respectively.

RESULTS

In Figure 1 we show electron energy loss spectra in the energy range 0 to 10 eV for pristine and for Li-doped PPP films. The spectra were taken with a momentum transfer $q = 0.1 \text{ \AA}^{-1}$ in order to avoid contributions from surface excitations. The chain axis of the polymer was oriented parallel to the momentum transfer. For undoped PPP two losses at 4 eV and at 7 eV have been observed above the gap of 2.8 eV corresponding to excitations from occupied π -bands to unoccupied π^* -bands.⁶ For the lowest Li-concentration (0.5 at.% Li

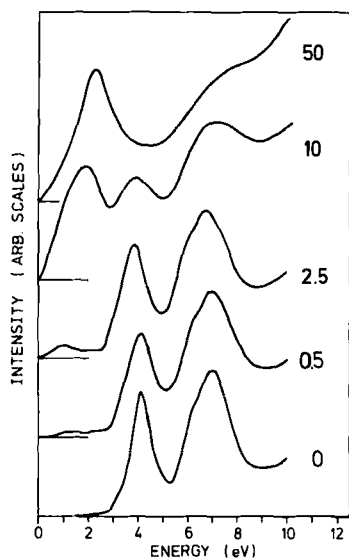


FIGURE 1 ELS spectra of pristine and Li-doped PPP. Li-concentrations as indicated in units of at.% per monomer.

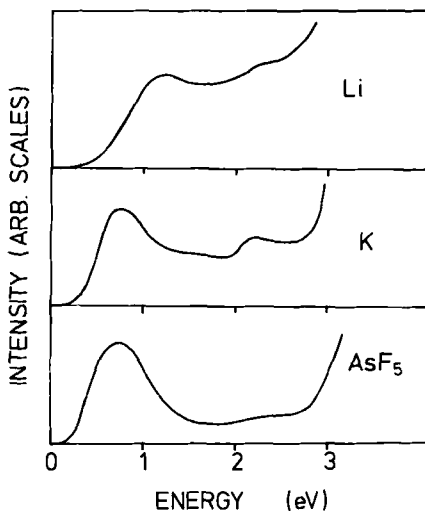


FIGURE 2 ELS spectra in the gap region for low n- and p-doped PPP.

per monomer) two small loss structures near 1 eV and near 2.2 eV appear in the gap. In Figure 2 these loss structures are shown in more detail. From a Kramers-Kronig analysis of the loss function the imaginary part of the dielectric function ϵ_2 can be derived, giving maxima at about 1.0 and 2.0 eV. We suggest to identify these maxima with transitions from the occupied bipolaron states to the conduction band (CB) as predicted by Brédas et al.¹ According to their calculations on Li-doped PPP, these states are located 0.5 eV above the HOMO and 0.62 eV below the LUMO. Thus the transition energies should be observed at 0.6 eV and 2.3 eV. Our measurements reveal that the bipolaron states are pushed more towards the centre of the gap as compared to the calculated energy position indicating a larger charge transfer from the Li-atoms to the C-atoms. For comparison, we show in Figure 2 similar transitions for K-doped and for AsF₅-doped PPP. The smaller energy of the lower transition in

the gap in K-doped PPP indicates a smaller separation of the bipolaron states from the band edges and thus a smaller charge transfer compared to Li-doping. In the AsF₅-doped PPP the higher bipolaron transition is hardly detectable, as already observed in previous measurements.³ In addition other experimental facts support our assignment of the transitions in the gap. The two maxima in the gap show no momentum dependence indicating localized transitions as is expected for transitions related to bipolarons. Furthermore, we point out that the intensity of the lower transition is much larger than that of the upper transition and that the transitions show an asymmetric line shape. Both facts are consistent with calculations of the oscillator strength for bipolaron related transitions by Fesser *et al.*⁷ Moreover, in the case of Li-doped PPP, we have observed that the two excitations disappear upon oxidation of the film in air.

Increasing the doping concentration leads to an increasing intensity and an upward shift of the low energy transition in the gap while the first π - π^* transition is decreasing in intensity. At the highest doping concentration, the gap has closed and a plasmon near 2.2 eV is observed, explaining the golden colour of this conducting polymer. The first π - π^* transition has disappeared and the second π - π^* transition has suffered a considerable broadening. A large part of the 2.2 eV plasmon shows a strong positive dispersion in momentum transfer which is characteristic for a free carrier plasmon. In Figure 3a we show the optical joint density of states (proportional to the optical conductivity) for undoped and for highly doped PPP as derived from a Kramers-Kronig analysis of the loss functions. In the undoped case, again two π - π^* transitions at 4 and 6 eV and the σ - σ^* transitions around 12 eV are seen. For highly doped PPP, the first π - π^* transition has transformed into Drude-like excitations at low energy. The second π - π^* transitions as well as the σ - σ^* transitions are shifted and broadened probably due to a transformation of the non-planar PPP structure into a planar struc-

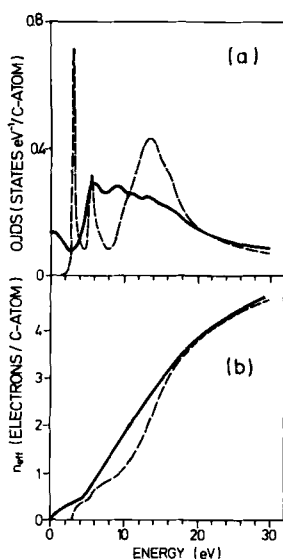


FIGURE 3 Optical joint density of states (a) and n_{eff} per C-atom (b) for pristine (broken line) and fully Li-doped (full line) PPP.

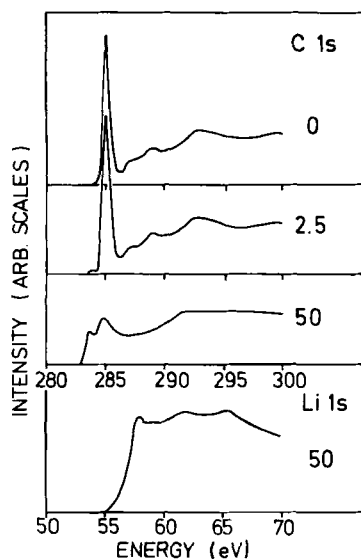


FIGURE 4 Core-level excitations of Li-doped PPP. The curves are labelled according to the Li-concentration.

ture of doped PPP. This change of structure upon doping was also predicted by Brédas et al.¹ In Figure 3b we show the effective number n_{eff} of valence electrons taking part in transitions up to a certain energy. In the undoped case, the π -electrons give rise to two steps, corresponding to the two highest occupied π -bands. Above 10 eV a third step appears mostly due to excitations of σ -electrons. In highly doped PPP the lowest step has moved to zero energy. A gap of 1.7 eV between the remaining VB and the CB as predicted by the theory¹ would lead to a small $n_{\text{eff}} \sim 0.05$ for $E < 1.7$ eV due to excitations of electrons in a partially filled CB. Above 1.7 eV a step-like increase to $n_{\text{eff}} \sim 0.6$ should appear due to excitations of π -electrons from the VB. This is clearly not observed, indicating that the gap between VB and CB is almost closed.

In Figure 4 we show the core-level excitations of carbon 1s

and Li 1s electrons. In undoped PPP, the lowest energy peak at 285 eV is identified as excitations from the carbon 1s states into antibonding π^* -bands. The peak does not reflect the density of states of the unoccupied π^* -states. Due to the strong interaction of the CB states with the core hole a resonance-like absorption into the bottom of the CB is observed.⁸ At higher energies satellites as well as $1s\text{-}\sigma^*$ transitions are observed. At a Li concentration of 2.5 % a shoulder at 284 eV appears. We suggest to identify this shoulder with excitations of carbon atoms in those benzene rings having an adjacent Li atom. Due to the charge transfer from the dopant to the polymer these carbon atoms have a lower binding energy of the 1s level. Using an approximate relation between change in binding energy (chemical shift) and charge on carbon atoms $\Delta E = 6 \text{ eV/e}^9$, the additional charge on the carbon atoms is about 0.15e. Assuming that most of the charge transferred from the Li atoms to the polymer goes to the next ring having 6 carbon atoms gives the result that the 2s electrons from the Li-atoms are almost completely transferred to the polymer. At 50 % Li-doping the C 1s core level spectrum shows two peaks at 284 and 285 eV having nearly the same intensity. Thus about one half of the carbon atoms have a lower 1s binding energy indicating that each second ring has an adjacent Li-atom. The broadening of the peaks can be explained by a stronger shielding of the core hole in the metallic state. Those C-atoms in rings having no adjacent Li atoms have still the same 1s-binding energy and thus the same charge as in undoped PPP. Our results are qualitatively in line with the calculations of Brédas *et al.*² Again the assumption of a stronger charge transfer from the Li-atoms to the carbon atoms (1 instead of 0.6 electrons) gives a closer agreement between theory and experiment. In the lower part of Figure 4 we show the core-level excitation of the Li 1s state in fully doped PPP. We tentatively ascribe the two maxima at 62 and 65 eV to the crystal-field splitted Li 2p states. The peak near 58 eV might be associated with the unoccupied Li 2s state mixed

with the carbon π -bands. The position of the Fermi threshold is not clear in the carbon 1s as well as in the Li 1s excitation spectrum.

SUMMARY

Our results give evidence for bipolaron states in the gap for p- and n-doped PPP. These defects have been observed now also in polypyrrol and in polythiophene.¹⁰ Thus the bipolaron model might be a general concept to explain the high conductivity in all conducting polymers having a nondegenerate ground state. In the fully Li-doped PPP we have observed a metallic state and the electronic structure has been investigated in detail. Qualitative but not quantitative agreement with theoretical calculations has been obtained. The discrepancies can be reduced by assuming a higher charge transfer between Li and the polymer compared to that used in the calculations.

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