Evidence of Intrinsic Extended π-Bonding Band and Metalliclike Behavior in Undoped and Doped Electropolymerized Poly(3-Methylthiophene) Films

Y. Jugnet,(1) G. Tourillon,(2) and Tran Minh Duc(1)

(1)*Institut de Physique Nucléaire and Institut National de Physique Nucléaire et de Physique des Particules, Université Claude Bernard Lyon 1, F-69622 Villeurbanne Cedex, France*

(2) *Laboratoire pour l'Utilisation du Rayonnement Electromagnétique, Université de Paris-Sud, F-91405 Orsay Cedex, France*

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Valence-band ultraviolet photoemission spectra of undoped poly(methylthiophene) show an extended π bonding at 1.05 eV from the Fermi level, E_F. Doping with ClO_4^- proceeds through uniform extraction of π-bonding electrons resulting in (i) an extension of the π band and (ii) an E_F shift by 0.8 eV relative to this band and 0.5 eV relative to the core levels. Band-gap narrowing reduces the $\pi \rightarrow \pi^*$ shakeup energy of the x-ray photoemission spectroscopy C1*s* peak from 2.7 to 1.7 eV with a strong intensity enhancement.

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Organic conducting polymers have attracted considerable attention this last decade because their electrical conductivities can be varied over 12 orders of magnitude by doping.[1] Their interest encompasses a large domain of applications.[1,2] Electronic structure calculations have been developed for an understanding of their properties.[3-7] The dependence of electronic structure on molecular architecture has been put forward, in particular for leading to extended π-electron states which are most important in transport properties and conduction.[6] However, most models of conduction by doping are based on carrier propagation through chains with disorder and/or localized charges. Bond-alternation defects possibly lead to nonlinear soliton excitation[8] and conduction in doped polypyrrole, polythiophene, etc., has been ascribed to levels localized in the gap associated to spinless bipolarons formed by lattice deformations around localized charges.[9] Experimentally some x-ray photoemission spectroscopy (XPS) core-level and valence-band studies have been reported on the subject[10-18] with fewer ultraviolet photoemission spectroscopy (UPS) valence-band investigations.[19-21] However, from these results no conclusive agreement comes out. Among conducting polymers, polythiophene and derivatives represent the first class of polymers chemically stable in air and moisture in both doped and undoped states.[22] We report in this Letter a UPS and XPS investigation of the electronic structure of poly(3-methylthiophene) (pMeT) films which are electropolymerized and doped with ClO_4^-. Present conclusions relevant to the conduction mechanism appear to be general for any thiophene-derivative polymer.[23]

The pMeT films are electrochemically grafted on Pt electrodes in CH_3CN $5\times10^{-1}M$ $LiClO_4$, $5\times10^{-1}M$ methylthiophene electrolytic medium. The Pt electrode is anodically polarized at +1.35 V (referred to a saturated calomel electrode) for obtaining the doped films and cathodically polarized at −0.2 V (referred to a saturated calomel electrode) for the undoped films.[24] Films are 800–1000 Å thick. Electron spectroscopies are most sensitive to the first atomic layers; thus sample surface cleanliness is crucial. Samples grown and transferred under a controlled argon atmosphere and those obtained in air show basically the same spectra in UPS and in ionization-neutralization spectroscopy.[25] Accordingly no surface-cleaning procedure has been applied further *in situ*, since instead of being useful it may rather induce defects on the polymer surfaces.

The UPS spectra have been measured in a Vacuum Generators ESCA III spectrometer with He I and He II resonance lines and resolution of 0.2 eV. XPS experiments have been run in the same spectrometer and with a Hewlett Packard 5950B spectrometer at better resolution, viz., 0.7 eV with monochromatized Al $K\alpha$ radiation. On both doped and undoped pMeT films the S/C stoichiometry is checked to be 0.18, i.e., very close to the 0.2 nominal value. The ClO_4^- dopant concentration as measured from either Cl/C or O/C ratio corresponds to a doping level of 30%.

Figure 1 shows the He II spectra of pMeT doped and undoped. For purpose of band assignment the gas-phase spectrum of the thiophene molecule[26] is also shown together with two theoretical UPS spectra of polythiophene from, respectively, the CNDO/S3 model[20] and a valence effective Hamiltonian (VEH) calculation.[9] If we superimpose the undoped pMeT spectrum with the thiophene one, we clearly see that the deepest valence levels are not fundamentally modified upon polymerization. Solid-state effects are manifest through a energy shift by 5 eV of the whole gas-phase spectrum towards lower binding energy (BE) to be aligned with the polymer spectrum and through a broadening of the molecular levels into bands. We rather focus our attention on the BE region below 4 eV. This part of the spectrum is dominated by a sharp peak at 3 eV BE assigned to the nonbonding π band. Physically more important, we find the emergence upon polymerization of a prominent broad band at ~2 eV on the lower BE side of this peak. This

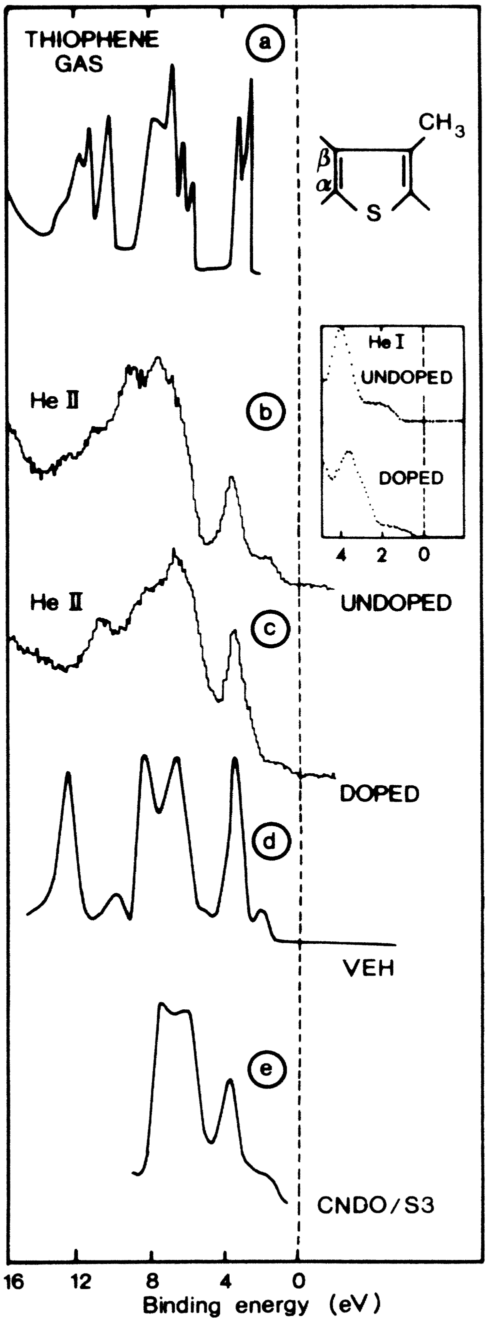

FIG. 1. He II and (inset) He I UPS spectra of ClO_4^--doped (curve *c*) and undoped (curve *b*) pMeT electropolymerized films. For the sake of band assignment there are also shown gas-phase thiophene (Ref. 26) (curve *a*) and theoretical UPS spectra of polythiophene polymers from VEH (Ref. 9) (curve *d*) and CNDO/S3 (Ref. 20) (curve *e*) calculations. The theoretical curves *d* and *e* result from calculations of density of occupied states broadened by a 0.7-eV Gaussian without any cross-section modulation. The formula for pMeT indicates the α and β positions for C.

emission is explicitly attributed within the CNDO/S3 model to the extended π-bonding frontier orbitals.[20] Experimentally these π-bonding states have not been detected in the case of polypyrrole[6,13] and polyacetylene[27] and only weakly detected in the case of poly(*p*-phenylene).[18]

The emergence of the π-bonding band clearly means that a long-range order exists along the polymeric chains with large interaction between the aromatic rings. In the competition between the topological disorder along the chain which tends to localize the electronic states and the intermolecular hopping integrals which tend to delocalize them, we find that the latter are playing the major part in the investigated films. However, the number of units constituting the chain cannot be deduced directly. Our measurement locates the upper π-band edge at 1.05 ± 0.1 eV below the Fermi level E_F. If we assume E_F to be intrinsically located at midgap, this value is in agreement with a band gap of 2.2 eV for polythiophene as predicted by VEH calculations[9] and inferred from optical measurements.[14]

Let us consider now the effect of doping. From the ClO_4^- spectrum[28] we can conclude that the dopant does not significantly interfere in the BE region of interest. In the UPS spectrum of doped pMeT films the π-bonding band is extending further towards lower BE up to 0.25 eV below E_F. This result associated to the core-level shakeup data (see later discussion) is consistent with a narrowing of the band gap upon doping and is to be put together with band-gap values of 0.35 eV from optical measurements[22] and of 0.14 eV as predicted by the bipolaron model for 100% doped polythiophene.[9]

The above UPS spectra give some significant indication on the position of E_F in undoped and doped states. Under oxidation, electrons are extracted from the π extended states of the polymeric chain as evidenced by the decrease of the total intensity of this band relative to the nonbonding which is, however, difficult to quantify (see Fig. 1). Since the density of these states is rather low and flat in the vicinity of the Fermi energy, there results a large shift of E_F into the valence band, measured here to be 0.80 eV. If we assume the rigid-band model to be valid, nonbonding bands (and core levels) should move towards lower BE following the E_F shift: actually the π-nonbonding band is shifted by 0.50 eV.

At this point it is worthwhile to comment on the reasons why such results have not been produced up to now. First, in the XPS valence band, because of the low cross section for π bands and large width of extended states, the band is smeared out.[18,23] When UPS more sensitive to π states has been employed, the investigated polymers probably contain structural disorder precluding emergence of a π delocalized band and its evolution upon doping.

Figure 2 shows the evolution of C1*s* and S2*p* core levels from the pMeT films upon ClO_4^- doping. The modifications are completely reversible, very pro-

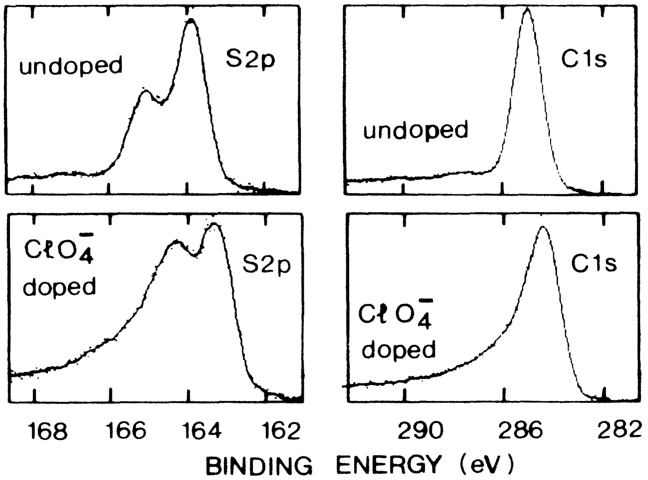

FIG. 2. C1*s* and S2*p* core levels of ClO$_4^-$-doped and undoped pMeT electropolymerized films.

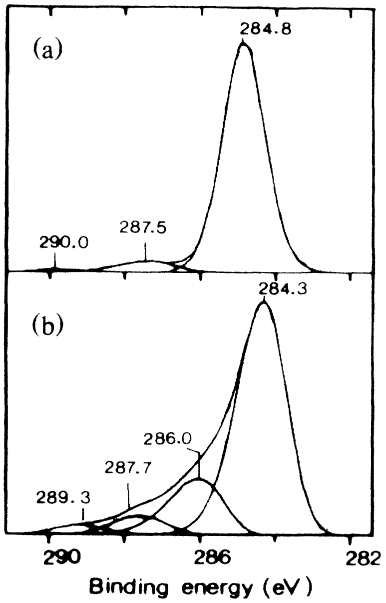

FIG. 3. Decomposition of C1*s* spectra into Gaussian Lorentzian line-shape components for (a) undoped and (b) ClO$_4^-$-doped pMeT electropolymerized films.

nounced and fundamentally identical for the two atoms: Both core levels are shifted towards lower BE by 0.5 eV while broadening markedly and asymmetrically on the high-BE side. Obviously the same origin must hold for both levels and their interpretation closely related to the UPS data on the electronic structure as well. Accordingly since spin-orbit splitting somewhat obscures the S2*p* spectrum, only detailed inspection of the C1*s* spectrum is given in Fig. 3. In reduced form, the C1*s* peak presents three components at, respectively, 284.8, 287.5, and 290.0 eV BE with relative intensities of 1, 0.07, and 0.02. In the main peak at 284.8 eV there contribute all the C atoms in the chain: The α and β components C1*s* in the thiophene molecule are separated by 0.3 eV[29] and unresolved in our spectrum. The energy separation of the two other components from the main peak—2.7 eV (5.2 eV)—corresponds exactly to (twice) the $\pi \rightarrow \pi^*$ transition excitation from the highest occupied state to the lowest unoccupied state as measured by the optical absorption band.[22] Consequently they are assigned as shakeup satellites.

In the doped state, the emergence of the prominent shoulder on the high-BE side of the main peak can be ascribed to a Doniach-Sunjić asymmetry as proposed for graphite intercalation compounds.[30] However, the density of occupied states at E_{F} is too low to explain the large observed asymmetry. Then the C1*s* spectrum is decomposed into four components at 284.3, 286.0, 287.7, and 289.3 eV with respective intensity ratios of 1, 0.26, 0.08, and 0.04. The direction and magnitude of the main-peak shift upon doping (-0.5 eV) is closly related to the previously discussed E_{F} shift. Our result is in contrast with the shift reported in the reverse direction for low-conductivity BF$_4^-$-doped polythienopyrrole[16] and for ClO$_4^-$-doped polypyrrole.[13] The appearance of the intense peak at 286 eV can be interpreted in different ways: presence of disorder and defects along the polymeric chains, formation of new chemical sites induced by the doping process, or enhancement of the shakeup satellite. The hypothesis (disorder and defects), proposed by Pfluger and Street,[15] is inconsistent with (i) the UPS results which clearly show the presence of extended π-bonding band and (ii) the complete reversibility of this peak during doping and undoping cycles. Moreover, S core levels should not experience shifts due to structural defects in the C backbone. Another interpretation invokes the creation of molecular cation charges localized on some moieties by P doping. Conductivity is then ensured by the bipolaron levels formed by local distortion of the lattice around these localized charges. Our results cannot reject this hypothesis. However, we point out that the intensity of this peak is not related to the dopant concentration as would be the case in the formation of localized chemical sites by oxidation.[23] Indeed the intensity of this peak is very weak with the doped poly (N-methylpyrrole) although the doping level is as high as 30% and in this case, steric effects twist the N-methylpyrrole units leading to localized positive charges but low conductivity ($\sigma \sim 10^{-3}\ \Omega^{-1}\cdot\mathrm{cm}^{-1}$).[31]

Therefore, we rather advocate the hypothesis of an enhancement of $\pi \rightarrow \pi^*$ shakeup satellite from the modification of the electronic structure of pMeT films by doping. This hypothesis explains the last two remaining peaks as well. The energy separation between the successive components of the C1*s* emission is constant, equal to 1.7 eV, and therefore gives the shakeup splitting. This reduction of the $\pi \rightarrow \pi^*$ transition energy agrees closely with the red shift of the broad optical absorption band peaking at 1.7 eV.[22]

In conclusion the electrochemically synthetized pMeT films display long-range order, evidenced by the observation not explicitly made previously of intrinsic extended π-bonding states. P doping does not inject localized charges but proceeds through a uniform extraction of electrons. It follows a narrowing of the band gap as evidenced by UPS valence-band spectra, a core-level shift due to the Fermi level shift, and a shakeup satellite modification. These results corroborate a metalliclike conduction mechanism as proposed for doped pMeT from EPR data.[32]

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