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# Temperature evolution of the electronic band structure of the undoped and doped regioregular analog of poly(3-alkylthiophenes): A spectroscopic and theoretical study

P. Barta,<sup>a)</sup> P. Dannetun, and S. Stafström

*Department of Physics (IFM), Linköping University, S-581 83 Linköping, Sweden*

M. Zagórska

*Department of Chemistry, Technical University of Warsaw, PL-00 664 Warsaw, Poland*

A. Proń

*Department of Chemistry, Technical University of Warsaw, PL-00 664 Warsaw, Poland and*

*Department of Material Science and Ceramics, Academy of Mining and Metallurgy, PL-30 059 Kraków, Poland*

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The undoped and ferric chloride *p*-doped “head-to-head” “tail-to-tail” analog of poly(3-decylthiophene) obtained from substituted bithiophenes, i.e., poly(4,4′-didecyl-2,2′-bithiophene)-PDDBT has been investigated. The samples were studied by means of ultraviolet photoelectron spectroscopy, optical absorption measurements, and polymer bands structure calculations. Experiments were carried out at different temperatures between 100 °C and –180 °C. The results indicate that PDDBT is nonplanar in the undoped state. No temperature effects have been observed in the  $\pi$ -electron properties. In the doped state, however, lowering of the temperature results in an increase of the system planarity that modifies the electronic band structure. This effect has been shown to be fully reversible with temperature.

## I. INTRODUCTION

The fact that  $\pi$ -conjugated polymers can be doped to a state of high electrical conductivity has been well known since the pioneering works of the mid-seventies.<sup>1</sup> A large number of organic  $\pi$ -conjugated systems that can be made conducting has been proposed since this time. These so-called electroactive polymers are very attractive from both a scientific and a technological point of view. Scientifically, interest arises from the large electron-phonon coupling which is characteristic for all low dimensional systems. This coupling leads to low lying self-localized excitations in the polymer system (polarons, bipolarons or solitons). These excitations can be created by chemical, electronic, or optical treatment of the conjugated polymer. Technologically, the interest is focused on the possibility of processing organic components for applications in electro-optical and microelectronic devices in industry.

The polyalkylthiophenes represent one of the most interesting of the conjugated systems, because of their solubility and processibility. During the 1980's, it was shown<sup>2,3</sup> that substitution of a hydrogen, in the 3-position of thiophene group, by an alkyl group longer than propyl, makes the polymer soluble in common organic solvents. Since then, much work has been devoted to the polyalkylthiophene system and its derivatives (mainly different substituents at the 3-position).<sup>4–7</sup> Simple polyalkylthiophenes usually polymerize by the C(5)–C(2′) coupling (“head to tail”), as indicated in Fig. 1(a). This kind of coupling is favored for steric reasons. The C(2)–C(2′) (“tail to tail”)

and the C(5)–C(5′) (“head to head”) couplings, however, cannot be totally excluded. Thus, the poly(3-alkylthiophenes) ought to be treated as nonregular, predominantly “head-to-tail” coupled, conjugated polymers with a less than ideal degree of chain regularity. In other words, the resultant structure should contain a numbers of thiophene rings twisted out of the plane of conjugation because of steric interactions, mainly among alkyl chains.

There are two ways to synthesize regiospecific poly(3-alkylthiophenes). The first method, by McCullough and co-workers,<sup>8</sup> allows significant regiocontrol at each coupling step in the polymerization process, which leads to pure “head to tail” couplings along the polythiophene chain. A second method, suggested by Zagórska and Krische,<sup>9–11</sup> yields directly the “head-to-head” (or “tail-to-tail”) analog of poly(3-alkylthiophene) by polymerization from the corresponding bithiophene dimers [see Fig. 1(b)]. Accordingly, the latter polymerization routine can be used to obtain strictly regular poly(4,4′-dialkyl-2,2′-bithiophene) systems as it is illustrated in Fig. 1(c). The chemical, electrochemical and electrical properties of this polymer have been described elsewhere.<sup>12–14</sup> These previous results indicate that this strictly stereoregular system possesses an electronic band structure in the neutral state which is different than conventional poly(3-alkylthiophene) prepared from the monomer.

The conventional poly(3-alkylthiophene)s are known to exhibit thermochromism, caused by thermally induced conformational defects in the  $\pi$  system of the polymer backbone, which are driven by side chain interactions.<sup>15,16</sup> Moreover, the changes in the electronic structure upon oxidative doping have been studied.<sup>17</sup> It is of significant interest to compare the temperature dependence of the

<sup>a)</sup>Permanent address, where correspondence should be addressed: University of Mining and Metallurgy, Faculty of Physics and Nuclear Techniques, PL-30059 Kraków, al.Mickiewicza 30, Poland.

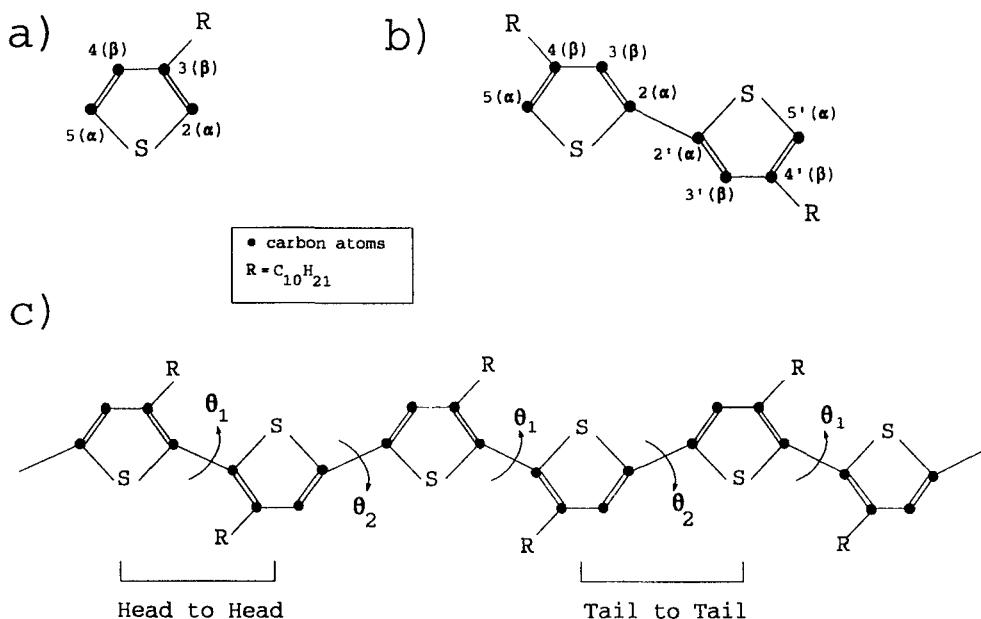


FIG. 1. (a) The common notation of atoms in 3-alkylthiophene—the monomer for the preparation of poly(3-alkylthiophene). Position of the alkyl group is marked by letter *R*. (b) The common notation of atoms in 4,4'-dialkyl-2,2'-bithiophene—the monomer for the preparation of regiospecific poly(4,4'-dialkyl-2,2'-bithiophene). (c) Schematic picture of the molecular structure of regiospecific poly(4,4'-dialkyl-2,2'-bithiophene) obtained by 5,5' coupling of 4,4'-dialkyl-2,2'-bithiophene. The  $\theta_1$  and  $\theta_2$  torsion angles indicate where the conformational defects could exist. These defects would induce non-planarity of the chain.

electronic structure of the regiospecific poly(4,4'-dialkyl-2,2'-bithiophene) system, with that of the conventionally prepared poly(alkyl-thiophene)s. In the present work, thin films of poly(4,4'-didecyl-2,2'-bithiophene), or PDDBT, have been studied by photoelectron spectroscopy and optical absorption spectroscopy. The application of photoelectron spectroscopy, both with ultraviolet photons (UPS) and x-ray photons (XPS), to the study of the electronic and chemical structure of conjugated polymers has been described elsewhere.<sup>18</sup> UPS is used to investigate the valence electron energy structure (the band structure), which can be strongly affected by charge-transfer processes occurring during the reduction/oxidation treatment of the conjugated system. The relatively high photoionization cross section for C(2*p*)-derived states renders UPS more useful than XPS for studying the  $\pi$  states at the valence band edge of polyconjugated organic systems. XPS, on the other hand, is used to study the core levels of the polymer constituents.

Doping induced changes in the electronic structure of polythiophene and polyalkylthiophene have been studied extensively in the past. It is well known that doping leads to formation of localized states which in the case of the polythiophene class of material are predominantly bipolarons. Unfortunately, the gap states created by oxidation (positively charged “hole” states) cannot be detected by means of the photoelectron spectroscopy, since they do not contain electrons. Instead, the optical absorption studies have been performed in order to follow the thermal evolution of mid-gap levels created by the doping process.

The temperature evolution of valence band levels and mid-gap states were studied over a wide temperature range,

from 400 K down to 90 K. To the best of our knowledge, the temperature evolution of the electronic band structure of conjugated polymers has not been investigated previously by means of the photoelectron spectroscopy.

There is a strong relationship between the structural homogeneity, on the one hand, and the electrical and optical properties of any conjugated system, on the other hand. For a planar system of fully conjugated monomer units, the  $\pi$  states are delocalized over the length of the polymer chain. A decrease in the planarity leads to a decrease in the degree of  $\pi$  overlap between  $p_z$  atomic orbitals of the carbon atoms at the sites where the monomer units are linked. The degree of planarity directly determines the effective conjugation length as well as the width of the  $\pi$  bands, including the optical band gap. Furthermore, the longer conjugation and the lower number of nonconjugated centers, the better electrical transport and optical properties.

In order to quantify the experimental results in parameters that are not directly subject to the measurements, theoretical studies play an important role. In the present study we have employed geometry optimization and band structure calculations to interpret the experimental spectra in terms of the coupling between the geometrical structure and the electronic properties of the material. An important parameter in this case, turns out to be the planarity of the system. It is well known from earlier studies of polythiophene that a change in the torsion angle between adjacent thiophene units affects the band gap and the bandwidth quite dramatically.<sup>19</sup> When polythiophene is planar or close to planar, the PDDBT system exhibits a large degree of nonplanarity in the ground state. As will be

shown later, this feature introduces a new type of coupling, namely, a change in the electronic system, for instance, by means of doping, which induces change in the torsion angle between thiophene rings (the electron-libron coupling). This phenomena has not been addressed in the case of the polythiophene class of materials until now, but is well known to exist in polyaniline.<sup>20</sup>

This paper is structured as follows. In Sec. II the sample preparation and the experimental techniques are described. The results are presented and discussed in Sec. III, first in terms of the core level spectra and then the valence band spectra and optical absorption spectra. In both cases the results for both the undoped and the doped polymer are presented. Finally, conclusions are given in Sec. IV.

## II. EXPERIMENT

The 4,4'-didecyl-2,2'-bithiophene substrates for polymerization were prepared from 3-alkylthiophenes by metalation with butyllithium followed by oxidative coupling with copper chloride. The polymerization of poly(4,4'-didecyl-2,2'-bithiophene) has been reported in detail by Zagórska.<sup>9</sup> Thin films of neutral PDDBT were obtained by spinning from chloroform solution onto (naturally oxidized) optically flat Si wafers, which were washed in chloroform and dried immediately before spin coating. The samples were mounted immediately on a heatable/coolable copper sample-holder and introduced to the spectrometer within minutes. The samples were then pumped down to  $10^{-6}$  Torr, moved into a UHV sample preparation chamber ( $P < 10^{-10}$  Torr), and heated to 100 °C for a few minutes, in order to remove the remaining solvent and any surface hydrocarbon contamination. Doping was carried out by removing a sample from the UHV system and placing it in a solution of dried, anhydrous  $\text{FeCl}_3$  in acetronile (0.1 M). The doping level was controlled by soaking time. It is known that doping with  $\text{FeCl}_3$  produces  $\text{FeCl}_2$  as a side product. Because the educed species as well as excess  $\text{FeCl}_3$  should be removed after the charge transfer (doping) process, the doping had to be carried out *ex situ*. Consequently, the ferrous/ferric chloride was removed from the sample by repeated washing in acetronile, followed drying in UHV (in the spectrometer preparation chamber). The drying temperature of the doped samples was kept below 70 °C to avoid the possibility of dedoping. The sample thickness was estimated by XPS from the intensity of the silicon substrate Si(2p) lines. A typical thickness was about 100 Å.

The UPS spectra were recorded using monochromatized He I (21.2 eV) radiation from He-resonance lamp, while unmonochromatized Mg  $K_{\alpha 1\alpha 2}$  was used for XPS. For both UPS and XPS, the electron energy analyzer resolution was 0.2 eV, such that the Au(4f<sub>7/2</sub>) line would be recorded with a full width at half maximum (FWHM) of 0.9 eV. The reproducibility of energy measurements is  $\pm 0.1$  eV. Sample charging effects in both XPS and UPS can also be excluded, since no change in apparent work function was detected, either with change in temperature or with illumination of 0.5 W from an Ar-ion laser (which normally reveals sample charging problems in thin film

insulator systems). The temperature setting was accomplished using a gas-flow variable temperature cryosystem. The temperature was controlled using a copper-constantan thermocouple mounted on the thermal bridge between the holder and cryosystem. Therefore, temperature was measured with a total accuracy better than 5 K. All of the spectra are completely reproducible with temperature cycling between high and low limits.

Samples for optical absorption spectroscopy studies were prepared by casting from chloroform solution onto quartz substrates. A previously determined amount of dopant solution was applied to the polymer surface. The polymer film gradually changed color from yellow, in neutral state, to dark navy blue, after doping. The samples were then washed in pure acetronile, installed on the copper sample holder, introduced to the spectrometer, and dried in instrument's UHV system.

Optical absorption spectroscopy was carried out using a new instrument of own design and construction. The spectrometer consists of a SPEX 1682 broadband tungsten radiation source covering 300–3000 nm, a SPEX 340E monochromator with a dual turret so that two gratings can be used, and two (Si and Ge) solid state detectors. Further details will be published elsewhere.<sup>21</sup>

The calculations performed for this study include geometry optimizations and electronic band structure calculations. The geometry optimizations are carried using the semiempirical modified neglect of diatomic overlap (MNDO) method<sup>22</sup> and, for comparison, the Austin Model 1 (AM1) method<sup>23</sup> on oligomers of thiophene and alkylthiophenes. Electronic structure calculations are performed using the pseudopotential valence effective Hamiltonian (VEH) approach<sup>24</sup> with the geometry optimized from MNDO calculations as input.

In a previous work Dos Santos *et al.*<sup>25</sup> have studied the effect of head-to-head and tail-to-tail couplings on the torsion angle between the thiophene rings in bithiophene. We have repeated the AM1 calculations of Dos Santos *et al.* for longer thiophene oligomers (tetrahexylthiophene) and obtained essentially the same results, namely, the nonplanarity of the PDDBT type of systems is due to the local interaction at the head-to-head coupling sites (see Sec. III). However, there is an intrinsic drawback of the AM1 method for obtaining reliable ground state geometries of thiophene systems, namely the  $C_\alpha-C_\beta$  and  $C_\beta-C_\beta$  distances are much smaller than that obtained in *ab initio* calculations reported by Boman *et al.*<sup>26</sup> or from MNDO optimization. The AM1 geometry fails to reproduce the experimental band gap of polythiophene whereas the MNDO result gives a much better agreement with experimental data. Therefore, in the case of PDDBT we have used the MNDO method and treated the torsion angle between adjacent thiophene rings as a parameter. Thus, the geometry is fully optimized for a set of torsion angles between the head-to-head coupled rings [ $\theta_1$  in Fig. 1(c)] while the tail-to-tail coupled rings are assumed to be planar ( $\theta_2=0$ ). We have performed electronic band structure calculations both for PDDBT and for polythiophene. The results show that the band structure around the Fermi

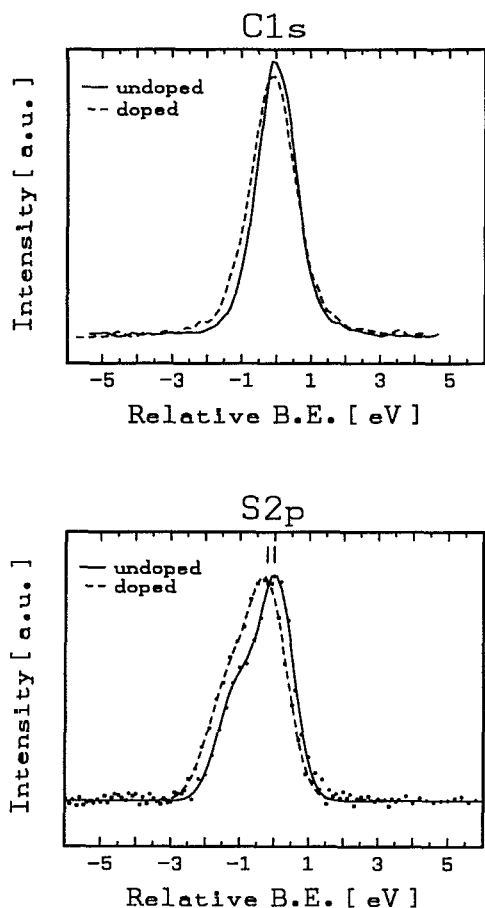


FIG. 2. Carbon C(1s) and sulphur S(2p) core level spectra for neutral and doped polythiophene. Binding energies are relative to the undoped chain.

energy is essentially unaffected by the presence of the alkyl chains, given that the geometry of the thiophene backbone is the same. Therefore, in order to save computational time the calculations are performed for polythiophene.

### III. RESULTS AND DISCUSSION

#### A. Core levels spectroscopy

The x-ray photoelectron spectroscopy (XPS) experiments were mainly carried out in order to check the sample quality. It was determined that the samples measured were oxygen and iron Fe(III) free (iron impurities could be present because  $\text{FeCl}_3$  was used as a polymerization agent). From a detailed examination of the individual core electrons peaks an estimation of the doping level can be obtained. Moreover, subtle changes in the core electron levels can indicate the nature of charge carrying species induced during oxidation of the sample. Typical XPS core spectra of undoped as well as doped PDDBT are shown in Figs. 2 and 3.

In the neutral state, the carbon C(1s) peak was detected at 284.7 eV (see Fig. 2—upper spectrum), containing the contributions of the ring and of the aliphatic side chain. The sulphur S(2p) line (lower spectrum) is located

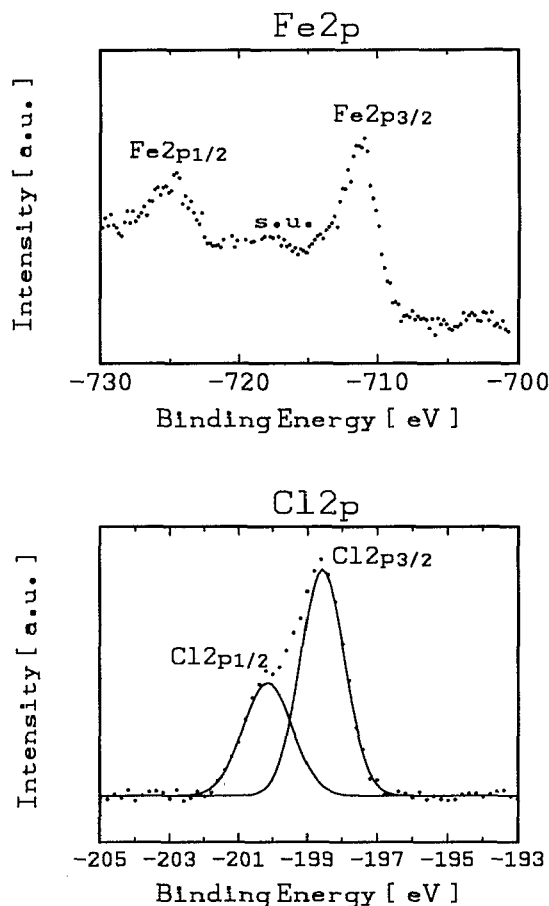


FIG. 3. Iron Fe(2p) and chlorine Cl(2p) core level spectra for polydiethylbithiophene doped with ferric chloride.

at 164 eV. The ratio of the intensities S(2p)/C(1s), averaged over several samples, indicates that there are about 13.6 carbon atoms per sulphur atom, in a good agreement with the ideal value from neutral polymer chemical formula,  $(\text{C}_{14}\text{H}_{22}\text{S})_n$ .

After doping, peaks corresponding to the dopant agent could be detected. The line at 711.3 eV, corresponding to electrons removed from the Fe(2p<sub>3/2</sub>) core levels, is shown in Fig. 3. The spin-orbit splitting can be observed for the Fe(2p) line and the line of singlet Fe(2p<sub>1/2</sub>) electrons was detected at about 724.5 eV. The wide peak at 717 eV corresponds to shake-up satellite of the triplet electrons. This spectrum is representative for Fe(III) iron. The spin-orbit splitting can be also observed for the chlorine Cl(2p) line. Because the splitting is weaker (1.6 eV), this effect can be visualized by numerical deconvolution of the experimental curve, as it is presented in Fig. 3 by solid lines. From the binding energies and from the Fe(2p)/Cl(2p) intensity ratio, it is determined that the dopant agent exists in the form of the  $\text{FeCl}_4^-$  complexes.

To study the evolution of the XPS peaks upon doping, it is necessary to take into account a shift of the Fermi energy as a result of chemical modifications of the sample. This is because the photoelectron spectra are referred to the Fermi level whereas the chemically significant reference is the vacuum level. The shift of the Fermi level was

estimated from the shift of the work function obtained from UPS spectra. The carbon and sulphur core level peaks, with already corrected binding energies, are shown in Fig. 2 (dashed line). The maximum doping level, estimated from relative intensities of S(2p) and Cl(2p) lines, including the weighting factor due to experimental cross sections parameters, was about 20 mol. %.

In principle, the doping process affects both the carbon and sulphur lines. The S(2p) line for the doped sample is broader than the corresponding peak for the undoped sample and is shifted by about 0.2 eV towards higher binding energy compared to this peak. For the C(1s) line, doping results only in a broadening. The position and the shape evolution of the carbon and sulphur peaks of the polymer backbone should be discussed from the point of view of charge carrying species (polarons, bipolarons) induced during doping. The position of the carbon C(1s) peak does not change upon doping, since it is dominated by aliphatic carbon atoms in the side groups. Since doping in this case corresponds to the electron transfer from the polymer chain, the lines corresponding to polymer backbone carbons are shifted towards higher binding energies, thereby resulting in the observed change in the peak shape. In case of bipolarons, theoretical results<sup>27,28</sup> predict the existence of a well-defined component of the spectrum located at 1.7 eV below the main line. But because of the large number of carbon atoms in the side chains, which are not affected by doping, this feature cannot be resolved.

The theoretical calculations<sup>28</sup> indicate that the doping (charge transfer process) also affects sulphur atoms. In the case of polarons, the charge density is almost equally distributed over all of the sulphur sites belonging to one polaronic topological excitation (delocalized over six thiophene rings). Therefore, the S(2p) line is shifted towards higher binding energy by about 0.3 eV. For bipolarons, three different types of sulphur are expected: the outer two sulphur atoms are mostly affected, the two atoms closest to the center are almost not affected and, finally, the atoms in between are only slightly polarized. The resultant charge distribution should lead to broadening of the XPS line, as well as to a shift slightly towards higher binding energy. The S(2p) line measured (Fig. 2, lower curve) for a doped sample is broadened and shifted by about 0.2 eV, relative to the S(2p) of an undoped sample. Note, that the core electron spectra did not change with decreasing temperature.

In summary, the XPS spectra obtained indicate the high degree of the sample quality. The studies of changes in the core spectra upon doping cannot be considered as a clear indication of the nature of the charge carrying species in case of a doped sample. The data, however, with the help of theoretical estimates<sup>28,29</sup> may lead to the conclusion that the shapes of the XPS spectra are in better agreement with the bipolaron model.

## B. Valence bands spectroscopy

### 1. Undoped state

The electronic band structure of the neutral, undoped, unsubstituted polythiophene system, which is known to be

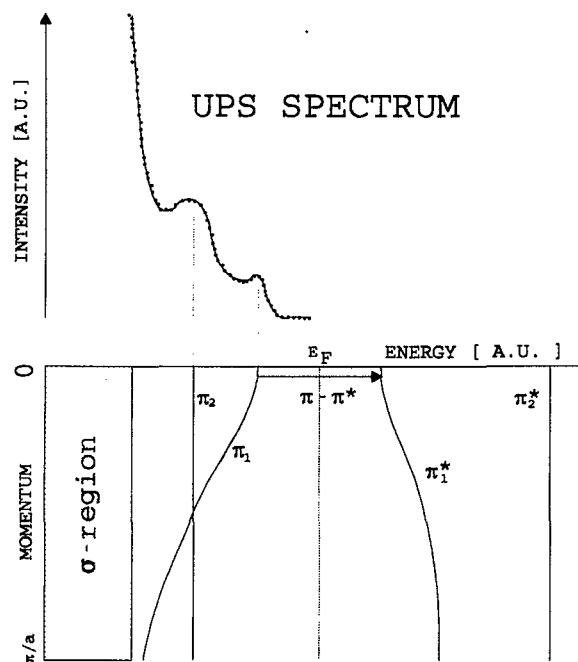


FIG. 4. Scheme of the polythiophene (or PDDBT)  $\pi$ -band structure near the Fermi energy. The corresponding low binding energy portion of the UPS spectrum is shown.

planar at room temperature, is schematically depicted in Fig. 4. In unsubstituted polythiophene, the optical absorption edge, derived from the lowest energy of  $\pi$ - $\pi^*$  transition, corresponds to an electronic band gap of about 2.1 eV.<sup>30</sup> In PDDBT, however, the optical absorption edge measured at room temperature is near 2.7 eV, with the absorption peak near 3.2 eV, as seen in Fig. 5. The larger optical gap indicates the existence of a larger band gap in

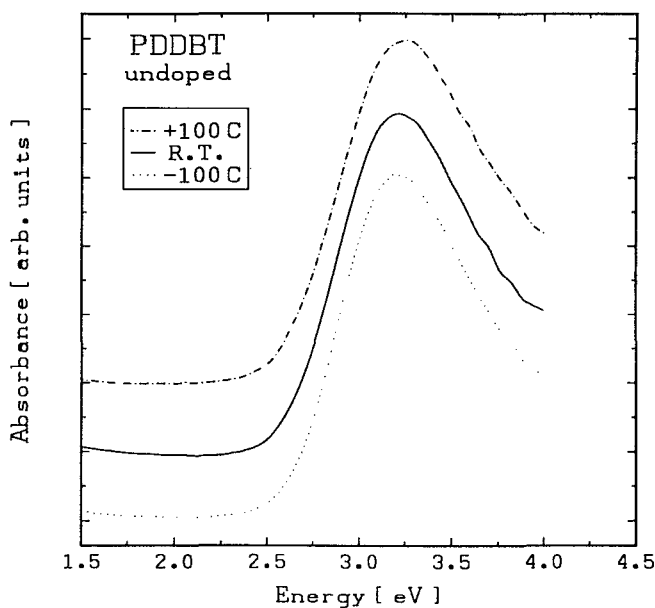


FIG. 5. Optical absorption spectra of PDDBT at three different temperatures.

PDDBT, i.e., a larger difference in energy between the highest occupied  $\pi$ -band ( $\pi_1$ ) and the lowest unoccupied  $\pi$ -band ( $\pi_1^*$ ) in Fig. 4. In PDDBT, as in the polyalkylthiophenes, the aliphatic groups do not contribute directly to the  $\pi$ -band structure, since these groups contain only  $\sigma$  bonds among carbon and hydrogen atoms. They are located at higher binding energies than the  $\pi$  bands. Accordingly, the presence of alkyl groups does not affect directly the value of  $\pi$ - $\pi^*$  transition energy. Indirectly, however, interactions among the alkyl groups on neighboring chains can lead to a departure from planarity of the polyalkylthiophene backbone, an effect which leads to the observed thermochromism in the polyalkylthiophenes.<sup>15,16</sup> Moreover, the magnitude of the effect strongly depends upon the length of the alkyl group.<sup>31</sup>

In the simple picture discussed, the relatively large value of the optical absorption edge is an indication of the presence of finite torsion angles among the thiophene rings in the PDDBT backbone. The fact that the optical absorption edge is as sharp as in conventional unsubstituted polythiophene indicates that there is a reasonably specific value of the torsion angle, rather than a broad distribution of torsion angles. In experimental studies of the polyalkylthiophenes referred to earlier, the materials were not regiospecific, but were mostly coupled in the head-to-tail configuration. It has been pointed out by dos Santos and co-workers<sup>25</sup> that the torsion angles in the polythiophene backbone depend strongly upon the regiochemistry of the alkyl group substitution. These calculations carried out for dialkylbithiophenes using the AM1 method have shown that the tail-to-tail substituted molecule [see Fig. 1(c)] has a minimum in the torsion potential for an angle of  $0^\circ$  between neighboring thiophene rings. On the other hand, in the head-to-head substituted molecule the minimum occurs at an angle of  $90^\circ$ , with a barrier to the planar configuration of 2.66 kcal. Even though the calculated value of this energy barrier may be only qualitatively accurate, it indicates that a regular array of conformational defects, of the type discussed in the polyalkylthiophenes,<sup>32</sup> are likely to exist in PDDBT. In addition, solid-state packing effects may, of course, affect the specific value of the average torsion angle.

The UPS spectrum of PDDBT is shown in Fig. 6. The overall features of this spectrum are very similar to those previously reported for poly(3-alkylthiophenes).<sup>33</sup> Assuming that the Fermi level lies in the middle of the band gap, a  $\pi$ - $\pi^*$  energy separation of about 2.8 eV ( $\pm 0.1$  eV) is derived from the position of the  $\pi$ -band edge. In comparison with the theoretically calculated band structure as a function of torsion angle  $\theta_1$  [see Fig. 1(c)] we obtain the best fit to the experimental result for  $\theta_1 = 70^\circ$  and  $\theta_2 = 0^\circ$ , for which the  $\pi$ - $\pi^*$  band gap is 2.7 eV. The corresponding electronic band structure for the bands around the Fermi energy, as obtained from a VEH calculations, is shown in Fig. 7. As compared to the band structure for the planar system, which is shown by the dashed line in Fig. 7, the effect of inter-ring torsion is clearly to reduce the  $\pi$ -band widths (note, that the unit cell consists of four thiophene rings in the case of the nonplanar system whereas the min-

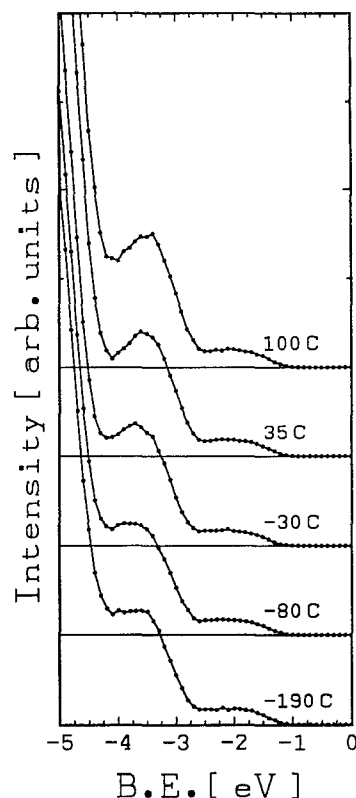


FIG. 6. UPS spectra (He I radiation, 21.2 eV) of neutral PDDBT taken at different temperatures and relative to the Fermi level. There are no temperature dependent changes in low binding energy parts of the spectra (i.e., for binding energies lower than 3 eV).

imum translationally invariant unit is one thiophene ring in the planar system).

The work function for PDDBT is experimentally determined to about 4.0 eV, as estimated from the UPS present spectra,<sup>27</sup> which is 0.4 eV larger than the corre-

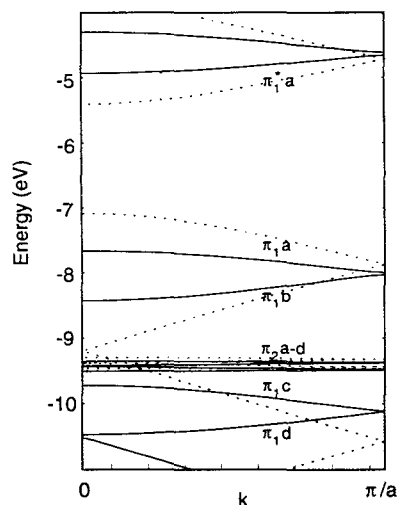


FIG. 7. VEH Electronic band structure of nonplanar polythiophene,  $\theta_1 = 70^\circ$ ,  $\theta_2 = 0^\circ$  (see Fig. 1). As a reference the band structure for planar PT chain, i.e.,  $\theta_1 = 0^\circ$ ,  $\theta_2 = 0^\circ$  is shown (dashed lines).



sponding value for P3AT.<sup>33</sup> This difference can be also explained in terms of the nonzero value of  $\theta_1$ . The increase of the ionization potential (IP) for the topmost occupied level of PDDBT compared to that of planar thiophene (dashed lines in Fig. 7) is 0.6 eV. In combination with a shift of the Fermi energy by 0.2 eV towards higher binding energies as a result of the nonplanarity ( $\theta_1=70^\circ$ ), this gives a theoretical estimate of 0.4 eV of the difference in the work function between a fully planar system and that with  $\theta_1=70^\circ$  and  $\theta_2=0^\circ$ . This is in perfect agreement with the experimental result.

Thus, we conclude that both the optical absorption and UPS measurements indicate that PDDBT is nonplanar in the ground state, exhibiting a "dimer structure" ring-twisting conformation. The torsion angle between adjacent (planar) dimers is about  $70^\circ$ .

As a function of temperature, there is no apparent change in the band gap of undoped PDDBT. The optical absorption spectra (Fig. 5), and  $\pi_1$ -band edge obtained from the UPS spectra in Fig. 6, show that the  $\pi$ - $\pi^*$  transition energy remains unchanged, i.e., the geometry of the polydidecylbithiophene backbone does not change with temperature, in contrast to the polyalkylthiophenes.<sup>15</sup> This indicates that the energy barrier against planarity due to interchain and intrachain interactions is high enough to prevent the decrease of the torsion angle  $\theta_1$  in Fig. 1(c). However, there is another observable temperature-dependent change in UPS spectrum. The intensity of the UPS signal near 4.2 eV binding energy increases with decreasing temperature. Since the  $\pi$  bands are unaffected, it is reasonable to assume that the changes are due to the alkyl chains. The temperature-dependent solid-state potential would tend to decrease the distance between adjacent polythiophene chains with decreasing temperature. The changes in the UPS spectrum might, therefore, be rationalized by increasing interactions between alkyl chains on neighboring polythiophene backbones, which would lead to an increase in the dimensionality of the  $\sigma$  bands which arise from the aliphatic groups. The electronic structure of these  $\sigma$  bands influences the total band structure for binding energy above 4.5 eV. Increasing of the dimensionality of the  $\sigma$  bands because of the interchain interactions, however, leads to a broadening of the corresponding peaks in UPS spectrum. Consequently, this affects the UPS valence band spectra by apparently filling of the valley which otherwise occurs at 4.2 eV in the room temperature UPS spectrum. Note that this decrease in interchain distance with decreasing temperature was observed directly by x-ray diffraction by Luzny.<sup>34</sup>

The results obtained from both UPS and optical absorption spectroscopy of undoped polydidecylbithiophene can be summarized as follows. At room temperature, the polymer backbone possesses dimer structure with a torsion angle of about  $70^\circ$  between adjacent dimers. This dimer structure does not change with temperature. With decreasing temperature, the interchain distance decreases, leading to the increasing of alkyl groups interactions, which affects UPS valence band spectra as described earlier.

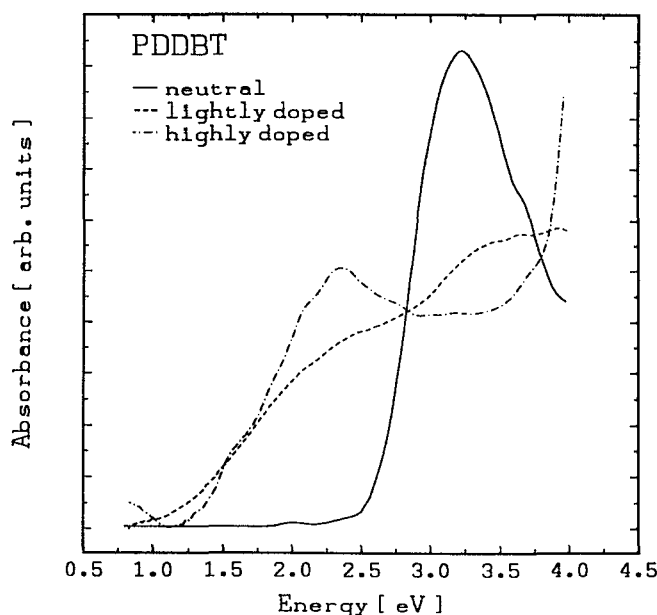


FIG. 8. Evolution of optical absorption spectra of PDDBT upon doping.

## 2. Doped state

It is well known that oxidative doping of polythiophene leads to formation of a new electronic levels within the otherwise forbidden energy band gap.<sup>29</sup> At the very lowest doping level, these new states are associated with polarons (molecular radical cations) positioned approximately symmetrically about mid gap. For the hole polaron, the lower state in the gap is half occupied and the upper state is empty. At higher doping levels, the second oxidation step removes the single electron from the lower polaron level. This leads to the formation of a bipolaron (molecular dication). Both the polaron and the bipolaron charge carrying species are known to induce a more quinoidlike structure in thiophene rings. Further doping leads to interactions among bipolarons. At high doping levels, two bipolaron bands are formed within energy band gap. It should be mentioned that polaron-bipolaron transition is common for all conjugated polymers with a nondegenerate ground state. However, *in situ* ESR experiments<sup>35</sup> have shown that in the polythiophene system bipolarons are the favorable charge storage configuration even at low dopant concentration. Therefore, we suggest that the electronic states induced by doping mainly correspond to bipolaronic states.

The evolution of the optical absorption spectrum upon oxidative doping of PDDBT is shown in Fig. 8. The effect of doping is to shift the intensity of the  $\pi$ - $\pi^*$  transition to new peaks that appear within the band gap of the undoped polymer. This effect is clearly shown in the theoretical electronic band structure for the doped polythiophene system presented in Fig. 9. The doping level is set to 25% in this case, corresponding to one bipolaron per eight thiophene rings. Even though this doping level is slightly higher than that in the experimentally studied samples, the theoretical band structure shows interband transitions that are in close



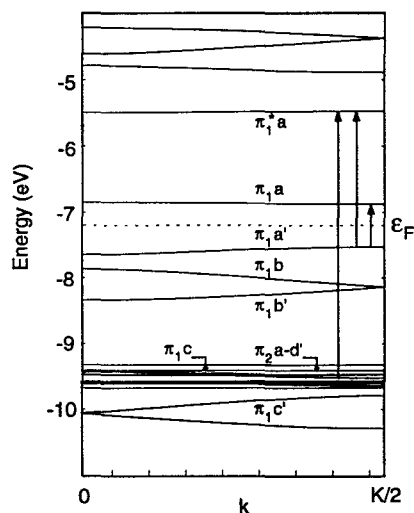


FIG. 9. Electronic band structure of doped (25%) nonplanar polythiophene,  $\theta_1=70^\circ$ ,  $\theta_2=0^\circ$ . The arrows indicate the doping induced optical transitions observed experimentally.

agreement with the experimental results. The doping induced absorption peak (see Fig. 8) at 2.3 eV is due to the excitation of electrons from the top of the valence band to the upper of the two bipolaron bands (the transition at 2.1 eV from  $\pi_1a'$ -to- $\pi_1^*a$  in Fig. 9). The high energy tail of the second absorption to the lower bipolaron band ( $\pi_1a'$ -to- $\pi_1a$ , 0.65 eV, see Fig. 9) is observed around 0.75 eV for the highly doped sample (the absorption peak appears at energies below the limit of our spectrometer). Moreover, a doping induced absorption peak also grows at energies about 4 eV. This absorption involves excitations from the  $\pi_2$  bands to the upper bipolaron band,  $\pi_1^*a$  in Fig. 9. According to our VEH calculations, this transition occurs in the energy regime 3.5–4.0 eV, in close agreement with experimental data. The calculated transition moments show that transition from the  $\pi_2$  bands to the lower bipolaron band ( $\pi_1a$  in Fig. 9) are about 2 orders of magnitude smaller than the corresponding value for the transition to the upper bipolaron level. This explains why the  $\pi_2$ -to- $\pi_1a$  transition, which occurs at 2.8 eV, is not observed experimentally.

The estimated value of the energy of the upper bipolaron transition (2.3 eV) is about 0.6 eV higher than that reported by Harbeke (1.6 eV) for poly(3-methylthiophenes).<sup>36</sup> This difference can be understood by taking into account the differences in geometry between the undoped polythiophene (Harbeke) and the present PDDBT. Because of the nonplanar geometry of polydidecylbithiophene backbone, the system possesses a lower effective conjugation length. Upon doping, the transition from aromatic to a more quinoidlike structure induces a double bond character of the bond between the C(2) and C(2') carbons (see Fig. 1). Thus, in this kind of system there is a competition between the alkyl-chain interactions which favors a nonplanarity of the system and  $p_z$  interactions between C(2), C(2') sites which favors a planar system.

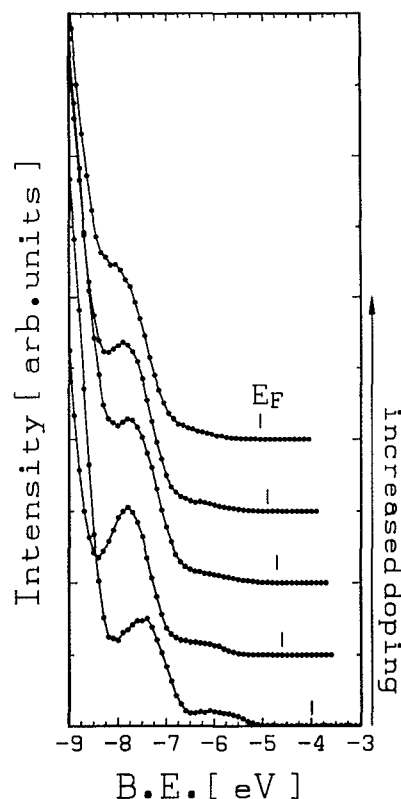


FIG. 10. Evolution of the UPS spectrum upon oxidative doping. Doping leads to a shift of the Fermi level which for the highest doped sample (upper curve) is of about 1 eV.

The large difference in the optical absorption spectrum between doped polythiophene<sup>37</sup> and doped PDDBT indicates that PDDBT remains highly nonplanar even in the doped state. This result is in contrast to the results of geometry optimization of a single PDDBT chain. These calculations show that for the doped system, both  $\theta_1$  and  $\theta_2$  are very close to  $0^\circ$ . Clearly, interchain interactions that are not considered in the theoretical study must be very important in this case. These interactions might lock the system in the non-planar conformation characteristic of the undoped system and prevent any rotation degrees of freedom (librons) upon doping. The band structure shown in Fig. 9 has been obtained for  $\theta_1=70^\circ$  and  $\theta_2=0^\circ$ , as in the case of the undoped system. This conformation is shown to give transition energies that are in a close agreement with the experimental data.

The effects of doping on the electronic properties of PDDBT was also studied by UPS. The evolution of the valence band spectrum as a function of the dopant concentration is illustrated in Fig. 10. The shift of the Fermi energy relative to vacuum level can be observed as the result of charge-induced changes in electronic bands structure of the polymer system. This shift was estimated in the standard way from the shift of work function.<sup>17</sup> The maximum shift observed is equal to 1 eV ( $\pm 0.1$  eV), which is in good agreement with the previously reported<sup>17</sup> value of 0.8 eV, for poly(3-hexylthiophene) doped with NOPF<sub>6</sub>. A

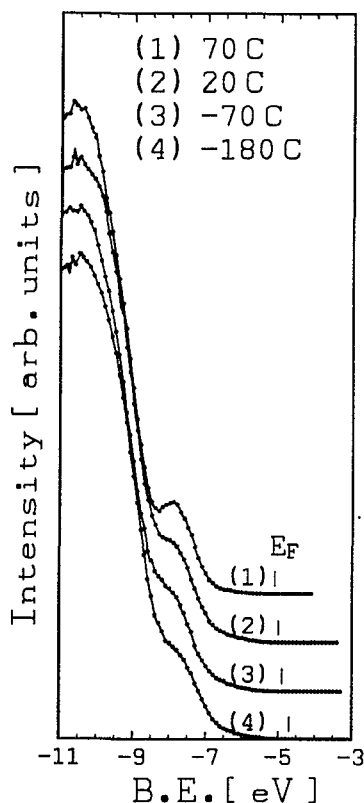


FIG. 11. The temperature evolution of the UPS spectrum for highly doped PDDBT. The shift of the Fermi energy is clearly observed. Spectrum (2) is the spectrum of PDDBT doped to the highest dopant concentration shown in Fig. 8.

qualitative change in  $\pi$ -band edge also occurs. The changes in intensity of the UPS spectra near the valence band edge are caused by either disorder induced by the counterions (Fe-Cl distance is large, about 2.2 Å) or by electrostatic interactions among negative counterions and positive charged species located on the polythiophene chain. The possibility of inhomogeneous doping may also be considered. Significant changes in the spectra occur at binding energies of about 4 eV (relative to the Fermi level). For undoped PDDBT (Fig. 8, lower curve), the main peak in this region is located at about 3.5 eV. This peak corresponds to electrons removed from  $\pi_2$  bands (see Fig. 9). These states are strongly localized on the  $\beta$  carbon atoms [C(3) and C(4) in Figs. 1(a) and 1(b)] and the sulphur atom. Due to more quinoidlike structure of the thiophene ring induced by charge transfer this peak shifts towards higher binding energies upon oxidation. Consequently, the bonding interactions between the C(3) and C(4) atoms increase, which, in turn, stabilize the corresponding electronic level. Moreover, the charge density associated with the bipolaron states results in a nonzero positive effective electronic charges on the sulphur atom, causing the shift of the peak corresponding to states localized on sulphur atom toward higher binding energies. In addition, electrons in states of the counterion might contribute to the tail of the strong bands located below 5 eV. It should be mentioned here, that in contrast to the planar (or quasiplanar) un-

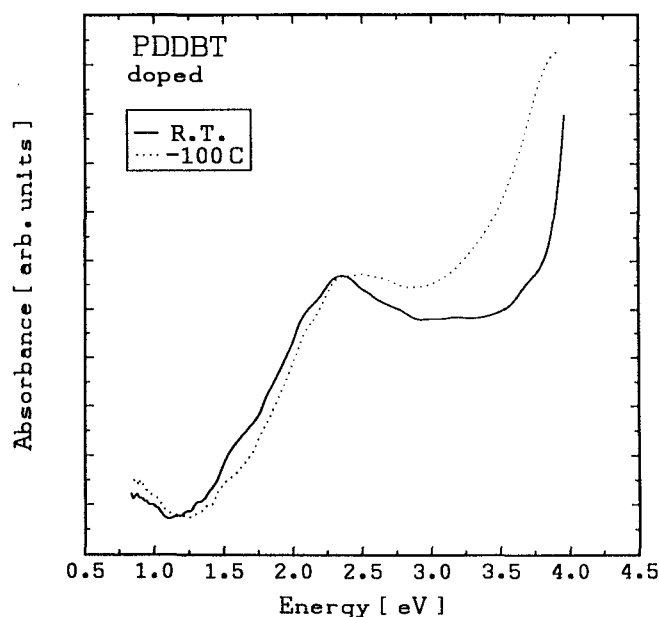


FIG. 12. Optical absorption spectra for the doped sample at room temperature (RT) and at  $-100^\circ\text{C}$ .

substituted polythiophene system it is impossible to dope the twisted polymer backbone system (as described earlier) by chemical treatment to the metallic state. On the other hand, forces associated with electrochemical doping may be able to force planarity, and, consequently, a higher degree of charge transfer. This suggestion is supported by the results of cyclic voltammetry experiments, where in the oxidation peak is sharper than that for poly(3-decylthiophene), and is located at a higher voltage.<sup>38,39</sup> The apparent smearing of the  $\pi$ -band edge observed can be rationalized as a combination of all of the factors mentioned earlier.

With decreasing temperature, an interesting and unexpected effect occurs in the UPS spectrum of PDDBT, as shown in Fig. 11. The Fermi energy shifts relative to the vacuum level by about 0.4 eV and the nature of the signal in the vicinity of 8–9 eV (in Fig. 9) changes. *The spectra changes are completely reversible with temperature.* The optical absorption spectra shown in Fig. 12, also suggest that significant changes in electronic band structure take place with decreasing temperature. The onset of the  $\pi_2$ - $\pi_1^*$  transition is shifted towards lower photon energies as the temperature is decreased. For lower temperature, the maximum of the absorption corresponding to the bipolaron absorption band becomes broader, and shifts slightly toward higher photon energy. These observed phenomena can be understood in the following way. The differences in ground state geometry in the undoped state between conventional polythiophene and PDDBT were pointed out earlier. In neutral PDDBT, the magnitude of the torsion angle,  $\theta_1$  in Fig. 1(c), is determined by a balance between different forces. In doped PDDBT, the quinoidlike structure of the thiophene rings corresponds to enhanced bonding between the C(2) and C(2') atoms (Fig. 1), thereby tending to increase the backbone planarity, leading to an

additional energy factor in energy balance. In equilibrium, the influence of the interacting alkyl-groups on the backbone tends to break up the  $\pi$  system into dimers [as in the P(3AT's) (Ref. 16)], while the  $\pi$ -electron delocalization energy and energy associated with quinoid-like ring formation tend to increase the planarity. In case of the undoped system, the equilibrium at room temperature leads to the dimer structure discussed earlier. While in the doped system, there is the influence of additional "quinoidal" factor. For this reason, in the doped system, as the temperature is lowered a new energy equilibrium is accomplished through lowering the  $\theta_1$  angle. The resultant increase in the backbone planarity leads to a redistribution of the charge which was transferred into the polymer during doping, similar to the case when the same amount of charge is transferred into more planar polythiophene backbone. In this case the Fermi energy level is less shifted from the mid-gap position, and the energy difference between  $\pi$  and  $\pi^*$  bands tends to become smaller. For the same reasons, the two in-gap bipolaron bands are wider thereby broadening the absorption bands. This, together with the evolution of the position of the in-gap states, results in the apparent shifting of the appropriate absorption peaks (Fig. 12).

The temperature-dependent changes in the UPS spectra near 4 eV binding energy (Fig. 11) occur for the same reasons in both the doped and undoped cases: from effects of the aliphatic groups. However, in the case of the doped system another effect can be taken into account. Increasing of the planarity increases the steric interactions between alkyl group and polymer chain. For that reason the angle between polymer backbone axis and alkyl group axis should increase. This, in turn, leads to the reorganization of the  $\sigma$ -band structure, thereby affecting the UPS spectrum. When the temperature is increased back to room temperature, the opposite transition occurs. The system becomes less planar, therefore the conjugation length decreases. This leads to the electronic bands narrowing and increasing of the density of states, thereby changing the position of the bipolaron bands and the Fermi level. In this transition, the temperature induced changes of the polythiophene backbone geometry caused transformation of electronic band structure. This transition is entirely reversible with temperature.

#### IV. CONCLUSIONS

Regioregular polythiophene, poly(4,4'-dialkyl-2,2'-bithiophene), has been studied by ultraviolet photoelectron spectroscopy, optical absorption measurements and molecular band structure calculations. The system possesses only "head-to-head" and "tail-to-tail" couplings between adjacent bithiophene monomer units. The regioregularity of the aliphatic group substitution is an important factor influencing the electronic band structure of polythiophene system in either neutral or oxidative states. Studies were carried out at different levels of oxidation at different temperatures. The results indicate that the undoped poly(4,4'-dialkyl-2,2'-bithiophene) chain is nonplanar and conformationally stable. The polymer system occupies a global thermodynamic potential minimum at

room temperature and thermochromic effects have not been observed. Charge transfer induces a new state of equilibrium, which is accomplished at lower temperatures. The transformation of the system geometry to this new potential minimum increases the system planarity and modifies the  $\pi$ -band structure. For a polymer doped to the saturation doping level the Fermi level appears to shift gradually towards lower binding energies between  $-180^\circ\text{C}$  and  $+70^\circ\text{C}$ . This is the first observation of a temperature-dependent change in the electronic structure of a charged (doped) conjugated polymer.

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