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# Ab initio study of the electronic structure and conduction properties of mislinked heterocyclic polymers

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Results of *ab initio* band structure calculations of completely mislinked ( $\alpha$ - $\beta$  linked) polypyrrole, polythiophene, and polyfuran are reported. Comparison of the important electronic properties such as ionization potential, electron affinity, and band gap of these mislinked polymers with those of the normally linked ( $\alpha$ - $\alpha'$  linked) polymer chains indicates that the introduction of mislinkages in the normally linked polymer chains makes them more insulating and less dopantphilic. Both the ionization potential and the electron affinity values of the mislinked polymer chains are found to be sensitive to both the nature of the heteroatom and substitution at the backbone. The effect of the distributions (both periodic and random) of the mislinkages on the conduction properties of normally linked heterocyclic polymers is also investigated using negative factor counting method in its tight binding approximation. A random distribution of mislinkages, in general, has been found to produce polymer chains which are less insulating and have better prospects for forming conductive materials on doping with both electron acceptors and electron donors than the corresponding periodic distribution of mislinkages. The possible effects of the distribution of mislinkages on the conduction properties of copolymers of the heterocyclic compounds are also discussed.

## I. INTRODUCTION

In recent years conjugated heterocyclic polymers such as polypyrrole (PPY), polythiophene (PTP), and polyfuran (PFU) have been the focus of enormous interest both theoretically and experimentally. Their most significant property is their ability to form highly conducting materials upon doping with electron acceptors (*p* doping).<sup>1</sup> In case of polythiophene, *n*-doped (with electron donors) samples have also been prepared.<sup>2</sup> A variety of applications such as in rechargeable<sup>3</sup> and solar batteries,<sup>4</sup> optoelectronic devices,<sup>5-6</sup> permanent information storage devices,<sup>7</sup> and sensors<sup>8</sup> have been proposed using their electrochemically synthesized films.

Among the three heterocyclic polymers, PPY has been the most studied polymer followed by PTP and PFU. All the three polymers can be obtained in their highly conducting form through the method of electrochemical polymerization<sup>1,9-11</sup> and display similar electrical and optical properties.<sup>12-15</sup> Both theoretical and experimental studies<sup>16,17</sup> of these polymers suggest the formation of polarons at low oxidation level followed by spinless bipolarons at higher oxidation levels. All the theoretical studies on the electronic structure and conduction properties of these heterocyclic polymers hitherto performed<sup>18-25</sup> have assumed the coplanar polymer structures made up of alternating neighboring rings with  $\alpha$ - $\alpha'$  linkages. These structures are consistent with <sup>13</sup>C NMR spectrum analyses<sup>26,27</sup> of both PPY and PTP chains which suggest that these chains are primarily composed of the  $\alpha$ - $\alpha'$  linkages of the monomer rings. In the case of PPY, the XPS study<sup>28</sup> reveals the existence of partial  $\alpha$ - $\beta$

linkages too. Yamamoto *et al.*<sup>29</sup> have found that it is possible to prepare PTP chains containing only  $\alpha$ - $\beta$  linkages by the polycondensation of  $\alpha,\beta$  substituted dibromothiophene with magnesium in the presence of nickel compounds. PTP chains containing both  $\alpha$ - $\alpha'$  and  $\alpha$ - $\beta$  linkages, on the other hand, have been obtained by the copolymerization of  $\alpha,\alpha'$  substituted and  $\alpha,\beta$  substituted dibromothiophenes under similar conditions. The distribution of  $\alpha$ - $\beta$  linkages in these chains has been shown to be random. On the basis of the investigation<sup>30</sup> of the affinity of the various types of PTP chains towards electron acceptors and the electric conductivities of resulting adducts, it has been found that both this affinity and electric conductivity decrease with an increase in the percentage of  $\alpha$ - $\beta$  linkages in the PTP chains.

In this paper we investigate the effect of mislinkages ( $\alpha$ - $\beta$  linkages) on the electronic structure and conduction properties of PPY, PTP, and PFU. A comparative study of the electronic structure and conduction properties of the normally linked (having only  $\alpha$ - $\alpha'$  linkages), PPY, PTP, and PFU has been recently carried out by us<sup>25</sup> and we have found PPY to be the strongest candidate for oxidative (*p*) doping, whereas PTP is predicted to have the greatest capacity for reductive (*n*) doping. It has also been found that the electron affinity values of these heterocyclic polymers depend more on the heterosubstitution, whereas the corresponding values of the ionization potential are influenced more by the backbone substitution. In the light of above results, it would really be of interest to see how the electronic structure and conduction properties of normally linked heterocyclic polymers are affected by the introduction of mislinkages ( $\alpha$ - $\beta$  linkages). The structure of  $\alpha$ - $\alpha'$  linked and  $\alpha$ - $\beta$  linked he-

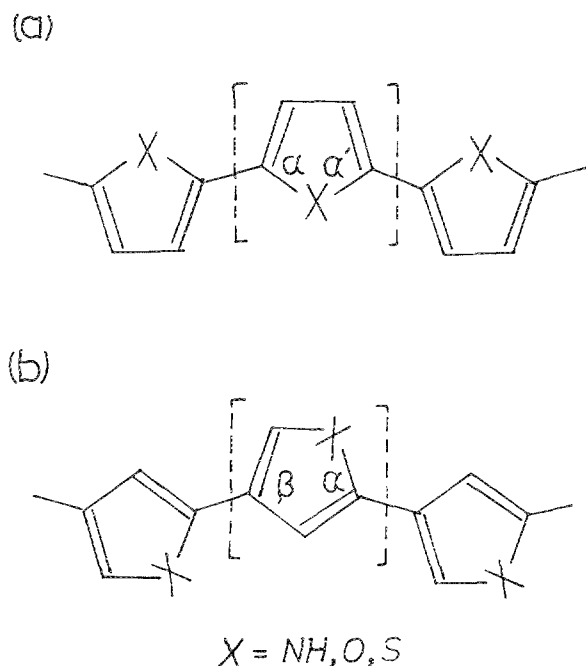


FIG. 1. Structures of (a) normally linked ( $\alpha$ - $\alpha'$  linked) and (b) completely mislinked ( $\alpha$ - $\beta$  linked) heterocyclic polymers. The unit cells are surrounded with broken lines.

terocyclic polymer chains are shown in Fig. 1. As is evident from these structures, the  $\pi$  electrons of  $\alpha$ - $\alpha'$  linked polymer chains are extensively delocalized, whereas the conjugation in  $\alpha$ - $\beta$  linked chains is very limited. This difference in the electron delocalization between the two types of polymer chains is expected to be reflected in their intrinsic electrical conductivities as well as in their chemical reactivities towards dopants and the electrical conductivities of the resulting adducts.

Tanaka *et al.*<sup>31</sup> have recently investigated the electronic properties of mislinked PPY and PTP chains using the CNDO/2 crystal orbital method and on the basis of their results concluded that as a result of the mislinkages, the dopantphilicity of these heterocyclic polymers decreases accompanied by a decrease in the highest occupied and lowest unoccupied  $\pi$  bandwidths. The aim of the present work is to test these conclusions using the more reliable *ab initio* Hartree-Fock crystal orbital method. We have, in addition, also investigated the effect of both the periodic and random distributions of mislinkages on the electronic structure and conduction properties of these heterocyclic polymers by using negative factor counting method in its tight binding approximation. The possible effects of these mislinkages on the conduction properties of the copolymers are also discussed.

The paper is organized as follows: In Sec. II we present the methods and computational details of the present work. Section III is devoted to the results and their discussion. Conclusions of this work are given in Sec. IV.

## II. METHODS AND COMPUTATIONAL DETAILS

The energy band structures of the quasi-one-dimensional periodic completely mislinked (having only  $\alpha$ - $\beta$  link-

ages) heterocyclic polymers were calculated using the *ab initio* Hartree-Fock crystal orbital method. This method has been described and discussed in detail in the literature.<sup>32,33</sup> The computations were carried out using Clementi's 7s/3p minimal basis set for the heavy atoms and four primitive Gaussians contracted to one *s* function for the hydrogen atom. All the multicenter-two-electron integrals larger than the threshold value of  $10^{-8}$  a.u. were calculated and interactions up to fourth neighbors were taken into account. A coplanar structure has been considered in the calculations for all the three heterocyclic polymers. The corresponding experimental geometries of the monomers<sup>34</sup> were used for the internal geometry of the heterocycles. Bond lengths between rings were set at 1.49 Å similar to what is used in our earlier calculations of normally linked heterocyclic polymers.<sup>24,25</sup>

The effect of the mislinkages on the conduction properties of the heterocyclic polymers was studied by determining the DOS distributions of the composite systems containing both the normal and mislinkages. The DOS distributions were calculated using the simple negative factor counting method<sup>35</sup> based on Dean's negative eigenvalue theorem.<sup>36</sup> According to this method the number of eigenvalues of a tridiagonal tight binding (Hückel) secular determinant of a polymer chain which are smaller than a given trial value  $\lambda$  equals the number of negative factors obtained by the recursion relation:

$$\epsilon_i(\lambda) = a_i - \lambda - b_{i-1,i}^2 / \epsilon_{i-1}(\lambda), \quad i = 2, 3, 4, \dots, N,$$

$$\epsilon_1(\lambda) = a_1 - \lambda$$

(the latter expressions are obtained by transforming the tridiagonal determinant to a didiagonal one by applying successive Gaussian elimination). Here  $a_i$  and  $b_{i-1,i}$  are the on-site and hopping parameters in the first neighbors interactions approximation. They are obtained for a given band (for instance, for the valence or the conduction bands, respectively, of the corresponding homopolymers) by taking the center of the band ( $a_i$ ) and one fourth of the band width ( $b_{i-1,i}$ ) [if one assumes a simple cosine form for the  $\epsilon_i(k)$  curve].

Thus by giving  $\lambda$  different values and taking difference of the number of negative  $\epsilon_i(\lambda)$ 's belonging to consecutive values one can obtain the distribution of eigenvalues (DOS).

In the present work, a chain length of 500 units has been chosen for the calculations of the DOS of the heterocyclic polymers containing mislinkages. For each heterocyclic polymer, the results of the present study (corresponding to completely mislinked  $\alpha$ - $\beta$  homopolymers) as well as those of our earlier study<sup>25</sup> (corresponding to normally linked homopolymers) are used. Three cases corresponding to both periodic and random distributions of mislinkages with their compositions as 25%, 50%, and 75%, respectively, have been studied for each heterocyclic polymer.

## III. RESULTS AND THEIR DISCUSSION

### A. Band structure results of completely mislinked heterocyclic polymers

The energy band structures of all the three completely mislinked heterocyclic polymers are shown in Fig. 2. Only

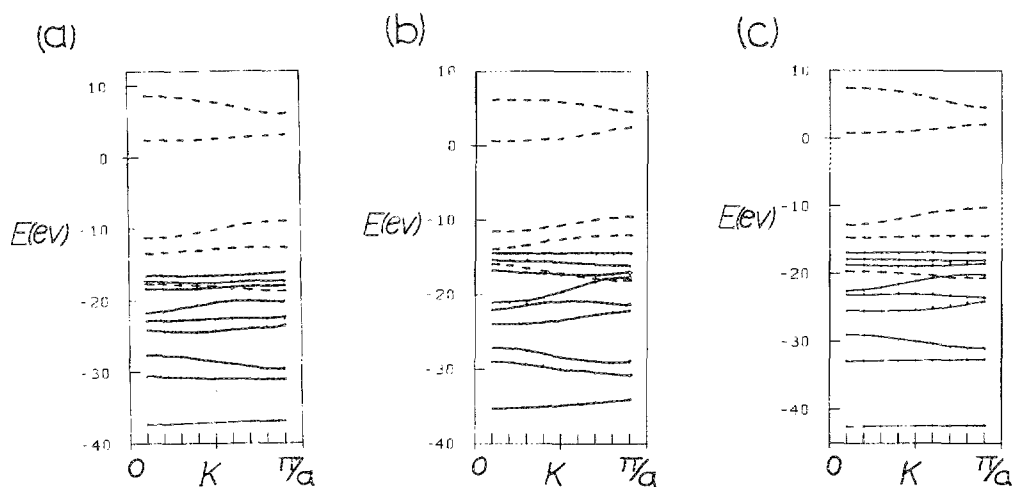


FIG. 2. Energy band structures of the completely mislinked ( $\alpha$ - $\beta$  linked) (a) polypyrrole (PPY); (b) polythiophene (PTP) and (c) polyfuran (PFU). Broken and solid lines represent  $\pi$  and  $\sigma$  bands, respectively.  $a$  is the length of the unit cell.

the higher lying valence bands and the two lowest unoccupied bands of each system are shown. Comparison of the energy band structures of these mislinked polymers with those of normally linked polymers<sup>25</sup> shows that in the case of mislinked polymers both valence and conduction bands are lower in energy than the corresponding bands of normally linked heterocyclic polymers. Both the highest occupied and the lowest unoccupied bands for each system, in both cases, however, remain  $\pi$  bands. An avoided crossing between the two highest occupied bands observed in the normally linked polymers is missing in the mislinked polymers.

The most important electronic properties such as the lowest ionization potential (corresponding to the top of the valence band), maximum electron affinity (corresponding to the bottom of the conduction band), band gap, and bandwidths are given in Table I. The corresponding values for the normally linked chains are also given for the sake of comparison in this table. It is seen that in the case of each heterocyclic polymer the replacement of the  $\alpha$ - $\alpha'$  linkages with the  $\alpha$ - $\beta$  linkages causes the band gap values to increase by about 2 eV. It therefore means that mislinked polymers shall be better insulators than normally linked polymers. The calculated trend in the band gap values for the mislinked polymer chain however remains the same as for the normally linked polymers (PTP still has the smallest band gap and PFU the largest). This trend is in agreement with the corresponding experimental trend, though our calculated band gap values are much larger than the corresponding experimental values. This is the well known overestimation of the band gap in the Hartree-Fock method. By using better basis sets and by taking into consideration correlation effects, the calculated band gap values would certainly come closer to the experimental values as has been previously observed by Suhai<sup>37</sup> in the case of polyacetylene.

As a result of the mislinkages, both the highest occupied and the lowest unoccupied  $\pi$  bandwidths decrease considerably as is evident from Table I. This decrease in the bandwidth values signifies the suppression of the inter-ring  $\pi$  conjugation of the highest occupied and the lowest unoccupied

crystal orbitals of the mislinked chains and consequently the decrease in the mobility of the charge carriers in these bands. The flattening of both the highest occupied and the lowest unoccupied bands causes an increase in the lowest ionization potential and a decrease in the electron affinity values of the mislinked polymers. It therefore means that the completely mislinked heterocyclic polymers shall have smaller capacity than the normally linked polymers to form conducting materials on doping with electron acceptors ( $p$  doping) and electron donors ( $n$  doping). Our results are in agreement with the earlier results<sup>31</sup> for PPY and PTP obtained by using CNDO/2 crystal orbital method. It needs, however to be noted, that the trend in the ionization potential and the electron affinity values of the completely mislinked polymers remains the same as that for normally linked polymers.

An analysis of the Bloch wave functions of the highest occupied and the lowest unoccupied bands of the completely mislinked heterocyclic polymers reveals that for all these

TABLE I. Calculated electronic properties (in eV) for completely mislinked ( $\alpha$ - $\beta$  linked) heterocyclic polymers.\*

	PPY	PTP	PFU
Valence bandwidth	2.350 (3.905)	1.949 (2.890)	2.477 (4.205)
Conduction bandwidth	0.734 (3.751)	1.767 (5.118)	1.237 (4.215)
Ionization potential (top of valence band)	8.977 (8.826)	9.656 (9.499)	10.257 (9.740)
Electron affinity (negative value of bottom of conduction band)	-2.394 (-0.275)	-0.651 (1.362)	-0.859 (0.891)
Band gap	11.371 (9.102)	10.307 (8.137)	11.158 (8.849)
Band gap (expt.)	3.0	2.0	2.7

\* Values in parentheses indicate the corresponding values for normally linked ( $\alpha$ - $\alpha'$  heterocyclic linked) polymer chains.

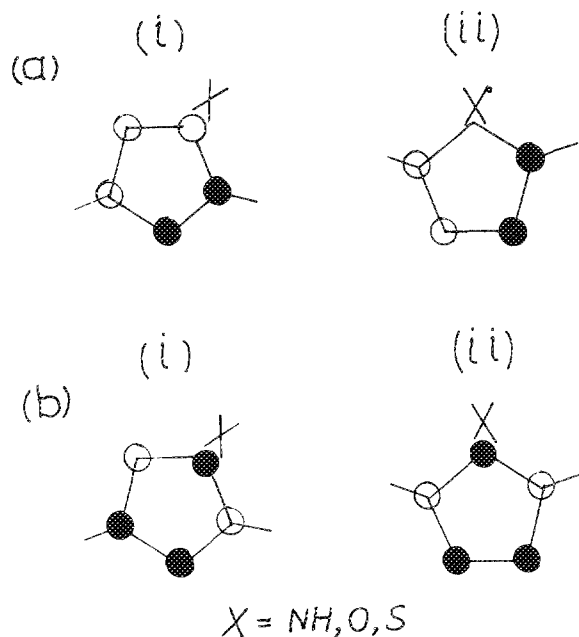


FIG. 3. Orbital patterns of (a) the top of the valence band and (b) the bottom of the conduction band ( $K=0$ ) of the (i) completely mislinked ( $\alpha$ - $\beta$  linked) and (ii) normally linked ( $\alpha$ - $\alpha'$  linked) heterocyclic polymers.

systems, the contributions to both the top of the highest filled band (corresponding to the lowest ionization potential) and to the bottom of the lowest unfilled band (corresponding to the highest electron affinity) come from the  $p_z$  orbitals of all the atoms including the heteroatom. Therefore when these mislinked polymer chains are doped with electron acceptors or electron donors, all the electrons of the ring are expected to be involved in the doping process. This is quite in contrast to the results obtained in the case of normally linked heterocyclic polymers<sup>25</sup> where the contribution of the orbitals of the heteroatom to the top of the highest filled band was found to be zero. It therefore means that the introduction of mislinkages to the normally linked heterocyclic polymers changes considerably the pattern of the highest occupied crystal orbital. From the contributions of the  $p_z$  orbitals of the heteroatom to both the highest filled and the lowest unoccupied bands, it can be concluded that the ESR signals of both  $p$ -doped and  $n$ -doped completely mislinked polymer chains shall be having similar  $g$  values.

In Fig. 3 are shown the orbital patterns corresponding to the highest occupied and the lowest unoccupied crystal

bands of the completely mislinked heterocyclic polymers. Also shown, in this figure are, for the sake of comparison the corresponding orbital patterns of the normally linked heterocyclic polymers. It is evident from this figure that the orbital patterns of the lowest unoccupied crystal band for both completely mislinked and normally linked heterocyclic polymers are the same. On the other hand, in the normally linked polymer chains heteroatoms have no highest occupied crystal orbital lobes, whereas the mislinked polymer rings have these on the heteroatoms.

It is also found that for both normal and completely mislinked polymer chains, the  $\alpha$  or  $\alpha'$  carbon atoms have larger LCAO coefficients of the  $p_z$  orbitals, thereby reflecting the relatively higher reactivity of these atoms.

From the foregoing discussion on the nature of the Bloch wave functions of the mislinked polymer chains, it follows that both the ionization potential and the electron affinity values are sensitive both to the nature of the heteroatom and to the substitution on the free  $\alpha$  or  $\beta$  carbon atoms. In our earlier work on the normally linked polymer chains, it was found that the ionization potential values unlike the electron affinity values of the heterocyclic polymer chains are not much dependent on the nature of the heteroatoms, though both of them were predicted to change with the substitution on the backbone. In those systems therefore, where both  $\alpha$ - $\alpha'$  and  $\alpha$ - $\beta$  linkages are present, both ionization potential and electron affinity values are expected to change with the nature of the heteroatom, though the change in the ionization potential values is predicted to be relatively smaller. Our results, are quite significant in view of the preparation of novel polymers.

The charge distributions for the mislinked heterocyclic polymers and also for the sake of comparison of the normally linked polymers, calculated on the basis of Mulliken population analysis are given in Table II. As expected, the symmetry of charge distributions present in the  $\alpha$ - $\alpha'$  linked polymer chains is lost in the  $\alpha$ - $\beta$  linked polymer chains. The net charges on the heteroatoms are as follows: +0.347 at S, -0.372 at O, and -0.484 at N. As in the normally linked polymer chains, here too, it has been found on the basis of the orbital population analysis of the heteroatoms under consideration that nitrogen is the strongest  $\pi$  donor (+0.384) followed by sulphur (+0.316) and oxygen (+0.310). Similarly nitrogen is also the strongest  $\sigma$  acceptor (-0.868) followed by oxygen (-0.682), whereas sulphur is not a  $\sigma$  acceptor at all (+0.079).

TABLE II. Calculated net charges on the basis of Mulliken population analysis (see Fig. 1).<sup>a</sup>

System	C <sup>1</sup>	C <sup>2</sup>	C <sup>3</sup>	C <sup>4</sup>	H <sup>1</sup>	H <sup>4</sup>	N/S/O
PPY	-0.070 (0.111)	0.132	-0.085 (-0.266)	-0.276	0.211 (0.197)	0.185	-0.484 (-0.477)
PTP	-0.289 (-0.178)	-0.165	-0.077 (-0.243)	-0.244	0.211 (0.230)	0.217	0.347 (0.382)
PFU	0.030 (0.209)	0.229	-0.091 (-0.268)	-0.276	0.244 (0.246)	0.236	-0.372 (-0.374)

<sup>a</sup> Values in parentheses indicate the corresponding values for normally linked ( $\alpha$ - $\alpha'$ ) heterocyclic polymer chains.

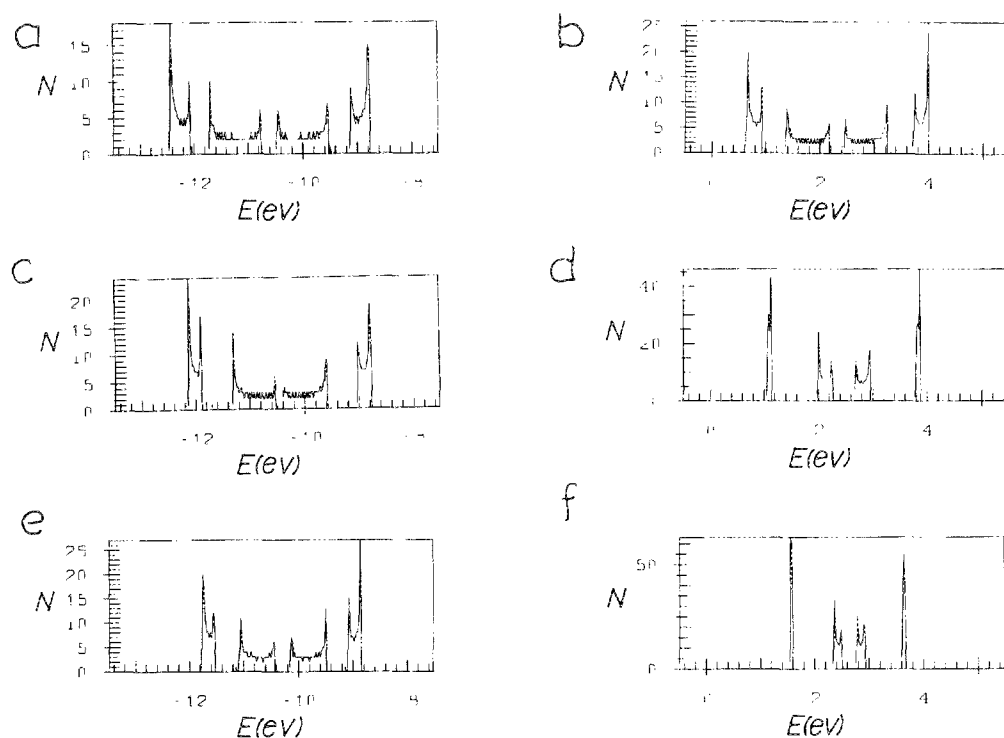


FIG. 4. The density of states (DOS) of (a) the valence band and (b) the conduction band of a 500 units long polypyrrole (PPY) chain containing 25%  $\alpha$ - $\beta$  mislinkages distributed periodically (the remaining 75% are, of course,  $\alpha$ - $\alpha'$  linkages). (c) and (d) indicate the corresponding DOS of 500 units long PPY chain containing 50%  $\alpha$ - $\beta$  mislinkages distributed periodically and (e) and (f) those of the same PPY chain but having 75% periodically distributed  $\alpha$ - $\beta$  mislinkages.

### B. Effect of the distribution of mislinkages (both periodic and random) on the conduction properties of the heterocyclic polymers

In the previous section we reported our results for the electronic structure and conduction properties of completely mislinked (100%  $\alpha$ - $\beta$  linkages) heterocyclic polymers.

In this section we report the results of our study of the effect of both the periodic and random distributions of mis-

linkages ( $\alpha$ - $\beta$ ) on the conduction properties of the normally linked ( $\alpha$ - $\alpha'$ ) heterocyclic polymer chains. In the case of each polymer, the DOS of the polymer chains of 500 units containing 25%, 50%, and 75% mislinkages ( $\alpha$ - $\beta$ ) (distributed both periodically and randomly) have been studied.

The electronic DOS for both the valence and conduction bands of the various cases of the distribution of mislinkages in the case of polypyrrole are shown in Figs. 4 and 5.

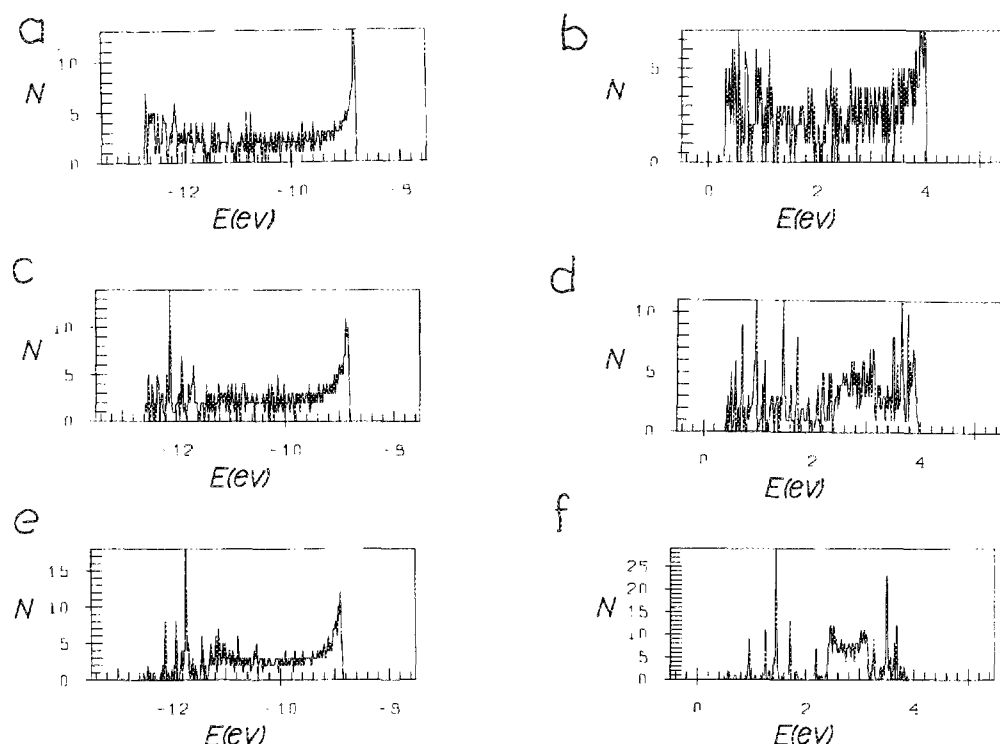


FIG. 5. The density of states (DOS) of (a) the valence band and (b) the conduction band of the 500 units polypyrrole (PPY) chain containing 25%  $\alpha$ - $\beta$  mislinkages distributed randomly (the remaining 75% are, of course,  $\alpha$ - $\alpha'$  linkages). (c) and (d) indicate the corresponding DOS of 500 units long PPY chain containing 50% linkages distributed randomly and (e) and (f) those of the same PPY chain but having 75% randomly distributed  $\alpha$ - $\beta$  mislinkages.



Figure 4 shows the DOS curves representing the periodic distribution of the mislinkages (A-25%, B-50%, C-75%), while those representing the random distributions of the mislinkages are shown in Fig. 5. As is evident from these figures, the valence and the conduction band regions in the periodic case consist of relatively narrower bands while those in the random case consist of a single very broad region of allowed energies (with a few extremely narrow gaps). The occurrence of relatively narrower peaks in the periodic case, in contrast to aperiodic case, may be explained on the basis of fact that in a DOS curve of, say the conduction band region, of a particular sequence of two units A and B, the energy position of the peak due to a unit, say A, is determined by two factors: (1) the position of the conduction band (center of the band) of the homopolymer poly (A); and (2) the electronic environment of A in the sequence under consideration. The shift in the energy position of the peak due to A in the given sequence relative to that in poly (A) shall depend upon how different the interaction of A is with its neighbors in a given sequence from its interaction with other neighboring A's in poly (A). Now in the case of the periodic sequence of A and B—say ABABAB...—the electronic environments of A and B throughout the sequence remain the same. Therefore one expects relatively two narrower peaks. On the other hand, in the case of random sequence of A and B, the respective environments of A and B keep on changing. Therefore their energy positions (peaks) are scattered over a much wider range of energy. Similar broadening in the aperiodic systems was observed by us in the case of aperiodic DNA and aperiodic polypeptides,<sup>38-40</sup> random copolymers of heterocyclic compounds,<sup>25</sup> nitrogen containing analogs of polyacetylene,<sup>41</sup> and polyfluoroacetylenes.<sup>42</sup> To check the dependence of the DOS on the sequence of the  $\alpha$ - $\beta$  linkages in both the valence and conduction band regions, the random distributions of mislinkages were studied with three different sequences generated with the help of a Monte Carlo program. The general features of the DOS curves remained the

same proving that a chain of 500 units is long enough to yield statistically meaningful results. Similar results were obtained in the case of the other two heterocyclic polymer chains of polythiophene and polyfuran and therefore we do not show their DOS curves here.

The most important electronic properties obtained from the corresponding DOS curves as a function of the percentage of mislinkages (for both periodic and random distributions) for each heterocyclic polymer are given in Table III. Also given in this table are the corresponding electronic properties for normally linked (0% mislinkages) and completely mislinked (100% mislinkages) heterocyclic polymers. It can be seen from this table that in the case of each heterocyclic polymer, as the percentage of mislinkages increases, the polymer tends to become more insulating. There is also an increase in the ionization potential and a decrease in the electron affinity of the polymer with an increase in the percentage of the mislinkages, thereby implying that the mislinkages decrease the ability of the polymers to form conductive materials on doping. These results are understandable in view of the fact that the extensive delocalization of electrons present in the normally linked polymer chains is disrupted by the introduction of mislinkages ( $\alpha$ - $\beta$  linkages). The resulting degree of delocalization of  $\pi$  electrons present in polymer chains (which of course varies inversely with the percentages of mislinkages) determines reactivities and electronic conducting properties of these chains. It is also interesting to note from this table that for a given percentage of mislinkages, the polymer chains with a random distribution of mislinkages have lower ionization potentials, higher electron affinities, and hence smaller band gaps than the corresponding polymer chains with periodic distribution of mislinkages. It, therefore, means that heterocyclic polymers with random distribution of mislinkages are not only better semiconductors but also more dopantphilic than the corresponding polymers with periodic distribution of linkages.

TABLE III. Effect of mislinkages ( $\alpha$ - $\beta$ ) (both for periodic and random distributions) on the electronic properties of heterocyclic polymers.

System	% of $\alpha$ - $\beta$ linkages	Ionization potential		Electron affinity		Band gap	
		Periodic	Random	Periodic	Random	Periodic	Random
PPY	0	8.826	8.826	-0.275	-0.275	9.102	9.102
	25	8.780	8.820	-0.640	-0.320	9.420	9.140
	50	8.780	8.820	-1.060	-0.440	9.840	9.260
	75	8.860	8.860	-1.560	-0.500	10.420	9.360
	100	8.977	8.977	-2.394	-2.394	11.371	11.371
PTP	0	9.499	9.499	1.362	1.362	8.137	8.137
	25	9.500	9.500	0.980	1.300	8.520	8.200
	50	9.540	9.520	0.540	1.160	9.000	8.360
	75	9.580	9.560	0.040	1.080	9.540	8.480
	100	9.656	9.656	-0.651	-0.651	10.307	10.307
PFU	0	9.740	9.740	0.891	0.891	8.849	8.849
	25	9.820	9.760	0.560	0.840	9.260	8.920
	50	9.920	9.820	0.200	0.720	9.720	9.100
	75	10.060	9.880	-0.240	0.460	10.300	9.420
	100	10.2570	10.2570	-0.8590	-0.8590	11.158	11.158

The abovementioned conclusions are quite important and may be exploited in the synthesis of novel polymers with desired conduction properties. On the basis of the above results, one can also say that the copolymers of the heterocyclic compounds having only normal linkages shall be better semiconductors and more dopantphilic than the copolymers containing mislinkages. Further, among the copolymers containing mislinkages, the ones with random distribution of mislinkages are expected to be not only better conductors of electricity but also better candidates for forming conducting materials through both oxidative and reductive doping than those with periodic distribution.

#### IV. SUMMARY AND CONCLUSIONS

In this paper we have investigated the electronic structure and conduction properties of completely mislinked neutral heterocyclic polymers—polypyrrole, polythiophene, and polyfuran on the basis of *ab initio* Hartree–Fock crystal orbital method. The general features of the energy band structures of all the three mislinked polymer chains are found to be similar: both the two highest occupied bands and the two lowest unoccupied bands in each case are  $\pi$  bands. In comparison to the corresponding normally linked heterocyclic polymers, the mislinked polymers are found to have higher ionization potentials, lower electron affinities, and thus higher band gap values, thereby implying that mislinkages increase the insulating character of the polymer chains and decrease their dopantphilicity for both oxidative and reductive doping. On the basis of the analysis of the Bloch wave functions both ionization potentials and electron affinities of the completely mislinked polymer chains are predicted to be sensitive both to the nature of the heteroatom and to the substitution at the ring carbon atoms. These results are important in view of the preparation of novel polymers with prescribed conduction properties.

In addition we have also investigated the effect of the distributions (both periodic and random) of the mislinkages on the electronic properties of the normally linked heterocyclic polymers, by determining the electronic DOS for the various percentages of mislinkages. The heterocyclic polymers with random distribution of mislinkages, in addition to being better semiconductors, are also found to have better prospects for forming conductive materials through both oxidative and reductive doping than the corresponding polymers with periodic distribution of mislinkages. Copolymers of the heterocyclic compounds are also predicted to become more insulating and less dopantphilic with the introduction of  $\alpha$ – $\beta$  linkages, though this effect is likely to be more pronounced for the periodic distribution of  $\alpha$ – $\beta$  linkages than for the random distribution.

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