

## Comparative study of the electronic structure and conduction properties of polypyrrole, polythiophene, and polyfuran and their copolymers

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A comparative study of the electronic structures and conduction properties of the three heterocyclic polymers polypyrrole, polythiophene, and polyfuran has been carried out using the results of *ab initio* crystal orbital calculations. Important electronic properties such as band gap, bandwidths, ionization potential, and electron affinity of these polymers are compared. The calculated trend in the values of the gap of the polymers is in excellent agreement with experiment. Our results predict polypyrrole to be the strongest candidate for oxidative (*p*) doping whereas polythiophene is predicted to have the greatest capacity for reductive (*n*) doping. It is shown that the electron affinity values depend more on the heterocyclic substitution whereas the values of the ionization potential are more influenced by substitution on the backbone. The problem of the copolymerization of these heterocyclic compounds is examined and the electronic density of states has been determined for various copolymers. The conduction properties of these copolymers are compared and discussed.

### I. INTRODUCTION

Conjugated heterocyclic polymers such as polypyrrole (PPY), polythiophene (PTP), and polyfuran (PFU) constitute an important class of conducting polymers. PPY has been, both theoretically and experimentally, the most studied polymer of this group followed by PTP and PFU. Though they are insulators in their neutral forms, these heterocyclic polymers become highly conducting on doping with electron acceptors (*p* doping).<sup>1</sup> Because of the ease of their preparation together with their environmental stability<sup>1</sup> a variety of applications such as rechargeable<sup>2</sup> and solar<sup>3</sup> batteries, optoelectronic devices,<sup>4,5</sup> permanent information storage devices<sup>6</sup> and sensors<sup>7</sup> have been proposed using these conducting films.

Among the three conducting polymers PPY films were the first to be synthesized.<sup>8</sup> The films of electrochemically synthesized PPY in the presence of tetraethyl ammonium tetrafluoroborate as electrolyte have room-temperature conductivities of 30–100  $\Omega^{-1} \text{cm}^{-1}$ .<sup>8</sup> They consist of cationic polypyrrole and the  $\text{BF}_4^{-1}$  anions with a ratio of pyrrole rings to anions of the order of 4:1. The nature of anions in the electrochemically oxidized PPY films has been found<sup>9</sup> to produce a variation up to  $10^4$  in the conductivity of the films for a variety of anions, though the concentration of anions remains nearly constant. The reason for the increase in the conductivity of PPY on oxidation is, however, not completely clear. The study of the various physical properties such as conductivity,<sup>10</sup> thermoelectric power,<sup>10</sup> infrared and visible spectra,<sup>10,11</sup> photoelectron spectra,<sup>12</sup>  $^{13}\text{C}$  NMR,<sup>11</sup> and electron diffraction patterns<sup>13</sup> of various pyrrole polymers rules out the validity of the conventional metallic band transport theory for these systems. The ESR measurements<sup>14</sup> on samples of neutral and oxidized PPY indicate that no ESR adsorption signal is found in the electrochemically cycled highly conducting PPY films. This observation of high conductivity without a paramagnetic susceptibility in oxidized

PPY has therefore been explained<sup>15</sup> on the basis of the formation of polarons at low oxidation level followed by spinless bipolarons at higher oxidation levels. Electrochemically synthesized PTP (Refs. 16 and 17) and PFU (Ref. 1) films are also found to have similar electrical and optical properties<sup>18–19</sup> as PPY films. A recent study<sup>20</sup> of the changes in adsorption spectra of PTP induced by photoexcitations and electrochemical doping also suggests the formation of polarons and bipolarons as charge carriers in oxidized PTP. It needs to be mentioned here that it has not been possible so far to dope PPY with electron donors (*n* doping), though *n*-doped PTP samples<sup>18</sup> have been prepared.

The structures of all the three heterocyclic polymers are shown in Fig. 1. Their benzenelike unit cells consist of  $(4n+2)\pi$  electrons and are therefore considered aromatic. All of them can be viewed as consisting of a backbone of  $sp^2$  hybridized carbon atoms analogous to that of trans-cisoid polyacetylene (*cis*-PA) (see Fig. 1), but stabilized by a heteroatom *X* (where *X*=NH, S, or O), which is covalently bonded to neighboring carbon atoms to form the heterocycle. The presence of three different heteroatoms (different both in size and electronegativity) in these three heterocyclic polymers brings about a great deal of diversity. Further sulphur, unlike oxygen and nitrogen, has also vacant *3d* orbitals whose overlap with the neighboring orbitals may lead to more effective coupling thereby improving the electron transfer necessary for conduction. One can therefore anticipate that there may be a systematic variation in the values of the parameters related to conduction properties such as band gap, ionization potential and electron affinity among these polymers. Band-gap values are related to the conduction properties of the undoped systems whereas ionization potential and electron affinity values determine the ability of the systems to form conducting polymers through oxidative and reductive doping, respectively.

The purpose of this work is to carry out a comparative

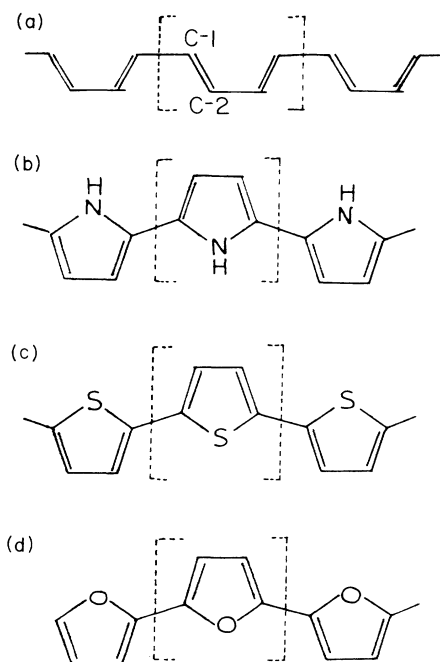


FIG. 1. Structures of (a) trans-cisoid polyacetylene (*cis*-PA); (b) polypyrrole (PPY); (c) polythiophene (PTP); and (d) polyfuran (PFU). The unit cells are surrounded with broken lines.

study of the electronic structures and conduction properties of these three heterocyclic polymers in their neutral forms. Quantum-mechanical methods are most suited for this purpose and are an efficient tool not only for the interpretation of the experimental results but also for the investigation of the finer details in the electronic structure which would be barely accessible in experiments. Band structures of undoped and doped polyparaphenylene, polypyrrole and polythiophene chains have already been calculated using the valence effective Hamiltonian (VEH) approach.<sup>21</sup> We also have investigated the problem of copolymerization of PPY, PTP, and PFU since in the recent years, there has been a great deal of effort devoted to the possibility of preparing copolymers of different monomers into more or less conducting polymers. It should, in principle, be possible to "tailor" polymers with prescribed properties by varying the nature and the composition of the monomers constituting the copolymer. Copolymers of acetylene with other compounds have already been prepared and studied.<sup>22</sup> There has also been some success in the field of heterocyclic copolymers: the copolymers of pyrrole with (i) *N*-methyl pyrrole,<sup>23</sup> (ii) *N*-nitro pyrrole,<sup>24</sup> and (iii) azulene<sup>25</sup> have been synthesized using the technique of electrochemical polymerization. It has also been found possible to achieve copolymerization through incorporation of nonelectroactive molecules into conducting polymers—for example, the copolymers from pyrrole and *N*-amino pyrrole have been obtained,<sup>26</sup> while it has not been possible to obtain a homopolymer out of *N*-amino pyrrole alone. Very recently the copolymers of pyrrole and thiophene in the composition (2:1) have been synthesized<sup>27</sup> through electrochemical copolymerization.

These copolymers are shown to have a random arrangement of the units with the properties intermediate between those of its constituent homopolymers; for example, their electrical conductivity is intermediate between that of its homopolymers ( $10^1$ – $10^2 \Omega^{-1} \text{cm}^{-1}$  for PPY and  $10^{-3}$ – $10^{-2} \Omega^{-1} \text{cm}^{-1}$  for PTP). We have determined the electronic density of states (DOS) of the copolymers of (i) pyrrole and thiophene; (ii) pyrrole and furan; and (iii) thiophene and furan using the negative factor counting method in the tight-binding approximation.<sup>28</sup>

The structure of this paper is as follows. In Sec. II, we present the method and computational details of the band structure calculations of the periodic homopolymers and of the density-of-states (DOS) calculations of the copolymers. Section III gives the results and their discussion. Finally, in Sec. IV, we present a summary of the present study and the conclusions.

## II. METHODS AND COMPUTATIONAL DETAILS

The energy band structures of the one-dimensional periodic neutral heterocyclic polymers and of *cis*- and *trans*-PA were calculated using the *ab initio* Hartree-Fock crystal orbital method. This method has been described and discussed in the literature.<sup>29</sup> The computations were performed employing Clementi's 7s/3p minimal basis set for the heavy atoms and four primitive Gaussian functions contracted to one *s* function for the hydrogens. All the multicenter two-electron integrals larger than the threshold value of  $10^{-8}$  a.u. were calculated and the interactions up to fourth-neighbors' interactions were taken into account. The precise structure of these heterocyclic polymers is not known. <sup>13</sup>C NMR data of PPY indicates the presence of pyrrole units bonded together by  $\alpha$ - $\alpha'$  linkages.<sup>11</sup> In the PPY films  $\alpha$ - $\beta$  and  $\beta$ - $\beta'$  linkages have also been found. The evidence that the polymerization occurs at the  $\alpha$  carbons comes primarily from the oxidative degradation studies of chemically prepared polypyrroles or pyrrole blocks, which lead predominantly to pyrrole-2,5, dicarboxylic acid.  $\alpha$ -substituted pyrroles do not undergo this type of polymerization but  $\beta$ -substituted pyrroles do, suggesting that  $\alpha$  substitution blocks the polymerization process.<sup>30</sup> A coplanar structure with an alternating orientation of neighboring rings has been considered in the calculations, for all the three heterocyclic polymers. This is in agreement with the solid-state conformations obtained from x-ray diffraction experiments for bipyrrrole and terpyrrrole<sup>31</sup> and for bithiophene.<sup>32</sup> The corresponding experimental geometries of the monomers<sup>33</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 CNDO/S3 calculations<sup>34</sup> (CNDO/S3 denotes modified complete neglect of differential overlap) and the extended Hückel calculations.<sup>35</sup> For *cis*- and *trans*-PA, the geometries were obtained from references.<sup>36,37</sup>

The DOS distributions of the various random copolymers have been calculated using the simple negative factor counting method<sup>28</sup> based on Dean's negative eigenvalue theorem.<sup>38</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 energy  $\lambda$  equal the number of negative factors  $\epsilon_i(\lambda)$  obtained by the recursion relation

$$\epsilon_1(\lambda) = \alpha_1 - \lambda$$

$$\epsilon_i(\lambda) = \alpha_i - \lambda - \frac{\beta_{i-1,i}^2}{\epsilon_{i-1}(\lambda)}, \quad i \geq 2.$$

(The latter expressions are obtained by transforming the tridiagonal determinant to a diagonal one applying successive Gaussian elimination.) Here  $\alpha_i$  and  $\beta_{i-1,i}$  are the on-site and hopping parameters in the first-neighbors' interactions approximation. They are obtained from the dispersion of the valence or the conduction bands (calculated with the help of the *ab initio* self-consistent-field linear combination of atomic orbitals crystal orbital method;<sup>29</sup> see first sentence of Sec. II) of the corresponding homopolymers. Their values are taken as the center of the band and one fourth of the bandwidth, respectively. It should be pointed out that the negative factor counting (NFC) method<sup>28</sup> in its simple form as described here treats the DOS's of a random copolymer only in the Hückel approximation. Since, however, the  $\alpha_i$  and  $\beta_{i-1,i}$  parameters occurring in the tridiagonal Hückel determinant are fitted to the band-structure results of *ab initio* crystal orbital calculations performed for the periodic chains of the components (polyacetylene, polypyrrole, etc.) the DOS curves obtained for a given energy region (one-band approximation) do not differ very much<sup>39</sup> from the total DOS curves (all-bands treatment) in the same energy region obtained with the help of the more accurate, but much more CPU-time-consuming *ab initio* matrix block version<sup>40</sup> of the method. Certainly the NFC method in its simple form, but using *ab initio* band structures to determine its parameters, gives the right trends for the DOS of two- and more component random polymers.

Thus by giving  $\lambda$  different values and taking the difference of the number of negative  $\epsilon_i(\lambda)$ 's belonging to consecutive values one can obtain the distribution of eigenvalues (density of states). In the present study the DOS have been determined for a chain length of 500 units.

### III. RESULTS AND THEIR DISCUSSION

#### A. Band-structure results

The energy band structures of the three heterocyclic polymers and of *cis*-PA (trans-cisoid) are shown in Fig. 2. For each system all the valence bands and the two lowest unoccupied bands are shown. In the case of *cis*-PA two-fold degeneracy of the bands is observed at the end of the Brillouin zone. This is because we have considered only a simple translation to define the unit cell (see Fig. 1) which consists of four CH units. The reason for considering this unit cell is to be able to see the change in the energy band structure which occurs when the unit cell of *cis*-PA forms a heterocycle with a heteroatom. The backbones of both the heterocyclic polymers and of the *cis*-PA thus consist of four carbon atoms, though helical symmetry is present in the former in contrast to the translational symmetry in the latter. As is evident from Fig. 2, the degeneracy of the bands of *cis*-PA is lifted as a result of the formation

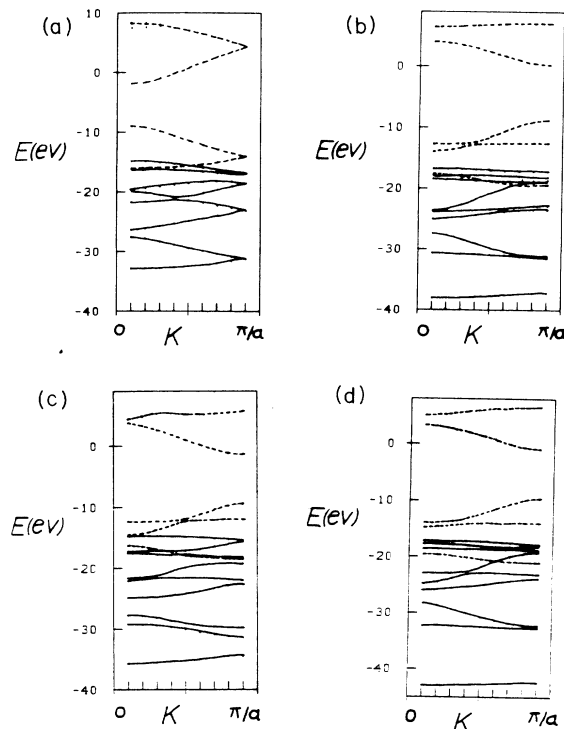


FIG. 2. Energy band structures of the (a) trans-cisoid polyacetylene (*cis*-PA); (b) polypyrrole (PPY); (c) polythiophene (PTP); and (d) polyfuran (PFU). Broken and solid lines indicate  $\pi$  bands and  $\sigma$  bands, respectively.  $a$  is the length of the unit cell.

of the heterocycle. The number of the  $\pi$  valence bands also increases from two in *cis*-PA to three in the heterocyclic polymers.

The most important electronic properties of the heterocyclic polymers and of both *cis*- and *trans*-polyacetylene are given in Table I. The band-gap values for all the three heterocyclic polymers are quite large and therefore they are expected to be good insulators. The calculated band gap in these polymers is found to decrease in the following order  $PPY > PFU > PTP$ . This trend is in agreement with the corresponding experimental results, as is evident from Table I, though the calculated values of the band gap are larger by about 6 eV than the corresponding experimental values. This is the well-known overestimation of the band gap in the Hartree-Fock method. Using better basis sets and taking into account correlation effects, the calculated band gap values would come closer to the experimental ones as has been observed previously in the case of *trans*-PA,<sup>41</sup> where the initially determined band-gap value of 8.282 eV [for STO-3G (Slater-type orbital with three Gaussian) basis sets] decreases to 2.980 through the use of 6-31G\*\* basis set and the consideration of correlation effects in the Moeller-Plesset form of many-body perturbation theory in second order.

The two highest occupied bands  $n$  and  $n - 1$ , which are mainly responsible for the conduction properties of the systems upon  $p$  doping, are  $\pi$  bands for all the three heterocyclic polymers (see Fig. 2). The highest occupied

TABLE I. Calculated electronic properties (in eV) for heterocyclic polymers and for *trans*- and *cis*-polyacetylene.

	<i>trans</i> -PA	<i>cis</i> -PA	PPY	PTP	PFU
Valence-band width	7.826	5.890	3.905	2.890	4.205
Conduction-band width	9.330	9.930	3.751	5.118	4.215
Ionization potential (top of valence band)	8.482	8.990	8.826	9.499	9.740
Electron affinity (negative value of bottom of conduction band)	1.968	1.858	-0.275	1.362	0.891
Band gap <sup>a</sup>	6.514 (1.5)	7.131	9.102 (3.0)	8.137 (2.0)	8.849 (2.7)

<sup>a</sup>Values in parentheses indicate the experimental band-gap values.

band ( $n$ ) is broader than the band ( $n - 1$ ) in all of them, though for PFU, the ( $n - 1$ ) band is very narrow. The lowest ionization potential values, corresponding to the top of the highest-filled band (using Koopman's theorem) of the three heterocyclic polymers decrease in the following order  $PPY < PTP < PFU$ . Amongst the three heterocyclic polymers, PPY is thus expected to have the greatest capacity to form well conducting materials through oxidative doping and PFU the least.

An examination of the Bloch wave functions of the highest filled band of the three heterocyclic polymers indicates that for all three systems, the contributions to the top of this band (corresponding to the lowest ionization potential) come only from the  $2p_z$  orbitals of the four backbone carbon atoms and not at all from  $p_z$  orbitals of the heteroatom. This implies that when these heterocyclic polymers are doped with electron acceptors, the latter attract the  $\pi$  electrons of the carbon skeleton and not of the heteroatom. These results are in agreement with the results of the ESR measurements<sup>14,42</sup> on both PPY and PTP (in both neutral and oxidized forms) which indicate a  $g$  value of 2.0025 to 2.0028, implying thereby that the species responsible for spin resonance is not a heteroatom containing moiety but a defect in the "*cis* polyene" backbone. We would like to mention here that any radical localized on or near a heteroatom, such as oxygen in carboxylic species or nitrogen in pyridines has a " $g$ " value shift<sup>43</sup> of at least  $10^{-3}$ . Extending these arguments further, it is therefore expected that the ESR signal of both insulating and conducting PFU shall also have a signal centered at a  $g$  value of 2.0026.

Also the two lowest unoccupied bands of all the three heterocyclic polymers are  $\pi$  bands. The electron affinity values (corresponding to the negative values of the bottom of the conduction band) for the polymers decrease in the order  $PTP > PFU > PPY$  (Table I). Therefore, among the three heterocyclic polymers, PTP is expected to be the strongest and PPY the weakest candidate for reductive ( $n$ ) doping. These results are substantiated by the experimental observation that it has now been possible to  $n$  dope

PTP,<sup>18</sup> whereas the attempts to  $n$  dope PPY so far have been unsuccessful. To the best of our knowledge no results on  $n$  doping of PFU have been reported until now. As is evident from Fig. 2, there are negative energy states near the bottom of the conduction band in case of PTP and PFU but not for PPY. This is in contrast to the corresponding VEH (Ref. 44) and CNDO/S3 (Ref. 34) results of PPY, both of which show negative energy states for the conduction band. As has been observed earlier in case of *trans*-PA,<sup>30</sup> the conduction bands are lowered and the valence bands raised in energy through the consideration of correlation (if better basis sets are used). Therefore it is expected that similar shifts in case of PPY shall lead also to the negative energy states near the bottom of the conduction band.

An analysis of the Bloch wave functions of the lowest unoccupied band of the three heterocyclic polymers indicates that unlike the valence band, the contribution to the bottom of the conduction band (corresponding to the highest electron affinity) comes from all the ring atoms including the  $p_z$  orbitals of the heteroatom. This is in complete contrast to the case of the valence band where by symmetry the contribution of the  $p_z$  orbitals of the rings heteroatom was zero. Hence the  $g$  factor of the ESR signal for  $n$ -doped heterocyclic polymers is expected to differ from the values of 2.0025 to 2.0028 observed for  $p$ -doped polymers.

As mentioned before, the  $p_z$  orbitals of the heteroatom do not contribute to the wave function belonging to the top of the valence band in all the three heterocyclic polymers. However, these orbitals make a significant contribution to the wave function belonging to the bottom of the conduction band. This is in agreement with the VEH calculation for PPY and PTP.<sup>21</sup> The LCAO coefficients for  $k=0$  are depicted schematically in Fig. 3. Both the orbitals corresponding to the top of the valence band and to the bottom of the conduction band for both heterocyclic polymers and *cis*-PA are shown. From the quite different nature of the wave functions it can be expected that the ionization potential values of these heterocyclic poly-

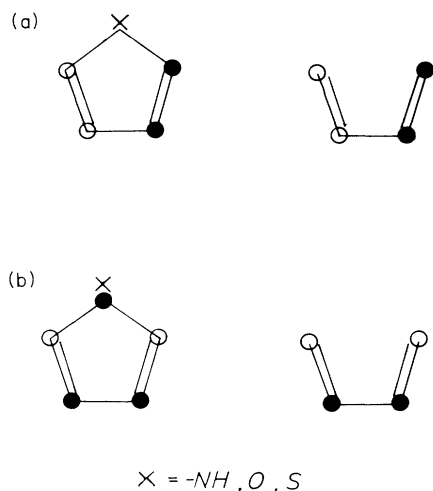


FIG. 3. Orbital patterns of (a) the top of the valence band and (b) the bottom of the conduction band ( $k=0$ ) of heterocyclic polymers and *cis* polyacetylene. White (black) circles indicate positive (negative) LCAO coefficients.

mers and of *cis*-PA shall not differ too much from each other. On the other hand, the electron affinity values of these polymers are expected to depend considerably on the nature of the heteroatom. The ionization potential and the electron affinity values of the polymers studied are shown diagrammatically in Fig. 4. The maximum deviation in the ionization potential from that of *cis*-PA is 0.750 eV in the case of PFU while the corresponding deviation in the electron affinity from *cis*-PA is 2.133 eV for PPY. From this follows that it should, in principle, be possible to change the electron affinity values by the choice of the heteroatom. The ionization potential, on the other hand, is much less sensitive to this substitution but should be changeable upon substitution on the backbone ( $\beta$ -carbon atoms) which would, of course, also influence the electron affinity values. This is important in view of the preparation of novel polymers with prescribed properties (for conduction properties of substituted heterocyclic polymers see Refs. 45–49). Of course, the foregoing discussion applies only as long as the substituent is not too bulky to modify the geometry (introducing nonplanarity) in which case the conduction properties may get further modified. One also has to point out that the experimental trend is very well reproduced by minimal basis set calculations only within a given class of polymers. Better basis sets (and correlation effects) have to be employed if electronic properties of polymers belonging to different classes are compared. For example, the calculated ioniza-

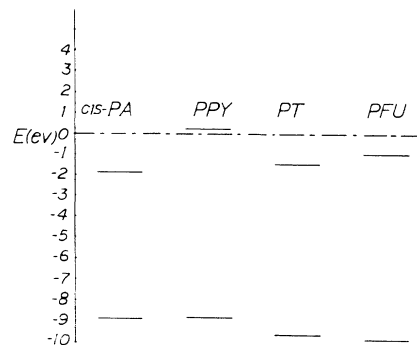


FIG. 4. Diagrammatic representation of the lowest ionization potential and the highest electron affinity values of the heterocyclic polymers and *cis*-polyacetylene.

tion potential of *trans*-polyacetylene is less than that of polypyrrole (see Table I)—contrary to experiment.<sup>50</sup>

The charge distributions for the heterocyclic polymers and for *cis*-PA, calculated on the basis of Mulliken's population analysis, are given in Table II. The charge distributions for the heterocyclic polymers are quite different from that of *cis*-PA. As compared to *cis*-PA, carbon atoms C-1 (see Fig. 1) become more positive in the heterocyclic polymers, though to different extents. This increase of positive charge is maximal for PFU and minimal for PTP. On the other hand, carbon atoms C-2 (Fig. 1) become more negative than the C-2 carbon atoms of *cis*-PA. Here too the increase of negative charge is maximal for PFU and minimal for PTP. This is because oxygen is the most electronegative and sulphur the least electronegative of the three heteroatoms. The net charges on the heteroatoms are as follows: +0.382 at S, -0.374 at O, and -0.477 at N. This is because in the ring, nitrogen is the strongest  $\pi$  donor (+0.369) followed by sulphur (+0.303) and oxygen (+0.291), but nitrogen is also the strongest  $\sigma$  acceptor (-0.846) followed by oxygen (-0.665) whereas sulphur is not a  $\sigma$  acceptor at all (+0.079). The charge distributions—for PPY and PTP, as are consistent with those calculated earlier for quaterpyrrole and quaterthiophene<sup>21</sup>—will certainly influence the position of donor or acceptor atoms or molecules.

#### B. Density of states of copolymers of heterocyclic compounds

Here we report the results for the DOS of copolymer chains of 500 units (for both periodic and random sequences) of (i) pyrrole and thiophene (copolymer *A*); (ii)

TABLE II. Calculated net charges on the basis of Mulliken population analysis (see Fig. 1).

System	C-1	C-2	H-2	N,O,S	H-1
<i>cis</i> -PA	-0.207	-0.207	0.207		0.207
PPY	0.111	-0.266	0.197	-0.477	0.391
PTP	-0.178	-0.243	0.230	0.382	
PFU	0.209	-0.268	0.246	-0.374	

pyrrole and furan (copolymer *B*); and (iii) thiophene and furan (copolymer *C*) in the same composition (2:1). Polymers similar to copolymer *A* with random sequence have been synthesized recently.<sup>27</sup>

The electronic DOS for both the valence and the conduction bands of the various copolymers studied are shown in Figs. 5 and 6. Figure 5 shows the DOS curves of the periodic copolymers (*A*, *B*, and *C*) while those of the random copolymers are shown in Fig. 6. All periodic and random copolymers were taken in the composition 2:1, the number 2 referring to the first-mentioned constituent in these binary chains (see legends to Figs. 5 and 6). It is certainly not true that in the real copolymer this ratio is maintained and also the sequence of the two components are not completely uncorrelated. To see, however, again the trends in the electronic structure changes of these copolymers due to disorder we have taken the two extreme cases: the periodic one, *ABAABAAB*..., and the completely random sequence (in 2:1 composition). To perform a more realistic calculation one would need experimentally determined sequences of these copolymers which are—according to our knowledge—not available.

As is evident from these figures, the valence and the conduction band regions of the periodic copolymers consist of three relatively narrow bands, while those of the random copolymers consist of a single very broad region

of allowed energies (with a few extremely narrow gaps). Such broadening in aperiodic systems is consistent with our earlier observations on aperiodic deoxyribose nucleic acid (DNA) and polypeptides<sup>51–53</sup> using the matrix block negative factor counting technique<sup>54,55</sup> and is mainly due to the changing environment of each unit in the random chain. To check the dependence of the DOS on the sequence of the units in both the valence and conduction band regions, the random copolymers 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. In Fig. 6 the averages of the three Monte Carlo runs are given (test calculations have shown that the differences of the average DOS curves with three and four runs, respectively, are negligible).

The most important electronic properties of the copolymers obtained from their DOS curves are given in Table III. In the case of each copolymer the band gap for the random sequence is found to be a little smaller than that for the periodic sequence and therefore to dope periodic copolymers *A* and *B* is somewhat more difficult than the corresponding random copolymers. Among the random copolymers, the smallest band gap is obtained for copolymer *A* (7.820 eV) followed by copolymer *C* (8.200 eV) and

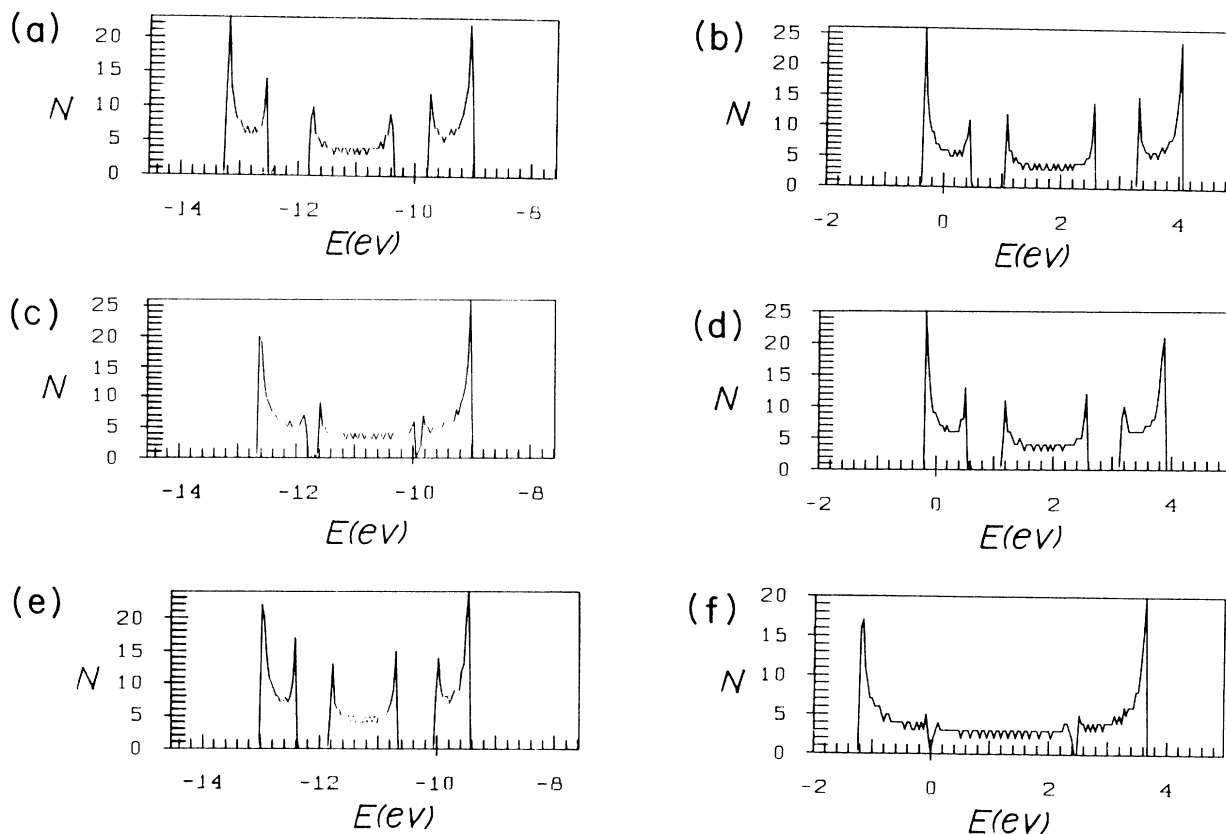


FIG. 5. Density of states (DOS) of (a) the valence band and (b) the conduction band of the periodic copolymer *A* (pyrrole and thiophene) in the composition (2:1). Figure (c) and (d) indicate the corresponding DOS of the periodic copolymer *B* (pyrrole and furan) and figures (e) and (f) those of the periodic copolymer *C* (thiophene and furan) in the same compositions.

$B$  (8.220 eV), while among periodic copolymers, the smallest band gap is obtained for copolymer  $C$  (8.260 eV) followed by copolymer  $A$  (8.700 eV) and  $B$  (8.860 eV), respectively. Therefore, for copolymer  $C$ , in which the decrease of the gap is only about 1% going from the periodic to the random sequence one cannot establish safely even a trend, because the error in the gap due to basis set errors and due to the lack of a correlation is much larger.<sup>41</sup> As is evident from Table III, the transition from the periodic sequence to the random sequence in the case of each copolymer leads to the increase of electron affinity but decreases the ionization potential (except in the case of copolymer  $C$  where the ionization potential slightly increases). This means that the random copolymers are generally expected to be somewhat better candidates for forming conducting materials through both oxidative and reductive doping in comparison to their periodic counterparts. Among the copolymers studied by us the random copolymers  $B$  and  $A$  have the smallest ionization potential (8.86 eV) which is slightly more than that of PPY whereas random copolymer  $C$  has the highest electron affinity (1.280 eV). A similar trend was observed by us for the copolymers of trans-polyacetylene and methineimine<sup>56</sup> as well as for aperiodic nucleotide base stacks and polypeptides.<sup>51,53</sup> This observed difference in the conduction properties of the random and the periodic copolymers may be exploited in synthesizing copolymers with a wide

range of conductivities. Whether the resulting copolymer is periodic or random depends upon the kinetics and the energetics of the radical cation attack, through which electropolymerization is believed to occur.<sup>57</sup> A radical cation may dimerize with another radical cation or may either attack the parent monomer or some other molecules, thereby leading to different polymer chains, depending upon the detailed coupling of the radicals.

Our results for the DOS of the copolymers are for the composition (2:1). A change in the composition of the copolymers shall certainly change the electronic properties of the copolymers, though they are expected always to remain between those of the corresponding homopolymers.

#### IV. SUMMARY AND CONCLUSIONS

In this paper we have reported the results of a comparative study of the electronic structures and conduction properties of the neutral heterocyclic polymers—polypyrrole, polythiophene, and polyfuran. The general features of the energy band structures of all the three heterocyclic polymers are found to be similar: both the two highest occupied bands and the two lowest unoccupied ones in each case are  $\pi$  bands. The calculated trend in the values of the gap is in excellent agreement with experiment. Our results predict PPY to be the strongest and

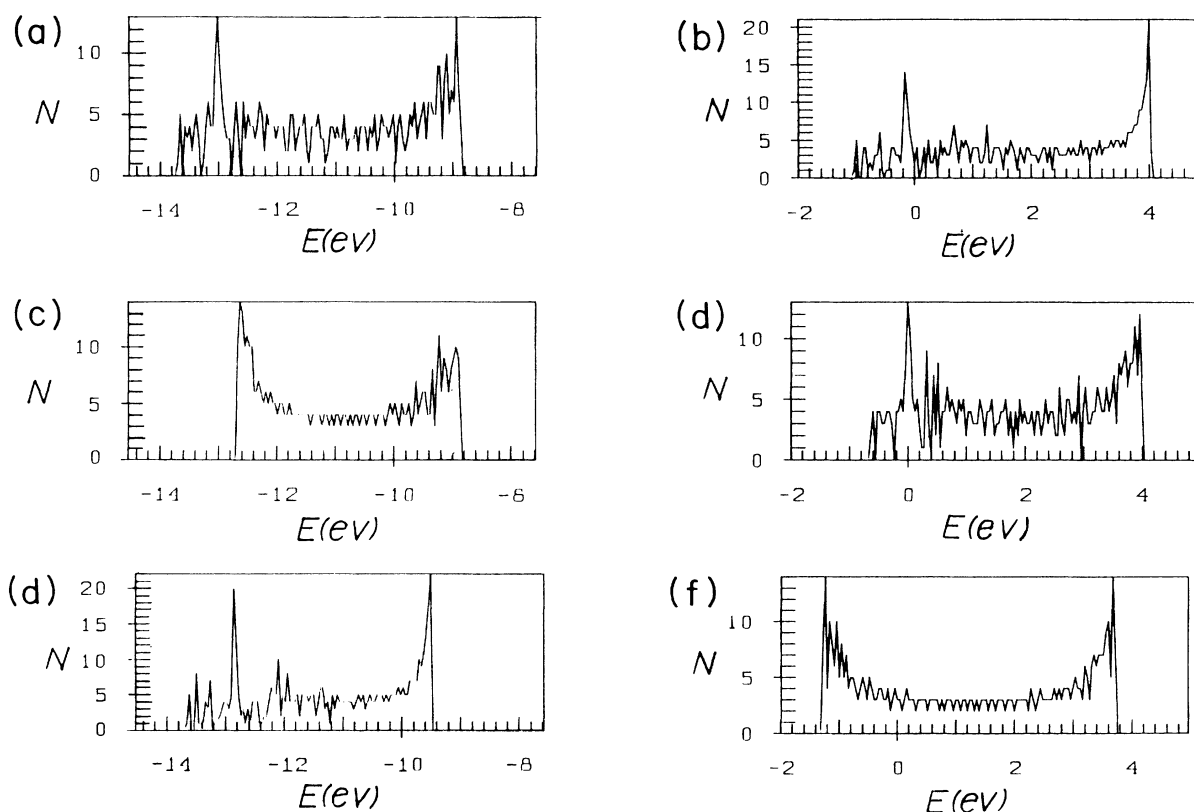


FIG. 6. Density of states (DOS) of (a) the valence band and (b) the conduction band of the random copolymer  $A$  (pyrrole and thiophene) in the composition (2:1). Figures (c) and (d) indicate the corresponding DOS of the random copolymer  $B$  (pyrrole and furan) and figures (e) and (f) those of the random copolymer  $C$  (thiophene and furan) in the same composition.

TABLE III. Electronic properties (in eV) of the copolymers. Copolymer *A* is of pyrrole and thiophene; copolymer *B* is of pyrrole and furan; copolymer *C* is of thiophene and furan.

	Copolymer <i>A</i>		Copolymer <i>B</i>		Copolymer <i>C</i>	
	Periodic	Random	Periodic	Random	Periodic	Random
Ionization potential	9.020	8.860	9.020	8.860	9.460	9.500
Electron affinity	0.320	1.04	0.160	0.640	1.200	1.280
Band gap	8.700	7.820	8.860	8.220	8.260	8.200

PFU to be the weakest candidate for forming conductive materials through oxidative doping. On the other hand, PTP is found to have the greatest capacity for reductive doping followed by PFU and PPY. From the analysis of the wave functions it could be shown that the electron-affinity values depend more on the heterocyclic substitution while the values of the ionization potential are more influenced by substitution on the backbone carbon atoms. In addition we have determined the DOS of various copolymers (both periodic and random) of these heterocyclic compounds. The study of periodic copolymers is a first step toward basic investigations of polymeric quantum well structures. The random copolymers are found to have better prospects for both *p* and *n* doping as compared to their periodic counterparts.

These primary calculations show that, for a given class of polymers, comparatively simple calculations can be

helpful in the search for novel polymers: other heteroatom substitutions have to be investigated in the future for polymers suitable for *n* doping. For *p* doping, substitutions on the backbone should be considered. Among the candidates investigated, copolymers with a high percentage of thiophene seem to be desirable if *n* doping is wanted. For *p* doping, on the other hand, a high percentage of pyrrole is still the best solution.

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