On the electronic structures and conduction properties of quasi-one-dimensional copolymers (type-II staggered) of donor-acceptor polymers

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Using ab-initio band structure results of two novel donor-acceptor polymers PPDCH [A]$_x$ and PPDCN [B]$_x$ as the input, the electronic structures and conduction properties of their various periodic and aperiodic copolymers ($A_mB_n$) have been investigated using negative factor counting method based on Dean's negative eigen value theorem. These polymers consist of a bicyclopentadienylene unit bridged by an electron accepting group Y (where $Y=\text{C}=\text{CH}_2$ in PPDCH and $\text{C}=\text{C}$(CN)$_2$ in PPDCN) as the repeat unit. The copolymers, on the basis of the band alignments of the two constituent homopolymers, are found to belong to the class of type-II staggered superlattices. The trends in their electronic structures and conduction properties as a function of (i) composition (m/n), (ii) block sizes m and n and (iii) arrangement of the blocks (periodic or aperiodic) in the various copolymer chains are discussed. The trends are important guidelines for designing novel electrically conducting copolymers.

Currently major efforts in the field of electrically conducting polymers are focussed on the molecular designing of novel polymers with tailor-made conduction properties$^{1,2}$. Organic conjugated polymers having relatively smaller band gap, smaller ionization potential, larger electron affinity and larger band widths are expected to be better conductors of electricity both intrinsically and extrinsically. Various routes are presently followed for designing such conducting polymers. Among these routes, the strategy of growing quasi-one-dimensional superlattices (or copolymers) is highly exciting and promising. The electronic properties of a copolymer$^3$ ($A_mB_n$)$_x$, though generally intermediate between those of its components [A]$_x$ and [B]$_x$, can be tuned by varying the molecular composition of the copolymer and by varying the arrangement of components (periodic or aperiodic) in the copolymer chain.

Donor-acceptor polymers, first proposed by Havinga and co-workers$^{4,5}$, consist of a regular alternation of donor and acceptor moieties in a conjugated backbone and have relatively smaller band gaps. The bandgap is expected to be the smallest for a combination in which the electronegativity difference between the donor and acceptor moieties is the largest. Various novel donor acceptor polymers differing in their electron donating and electron accepting moieties have been designed and investigated$^6,7$. Novel thermally stable donor-acceptor polymers such as poly-squaraines and polycroconaines synthesized by Havinga et al. have bandgap values as low as 0.5 eV$^4,8$. Lambert and Ferraris$^9$ have synthesized polymers such as poly-4H-cyclopentadithiophene-4-one (PCDT) and polydicyanomethylene cyclopentadithiophene (PCNTh) with bandgap values of 1.2 eV and 0.8 eV respectively, using a similar approach.

In this paper we report the results of our investigations of the electronic structures and conduction properties of the various periodic and aperiodic quasi-one-dimensional polymeric superlattices (copolymers) ($A_mB_n$)$_x$ of two novel donor-acceptor polymers PPDCH [A]$_x$ and PPDCN [B]$_x$ based on poly (cyclopentadienylene) (PPD) using simple negative factor counting method. The repeat unit of these polymers is a bicyclopentadienylene unit bridged by an electron accepting group $Y(Y=\text{C}=\text{CH}_2$ in PPDCH and $\text{C}=\text{C}$(CN)$_2$ in PPDCN) (Fig. 1). Though these polymers have not been synthesized yet, the band structure calculations$^7,10$ of these two donor-acceptor copolymers have already been performed on the basis of ab-initio Hartree Fock crystal orbital method.
Fig. 1—Schematic structures of [A] sub x PPDC and [B] sub x PPDCN.

The band alignments of the two homopolymers (PPDC and PPDCN) show that the copolymers belong to the class of type-II (staggered) superlattices 11 (Fig. 2). The values of the two fundamental parameters, the conduction band discontinuity $\Delta E_c$, and the valence band discontinuity $\Delta E_v$ controlling the electronic properties of the PPDC and PPDCN copolymers are 1.562 and 1.114 eV, respectively. ($\Delta E_c$ is defined as the difference in the electronic affinities of the two components, while $\Delta E_v$ equals the corresponding difference in the ionization potentials). Since the ab-initio Hartree Fock crystal orbital method is known to overestimate the electronic properties owing to the basis set truncation and neglect of electron correlation effects, the results given herein should be considered only as qualitative predictions referring to a stretched energy scale.

We have investigated the trends in the electronic structures and conduction properties of these copolymers $(A_mB_n)_x$ as a function of; (i) the block size m of A, (ii) the block size n of B, (iii) the block sizes m and n keeping m/n constant and (iv) the arrangement of units (periodic or aperiodic) in the copolymer chain. This study is expected to provide important guidelines for the molecular engineering of the copolymers with tailor-made conduction properties.

**Methodology**

The electronic density of states (DOS) of a quasi one-dimensional copolymer $(A_mB_n)_x$ chain can be determined using a simple negative factor counting method 13,14 based on Dean's negative eigen value theorem 15. The details of the method used in the present calculations of the copolymers are given in one of our recent papers 16. In this method one computes the electronic DOS by finding the number of eigenvalues of a tridiagonal tight-binding (Huckel) secular determinant of a copolymer chain which are smaller than a given trial energy $\lambda$, by using the recursion relations,

$$
\varepsilon_i(\lambda) = \alpha_i - \lambda, \quad \text{... (1)}$$

$$
\varepsilon_i(\lambda) = (\alpha_i - \lambda) - \frac{\beta_i}{\varepsilon_{i+1}(\lambda)}; \quad i = 2, 3, \ldots, N, \quad \text{... (2)}$$

(the later expressions are obtained by transforming the tridiagonal determinant to a didiagonal one by applying successive Gaussian elimination 16).

In the present calculations of the DOS, the $\alpha$ and $\beta$ values for the valence and the conduction bands which are needed as input for the above method, have been obtained from the corresponding band structure results 7,10 of each component (PPDC and PPDCN) constituting the copolymer chain. A chain length of 300 units has been considered for determining the
electronic density of states (DOS) of copolymers. For the copolymers \((\text{AmBn})_x\) of the donor-acceptor polymers, the \(\alpha(\beta)\) values in eV for the valence band of the donor-acceptor polymers based on PPDCH \([\text{A}]\), and PPDCN \([\text{B}]\), are \(-8.9325\) (0.784) and \(-10.074\) (0.798) respectively, while the corresponding values for the conduction band are \(-1.1795\) (0.389) and \(-3.1535\) (0.1832) respectively.

Results and Discussion

Electronic properties of the copolymers

The copolymers \((\text{AmBn})_x\), \((\text{ABn})_x = \text{PPDCH}\) and \([\text{B}]_x = \text{PPDCN}\) in the present study have been divided into three classes: Class 1: \((\text{ABn})_x\); this includes systems in which the block size \((m)\) of component A is kept constant \((m=1)\) and the block size \((n)\) of component B is varied; Class 2: \((\text{AmB})_x\); this includes systems in which the block size \((n)\) of component B is kept constant \((n=1)\) and the block size \((m)\) of component A is varied; and Class 3: \((\text{AmBn})_x\) this includes systems in which the block sizes \(m\) and \(n\) of both the components A and B are varied keeping the ratio \(m/n\) constant.

For all the three classes, both periodic as well as aperiodic copolymers have been studied. The calculated electronic properties such as ionization potential \((E_i)\), electron affinity \((E_{ea})\) and bandgap \((E_g)\) of the various periodic and aperiodic copolymer chains of the above three classes are given in Tables 1 and 2, respectively.

In the case of periodic copolymers of the class \((\text{ABn})_x\), the bandgap is found to increase with an increase in the block size \(n\) of B units (Table 1). This increase in the bandgap values in these copolymers is the result of an increase in both \(E_i\) and \(E_{ea}\) values. Since, the increase in the \(E_i\) increases the bandgap while an increase in \(E_{ea}\) decreases it, the observed increase in bandgap implies that the decrease in \(E_i\) is much more than the corresponding decrease in the \(E_{ea}\) values. It, therefore, means that the copolymers become not only better intrinsic conductor of electricity but also better candidates for p-doping as the block size \(m\) of the component A (PPDCH) increases.

An increase in the block sizes of A and B units for a given composition \((m/n=1)\) is also found to decrease the bandgap. This decrease in the bandgap is accompanied by a decrease in \(E_i\) and an increase in \(E_{ea}\) implying that increasing the block size has the effect of increasing both the intrinsic conductivity and the extrinsic conductivity of the copolymer. Therefore, with increase in the block sizes for a given composition, the copolymer chain not only becomes more and more conducting intrinsically but also its tendency to form conducting materials on doping with electron acceptors (p-doping) and electron donors (n-doping) increases. Similar trends are observed for copolymer chains with composition \(m/n=2\) and \(m/n=1/2\).

From the data in Table 2 one can see that the trends in the electronic properties of the aperiodic copolymers are found to be generally similar to those for the corresponding periodic chains except that in the aperiodic copolymers, the saturation in the electronic properties is reached relatively faster. The range of bandgap values over which the periodic copolymers can be tuned is much larger than that for the aperiodic copolymers. It, therefore, means that tuning the bandgap to a particular value is easier by synthesizing periodic copolymers. Further, it is

<table>
<thead>
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<th>System</th>
<th>(E_i)</th>
<th>(E_{ea})</th>
<th>(E_g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\text{AB})_x)</td>
<td>7.820</td>
<td>3.305</td>
<td>4.515</td>
</tr>
<tr>
<td>((\text{AB})_9)</td>
<td>8.090</td>
<td>3.530</td>
<td>4.560</td>
</tr>
<tr>
<td>((\text{AB})_{10})</td>
<td>8.115</td>
<td>3.530</td>
<td>4.585</td>
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<tr>
<td>((\text{AB})_{11})</td>
<td>8.115</td>
<td>3.530</td>
<td>4.585</td>
</tr>
<tr>
<td>((\text{AmB})_1)</td>
<td>7.465</td>
<td>3.280</td>
<td>4.200</td>
</tr>
<tr>
<td>((\text{AmB})_{10})</td>
<td>7.400</td>
<td>3.265</td>
<td>4.135</td>
</tr>
<tr>
<td>((\text{AmB})_{11})</td>
<td>7.365</td>
<td>3.265</td>
<td>4.100</td>
</tr>
<tr>
<td>((\text{AmB})_{12})</td>
<td>7.515</td>
<td>3.535</td>
<td>3.981</td>
</tr>
<tr>
<td>((\text{AmB})_{13})</td>
<td>7.415</td>
<td>3.540</td>
<td>3.875</td>
</tr>
<tr>
<td>((\text{AmB})_{14})</td>
<td>7.365</td>
<td>3.540</td>
<td>3.825</td>
</tr>
</tbody>
</table>
interesting to note from Tables 1 and 2 that aperiodic copolymers in general have lower $E_1$ and $E_g$ values but higher $E_{ca}$ values than their periodic counterparts. This means that, for a given composition, aperiodic copolymers are better candidates for both intrinsic and extrinsic conductivities than the corresponding periodic copolymers.

**DOS distributions**

Some selected DOS curves for both the valence and the conduction bands of the periodic and aperiodic copolymers of type $(AB_n)_x$ (Class 1) are shown in Figs 3 and 4 respectively. In the case of periodic copolymers, the DOS curves consist of narrow and well-separated peaks. In contrast, the DOS distributions of the aperiodic copolymers consist of

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**Table 2—Calculated electronic properties (in eV) of aperiodic copolymers $(AB_n)_x, (A,B)_x$ and $(A_n, B)_x$ ([A] = PPDC and [B] = PPOCN)**

<table>
<thead>
<tr>
<th>System</th>
<th>$E_1$</th>
<th>$E_{ca}$</th>
<th>$E_g$</th>
</tr>
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<tbody>
<tr>
<td>$(AB)_x$</td>
<td>7.500</td>
<td>3.530</td>
<td>3.970</td>
</tr>
<tr>
<td>$AB_3$</td>
<td>7.515</td>
<td>3.540</td>
<td>3.975</td>
</tr>
<tr>
<td>$AB_{10}$</td>
<td>7.570</td>
<td>3.540</td>
<td>4.030</td>
</tr>
<tr>
<td>$AB_{50}$</td>
<td>7.660</td>
<td>3.540</td>
<td>4.120</td>
</tr>
<tr>
<td>$(A,B)_x$</td>
<td>7.370</td>
<td>3.535</td>
<td>3.835</td>
</tr>
<tr>
<td>$A_3B$</td>
<td>7.365</td>
<td>3.520</td>
<td>3.845</td>
</tr>
<tr>
<td>$A_{10}B$</td>
<td>7.360</td>
<td>3.785</td>
<td>3.575</td>
</tr>
<tr>
<td>$(A_n,B)_x$</td>
<td>7.360</td>
<td>3.540</td>
<td>3.840</td>
</tr>
<tr>
<td>$A_{10}B_{10}$</td>
<td>7.365</td>
<td>3.540</td>
<td>3.825</td>
</tr>
<tr>
<td>$A_{50}B_{50}$</td>
<td>7.365</td>
<td>3.540</td>
<td>3.820</td>
</tr>
</tbody>
</table>

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Fig. 3—DOS curves of some periodic block copolymers of type $(AB)_n (\{A\}_x = PPDC and \{B\}_x = PPDCN)$. Energy in eV, number of states $N$ in relative units.
relatively broader regions of allowed energy states with fewer band gaps in between. The result is that the band gap for the aperiodic copolymer is less than that for the corresponding periodic copolymer. These features result from the changing environment of a unit in an aperiodic copolymer chain in contrast to the periodic chain where the environment of a unit throughout the chain remains the same. Since, similar features are present in the DOS curves of other periodic and aperiodic copolymers, we do not show them here.

Conclusion
In this paper, we have studied systematically the electronic structures and conduction properties of periodic and aperiodic copolymers of PPDCH \([A_x]\) and PPDCH \([B_x]\), which represent the prototypes of the quasi-one-dimensional superlattices of type-II staggered. Our results show that the electronic properties of periodic copolymers cover a wider range than those of aperiodic copolymers. It, therefore, means that the tuning the electronic properties to a particular value is easier by synthesizing periodic copolymers. In the case of aperiodic copolymers, on the other hand, the saturation in electronic properties is reached much faster. Aperiodic copolymers are also predicted to be better intrinsic and extrinsic conductors of electricity than the corresponding periodic copolymers. Further, our results show that increasing the proportion of low bandgap component
in the copolymer chain improves its $n$-dopantphilicity while increasing the percentage of large bandgap component improves its intrinsic conductivity and also makes it a better candidate for oxidative doping. To improve both intrinsic conductivity as well as extrinsic conductivity ($p$- and $n$-dopantphilicity), increasing the proportion of both components seems to be the best solution.

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**References**


