On the electronic structures of quasi-one-dimensional model superlattices of type-I

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The electronic structures of the three different quasi-one-dimensional model superlattices (copolymers)\( \text{A}_m\text{B}_n \), belonging to the class of type-I have been calculated in the tight-binding approximation using the direct numerical approach. For each of the three systems, component A is the same while component B, though having same band widths and band gap, differs in its alignment with respect to A. The trends in their electronic structures as a function of (i) composition (m/n), (ii) block sizes m and n and (iii) arrangement of units (periodic or aperiodic) in the copolymer chain are discussed. The results obtained are important guidelines for designing copolymers with tailor-made conduction properties.

The molecular engineering of novel polymers with tailor-made conduction properties\(^1\), including designing of polymers that are intrinsically good electrical conductors, is a problem of considerable interest in the field of electrically conducting polymers. To achieve this tailoring of conducting polymers, the following five routes are presently followed; (a) substitution; (b) ladder polymerisation\(^2\); (c) topological methods; (d) donor-acceptor polymerisation\(^3\) and (e) polymeric superlattices. The last route that achieves designing through copolymerisation is of current interest to us. Depending upon the band alignments of the two constituent polymers, polymeric superlattices like the inorganic superlattices may be divided into four types\(^4\), viz. type-I, type-II-staggered, type-II-misaligned and type-III (Fig. 1). Type-I applies to such systems, where the energy gap of one component is contained entirely within the band gap of the other component. Type-II-staggered involves systems such as in which the top of valence band of one component lies within the band gap of the other and the bottom of the conduction band of the second lies in the band gap of the first. In the type-II-misaligned superlattices the band match-up is such that the conduction band minimum of one is below the valence band maximum of the second component. In the type-III\(^7\) superlattice, one component is semimetallic (i.e. a zero-band-gap semiconductor), while the other is a normal semiconductor.

It is also possible to conceive of polymeric quasi-one-dimensional superlattices (or copolymers) which can have tailor made properties depending on the choice of two semiconducting components, their relative amounts and their arrangement in the polymer chain. It is already well known that copolymerisation\(^7,10\) (periodic or random) has

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Fig. 1—Types of superlattices
considerable influence on the electronic properties although these always remain intermediate between those of the homopolymers. Our earlier studies\textsuperscript{12} have shown that random copolymers, in general, are not only better intrinsic conductors, but also better candidates for forming conducting materials through both oxidative (p-) and reductive (n-) doping than the corresponding periodic copolymers. These results have been verified\textsuperscript{13} experimentally for copolymers of phenylene and thiophene.

Different model quasi-one-dimensional superlattices (or copolymers) of conducting homopolymers can be studied, and through such studies many interesting and important trends can be obtained. In the present study, three different systems each belonging to the class of Type-I have been studied using the simple negative factor counting (NFC) method. All the three systems have one component (homopolymer A) common, while the second component (homopolymer B) has different alignments with respect to component A in the three systems. This study is expected to provide guidelines for molecular engineering of copolymers with tailormade conduction properties.

**Methodology**

The electronic density of states (DOS) of the quasi-one-dimensional superlattices can be determined using the NFC (simple or matrix block) method\textsuperscript{14-16} based on Dean’s negative eigen-value theorem.\textsuperscript{17}

Consider a linear chain containing \( N \) units. If we take into account, as is the case with the simple tight-binding or Hückel approximation, only one orbital per unit cell, then the secular equation in the first neighbours interaction approximation (no cyclic boundary condition) is:

\[
|H(\lambda)| = \begin{vmatrix}
\alpha_i-\lambda & \beta_i & 0 & 0 & 0 \\
\beta_i & \alpha_i-\lambda & \beta_i & 0 & 0 \\
0 & \beta_i & \alpha_i-\lambda & \beta_i & 0 \\
0 & 0 & \beta_i & \alpha_i-\lambda & \beta_i \\
0 & 0 & 0 & \beta_i & \alpha_i-\lambda \\
\end{vmatrix} = 0 \quad \ldots (1)
\]

with

\[
\alpha_i = \chi^* |H_{\text{eff}}| \chi' ; j = 1,2,\ldots,N .
\]

\[
\beta_i = \chi^* |H_{\text{eff}}| \chi' ; j = 2,3,\ldots,N
\]

\[
\chi' = \chi(r-R_i)
\]

if we take an LCAO ansatz for the chain orbitals \( \phi^p(r) \):

\[
\phi^p(r) = \sum_{i=1}^{N} c(p) \chi_i
\]

\( \hat{H}_{\text{eff}} \) is the effective one-electron Hamiltonian of the form:

\[
\hat{H}_{\text{eff}} = -\frac{1}{2} \sum_{i=1}^{N} V(r-r_i)
\]

The secular determinant \( |H(\lambda)| \) can be factorized as:

\[
|H(\lambda)| = \prod_{i=1}^{N} (\lambda_i - \lambda)
\]

Assuming that some other convenient factorization is found:

\[
|H(\lambda)| = \prod_{i=1}^{N} \epsilon_i(\lambda)
\]

Dean’s negative eigenvalue theorem (3) states that the number of eigenvalues less than \( \lambda \) is equal to the negative factors \( \epsilon_i(\lambda) \), where the \( \epsilon_i(\lambda) \)s are given by the recurrence relation:

\[
\epsilon_i(\lambda) = \alpha_i - \lambda
\]

\[
\epsilon_i(\lambda) = (\alpha_i - \lambda) - \frac{\beta_i^2}{\epsilon_{i-1}(\lambda)} ; j = 2,3,\ldots,N
\]

Thus, the spectrum of the system can be calculated simply by counting the number of negative factors \( \epsilon_i(\lambda) \). By giving \( \lambda \) different values throughout the range of the spectrum and then taking the difference of the negative \( \epsilon_i(\lambda) \)s belonging to consecutive \( \lambda \) values, the distribution of eigenvalues of \( |H(\lambda)| \) can be determined to any desired accuracy.

In the present calculations, the diagonal (\( \alpha_i \)) and the off-diagonal (\( \beta_i \)) matrix elements of the secular determinant (1) are determined from the corresponding band structure results of each component constituting the copolymer chain (Fig. 2). Assuming the dispersion of the band (valence or conduction) to be given by the simple relation:

\[
\epsilon_i(k) = \alpha_i + \beta_i \cos(ka)
\]

\( \alpha_i \) of a component for a given band is taken to be the middle point of the corresponding band. \( \beta_i \) is taken to
be one fourth of the band width if the same component is repeated (i.e. component i is followed by component i in the copolymer chain). If, on the other hand, component i is followed by component j, then the off-diagonal matrix element $\beta_{ij}$ is assumed to be given by the simple relation:

$$\beta_{ij} = \frac{1}{2}(\beta_{ij} + \beta_{ji})$$  \hspace{1cm} \ldots (8)

### Results and Discussion

#### Type of superlattices

The valence and conduction bands of two homopolymers forming copolymers in the systems 1-3 are shown in Fig. 2. The calculated $\alpha$ and $\beta$ values for both the valence and conduction bands calculated from the band structure results are given in Table 1. (All the electronic DOS calculations were performed for a chain of 300 units using an energy grid of 0.005 eV). In all the systems the band gap of one homopolymer (component B) is contained entirely within the band gap of the other homopolymer (component A) and therefore all these systems belong to type-I superlattice.

#### Electronic properties of the copolymers

The various polymeric superlattices (copolymers) $(A_mB_n)_x$ were modeled by coupling $m$ units of A and $n$ units of B blockwise periodically or aperiodically. Tables 2-4 contain the calculated electronic properties.

### Table 1—Values of $\alpha$’s and $\beta$’s for valence and conduction bands

<table>
<thead>
<tr>
<th>Bands</th>
<th>$\alpha_A$</th>
<th>$\alpha_{B1}$</th>
<th>$\alpha_{B2}$</th>
<th>$\alpha_{B3}$</th>
<th>$\beta_{AA}$</th>
<th>$\beta_{BB}$</th>
<th>$\beta_{AB}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Valence band</td>
<td>-11.000</td>
<td>-6.875</td>
<td>-9.875</td>
<td>-5.875</td>
<td>0.500</td>
<td>0.437</td>
<td>0.4685</td>
</tr>
<tr>
<td>Conduction band</td>
<td>-1.250</td>
<td>-3.500</td>
<td>-7.500</td>
<td>-2.500</td>
<td>0.375</td>
<td>0.250</td>
<td>0.3125</td>
</tr>
</tbody>
</table>

where $\alpha_A$ is consistent for all the systems; $\alpha_{B1} = \alpha$ of the second component for the system 1; $\alpha_{B2} = \alpha$ of the second component for the system 2; $\alpha_{B3} = \alpha$ of the second component for the system 3; and $\beta_{AA}, \beta_{BB}, \beta_{AB}$ are consistent for all the systems.

### Table 2—Calculated electronic properties in (eV) of periodic (P) and aperiodic (A) $(AB_x)_x$ copolymers of the systems 1-3

<table>
<thead>
<tr>
<th>System</th>
<th>Band gap</th>
<th>Band gap</th>
<th>Band gap</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_0$</td>
<td>$E_x$</td>
<td>$E_0$</td>
</tr>
<tr>
<td>AB</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AB$_2$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>6.055</td>
<td>3.995</td>
<td>2.010</td>
</tr>
<tr>
<td>P</td>
<td>6.030</td>
<td>3.980</td>
<td>2.005</td>
</tr>
<tr>
<td>AB$_5$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>6.005</td>
<td>3.995</td>
<td>2.010</td>
</tr>
<tr>
<td>P</td>
<td>6.000</td>
<td>3.995</td>
<td>2.005</td>
</tr>
<tr>
<td>AB$_{10}$</td>
<td>0.05</td>
<td>3.995</td>
<td>2.010</td>
</tr>
<tr>
<td>A</td>
<td>6.000</td>
<td>3.995</td>
<td>2.005</td>
</tr>
</tbody>
</table>

Fig. 2—Showing all the 3 systems.
such as $E_i$ (ionization potential corresponding to the top of the valence band), $E_a$ (electron affinity corresponds to the bottom of the conduction band) and the band gap of the periodic and aperiodic copolymer chains of the type $(A_mB)_n$, $(AB)_n$, and $(A_mB)_n$, respectively for all the three systems, obtained from their corresponding DOS curves. In the case of periodic copolymers of the type $(AB)_n$, (Table 2) band gap is found to decrease with an increase in block size $n$ of $B$ units. This decrease in band gap is the result of a decrease in the ionization potential and the increase in the electron affinity values of the copolymers. It means, therefore, that the copolymers become not only better intrinsic conductors of electricity but also better candidates for both p- and n-doping as the block size of the low-bandgap component $B$ units increases in the copolymer chain.

The band gap value is, however, found to increase in the case of the copolymers of the type $(A_mB)_n$ with an increase in the block size of $A$ units (Table 3). This increase is accompanied by an increase in $E_i$ and a decrease in $E_a$, implying that an increase in blocksize $m$ of $A$ units makes the copolymer not only less intrinsically conducting but also less dopant-philic.

An increase in the block sizes of $A$ and $B$ units for a given composition $m/n$ is found to decrease the band gap (Table 4). This decrease in band gap is accompanied by a decrease in $E_i$ and an increase in $E_a$, implying that increasing the block size has the effect of increasing both the intrinsic conductivity and the dopant-philicity of the copolymer.

For all the three systems, periodic copolymers show similar trends in their electronic properties implying hereby that all copolymers belonging to the class of Type-I superlattice behave in a similar manner.

The trends in the electronic properties of the periodic copolymers described above are also found to be valid in case of aperiodic chains (Tables 2-4) with the only difference being that, in the latter, the saturation in the electronic properties is achieved much faster. This is due to the fact that some blocks of sufficient size $n$ of the low-band gap component

### Table 3—Calculated electronic properties in (eV) of periodic (P) and aperiodic (A) $(A_mB)_n$ copolymers of the systems 1-3

<table>
<thead>
<tr>
<th>System</th>
<th>$E_i$</th>
<th>$E_a$</th>
<th>Band gap</th>
<th>$E_i$</th>
<th>$E_a$</th>
<th>Band gap</th>
<th>$E_i$</th>
<th>$E_a$</th>
<th>Band gap</th>
</tr>
</thead>
<tbody>
<tr>
<td>A A</td>
<td>6.079</td>
<td>3.950</td>
<td>2.219</td>
<td>7.949</td>
<td>1.125</td>
<td>5.085</td>
<td>2.950</td>
<td>2.135</td>
<td></td>
</tr>
<tr>
<td>A B</td>
<td>6.110</td>
<td>3.934</td>
<td>2.176</td>
<td>9.090</td>
<td>1.156</td>
<td>5.511</td>
<td>2.940</td>
<td>2.571</td>
<td></td>
</tr>
<tr>
<td>A nB</td>
<td>6.385</td>
<td>3.785</td>
<td>2.600</td>
<td>9.295</td>
<td>1.531</td>
<td>5.394</td>
<td>2.815</td>
<td>2.579</td>
<td></td>
</tr>
</tbody>
</table>

### Table 4—Calculated electronic properties in (eV) of periodic (P) and aperiodic (A) $(A_mB)_n$ copolymers of the systems 1-3

<table>
<thead>
<tr>
<th>System</th>
<th>$E_i$</th>
<th>$E_a$</th>
<th>Band gap</th>
<th>$E_i$</th>
<th>$E_a$</th>
<th>Band gap</th>
<th>$E_i$</th>
<th>$E_a$</th>
<th>Band gap</th>
</tr>
</thead>
<tbody>
<tr>
<td>A A</td>
<td>6.079</td>
<td>3.950</td>
<td>2.219</td>
<td>7.949</td>
<td>1.125</td>
<td>5.085</td>
<td>2.950</td>
<td>2.135</td>
<td></td>
</tr>
<tr>
<td>P A</td>
<td>6.110</td>
<td>3.934</td>
<td>2.176</td>
<td>9.090</td>
<td>1.156</td>
<td>5.511</td>
<td>2.940</td>
<td>2.571</td>
<td></td>
</tr>
<tr>
<td>A B</td>
<td>6.015</td>
<td>3.990</td>
<td>2.035</td>
<td>9.015</td>
<td>1.025</td>
<td>5.015</td>
<td>2.990</td>
<td>2.025</td>
<td></td>
</tr>
<tr>
<td>P B</td>
<td>6.035</td>
<td>3.980</td>
<td>2.055</td>
<td>9.029</td>
<td>1.049</td>
<td>5.035</td>
<td>2.980</td>
<td>2.055</td>
<td></td>
</tr>
<tr>
<td>A nB</td>
<td>6.005</td>
<td>3.995</td>
<td>2.010</td>
<td>9.005</td>
<td>1.001</td>
<td>5.005</td>
<td>2.997</td>
<td>2.008</td>
<td></td>
</tr>
<tr>
<td>P nB</td>
<td>6.000</td>
<td>3.995</td>
<td>2.005</td>
<td>9.000</td>
<td>1.006</td>
<td>5.000</td>
<td>2.997</td>
<td>2.003</td>
<td></td>
</tr>
</tbody>
</table>
will occur in the aperiodic sequence. However, since their probability of occurrence in random chain is less, the DOS values at the band edge are relatively smaller.

*DOS distributions*

Few DOS curves for both the valence and the conduction bands of the periodic and aperiodic copolymers of type (AₙB)ₙ, (AₙBₙ) and (AₙBₙ)ₙ, for different systems are shown in Figs 3-6. In case of periodic copolymers, the DOS curves consist of relatively narrow and well separated peaks. In contrast, the DOS distribution of the random copolymers consists of relatively broader regions of allowed states with fewer gaps in between. The result is that the band gap for a random copolymer is less than that for the corresponding periodic copolymer. These results are the result of changing environment of a unit in a random copolymer chain in contrast to the periodic chain where the environment of a unit throughout the unit remains 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 investigated systematically the electronic structures of the various model periodic and aperiodic copolymers \((A_nB_m)_x\), which represent the prototypes of the quasi-one-dimensional superlattices of type-I. Our results show that higher percentage of smaller gap component makes the copolymer chain more p-dopant-philic besides increasing its intrinsic conductivity while increasing the amount large band gap component makes it more insulating and less dopant-philic. Increasing the block-sizes of the two components for a given composition is predicted to make the copolymer chain a better conductor of electricity both intrinsically and extrinsically. Further, it is found that tuning the electronic properties intermediate between those of two homopolymers is easier by synthesizing periodic copolymers. Random copolymerisation, on the other hand, is expected to lead relatively faster to the saturated electronic properties characteristic of the lower band gap component and largely independent of the larger gap component.

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References