Designing novel donor-acceptor copolymers using genetic algorithm

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Using *ab initio* band structure results of five donor-acceptor polymers, the electronic structure and conduction properties of their novel binary copolymers have been investigated. One of the donor-acceptor polymers based on thiophene (PCNTh) is common in all the copolymers while second one is varied by replacing S atom with CF$_2$, O, SiH$_2$ or CH$_2$ respectively. The effect of substitution on the electronic properties of the copolymer is investigated. In order to calculate the electronic properties of the copolymers and to obtain the copolymer possessing minimum band gap, genetic algorithm is used along with negative factor counting and inverse iteration technique. The copolymer containing CF$_2$ units is found to have the lowest band gap and hence maximum intrinsic conductivity. Investigations involving variation in block sizes of the homopolymer units suggest that copolymers containing lower concentration of PCNTh are better candidates for both intrinsic as well as extrinsic conductivity.

**Keywords:** Genetic algorithm, Polymers, Conducting polymers, Copolymers, Donor-acceptor polymers, Electronic properties, Band gap, Thiophene

In recent times, the field of electrically conducting polymers has witnessed remarkable progress resulting in vastly improved electronic performance of various opto-electronic and molecular devices$^{1-4}$. The key characters of a potential electrically conducting polymer include, low band gap, high electronic delocalization, ability to exhibit large electronic conductivity, reversibility with respect to doping and undoping cycles along with excellent stability in electrochemical environment and processes. While the initial progress in the field of electrically conducting polymers was mainly attributed to various efforts in synthesis of new molecular species with enhanced regularity and properties$^{5,7}$, more recently it has been the advancement of physico-chemical aspects and material processing. Hence, a fundamental understanding of all these issues is important in order to realize the full intrinsic potential possessed by these materials. The growing utility of these materials also calls for the need to discover novel variants whose properties and functions can be tailor-made as per requirement.

Enormous theoretical efforts$^{8-11}$ are also being made in this field because of the versatile behaviour of these materials which combine the high conductivity of pure metals along with properties such as resistance to corrosion, lighter weight and easier process ability. In order to design novel electrically conducting polymers, the first and important step is to achieve an understanding of the structure-property-activity relationship. Therefore, efforts are being made to make intrinsically conducting polymers which have smaller band gap and are easier to process and handle. Though several routes are being followed for designing novel electrically conducting polymers, a widely used approach is the donor-acceptor (D-A) polymerization technique suggested by Havinga *et al.*$^{12}$ The basic idea followed in this strategy is that the regular alternation of donor (electron rich) and acceptor (electron deficient) moieties along a conjugated chain is expected to lower the band gap. It has been generally observed that higher the electronegativity difference between the donor (D) and acceptor (A) moieties, lower would be the band gap of the resulting polymer. Moreover, D-A polymers possess higher stability because of π-conjugation in the chain. Using a somewhat similar approach recently, Salaoru *et al.*$^{13}$ have designed a new D-A molecule pair consisting of TTF (tetrathiafulvalene) as electron donor and TCNE (tetracyanoethylene) as electron acceptor.

Copolymerization is a very efficient strategy for designing polymers having properties intermediate between those of the constituent homopolymers. In the present study, we have combined the strategy of copolymerization with that of D-A polymerization to
investigate the conduction properties of copolymers of D-A polymers containing dicyanomethylene groups. We have investigated four novel binary copolymers. The basic structures of the unit cell of the various homopolymers being investigated are shown in Fig. 1. The primary structure of the polymer chain hence formed consists of each of these unit cells aligned at 180° helical angle to each other. Thus, no two consecutive unit cells have the same alignment with respect to each other in the chain. In all the four copolymers, one of the homopolymer components (A), polydicyanomethylene-cyclopentadithiophene (PCNTh) containing S as one moiety, is kept common, while the other has been varied by replacing the hetero atom S of the aromatic ring with group X which can be CF$_2$ (or B), O (or C), SiH$_2$ (or D) or CH$_2$ (or E) thereby forming copolymers of the type A$_x$B$_y$, A$_x$C$_y$, A$_x$D$_y$, or A$_x$E$_y$ respectively. The >C=C(CN)$_2$ bridging groups help extend conjugation in the chain. The heterocycle part of the unit cell acts as the electron donor moiety whereas the bridging group acts as the electron acceptor moiety. Hence, regular alternation of D-A moieties in the chain is expected to result in copolymers possessing low band gap.

We choose to keep PCNTh as the common D-A polymer in all the copolymers since it is an established and synthesized polymer having an experimental band gap value of 0.8 eV, which makes it extremely favourable for use in designing many devices.

Systematic search involving theoretical designing is a very cumbersome task and requires a lot of computational time. Since there can be several ways of arranging these different units in the polymeric chain, in order to design a polymer possessing properties as desired, we have used a metaheuristic technique known as the genetic algorithm (GA). GA is basically an optimization and search algorithm derived from the class of artificial intelligence. In our earlier approaches, we have successfully used GA for theoretical designing of model polypeptide chains as well as for tailoring novel copolymers of D-A polymers. The versatility of the algorithm lies in the fact that it is highly flexible and can be easily adapted to solve a variety of problems.

Another bio-inspired evolutionary algorithm which is being widely applied is the Ant Algorithm (AA) technique. It demonstrates the collective or swarm behaviour of social insects like ants. Both GA and AA are specialized in their own ways for solving discrete combinatorial optimization problems. The choice of algorithm for any problem is primarily application dependent while its success rate depends on the optimal solution returned at the end of a run as well as the time taken for computation. An interesting advantage of GA, however, is that, once convergence is achieved, the algorithm not only produces an optimal individual, but also a population of good individuals, thus enabling the user to choose from a collection of possible solutions.

In this study we have proposed a novel set of copolymers which are suitable candidates for designing intrinsically conducting materials possessing low band gap using the genetic algorithm technique.

**Methodology**

**Combining the Hückel molecular orbital theory with GA**

In order to design novel binary copolymers possessing low band gap and high delocalization in the chain, we have made use of the GA technique. Let us suppose that A$_x$B$_y$ is the desired copolymer, comprising of $x\%$ and $y\%$ units of A and B homopolymers respectively. Using the condition, $x + y = 100$, we aim to obtain that particular value of percentages $x$ and $y$ (of the homopolymers) which results in the copolymer possessing the minimum band gap and maximum intrinsic conductivity. To achieve the optimum solution from GA, we combined it with two numerical methods, NFC (negative factor counting) and IIM (inverse...
We initiated a GA run with random generation of a population of individuals (or chromosomes), each of which is represented by a bit sequence whose value in decimal form represents a particular percentage \( x \) (and hence \( y = 100-x \)) of the homopolymer A (and B respectively) in the resulting copolymer. Considering a polymer chain of 300 units, we then constructed the Hückel determinant taking nearest neighbour interactions into account. A tridiagonal determinant of the form,

\[
\begin{bmatrix}
\alpha_1 \lambda & \beta_2 & 0 & \cdots & 0 \\
\beta_2 & \alpha_2 \lambda & \beta_3 & \cdots & 0 \\
0 & \beta_3 & \alpha_3 \lambda & \beta_4 & \cdots \\
\vdots & \vdots & \vdots & \ddots & \vdots \\
0 & 0 & 0 & \cdots & \alpha_n \lambda
\end{bmatrix} = 0
\]

is obtained with \( \alpha \)'s and \( \beta \)'s as the diagonal and off-diagonal elements respectively and \( \lambda \)'s as the eigenvalues. Using the NFC method, we solved this determinant for the eigenvalues of energy such as the ionization potential (IP), electron affinity (EA) and band gap (\( E_g \)). We then made use of the IIM to obtain the coefficients \( c_{jr} \) for various units in the chain, which were then substituted in the following formula to calculate the inverse participation number or IPN \( I_j \). IPN can vary from 0 to 1 and is a measure of the level of delocalization of a MO in the chain.

\[
I_j = \frac{\sum_{r=1}^{n} |c_{jr}|^4}{\left( \sum_{r=1}^{n} |c_{jr}|^2 \right)^2}
\]

Defining the fitness criteria

GA is inspired by the selection rules of nature. Just like nature selects the best or “fittest” individuals according to survival of the fittest rule, we also defined a criterion in order to evaluate each individual in the population, which we call as the fitness function, \( f(x) \), defined as,

\[
f(x) = \frac{1}{(1/\rho) \text{ gap} + \text{IPN}}
\]

in terms of parameters such as IPN, band gap and \( \rho \). Here ‘\( \rho \)' is the difference between the highest occupied energy level (of valence band) and the lowest unoccupied energy level (of conduction band) of the two homopolymers constituting the copolymer. We further allowed the population to evolve over several iterations until the desired convergence criterion was reached. The steps involved in the optimization process using GA are depicted in Fig. 2. To ensure that we obtained the best possible solution in the entire configuration space we used the elitism approach since cross-over of the fittest individual is more valuable than cross-over involving any other individual in the new population. Hence, at the end of a GA run, we obtained not only an optimal solution (the fittest individual) but an entire collection of good individuals to choose from.

Varying the block size of copolymer

We also investigated the effect of variation in block sizes (of the D-A homopolymer units) on the electronic properties of the resulting copolymer. For this we made use of simple NFC in the tight binding approximation to study the trends in electronic properties for both periodic and random copolymers.
of the type \((A_mB_n)_x\), where \(m\) and \(n\) are the block sizes of components A and B respectively in the copolymer and \(x\) denotes the number of times the block \((A_mB_n)\) is repeated in the copolymer chain consisting of 300 units, i.e., \(x = \frac{300}{(m+n)}\).

To determine the electronic properties and density of states (DOS), an energy grid of 0.001 eV was consistently used in the calculations. The relative band alignments of homopolymer units comprising the copolymers are shown in Fig. 3. On the basis of relative band alignments of homopolymers all four copolymers were found to be of Type-I category. The band structures used in the calculations were obtained through \textit{ab initio} Hartree-Fock CO method using Clementi’s minimal basis set. As a result, the electronic properties obtained might be slightly over-estimated due to neglect of correlation effects. However, these theoretical results are expected to provide able guidelines for synthesis of these copolymers with “tailor-made” conduction properties.

**Results and Discussion**

**Trends in electronic properties**

In the present study we have focussed on designing of novel conjugated polymers possessing low band gap and high electronic delocalization. In our investigations, we have calculated the electronic properties of these novel binary copolymers. Table 1 shows electronic properties (obtained using Koopman’s theorem) as obtained for the resulting copolymers using GA. The values of IP (ionization potential; corresponding to the top of valence band, VB), EA (electron affinity; corresponding to the bottom of conduction band, CB), \(E_g\) (band gap) and the percentage compositions of the optimum solutions obtained from GA are listed for various systems. The resulting percentage of each homopolymer suggests its relative concentration in the copolymer (the optimum solution) which has the minimum band gap value and maximum level of electron delocalization in the polymeric chain.

The \(>\text{C=C(CN)}_2\) group is kept common in all the homopolymers since we mainly want to infer and investigate the effect of change in group X (X = S, in PCNTh, is also a common component in all copolymers) on the electronic properties of the copolymers. The two CN groups in the dicyanomethylene bridging links make the latter highly electron deficient, thus facilitating the movement of electron cloud towards the bridging groups from the backbone of the copolymer.

The trends in electronic properties suggest that IP value is found to be the lowest when X = CH\(_2\) (IP = 8.478 eV). As a result the copolymer containing PCNTh and X = CH\(_2\) groups is expected to be the best possible candidate for p-doping since the electron can be easily knocked off from the top most energy level of HOMO. The IP values of the copolymers containing X = O as well as SiH\(_2\) are found to be comparable while for the copolymer made of PCNTh with X = CF\(_2\) group, IP value is maximum at 9.192 eV, therefore making it most unsuitable for the p-doping process. The electron acceptor group X on the ring affects the EA more than the IP and hence EA has more contribution in lowering the \(E_g\) value. The copolymer comprising PCNTh and X = SiH\(_2\) has maximum EA value of 8.303 eV and is hence expected to be a better candidate for n-type or reductive doping.

In all the four copolymers, the IP, EA and \(E_g\) values of the copolymers are found to be characteristic of the lower band gap component of

<table>
<thead>
<tr>
<th>X</th>
<th>IP (eV)</th>
<th>EA (eV)</th>
<th>(E_g) (eV)</th>
<th>Optimum solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF(_2)</td>
<td>9.192</td>
<td>5.697</td>
<td>3.495</td>
<td>(A_3B_{97})</td>
</tr>
<tr>
<td>O</td>
<td>8.996</td>
<td>4.172</td>
<td>4.824</td>
<td>(A_1C_{99})</td>
</tr>
<tr>
<td>SiH(_2)</td>
<td>8.996</td>
<td>3.803</td>
<td>5.194</td>
<td>(A_1D_{99})</td>
</tr>
<tr>
<td>CH(_2)</td>
<td>8.478</td>
<td>3.520</td>
<td>4.958</td>
<td>(A_1E_{99})</td>
</tr>
</tbody>
</table>

\(^{\text{a}}\)PCNTh (denoted by A) is common in all copolymers whereas different groups (X) of the second component are listed in the table.
the copolymer. This implies that, if we replace one component by another with a smaller $E_g$, the values of these electronic properties can be further fine-tuned to obtain the optimum copolymer. In general, the electronic properties are found to be intermediate between those of the constituent homopolymers. The calculated band gap values of the four polymers increase in the order: $\text{CF}_2 < \text{O} < \text{CH}_2 < \text{SiH}_2$, where S containing PCNTh is common to all copolymers. The copolymer containing $X = \text{CF}_2$ has the lowest $E_g$ value and is hence expected to show maximum intrinsic conductivity. The lowest gap value, 3.495 eV, also suggests that there is maximum difference in electronegativity of donor ($X = \text{S}/\text{CF}_2$) and acceptor species (>$\text{C}=\text{C}($CN$)_2$) in this particular system. On the other hand, the homopolymer having $X = \text{SiH}_2$ combines with PCNTh to form the copolymer possessing a high $E_g$ value, 5.194 eV. Therefore, we can straightaway conclude that there is least difference in the electronegativities of donor ($X = \text{S}/\text{SiH}_2$) and acceptor species (>$\text{C}=\text{C}($CN$)_2$) in this case, which makes this particular copolymer to be least conducting out of the four copolymers. Moreover, the SiH$_2$ group is expected to interact with the conjugated backbone less strongly than the other hetero atoms since the HOMO of SiH$_2$ group is lower in energy than the $p$-orbitals of the hetero atoms$^{28}$.

**Optimum solution from GA**

The percentage compositions of the optimum solutions in all four cases suggest that PCNTh (denoted by A in Table 1) should be present in less amount and the other component having $X = \text{CF}_2/\text{O}/\text{SiH}_2/\text{CH}_2$ (denoted by B/C/D/E respectively in Table 1) should be present in major amount in the copolymer in order to generate the optimum solution, i.e., copolymer possessing minimum band gap and maximum electron delocalization. This trend is consistent with the fact that the homopolymer other than the polythiophene derivative has inherently smaller gap value (as is evident from the relative band structure alignments of the homopolymers; Fig. 3) which is, as a result, reflected in the properties of the copolymer being formed. Hence, the replacement of S atoms from the homopolymer units by the less electron donating groups like CF$_2$, O, SiH$_2$ and CH$_2$ not only makes the polymers better intrinsic conductors but also better candidates for forming conducting materials through doping (both p- and n-doping).

**Analysis of DOS curves**

The electronic DOS for all the Type-I systems corresponding to the GA optimized solution are shown in Fig. 4a-d. Since the homopolymer units are randomly arranged in the copolymer sequence, the respective environments of the units keep changing (as per the immediate neighbour) and therefore, the DOS distribution consists of broad regions of allowed energy states. The lowest band gap value of 3.495 eV observed in the case of $A_3B_{97}$ is also clearly evident from the corresponding DOS curve (Fig. 4a). Band gap can be calculated from DOS by subtracting EA from IP. As observed from DOS curves, the IP value is around 9.2 eV while the EA is approximately 5.7 eV hence leading to a band gap ~3.5 eV which is in very good agreement with the value of $E_g$ obtained from GA. The separation between peaks of the VB and CB is least in this case while it is largest when PCNTh combines with the D-A polymer containing $X = \text{SiH}_2$.
X = SiH₂ to form the copolymer. Similarly, in all other copolymers, the trends in values of electronic properties obtained from DOS are in very good agreement with those obtained from GA.

**Effect of variation in block size of copolymer on electronic properties**

The trends in electronic properties on variation in block sizes of components were investigated for two copolymers, one, containing X = S and X = CF₂ (since it is found to possess minimum gap value from GA) and the other containing X = S and X = SiH₂ (having maximum band gap value out of all four copolymers). The results obtained for some \((A_mB_n)_x\) and \((A_mD_n)_x\) type of copolymers are listed in Tables 2 and 3 respectively, for both periodic as well as random block sequences.

From these results, it is clearly evident that irrespective of the block size, random placement of blocks in the sequence gives rise to copolymers with lower band gap in comparison to their periodic counterparts. We observe that as the ratio of component B \((X = \text{CF}_2)\) or component D \((X = \text{SiH}_2)\) is increased in comparison to component A, the band gap decreases. This signifies that better intrinsic conductors can be designed keeping the amount of PCNTh lower than the other homopolymer. Similar trends were noticed when block size ratio \(m/n\) is kept constant and the block sizes are increased, i.e., the gap value decreases.

Moreover, when the amount of B (or D) is increased in \((A_mB_n)_x\) \((\text{or } (A_mD_n)_x)\) the EA value increases, which means that the copolymer has high n-dopant philicity and thereby high extrinsic conductivity. Similar is the trend when block sizes are increased in the same ratio. Based on the trends in IP values, we also conclude that when the amount of SiH₂ containing homopolymer is increased in \((A_mD_n)_x\), the IP values become lower and lower with increase in value of \(n\). This makes the copolymer suitable for p-doping and hence improves its extrinsic conductivity. Similar is the trend when both \(m\) and \(n\) are increased in the same proportion. Hence, the trend in IP values for \((A_mB_n)_x\) is reverse of that in \((A_mD_n)_x\).

Therefore, \((A_mD_n)_x\) is a suitable candidate for both p- as well as n-type of doping if we increase the proportion of homopolymer D in the copolymer.

**Conclusions**

In this paper, we have designed novel binary low band gap copolymers of donor-acceptor polymers which contain heterocyclic rings as the main framework of the polymer backbone. While one of the D-A polymer PCNTh is common in all the copolymers, we have varied the other D-A polymer in each of these binary copolymers by taking groups such as CF₂, O, SiH₂ and CH₂ instead of S atom. The bridging group \(>\text{C}=(\text{CN})_2\) is kept the same in all the copolymers. This facilitates in investigation of the effect of hetero atom substitution on the electronic properties of electrically conducting polymers. The energy band gap values for the different copolymers follow the order \(\text{CF}_2 < \text{O} < \text{CH}_2 < \text{SiH}_2\). As expected, the regular alternation of donor and acceptor type of moieties helps attain low band gap copolymers due to extension of conjugation in the polymeric chain.

The copolymer containing CH₂ units is expected to be the best candidate for p-doping since it has the lowest IP. On the other hand, since the copolymer containing SiH₂ units has the maximum EA, it would be better suited for n-doping. From the results we also conclude that there is maximum electronegativity difference in the donor-acceptor pair which contains CF₂ groups since it results in the copolymer
possessing the lowest band gap. In short, our results predict that the replacement of S atoms (from the homopolymer units) with less electron donating groups like CF\textsubscript{2}, O, SiH\textsubscript{2} and CH\textsubscript{2} improves, both intrinsic as well as extrinsic, conductivities of the polymers.

The trends in electronic properties on variation of block size of the copolymers, show that random sequencing of blocks in the chain leads to lower band gap copolymers as compared to periodic arrangement. Keeping the relative concentration of the thiophene-based homopolymer lower than that of the other homopolymer leads to not only better intrinsic conductors but also improves extrinsic conductivity by making them better candidates for p and n-doping.

Hence we conclude that copolymers of donor-acceptor polymers offer several advantages as compared to their carbon analogues. The extensive $\pi$-conjugation in the backbone adds to the stability of the copolymer. Substituents can be easily introduced in such systems via electrophilic substitution reactions. Therefore, chemical engineering at the molecular level of the polymer can be used along with theoretical designing in order to fine tune the properties of the polymer and serve as important aids in designing novel materials.

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