Band Gap Engineering of a Ternary Copolymer Based on Polythiophene and Its Derivatives Using Genetic Algorithm

Avneet Kaur[1] and A. K. Bakhshi[1*]

[1]*Department of Chemistry, University of Delhi, Delhi 110007, India.*

Research Article

ABSTRACT

The electronic and conduction properties of a copolymer, based on polythiophene (PTP) and its derivatives: polyisothianaphthene (PITN) and polyisonaphthothiophene (PINTP), have been studied. The optimum percentages of the homopolymer units PTP, PITN and PINTP in the copolymer have been successfully obtained using Genetic algorithm (GA). In order to test the effectiveness of GA and also to substantiate the optimum solution in case of the present copolymer, a systematic search varying the block sizes of the constituent homopolymer units has been done. It has been found that increasing the block size of all the three components simultaneously, decreases the band gap of the copolymer. Also, it is seen that the band gap values become constant after block size of 20 for the three components and do not reach the band gap of the optimum solution obtained from GA. By varying the block sizes, the trends obtained for electronic properties validate that the solution obtained from GA is an optimum solution.

Keywords: Copolymers; electronic properties; genetic algorithm; theoretical chemistry; artificial intelligence; conducting polymers; polythiophene.

_____

Corresponding author: Email: akbakhshi2000@yahoo.com;

1. INTRODUCTION

Band gap engineering of conjugated polymers refers to the tuning of band gap to obtain desired properties or functionality. It includes band gap minimization and processibility improvement. Many researchers have focused on synthesizing conjugated polymers with small or even zero band gaps because of their expected good intrinsic electrical conductivity (Snook et al., 2011) and nonlinear optical properties (Shin et al., 2007). Still at the present moment, the development of stable, processable polymeric materials with a low band-gap is an important issue for further advancements in these fields. Thus, substantial efforts have been devoted to the design of conjugated organic polymers with small band-gaps. One of the approaches towards small band gap conjugated polymers is the copolymerization approach. Copolymer synthesis offers the ability to alter the properties of a homopolymer in a desired direction by the introduction of an appropriately chosen second repeating unit.

The work presented here is related to the designing of low band-gap electrically conducting copolymers. The properties of copolymers can be tuned by varying either the ratio of various constituents or the manner by which these are chemically attached. Considering the large number of possible combinations of homopolymers, experimentally preparing polymers becomes very expensive. Therefore, in the present work genetic algorithm (GA) (Haupt, R.L., 2004) has been used to generate optimum units of homopolymers that would result in a copolymer with minimum band-gap and maximum delocalization. This has enormous potential for cost savings in the polymer industry.

In the search for novel electrically conducting polymers, an exciting possibility is provided by the derivatives of polythiophene (PTP) because of their stability, fusibility and solubility. Various derivatives of PTP have been studied- notable among these are polyisothianaphthene (PITN) (Lapkowski, M., 1997), polyisonaphthothiophene (PINTP) (Bakhshi, A.K., 1995), poly (5,6,dioxymethyleneisothianaphthene) (PDOMITN) (Ikenoue et al., 1991), poly dithieno [3,4 b-3',4',d] dithiophene (PDTT') (Taliani et al., 1989) all with a bandgap of the order of 1.1 eV. In the present study, we have considered quasi-one-dimensional superlattice of heterocyclic polymer based on PTP and its derivatives PITN and PINTP. The structures of PTP, PITN and PINTP are shown in figure 1. The monomer of PITN can be viewed as consisting of a thiophene unit with a benzene ring fused at its two β carbon atoms. Similarly, the monomer of PINTP can be considered as consisting of a thiophene unit with a naphthalene ring fused at its two β carbon atoms.

The theoretical published data (Bakhshi, A.K. and Ladik, J., 1987) on the electronic structure of PITN and PINTP can be used to benchmark the optimum solutions obtained in the present study using GA. In order to substantiate the optimum solution, we have carried out a systematic search varying the block sizes m, n and k of the constituent homopolymer units.
Our main aim, here is to demonstrate the promise that molecular electronics based on polymers hold: that electronic properties and hence conduction properties can be tuned by varying the molecular composition and the arrangement of the homopolymer units in the copolymers.
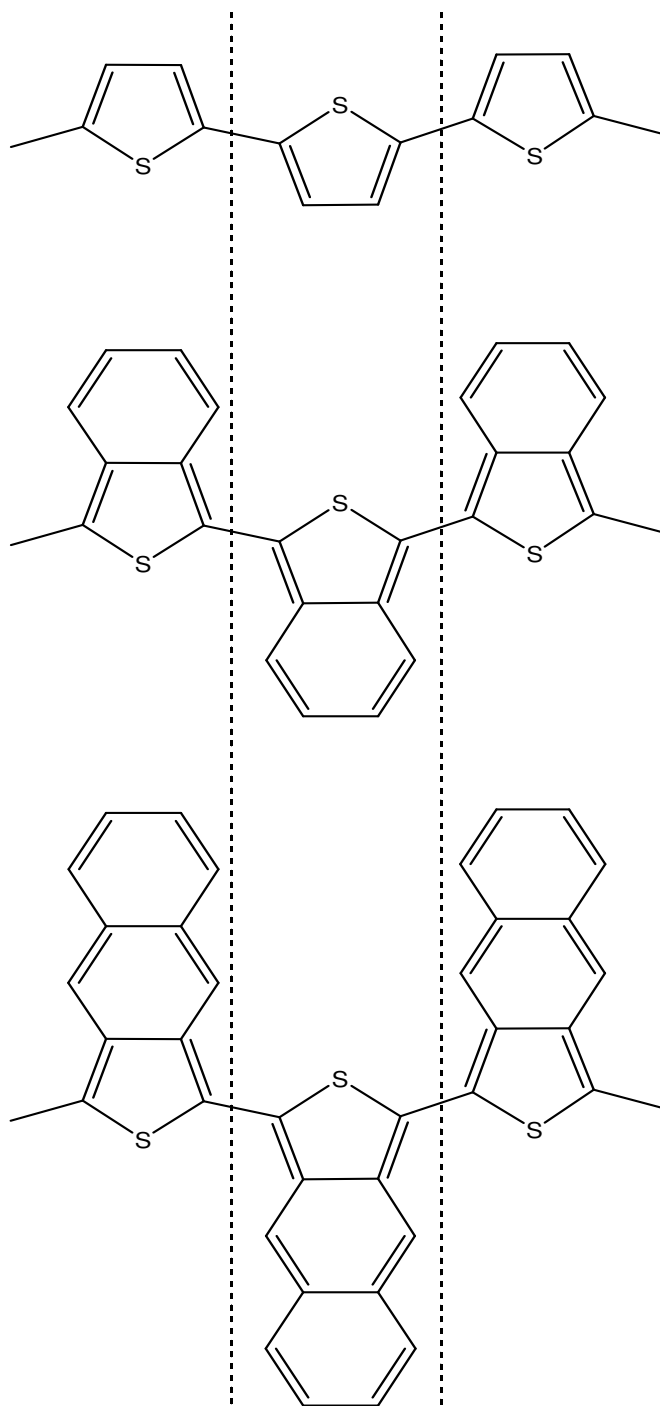
Fig. 1. Structures of (a) polythiophene (PTP), (b) polyisothianaphthene (PITN) and (c) polyisonaphtothiophene (PINTP). The unit cells are surrounded with broken lines.

2. METHODOLOGY

2.1 The algorithm

GA starts with a group of randomly generated initial solutions. Each solution can be represented as bit-strings (sequences of zeros and ones) of specified length. Each string is named as a 'chromosome', 'genes' are parts of a chromosome, and 'population' is a group of chromosomes used in a GA iteration (generation). Once the first population is generated the 'fitness' (how "good" is the proposed solution) of each individual (chromosome) is calculated through an evaluation function. The next populations ("offspring" generated from "parents") are composed using the elitism option and crossover among chromosomes. These steps are repeated until the criteria convergence is reached (Melanie, M.,1998).

2.2 GA parameters for the polymer problem

Consider ternary copolymer with three different constituent units A, B and C ($A_xB_yC_z$; $x + y + z$ = 100%), where the relative concentrations of A, B and C define the overall conductivity of the copolymer. The objective is to find out the percentages of A, B and C that would give us the most conducting polymer, i.e., the one with minimum band gap and maximum electronic delocalization. We have imposed a restriction that the concentration of none of the homopolymers can be zero, i.e., x, y and z cannot be zero.

Percentage '*x*' of homopolymer unit A in the copolymer can be represented as bit-string of specified length (chromosome). The GA adopted by us considers a population of five chromosomes, each one encoding a different solution to the optimization problem. Since the maximum value of a chromosome on decoding can be 99, the length of each chromosome is seven. From the given generation, a new population is generated keeping the fittest chromosome (elitism) and by single point crossover between chromosomes selected with probability proportional to their fitness. Single point crossover was implemented taking the fifth bit position (out of 7 bits) as the point of crossover (i.e. swapping of last three bits).

2.3 Constructing fitness function

Fitness function is a mathematical formula used to calculate efficiency of a chromosome. There are alternative ways to define it, but in the present case the fitness function must necessarily include two variables (band gap and IPN). In this paper, we have considered the following fitness function (Eq. 1),

$$f(x, y) = \frac{1}{(1/\rho)\, E_g(x,y) +\ IPN(x,y)} \qquad \ldots (1)$$

where ρ is the energy difference between the uppermost lowest unoccupied molecular orbital (LUMO) and lowermost highest molecular orbital (HOMO) out of the constituent homopolymers. Here, the fitness function, $f(x, y)$ has been defined by attributing the same statistical weight to band gap (E_g) and inverse participation number (IPN) of the copolymer. As they have different range definition (band gap varying from 0.0 to ρ, and IPN from 0.0 to 1.0), we have used a scale constant $(1/\rho)$ to satisfy this condition.
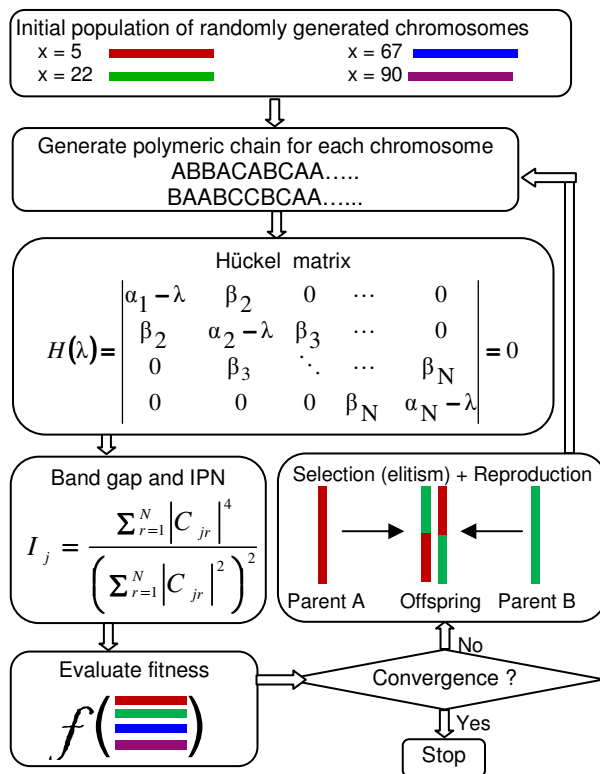
Fig. 2. Pictorial representation of steps involved in GA and evaluation of fitness function.

The band gap and IPN values can be found out considering copolymer chain consisting of N units whose energy states can be obtained by solving the Hückel Hamiltonian (in tight binding approximation) (Eq. 2),

$$H = \sum_{i=1}^{N} \alpha_i |i\rangle\langle i| + \sum_{\substack{i,j \\ i \neq j}}^{N} \beta_{i,j} |i\rangle\langle j|$$

… (2)

where α's and β's are the usual Coulomb and hopping integrals. The α and β values were obtained from the corresponding band structure of the homopolymers. This determinant on solving using Negative Factor Counting (NFC) method (Sutjinato et al., 1989) gives the value of the band gap. The electronic density of states (DOS) is obtained using NFC. The delocalization parameter is defined by the IPN, I_j of the HOMO, which can be obtained through the use of inverse iteration method (Wilkinson, J.H., 1965).

$$I_j = \frac{\sum_{r=1}^{N} |C_{jr}|^4}{\left(\sum_{r=1}^{N} |C_{jr}|^2 \right)^2}$$

… (3)

where C_{jr} are the LCAO expansion coefficients.

Various steps involved in GA and evaluation of fitness function are pictorially depicted in figue 2. Complete details of the methodology are mentioned in our earlier studies (Kaur A., Bakhshi, A.K., 2009, 2010)

3. RESULTS AND DISCUSSION

The band alignments along with band widths of homopolymers PTP, PITN and PINTP are given in Figure 3. The most important electronic properties such as ionization potential (IP), electron affinity (EA), band widths and the band gap of PTP, PITN and PINTP are given in Table 1.
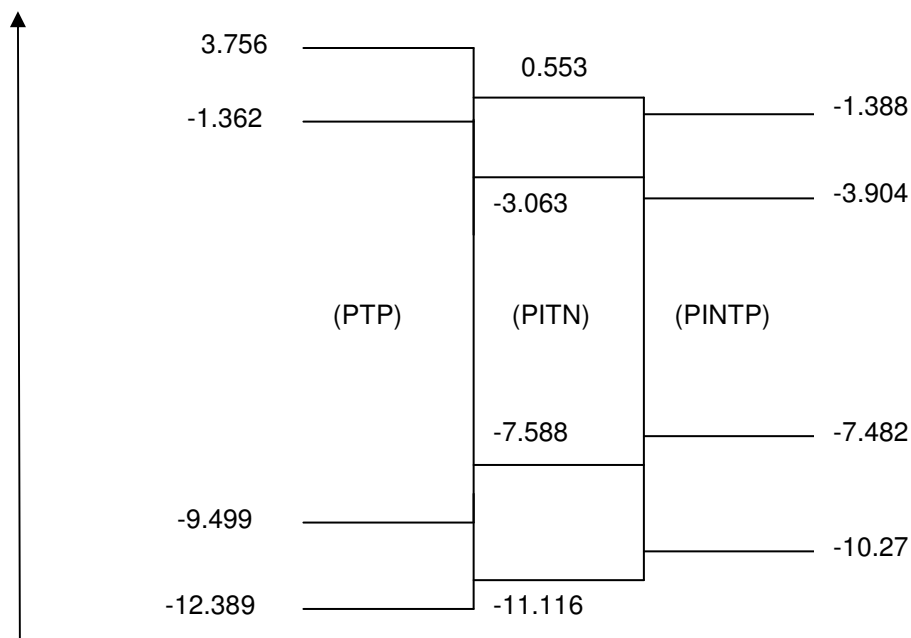

Fig. 3. Sketch of the HOMO and LUMO electronic levels calculated by means of the *ab - initio* technique for homopolymer chains of PTP, PITN, PINTP. All values are in eV. (1eV = 1.6 x 10^{-19} J)

These properties have been calculated using the band structure results obtained from *ab initio* crystal orbital (CO) calculations (Bakhshi, A.K., Ladik, J., 1987). These calculations 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. Consequently, the electronic properties might be slightly over estimated due to neglect of correlation effects. However, the results obtained are expected to provide able guidelines for synthesis of copolymers with "tailor-made" conduction properties. It can be seen from table 1 that of these three polymers, PINTP has the smallest energy gap followed by PITN and PTP. It, therefore, means that PINTP is the best intrinsic electric conductor of these three polymers.

Also, with increase in number of benzene rings, the ionization potential decreases whereas the electron affinity increases. It, therefore, means that PINTP has the greater capacity than both PITN and PTP to form conducting materials through oxidative and reductive doping.

Table 1. Calculated electronic properties (in eV) of polyisonaphtothiophene (PINTP), polyisothianaphthene (PITN) and polythiophene (PTP).

	PINTP	PITN	PTP
Valence band width	2.788	3.528	2.890
Conduction band width	2.516	3.616	5.118
Ionization potential	7.482	7.588	9.499
Electron affinity	3.904	3.063	1.362
Band gap	3.578	4.524	8.137

3.1 Optimum solution from GA

Table 2 shows the optimized percentage composition (or optimized solution) obtained from GA and the calculated electronic properties of the random copolymer chain (of $A_xB_yC_z$ type). The optimized solution gives the values of the relative concentrations of the three constituent homopolymer units in the resulting copolymer with minimum gap value and maximum level of delocalization in the chain. An analysis of the optimized solution obtained from GA reveals that the homopolymer units C (PINTP units) should be present in maximum amount in the resulting copolymer so that the copolymer hence formed possesses maximum conducting ability and minimum band gap. Here it would be worth mentioning that out of the three homopolymers units, C is the one with lowest value of IP (7.482 eV). We therefore conclude that the resulting ternary copolymer with highest percentage of PINTP skeleton is expected to be a suitable candidate for p doping.

Table 2. Optimum concentrations of homopolymer units PTP, PITN and PINTP in the copolymer obtained through genetic algorithm. The values of various electronic parameters for the optimum solution are also reported.

Optimum solution	$A_1B_1C_{98}$	
	Ionization potential	7.4820
Electronic properties (eV)	Electronic affinity	3.9031
	Band gap	3.5789

The electronic DOS, obtained from NFC, for the present system corresponding to the optimized composition returned by GA is shown in figure 4. The values of important electronic properties such as IP, EA and E_g of a copolymer are determined from the upper and lower edges of the valence and conduction band respectively using the Koopmans' theorem, i.e., from negative of the top of valence band and from negative of the bottom of

conduction band respectively. The DOS curve of the optimum solution consists of well separated peaks as the copolymer consists of 98% C, the electronic environment remains same throughout the chain.
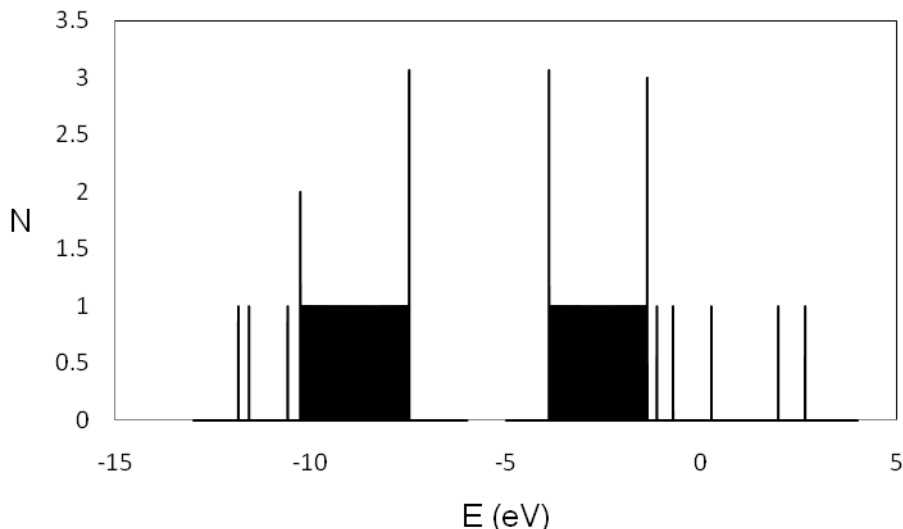

Fig. 4. Plot between number of states (N) and energy (E) for the proposed GA solution.

3.2 Systematic search varying block sizes

In addition to obtaining optimum solution, a further study was done by modeling various polymeric superlattices of the type $(A_mB_nC_k)_x$ by coupling m units of A (thiophene), n units of B (isothianaphthene) and k units of C (isonaphthothiophene) in random manner.

The study of these copolymers has been divided into four categories:

Category I: Here, the block sizes m, n and k of the components are varied keeping the ratio m:n:k constant.
Category II: Here, the block size m of the first component is varied keeping the block size n of second component and k of the third component at a constant value of 1.
Category III: Here, the block size m of first component and k of third component is kept at a constant value .i.e., 1 while the block size n of the second component is varied.
Category IV: Here, the block size m of first component and n of second component is kept at a constant value .i.e., 1 while the block size k of the third component is varied.
Tables 3, 4, 5 and 6 respectively contain results of the study of systems belonging to category I, II, III and IV.

3.2.1 Varying block sizes of all the homopolymer units simultaneously

It is found that the ionization potential values decrease and electron affinity values increase with the increase in the block size of A, B and C units for a given composition of the copolymer. The IP values are found to decrease from 7.528 eV to 7.483 eV as the block size of each component (m, n and k) was increased from 1 to 30. However, an increase of about 0.05 eV was observed in the value of EA from 3.854 to 3.902 eV on carrying out a similar increase in the block size. the band gap decreased from 3.6739 to 3.5809 eV. The decrease

in band gap in the case of aperiodic copolymers is the result of a decrease in IP and an increase in EA implying hereby that an increase in block sizes of the components results in an increase in the intrinsic conductivity of the copolymer. Also, decrease in the IP values and the increase in the EA values suggests that the copolymers can be doped easily by oxidation as well as reduction. It can be seen from Table 3 that the values of electronic parameters do not change with changing block size from 20 to 30 i.e. they reach saturation.

Table 3. Calculated electronic properties (in eV) of aperiodic copolymer chains of type $(A_mB_nC_k)_x$ obtained from their corresponding DOS curves in tight binding approximation.

System	IP	EA	E_g
$A_1B_1C_1$	7.528	3.854	3.6739
$A_2B_2C_2$	7.517	3.846	3.6709
$A_3B_3C_3$	7.522	3.854	3.6679
$A_5B_5C_5$	7.501	3.882	3.6189
$A_{10}B_{10}C_{10}$	7.487	3.897	3.5899
$A_{20}B_{20}C_{20}$	7.483	3.902	3.5809
$A_{25}B_{25}C_{25}$	7.483	3.902	3.5809
$A_{30}B_{30}C_{30}$	7.483	3.902	3.5809

3.2.2 Varying block size of A only

It is found that the ionization potential values increase and electron affinity values decrease with the increase in the block size of A from 1 to 8 while keeping the block sizes of B and C constant at 1. The IP values are found to increase from 7.528 eV to 7.605 eV as the block size of component A (m) was increased from 1 to 8. Also, a decrease in the value of EA from 3.854 to 3.677 eV was observed on carrying out a similar increase in the block size. This results in a decrease in the band gap from 3.674 to 3.928 eV. On further increasing the block size m of A, there was no change in the value of either IP or EA i.e. the band gap remained constant. The decrease in the IP values and the increase in the EA values suggest that the copolymers can be doped easily by oxidation as well as reduction.

Table 4. Calculated electronic properties (in eV) of aperiodic copolymer chains of type $(A_mBC)_x$ obtained from their corresponding DOS curves in tight binding approximation.

	Aperiodic $(A_mBC)_x$		
m	IP	EA	E_g
1	7.528	3.854	3.674
8	7.605	3.677	3.928
13	7.605	3.677	3.928
23	7.605	3.677	3.928

3.2.3   Varying block size of B only

It is found that the ionization potential values increase and electron affinity values decrease with the increase in the block size of B keeping block sizes of A and C constant. The IP values are found to increase from 7.528 eV to 7.568 eV as the block size of component B (n) was increased from 1 to 23. Also, a decrease in the value of EA from 3.854 to 3.671 eV was observed on carrying out a similar increase in the block size. This results in an increase in the band gap from 3.674 to 3.897 eV.

Table 5: Calculated electronic properties (in eV) of aperiodic copolymer chains of type $(AB_nC)_x$ obtained from their corresponding DOS curves in tight binding approximation.

	Aperiodic $(AB_nC)_x$		
n	**IP**	**EA**	**E_g**
1	7.528	3.854	3.674
8	7.570	3.680	3.890
13	7.569	3.671	3.898
23	7.568	3.671	3.897

3.2.4   Varying block size of C only

It is found that the ionization potential values decrease and electron affinity values increase with the increase in the block size of C keeping block sizes of A and C constant. The IP values are found to decrease from 7.528 eV to 7.483 eV as the block size of component C was increased from 1 to 23. However, an increase of about 0.05 eV was observed in the value of EA from 3.854 to 3.902 eV on carrying out a similar increase in the block size. This results in a decrease in the band gap from 3.674 to 3.581 eV.

Table 6: Calculated electronic properties (in eV) of aperiodic copolymer chains of type $(ABC_k)_x$ obtained from their corresponding DOS curves in tight binding approximation

	Aperiodic $(ABC_k)_x$		
k	**IP**	**EA**	**E_g**
1	7.528	3.854	3.674
8	7.489	3.895	3.594
13	7.485	3.900	3.585
23	7.483	3.902	3.581

3.2.5   Density of States (DOS) of block copolymers

Figure 5 shows the DOS curves of some selected $(A_mB_nC_k)_x$ copolymer chains. As compared to the DOS curve of the optimum solution, the DOS curves of block copolymers $(A_5B_5C_5)_{20}$ and $(A_{25}B_{25}C_{25})_3$ consist of relatively broader regions of allowed energy states with fewer gaps in between. The electronic environment around a particular unit keeps on changing in case of an aperiodic block copolymer, therefore the energy positions are scattered over a wide range of energy.
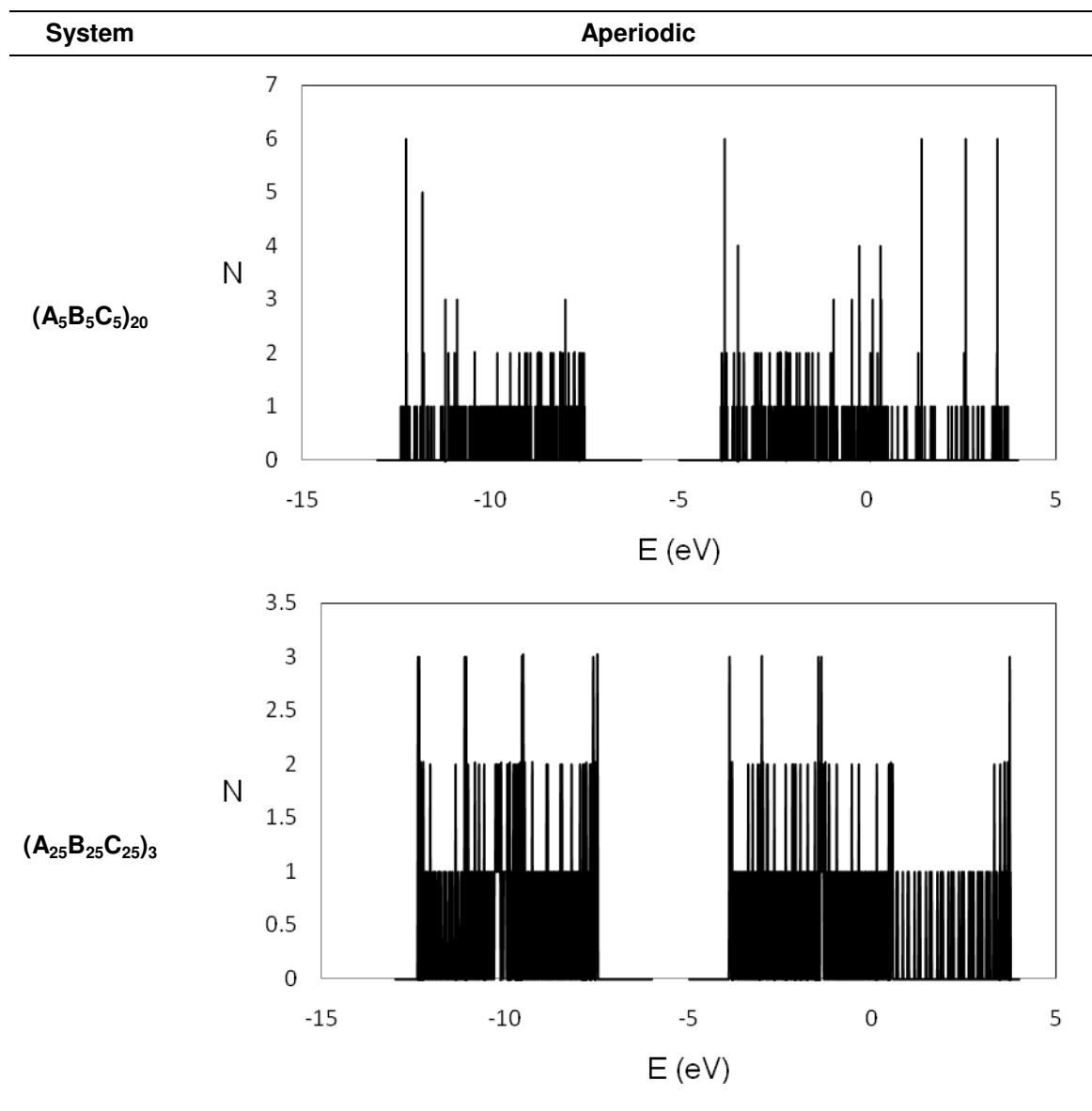
System	**Aperiodic**
$(A_5B_5C_5)_{20}$	
$(A_{25}B_{25}C_{25})_3$	

Fig. 5. Representative DOS curves of copolymer chains of type $(A_mB_nC_k)_x$.

4. CONCLUSIONS

We have systematically studied the electronic structures and conduction properties of the copolymer based on polythiophene and its derivatives, which represents the prototype of quasi-one –dimensional superlattices of type-I, using negative factor counting method in the tight binding approximation. In order to test the effectiveness of GA and also to substantiate the optimum solution in case of the present copolymer, a systematic search varying the

block sizes was done. It was found that increasing the block size of all the three components simultaneously decreased the band gap of the copolymer. Also, it was seen the band gap values became constant after block size of 20 and did not reach the band gap of the optimum solution obtained from GA. This implies that on increasing the block size of each homopolymer unit simultaneously GA optimum solution cannot be reached which shows that all of them contribute differently to optimum solution. Since there is no variation in band gap with increasing the block size of A, it implies that A will certainly contribute less to the optimum solution. This was validated by optimum solution which contains A as 1%. It was seen that an increase in block size of B increased the band gap of the copolymer which implies that certainly B will not have high percentage in optimum solution. The increase in block size of C resulted in major decrease in band gap of the copolymer implying that the optimum solution must be contain maximum amount of C. The observed trends in electronic properties indicate that the solution obtained from GA must be an optimum solution. Conclusively, it can be said that these results are important guidelines, which can be used for tuning the properties of conducting copolymers to desired electronic properties and consequently to desired conduction behavior.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

Bakhshi, A.K. (1995). Theoretical Tailoring of Electrically Conducting Polymers: Some New Results. Materials Science and Engineering: C, 3, 249- 255.

Bakhshi, A.K., Ladik, J. (1987). Electronic Structure of Polyisonaphtothiophene: Design of a new conjugated organic polymer. Solid State Commun., 63, 1157- 1160.

Haupt, R.L. (2004). Practical Genetic Algorithms, second ed, Wiley-IEEE, USA.

Ikenoue, Y., Wudl, F., Heeger, A.J. (1991). A novel substituted poly(isothianaphthene). Synthetic Metals, 40, 1- 12.

Kaur, A., Bakhshi, A.K. (2009). Tailoring Electrically Conducting Polymers using Genetic Algorithm. Indian Journal of Chemistry, 48A, 631- 636.

Kaur, A., Bakhshi, A.K. (2010). Change in optimum genetic algorithm solution with changing band discontinuities and band widths of electrically conducting copolymers. Chemical Physics, 369, 122- 125.

Lapkowski, M., Kiebooms, R., Gelan, J., Vanderzande, D., Pron, A., Nguyen, T. P., Louarn, G., Lef, S. (1997). Poly(isothianaphthene) from 2,5-bis(trialkylsilyl)isothianaphthenes: preparation and spectroscopic characterization. J. Mater. Chem., 7, 873- 876.

Melanie, M. (1998). An Introduction to Genetic Algorithms Complex Adaptive Systems, MIT Press, USA.

Shin, W.S., Kim, S.C., Lee, S.-J., Jeon, H.-S., Kim, M.-K., Naidu, B., Jin, S.-H., Lee, J.-K., Lee, J.W., Gal, Y.-S. (2007). Synthesis and photovoltaic properties of a low-band-gap polymer consisting of alternating thiophene and benzothiadiazole derivatives for bulk-heterojunction and dye-sensitized solar cells. J. Polym. Sci., 45, 1394- 1402.

Snook, G.A., Kao, P., Best, A.S. (2011). Conducting-polymer-based supercapacitor devices and electrodes. J. Power Sources, 196, 1- 12.

Sutjinato, A., Leigener, C. M., Otto, P., Ladik, J. (1989). Extension of the simple negative-factor-counting method to more neighbours' interactions. Solid State Commun., 70, 455- 458.

Taliani, C., Ruani, G., Zamboni, R., Bolognesi, A., Catellani, M., Destri, S., Porzoi, W., Ostoja, P. (1989). Optical Properties of a Low Energy Gap Conducting Polymer: Polydithieno [3,4 -b:3',4' –d]Thiophene. Synthetic Metals, 28, C507- C514.

Wilkinson, J.H. (1965). The algebraic eigenvalue problem, Clarendon press, Oxford.

_____