



Theoretical Designing of Novel Donor Acceptor Type Copolymer Comprising of Thiophene

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Using *ab initio* band structure results of three novel donor acceptor polymers (A)_x PCDT, (B)_x PMCT and (C)_x PFTh as the input, the electronic structures and conduction properties of their periodic and aperiodic copolymer (A_mB_nC_k)_x have been investigated. The method involves using negative factor counting method based on Dean's negative eigenvalue theorem. In this article, the quasi-one-dimensional Type II staggered copolymers comprising of thiophene units on the basis of the band alignments of the constituent homopolymers were studied. The trends in their electronic structures and conduction properties as a function of (i) block sizes (m, n, k) and (ii) arrangement of the blocks (periodic or aperiodic) in the various copolymer chains are discussed. These trends are important guidelines to the experimentalists for designing novel electrically conducting polymers with tailor made conduction properties.

Keywords: Copolymer, Thiophene, Conducting polymer, *ab initio* studies.

INTRODUCTION

Electrical conduction in polymers on application of certain oxidising or reducing agents was a landmark discovery in the field of polymers. Now a days, these electrically conducting polymers are attractive candidates for applications in biosensors [1], supercapacitors [2] and biomedical engineering [3,4] as these have several advantages over traditional metals or semiconductors. It is however, desirable to obtain polymers that are intrinsically conducting without the need of doping as doping can lead to decrease in solubility and processibility of the polymers. This can be done by carrying out theoretical designing of conducting polymers [5,6] to obtain information on intrinsically conducting polymers which have low band gaps and can conduct electricity without the need of doping. One exciting possibility for theoretical designing of conducting polymers is provided by growing quasi-one dimensional systems or copolymers [7-10]. The electronic properties of copolymers are found to be generally (though not always), intermediate between the properties of the constituent homopolymers. These copolymers can have desired conduction properties, depending on the choice of the constituting components, their relative

amounts and their arrangement in the polymer chain. The copolymers just like inorganic superlattices, can be classified into four types [11,12] (Fig. 1). In Type I copolymers, the band gap of one component lies completely in the band gap of the other component. Type II staggered copolymers have the top of valence and conduction bands of one component below the top of valence and conduction bands of other component. In case of Type II misaligned copolymers, the top of conduction band of one component is below the top of valence band of the other component and in Type III copolymers, one component is semi-metallic while other is the normal semiconductor. Among conducting polymers, polythiophene [13] is one of the most widely studied and used polymer for electronic devices. In this article, the effect of block size on the electronic properties of a novel thiophene based triblock copolymer (A_mB_nC_k)_x are studied. The components (A)_x, (B)_x and (C)_x constituting the copolymers are donor-acceptor polymers comprising of *trans-cisoid* polyacetylene (PA) chains joined with the help of electron accepting group X (S for all components) and electron withdrawing group Y. For component (A)_x (poly-4H-cyclopentadithiophene-4-one, PCDT), Y = O, for (B)_x (poly-4-methylene-4H-cyclopentadithiophene, PMCT) Y = CH₂ and

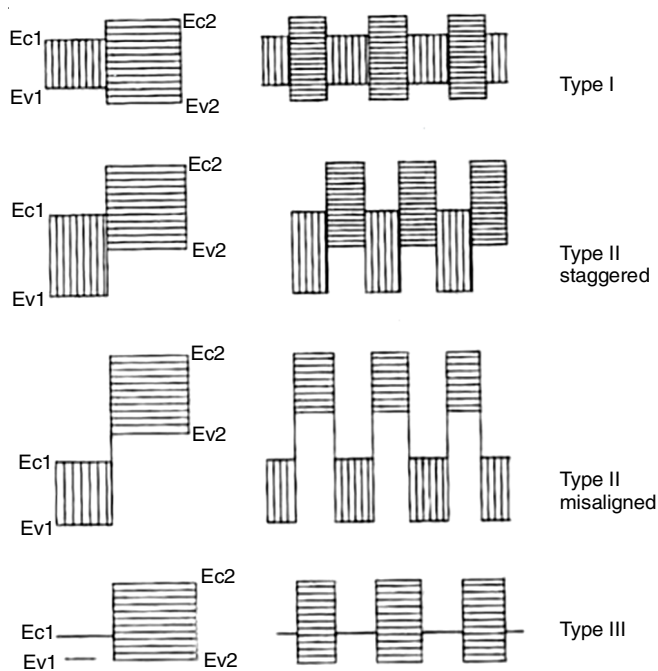


Fig. 1. Band alignments of various diblock copolymeric superlattices

that for component (C)_x (polydifluoromethylenecyclopentadithiophene, PFTh) Y: =CF₂. Ionization potential (IP), electron affinity (EA), band gap (E_g) and band widths of valence band (VB) and conduction band (CB) of the three components are given in Table-1. Band alignment of the three components in copolymer is shown in Fig. 2. It can be seen that the copolymer will belong to Type II staggered copolymers. The results obtained through these studies should provide guidelines for molecular designing of intrinsically conducting copolymers.

TABLE-1

Component	IP (eV)	EA (eV)	E _g (eV)	Band widths (eV)	
				VB	CB
A	8.774	2.514	6.260	3.363	1.427
B	8.198	1.960	6.238	2.910	1.547
C	8.434	2.176	6.257	2.613	1.471

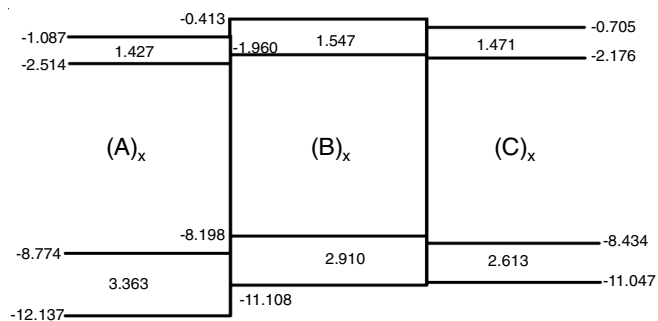


Fig. 2. Band alignment of components in copolymer (A_mB_nC_k)_x

EXPERIMENTAL

The electronic density of the states (DOS) of the quasi-one-dimensional copolymer chain can be determined by using simple negative factor counting method [14,15] based on

Dean's negative eigen value theorem [16,17]. The details of the method are already reported earlier [18]. In this method, the DOS are determined by finding the number of eigen values of the tridiagonal secular determinant in tight-binding approximation, which is smaller than a given trial energy λ by using the recursion relationships (eqns. 1 and 2):

$$\epsilon_i(\lambda) = \alpha_i - \lambda \quad (1)$$

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

where $i = 2, 3, 4, \dots, N$

Eqns. 1 and 2 are obtained by transforming the tridiagonal determinant to a bidiagonal one by applying successive Gaussian elimination.

In present calculations of electronic DOS of the copolymer chain, a chain length of 300 units and a grid size of 0.001 eV is used.

RESULTS AND DISCUSSION

Various polymeric chains of the type (A_mB_nC_k)_x were modelled by coupling m units of A, n units of B and k units of C in periodic and random manner. A computer program can easily generate various sequences of periodic and aperiodic copolymers. From study of the density of states of these copolymers, we obtained the values of IP (corresponding the top of valence band), EA (corresponding to the bottom of conduction band) and E_g (band gap) of these copolymer chains. The trends for these copolymer chains studied are as follows:

On increasing block size of all the components: It can be seen from the values of electronic properties like IP, EA and E_g for these copolymers that, in general, on increasing the block sizes m , n and k , there occurs a decrease in the value of IP and the value of EA increases. This leads to a decrease in the band gap, E_g which is the difference of IP and EA. These trends are shown as a chart (Fig. 3a). It can be seen that after a certain block size, the values of IP, EA and band gap do not change. There is a saturation observed in the electronic properties for large block size of the components. It can also be seen that the saturation in properties reaches faster for aperiodic copolymers than periodic copolymers. This implies that periodic copolymers can be tuned more efficiently for desired conduction properties.

On increasing the block size of component (C)_x: If we increase only the block size of component (C)_x in the system, that is change the value of k in (A_mB_nC_k)_x, keeping the values of m and n equal to unity, a slight increase in the IP values and a decrease in EA values is observed. This leads to an increase in band gap of the copolymers. Hence, we can conclude from these studies, that increase in component (C)_x will not be beneficial to formation of an intrinsically conducting copolymer. This is expected as the properties of copolymers are lying in between the properties of homopolymers and in this case, component (C)_x is the component of copolymer with maximum band gap.

On increasing the block size of component (B)_x: If the block size of component (B)_x, n , is increased in the copolymer,

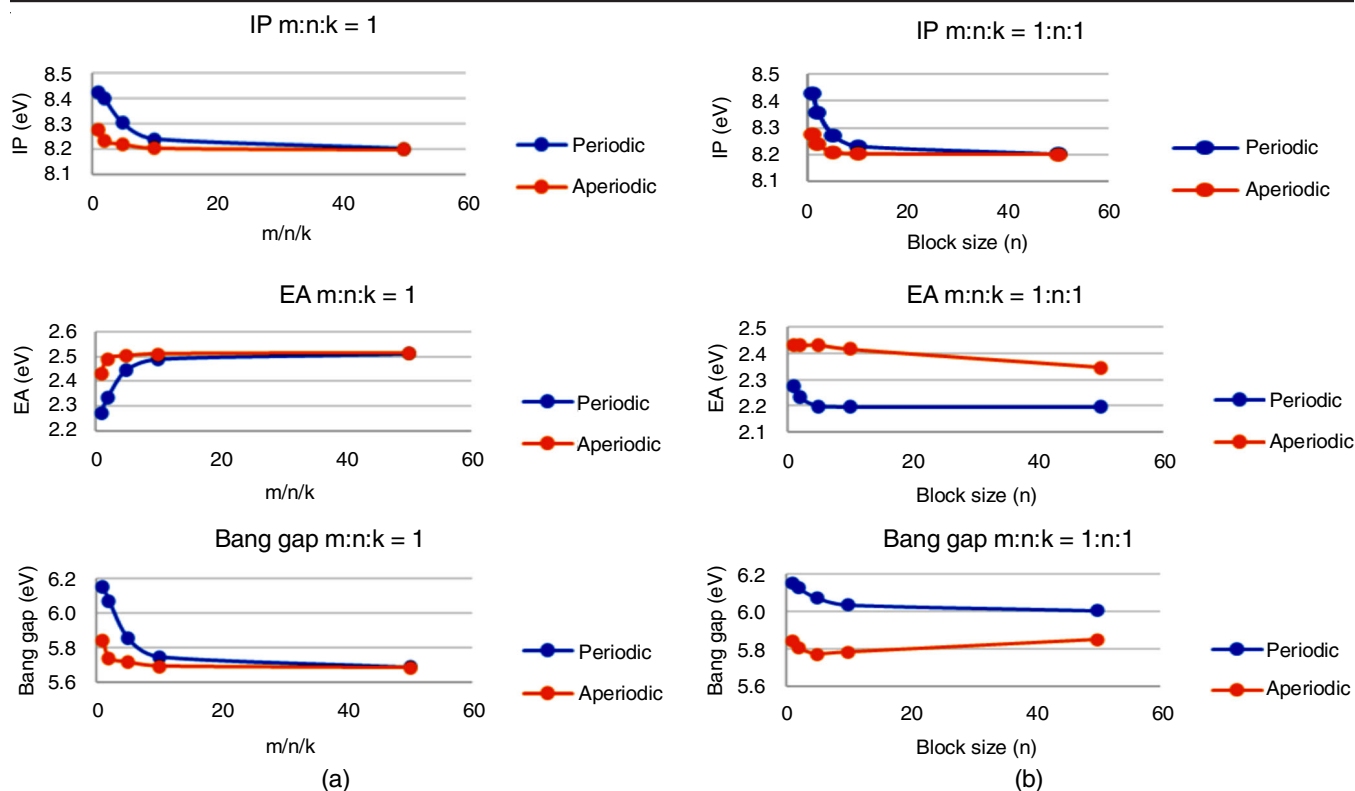


Fig. 3. (a) Variation of IP, EA and band gap with increase in block size for $m:n:k = 1$; (b) Variation of IP, EA and band gap with increase in block size for $m:n:k = 1:n:1$

keeping the values of m and k equal to 1, there occurs a decrease in IP and EA of the copolymers. This is leading to an overall decrease in the band gap of the copolymers making it more intrinsically conducting. Moreover, a decrease in IP values suggests that the copolymer will be more p-dopantphilic, *i.e.*, we can make it conducting by doping it with oxidising agents. In this case, one can also observe that the decrease in EA is somewhat slower in case of periodic copolymers while the decrease in EA is much faster. This decrease is leading to a rise in the value of band gap for aperiodic copolymers and it seems to be getting closer to the values obtained for periodic copolymers as the block size n is increased to sufficiently large values (Fig. 3b).

On increasing the block size of component (A)_x: If we increase only the block size of component (A)_x in the system, it can be seen that both the IP and EA of the copolymer increase. However, since the increase in IP is slightly lesser than the increase in the EA of the systems, it results in the decrease in E_g of the system. As the EA of the system is increasing on increasing the block size of component (A)_x, this implies that the system can be made conducting by doping using reducing agents. Technically speaking, this means that the copolymer becomes more n-dopantphilic on increasing block size of component (A)_x.

Periodic copolymers versus aperiodic copolymers: For both periodic and aperiodic copolymers, the trends in the values of electronic properties are similar. It can be seen that the properties of all the copolymers studied are intermediate between the properties of homopolymers. One can observe, in general,

that overall values of band gap (E_g) are smaller in the case of aperiodic copolymers than periodic copolymers. This is expected as the values of IP are lower and EA are higher for all the aperiodic copolymers as compared to corresponding periodic copolymers (Table-2).

DOS of copolymers: The DOS curves for homopolymers consist of well separated bands. The lower energy band in DOS curves belong to valence band while the higher energy band belongs to conduction band. The IP and EA of the homopolymers as well as the copolymers are determined by using Koopman's theorem. According to this, the negative of top of valence band corresponds to the IP of the polymer while the negative of bottom of conduction band gives the value of electron affinity. The difference between the values of IP and EA gives the band gap of the polymers.

Fig. 4 shows DOS curves for a few selected periodic and aperiodic copolymers. It can be seen that the DOS curves of the periodic copolymers consist of narrow and well separated peaks. This is a result of lifting of discontinuities around Brillouin zone for these copolymers. In contrast, the DOS for aperiodic copolymers consist of broad regions of allowed energy states with few gaps in between them. This happens due to the fact, that for a particular aperiodic sequence, the environment around A, B and C keeps on changing and therefore, the energy peaks are scattered over wider range. This scattering of energy peaks is the reason why aperiodic copolymers generally have smaller band gaps as compared to periodic copolymers.

Another observation that comes from DOS curves is that in case of periodic copolymers, the valence band and conduction

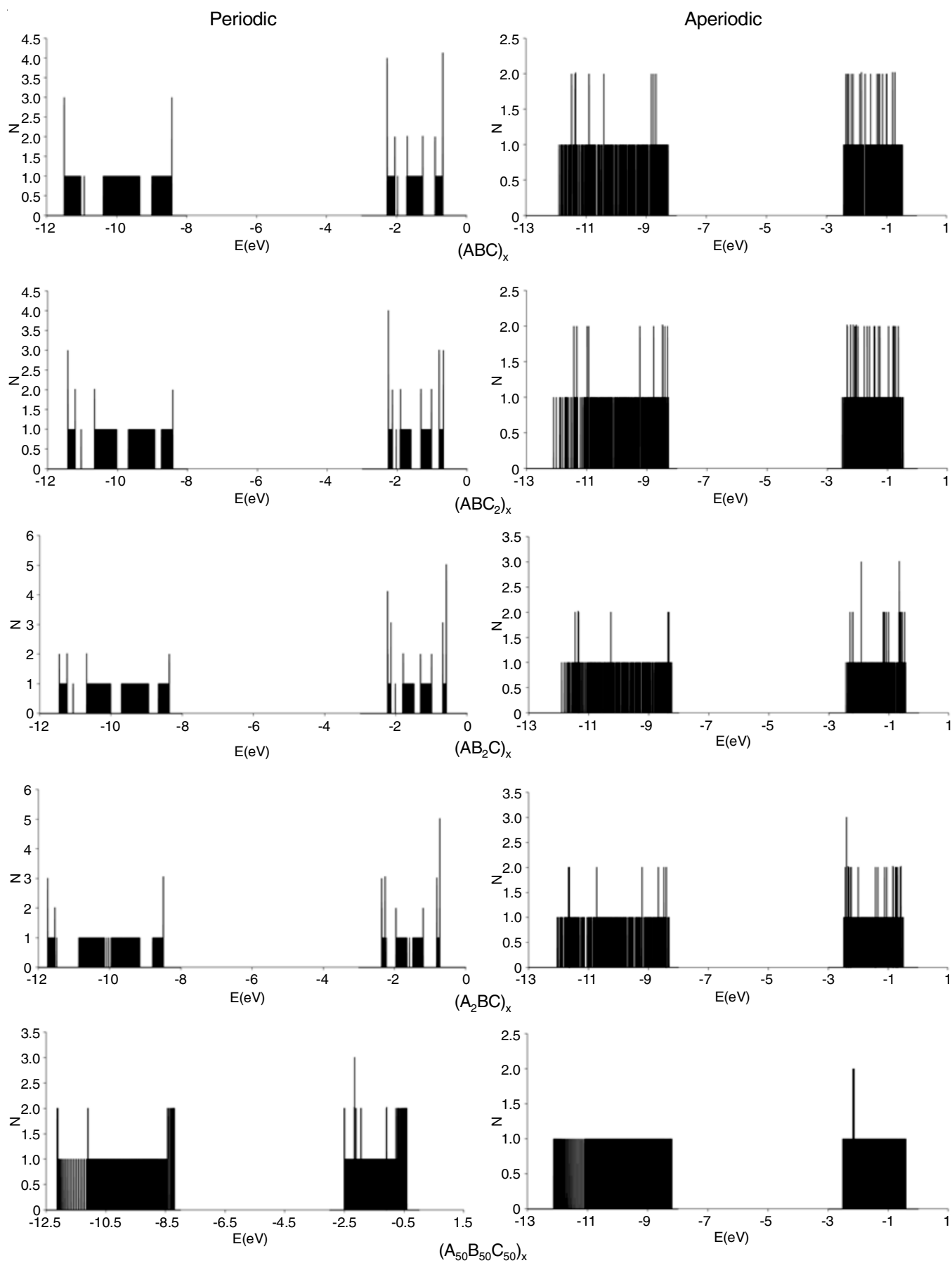


Fig. 4. DOS curves for some selected periodic and aperiodic copolymers

TABLE-2
CALCULATED VALUES OF ELECTRONIC PROPERTIES
IP (CORRESPONDING THE TOP OF VALENCE BAND),
EA (CORRESPONDING TO THE BOTTOM OF CONDUCTION
BAND) AND E_g (BAND GAP) OF PERIODIC AND APERIODIC
COPOLYMER $(A_m B_n C_k)_x$ IN TIGHT BINDING APPROXIMATION

$(A_m B_n C_k)_x$ (m,n,k)	Periodic			Aperiodic		
	IP (eV)	EA (eV)	E_g (eV)	IP (eV)	EA (eV)	E_g (eV)
(1,1,1)	8.427	2.273	6.154	8.275	2.43	5.845
(2,2,2)	8.402	2.332	6.07	8.232	2.492	5.74
(5,5,5)	8.303	2.447	5.856	8.221	2.503	5.718
(10,10,10)	8.24	2.491	5.749	8.205	2.511	5.694
(50,50,50)	8.201	2.513	5.688	8.199	2.514	5.685
(1,1,2)	8.427	2.258	6.169	8.284	2.502	5.782
(1,1,5)	8.429	2.237	6.192	8.314	2.487	5.827
(1,1,10)	8.431	2.229	6.202	8.343	2.393	5.95
(1,1,50)	8.433	2.227	6.206	8.379	2.342	6.037
(1,2,1)	8.358	2.232	6.126	8.238	2.43	5.808
(1,5,1)	8.272	2.198	6.074	8.207	2.434	5.773
(1,10,1)	8.231	2.194	6.037	8.201	2.417	5.784
(1,50,1)	8.201	2.194	6.007	8.199	2.346	5.853
(2,1,1)	8.486	2.362	6.124	8.314	2.482	5.832
(5,1,1)	8.551	2.456	6.095	8.319	2.507	5.812
(10,1,1)	8.571	2.493	6.078	8.389	2.512	5.877
(50,1,1)	8.574	2.513	6.061	8.398	2.514	5.884

band split in to peaks whose number is equal to the $(m+n+k)$. This is happening due to splitting of Brillouin zone for these copolymers making it discontinuous and resulting in separate peaks. Lastly, it can be seen that for large values of m , n and k , the DOS of periodic copolymers start resembling the DOS of aperiodic copolymers which happens because for a fixed length of copolymer chain, the number of possibilities of arrangement of different components in the polymer chain decreases so the environment around a particular component does not change much, just as in a periodic copolymer.

Conclusion

Electronic structure and conduction properties of various quasi one-dimensional Type II staggered copolymers comprising of thiophene units were studied. The electronic properties of the copolymer lies in between the properties of its constituents. It is seen that increasing the block size of all the components results in lowering of IP, increase in EA and a decrease in band gap of the copolymers. Increasing the block size of component $(A)_x$ leads to a copolymer that is more p-dopantphilic as the IP value is decreased, while increasing block size of $(B)_x$ leads to increase in EA and more n-dopantphilicity of the polymer. It is also found that it is easier to tune the properties of periodic copolymers than aperiodic copolymers. The values of band

gap observed for the copolymer is falling in range of 5-6 eV, which is too large for considering the copolymer as a good candidate for use as conducting polymer. But nevertheless, the results obtained can provide a better understanding about tuning the electronic structure of copolymer to obtain a copolymer with good conduction properties. Starting with homopolymers having smaller band gap can serve this purpose.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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