

Designing of quasi-one-dimensional compositional superlattices of donor–acceptor polymers

A. K. Bakhshi* and Pooja

Department of Chemistry, Panjab University, Chandigarh-160014, India

The electronic structure and conduction properties of quasi-one-dimensional compositional superlattices (copolymers) $(C_m D_n)_x$ belonging to the class of type II-staggered donor–acceptor polymers poly(cyanomethylene cyclopentadienylpyrrole) (PCNPY) $(C)_x$ and poly(cyanomethylene cyclopentadithiophene) (PCNTh) $(D)_x$ have been investigated using the negative-factor counting method in the tight binding approximation. It is found that increasing the proportion of either of the two components (C or D) in the copolymer chain improves the intrinsic conductivity of the chain. This is accompanied by the increased n-dopant-philicity in the case of low band-gap component PCNTh and increased p-dopant-philicity in the case of large band-gap component PCNPY.

The designing of novel polymers with tailor-made conduction properties has been an area of intensive activity and frequent reviews during recent years.^{1–4} Recently a new route to the design and synthesis of small band-gap polymers has been proposed by Havinga and co-workers.^{5,6} The principal idea behind this route is that the conjugated polymers with alternate donor and acceptor moieties in the main chain are expected to have a small band gap. Using this idea new classes of polysquaraines and polycroconaines with band gap values as low as 0.5 eV have been synthesized.^{5,7} Lambert and Ferraris,⁸ using a somewhat similar approach, have synthesized poly(cyanomethylene cyclopentadithiophene) (PCNTh), a polymer made by succession of bithiophene units in which the two aromatic rings are linked by a dicyanomethylene group. Theoretical studies on the geometric and electronic structures of PCNTh and its nitrogen containing analogue poly(cyanomethylene cyclopentadienylpyrrole) (PCNPY) have been reported by Toussaint and Bredas⁹ and show that the introduction of the electron-accepting group dicyanomethylene between the two thiophene or pyrrole rings of the unit cell induces major geometry differences within the rings, resulting in a geometrical structure that can be viewed as a combination of aromatic and quinoid geometries. Recently theoretical studies on the electronic and geometric structures of some novel donor–acceptor polymers based on polythiophene ($X = S$), polyfuran ($X = O$) and polypyrrole ($X = NH$), obtained using the one-dimensional tight-binding self-consistent field-crystal orbital (SCF-CO) method at the MNDO-AM1 level of approximation, have been carried out by Bakhshi *et al.*¹⁰ The repeat unit of these polymers consists of a bithiophene, bifuran or bipyrrrole unit bridged by an electron accepting group Y [$Y = >C=CH_2$, $>C=O$, $>C=CF_2$ or $>C=C(CN)_2$]. The optimized geometries of the polymers show a strong dependence on the nature of the electron-donating group X ($X = S, O$ or NH). All the polymers studied are predicted to have band gap values between 1 and 2 eV.

In this paper we study the design of novel conducting polymers through the technique of quasi-one-dimensional superlattices (copolymers). The conduction properties of such copolymers depend on the choice of the components and on their arrangement in the copolymer chain. Our aim is to investigate theoretically the electronic structures and conduction properties of periodic and aperiodic copolymers $(C_m D_n)_x$ of donor–acceptor polymers based on pyrrole (PCNPY) (C) and thiophene (PCNTh) (D). The structures of unit cells of these donor–acceptor polymers are shown in Fig. 1. Fig. 2

shows the band alignments of the above pair of polymers $(C)_x$ and $(D)_x$ obtained on the basis of band-structure results.¹⁰ The top of the valence band of component $(C)_x$ lies in the band gap of component $(D)_x$ and the bottom of the conduction band of $(D)_x$ lies in the band gap of $(C)_x$ and therefore this pair of polymers belongs to type II-staggered superlattices. The purpose of the present study is to see how the electronic structures and conduction properties of these types of copolymers change as a function of: (i) the block size m of C, (ii) the block size n of D, (iii) the block sizes m and n keeping m/n constant and (iv) the arrangement of units in the copolymer chain (periodic or aperiodic).

These investigations have been carried out using the negative factor counting method in the tight-binding approximation. The results are expected to provide important

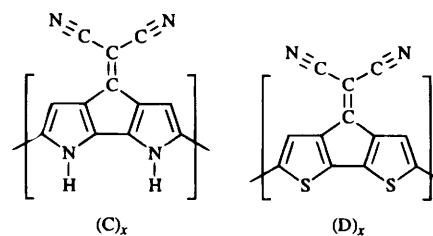


Fig. 1 Structures of the unit cell of poly(dicyanomethylene cyclopentadienylpyrrole) (PCNPY) $(C)_x$ and poly(dicyanomethylene cyclopentadithiophene) (PCNTh) $(D)_x$

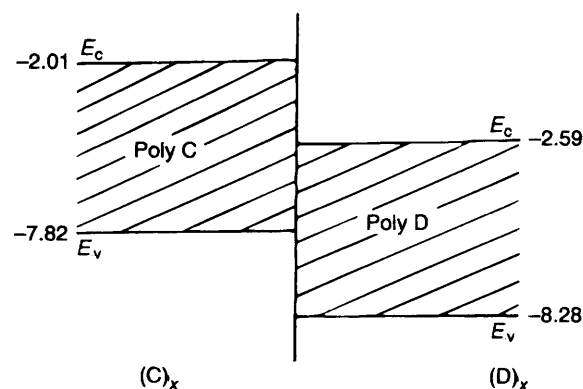


Fig. 2 Band alignments of poly(dicyanomethylene cyclopentadienylpyrrole) (PCNPY) $(C)_x$ and poly(dicyanomethylene cyclopentadithiophene) (PCNTh) $(D)_x$ (all values in eV)

guidelines for the design of novel conducting copolymers of these systems.

Methodology

The electronic density of states (DOS) of a quasi-one-dimensional copolymer $(C_mD_n)_x$ chain can be determined using a simple negative factor counting method^{11,12} based on Dean's eigenvalue theorem.¹³ The DOS are determined from the secular determinant which is tridiagonal in the case where only first-neighbour interactions are taken into account (tight binding approximation). The number of eigenvalues of the tridiagonal secular determinant, which are smaller than a given trial energy, equals the number of negative factors obtained by the relations;

∏_{i=1}^N (λ_i - λ) = ∏_{i=1}^N ε_i(λ) (1)

ε_1(λ) = α_1 - λ (2)

ε_i(λ) = α_i - λ - β_j^2 / (ε_{i-1}(λ)) (3)

Eqn. (2) and (3) are obtained by transforming the tridiagonal determinant into a didiagonal determinant by applying successive Gaussian eliminations. α_i and β_j are the diagonal and off-diagonal matrix elements, respectively, of an effective one-electron Hamiltonian, and λ is its eigenvalue. The diagonal (α) and the off-diagonal (β) matrix elements of the secular determinant are determined from the corresponding band-structure results of each component (PCNTh and PCNPY)¹⁰ constituting the copolymer chain. For a given band, α_i of a component is taken to be the middle point (or weighted middle point) of the corresponding band. Assuming the dispersion of the band to be given by the simple relation:

ε_C(k) = α_C + 2β_{C,C} cos(ka) (4)

where k is the wavevector, a is the translational period and β_{C,C} is taken to be one-quarter of the bandwidth if the same component is repeated. If on the other hand, component C is followed by component D, then the off-diagonal matrix element β_{C,D} is assumed to be given by the simple relation.

β_{C,D} = 1/2 (β_{C,C} + β_{D,D}) (5)

In the present calculations of the DOS the α and β values for the various components were obtained from their band-structure results.¹⁰ For the copolymers (C_mD_n)_x of the donor-acceptor polymers, the α(β) values in eV for the valence band of the donor-acceptor polymers based on pyrrole (C)_x and thiophene (D)_x, are 8.675(0.4275) and 8.865(0.2975), respectively, while the corresponding values for the conduction band are -1.91(0.05) and -2.37(0.11), respectively. The DOS calculations were carried out for a chain of 300 units.

Results and Discussion

The copolymers (C_mD_n)_x in the present study have been divided into the following classes.

- Class 1: (CD_n)_x; this includes systems in which the block size (m) of component C is kept constant (m = 1) and the block size (n) of component D is varied.
- Class 2: (C_mD)_x; this includes systems in which the block size (n) of the component D is kept constant (n = 1) and the block size (m) of component C is varied.
- Class 3: (C_mD_n)_x; this includes systems in which the block sizes m and n of both the components C and D are varied keeping the ratio m/n constant.

The calculated electronic properties such as ionisation potential (E_i), electron affinity (E_ea) and band gap (E_g) of the various periodic and aperiodic copolymer chains of the above three classes are given in Tables 1 and 2, respectively.

Table 1 Calculated electronic properties (in eV) of periodic copolymers (CD_n)_x, (C_mD)_x and (C_mD_n)_x

system	E _i	E _{ea}	E _g
(CD _n) _x			
CD	8.037	2.419	5.617
CD ₅	8.157	2.562	5.595
CD ₁₀	8.170	2.580	5.590
CD ₅₀	8.172	2.587	5.585
(C _m D) _x			
C ₅ D	7.875	2.394	5.480
C ₁₀ D	7.840	2.394	5.445
C ₅₀ D	7.820	2.394	5.425
(C _m D _n) _x			
C ₅ D ₅	7.902	2.560	5.342
C ₁₀ D ₁₀	7.847	2.580	5.267
C ₅₀ D ₅₀	7.820	2.587	5.232

In the case of periodic copolymers of the class (CD_n)_x the band gap is found to decrease with an increase in the block size n of D units (Table 1). A similar decrease was observed in the case of copolymers of type I.¹⁴ However, unlike type I, the decrease in band-gap values in these copolymers results from the increase in both E_i and E_ea values. Since the decrease in E_i reduces the band gap while the increase in E_ea also reduces it, the observed decrease in the band gap in these systems implies that the increase in E_ea is much more than the corresponding increase in E_i values. It, therefore, means that the copolymers of the type (CD_n)_x become not only better intrinsic conductors of electricity but also better candidates for n-doping. In the case of copolymers of type I, on the other hand, such an increase in the intrinsic conductivity was accompanied by an increasing tendency to form both p- and n-doped copolymers.

The band-gap values are found to decrease in the copolymers of the class (C_mD)_x with an increase in the block size m of C units. This decrease is accompanied by a decrease in both E_i and E_ea values implying that an increase of the block size m of C units makes the copolymer both a better intrinsic conductor and a better p-doped copolymer. The band-gap value, however, was found to increase with increase in m in the case of copolymers of type I making the copolymers not only poor intrinsic conductors but also poor candidates for n- and p-doping.

The band gap in (C_mD_n)_x class of copolymers is found to decrease with an increase in the block sizes of C and D units for a given composition m/n. This decrease in the band gap here 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 dopant-philicity of the copolymer. A similar trend was observed for type I copolymers.

Table 2 Calculated electronic properties (in eV) of aperiodic copolymers (CD_n)_x, (C_mD)_x and (C_mD_n)_x

system	E _i	E _{ea}	E _g
(CD _n) _x			
CD	7.867	2.560	5.307
CD ₅	7.902	2.587	5.315
CD ₁₀	7.902	2.587	5.315
CD ₅₀	7.977	2.587	5.390
(C _m D) _x			
C ₅ D	7.825	2.560	5.265
C ₁₀ D	7.820	2.560	5.260
C ₅₀ D	7.820	2.547	5.272
(C _m D _n) _x			
C ₅ D ₅	7.825	2.587	5.237
C ₁₀ D ₁₀	7.820	2.587	5.232
C ₅₀ D ₅₀	7.820	2.587	5.232

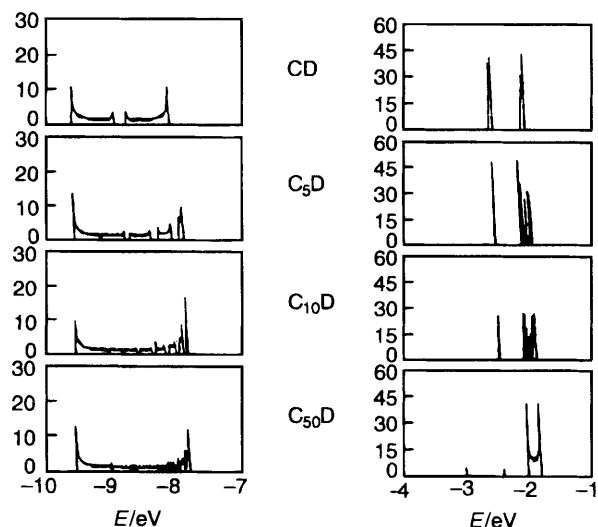


Fig. 3 DOS curves for periodic block copolymers of class $(C_m D)_x$ (energy in eV, number of states N in relative units)

The trends in the electronic properties of the aperiodic copolymers are found to be similar to those of periodic copolymers, the only difference being that for the former the saturation in the electronic properties is achieved much faster. It means that tuning the band gap to a particular value between that for $(C)_x$ and $(D)_x$ is made easier by synthesizing periodic copolymers, while achieving a small band gap (almost independent of the nature of the large-gap component C) is easier for aperiodic copolymers.

The electronic DOS curves of periodic and aperiodic copolymers of class $(C_m D)_x$ are shown in Fig. 3 and 4, respectively. The general features of the DOS curves for both periodic and aperiodic copolymers are the same as those observed in the case of type I superlattices *i.e.* narrower and well separated peaks for periodic copolymers while relatively broader regions of the allowed energy states with fewer gaps in between for aperiodic copolymers. Here too the band gap for an aperiodic arrangement is always smaller than the band gap for the corresponding periodic arrangement. Since similar

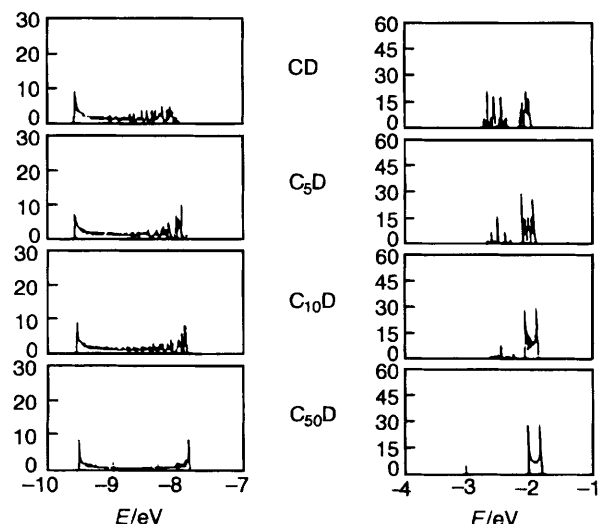


Fig. 4 DOS curves for aperiodic block copolymers of class $(C_m D)_x$ (energy in eV, number of states N in relative units)

features are also observed in other classes of periodic and aperiodic copolymers, their DOS curves are not shown.

Conclusion

A systematic study was carried out on the electronic structures and conduction properties of periodic and aperiodic copolymers of poly(cyanomethylene cyclopentadienylpyrrole) (PCNPy) and poly(cyanomethylene cyclopentadithiophene) (PCNTh) which represent the prototype of the quasi-one-dimensional superlattices of type II-staggered. Results show that in these copolymers $(C_m D_n)_x$, a higher percentage of either of the two components improves the intrinsic conductivity with correspondingly higher n-dopant-philicity for the smaller band gap component (PCNTh) and higher p-dopant-philicity for the larger band gap component (PCNPy). This is in contrast to type I copolymers¹⁴ where the higher percentage of the smaller band gap component makes the copolymer more dopant-philic (both p and n) while the higher percentage of larger band-gap component makes the copolymer more insulating and less dopant-philic. Our results also show that as in the case of type I copolymers, here too tuning the electronic properties intermediate between those of two homopolymers is made easier by synthesizing periodic copolymers. Aperiodic 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 band-gap component. In these copolymers, 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.

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