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Electronic confinement in quasi-one-dimensional triblock copolymers*

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A tight-binding calculation to describe the triblock copolymer xPA(polyacetylene)/nPPP (poly(p-phenylene))/yPA or xPPP/nPA/yPPP is presented. The interfacial coupling between homopolymer segments is attributed to the hopping of π-electrons and the coupling of σ-bonds. The dependence of the band gap of triblock copolymers on the interfacial couplings or on the composite segment lengths is studied. The influence of composite segment lengths on the electron density is also studied. For nPPP/xPA/nPPP structures, the band gap varies with PA segment length over a wide range of 1.32–2.74eV. For nPA/xPPP/nPA structures, the band gap is invariant with PPP segment length. It is found that a spontaneous tunnelling phenomenon could take place in nPA/xPPP/nPA structures. Furthermore, the polaron caused by doping an electron into nPA/xPPP/nPA will tend to be confined in one of the well (PA) parts. This kind of confinement may increase the electron–hole recombination probability.

Keywords: organic quantum well, copolymer, electronic confinement
PACC: 7125V, 7138, 6848, 6170T

1. Introduction

On the analogy of the traditional semiconductor superlattice and heterostructure, a copolymer chain with a periodic alternating sequence can be considered as a one-dimensional superlattice, such as a periodic $(A/B)_n$ copolymer chain, and a triblock A/B/A as a quantum well-barrier-well (or barrier-well-barrier) system. The connecting bonds between the composed homopolymers act as the interfacial coupling. The π-electrons can transfer from one segment to another through the connecting bonds. In the past few years, extensive investigations on the electronic properties of copolymers have been carried out both experimentally[1−9] and theoretically.[10−19] For instance, Ruckh *et al*[18] first studied a copolymer consisting of polyacetylene and polydiaetylene in a framework of organic quantum wells at the simple Hückel level. Then Mulazzi *et al*[17] reported their research on polynorbornene-polyacetylene copolymers with polarized infrared absorption method. Hernández *et al*[9] studied two neutral thiophene-based oligomers and indicated that these copolymers had a well-barrier-well structure, where the well parts were two bithiophene or terthiophene end-moieties, connecting through a barrier part with a larger energy gap. The evolution of the geometric structure and electronic properties of copolymers was studied by Meyers *et al*[10] with Austin Model 1 (AM1) geometry optimization and valence effective Hamiltonian (VEH). Piaggi *et al*[19] presented a model for calculation of a copolymer superlattice and showed that a confinement occurred and depended on the well-barrier alternation sequence. All these studies reveal that copolymers have more abundant electronic characteristics than the normal homopolymers. Especially, the quantum well characteristic of copolymers shows an advantage in designing and developing organic quantum devices. In this paper, we study the triblock xPA/yPPP/xPA or xPPP/yPA/xPPP copolymers both in neutral state and doped state. Calculations in a tight-binding approach have been carried out for some shorter copoly-

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mer chains and longer ones.

2. Model and formula

PA has a small band gap of 1.5–1.9eV,[20] while PPP has a larger band gap of 2.7–3.4eV.[21] A PA/PPP /PA copolymer chain is constructed and sketched in Fig.1. It has an alternating well-barrier structure. In the tight-binding approximation, the Hamiltonian of the copolymer chain can be composed of the Hamiltonian of the homopolymers plus the interfacial coupling between the composite homopolymer segments, which is given by

$$\begin{aligned} H_j = & -\sum_{n,s}[t^0_{j,n} - \alpha_{j,n}(u_{j,n+1} - u_{j,n})] \\ & \times (C^+_{j,n+1,s}C_{j,n,s} + C^+_{j,n,s}C_{j,n+1,s}) \\ & + \frac{1}{2}\sum_n K_{j,n}(u_{j,n+1} - u_{j,n})^2 \\ & + \sum_n K'_{j,n}(u_{j,n+1} - u_{j,n}), \end{aligned} \tag{1}$$

where j and n are the indices of segments and sites, respectively, s is the electron spin, $t^0_{j,n}$ is the hopping integral in the undimerized configuration, which is independent of the site index n in PA, so $t^0_{j,n} = t^0_{PA}$. In the PPP segment a factor is introduced to eliminate the degeneracy of the ground state of PPP, i.e. $t^0_{j,n} = t^0_{\rm PPP} - t'_{\rm PPP}\cos\dfrac{n\pi}{2}$.[22] $\alpha_{j,n}$ is the electron-phonon coupling strength, $u_{j,n}$ is the displacement of the nth (CH) unit, $C^+_{j,n,s}(C_{j,n,s})$ is the creation (annihilation) operator of the π-electron, and $K_{j,n}$ is the force constant between adjacent units. The last term, with $K'_{j,n} = -4\alpha_{j,n}/\pi$, is introduced to stabilize the system in a free-end boundary condition. In the case of a periodic boundary condition, it will vanish spontaneously. All these parameters are set before the following calculation by referring to Ref.[23].

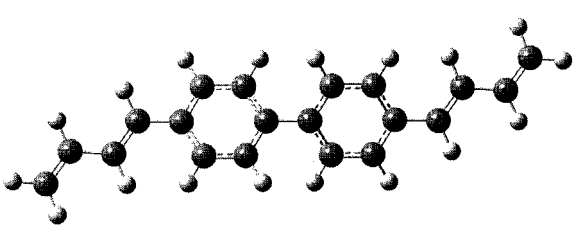


Fig.1. Molecular structure of 2PA/2PPP/2PA.

Different from ordinary semiconductor heterostructure or superlattice cases, the interface in polymer heterostructures is in perfect bond or antibond states. The interfacial couplings include the π-electron transfer and the σ-electron bonding coupling. Both of them will affect the structure and electronic properties of the copolymer. Therefore, two coupling parameters have been introduced. Parameter $\beta_{\rm e}$ is introduced to characterize the π-electron transfer, where $t^0_{\rm PA/PPP} = \beta_{\rm e}\cdot\dfrac{1}{2}\left(t^0_{\rm PA} + t^0_{\rm PPP} - t'_{\rm PPP}\cos\dfrac{n\pi}{2}\right)$ and $\alpha_{\rm PA/PPP} = \beta_{\rm e}\cdot\dfrac{1}{2}(\alpha_{\rm PA} + \alpha_{\rm PPP})$; β_K is used to describe the σ-electron coupling by $K_{\rm PA/PPP} = \beta_K\cdot\dfrac{1}{2}(K_{\rm PA} + K_{\rm PPP})$. If $\beta_{\rm e} = \beta_K = 0$, the homopolymers cannot be synthesized to a copolymer, but a simple blend of PA and PPP fragments. For simplicity of calculation, we take $\beta_{\rm e} = \beta_K = \beta$.

Considering a polymer heterostructure consisting of PA and PPP segments, the static equilibrium condition can be derived through a second-order perturbation theory by minimizing the total energy of the system. With the eigen equation of π-electrons together, a set of circulated iterative equations is obtained,

$$\begin{aligned} & [-t^0_{j,n} + \alpha_{j,n}(u_{j,n+1} - u_{j,n})]Z_{j,n+1,\mu,s} \\ & + [-t^0_{j,n} + \alpha_{j,n}(u_{j,n} - u_{j,n-1})]Z_{j,n-1,\mu,s} \\ & = \varepsilon_{\mu,s}Z_{j,n,\mu,s}, \end{aligned} \tag{2}$$

$$f(n) = \frac{1}{N-1}\sum_n^{N-1} f(n), \tag{3}$$

where

$$\begin{aligned} f(n) = & (-1)^n K_{j,n}(u^0_{j,n} - u^0_{j,n+1}) \\ & - 2\alpha_{j,n}\sum_\mu{}' Z_{j,n,\mu,s}Z_{j,n+1,\mu,s} - K'_{j,n}. \end{aligned}$$

For a given starting lattice configuration, the eigenvalues and eigenstates can be obtained from the eigen Eq. (2). By substituting the eigenstates into the equilibrium condition, i.e. Eq.(3), a new lattice configuration is obtained. Repeating this process until the differences between the values of $u_{j,n+1} - u_{j,n}$ for two successive iterations are smaller than 10^{-6} (in unit of nm) for each j and n, then the iteration stops.

3. Results and discussion

In this paper, we have studied a triblock copolymer xPA / nPPP / yPA, where x (or y) and n are the unit numbers of PA and PPP respectively. We take $t^0_{\rm PPP}$=2.5eV, $t'_{\rm PPP}$=1.0eV, $\alpha_{\rm PPP}$=45.0eV/nm, $K_{\rm PPP}$=2100.0eV/nm^2 for PPP sequence, and $t^0_{\rm PA}$=2.5eV, $\alpha_{\rm PA}$=41.0eV/nm, $K_{\rm PA}$=2100.0eV/nm^2 for PA.[23] Then the calculated band gaps are 2.74eV for PPP and 1.32eV for PA, which are consistent with the experimental data.[21,20] Therefore,

xPA / nPPP / yPA has a well-barrier-well structure, and xPPP / nPA / yPPP has a barrier-well-barrier one.

The band gaps versus the strength of interfacial coupling with different segment lengths in xPA/xPPP/xPA cases are shown in Fig.2. For small x, the gap decreases obviously with increasing interfacial coupling. Actually, if x is small, the copolymer be comes a polymer, and the boundary effect plays a dominant role. It is well known that the band gap increases with the shortening of the polymer chain. For copolymers, similar behaviour is obtained, as shown in Fig.2. For x=20 units the gap has little change with interfacial coupling. Furthermore, when $x \geq 20$ (CH) units, the gap has little dependence on the number of unit x of the homopolymer segments. Therefore, in the following calculations, we choose the strength of the interfacial coupling β=1, unless otherwise stated.

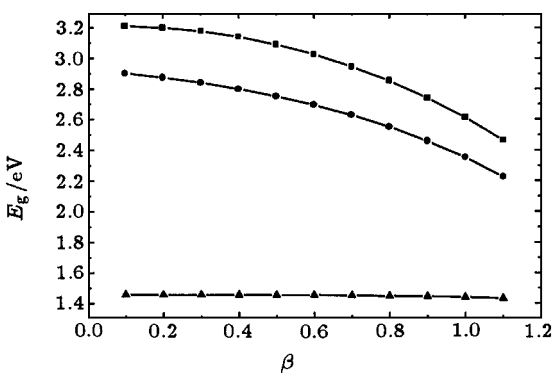


Fig.2. Evolutions of the band gaps of x PA/ x PPP/ xPA with the strength of interfacial coupling, ■: x=2; ●: x=4; ▲: x=20.

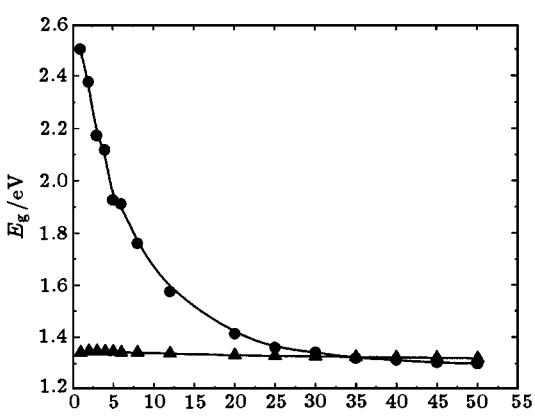


Fig.3. Evolutions of band gaps with the lengths of segments in 20PA/ x PPP/ 20PA and 20PPP/ x PA/ 20PPP separately (β=1). ▲: 20PA/ n PPP/ 20PA; ●: 20PPP/ x PA/20PPP.

Figure 3 shows the dependence of the band gap of the 20A/xB/20A system on the number of unit of the spacer homopolymer. For the barrier-well-barrier structure of 20PPP/xPA/20PPP, the gap of copolymers decreases rapidly with increasing PA unit when x <20. However, for the well-barrier-well structure of 20PA/xPPP/20PA, the band gap seems invariant with the length of PPP. Thus, the number of unit of the spacer homopolymer has a greater influence on the band gap of the barrier-well-barrier structure than on that of the well-barrier-well structure.

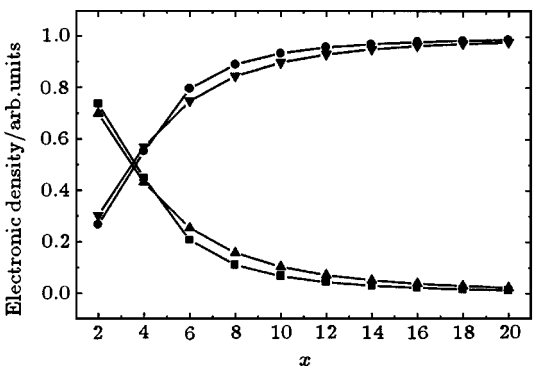


Fig.4. Dependence of the probability density of the lowest CB state in each homopolymers upon the x in triblock copolymer xPA / x PPP / xPA and x PPP / xPA / x PPP (β=1). ●: PA; ■: PPP in x PA / x PPP / x PA, and ▼: PA; ▲: PPP in x PPP/ x PA / x PPP.

Figure 4 shows the dependence of the electron density of the lowest level of the conduction band on the segment unit x of x PPP / x PA / x PPP or xPA/xPPP/xPA structures. When x is smaller than 4, for both structures the electron density on the PPP segment is a little higher than that on PA segment. When x is larger than 4, the electron density on PA is much higher than that on PPP. However, when x is over about 12, the electron density on the PPP segment is close to zero and the density on PA is close to 1. This means that electrons are confined in PA parts with increasing x. From the configuration shown in Fig.5, for $x > x_c$=4, it can be seen that xPPP/xPA/xPPP acts as a quantum well, and xPA/xPPP/xPA a quantum barrier. For $x < x_c$, there is no distinct confinement of electrons, and the composite structure does not show any characteristic of copolymer; but it shows a characteristic of a normal polymer-like material.

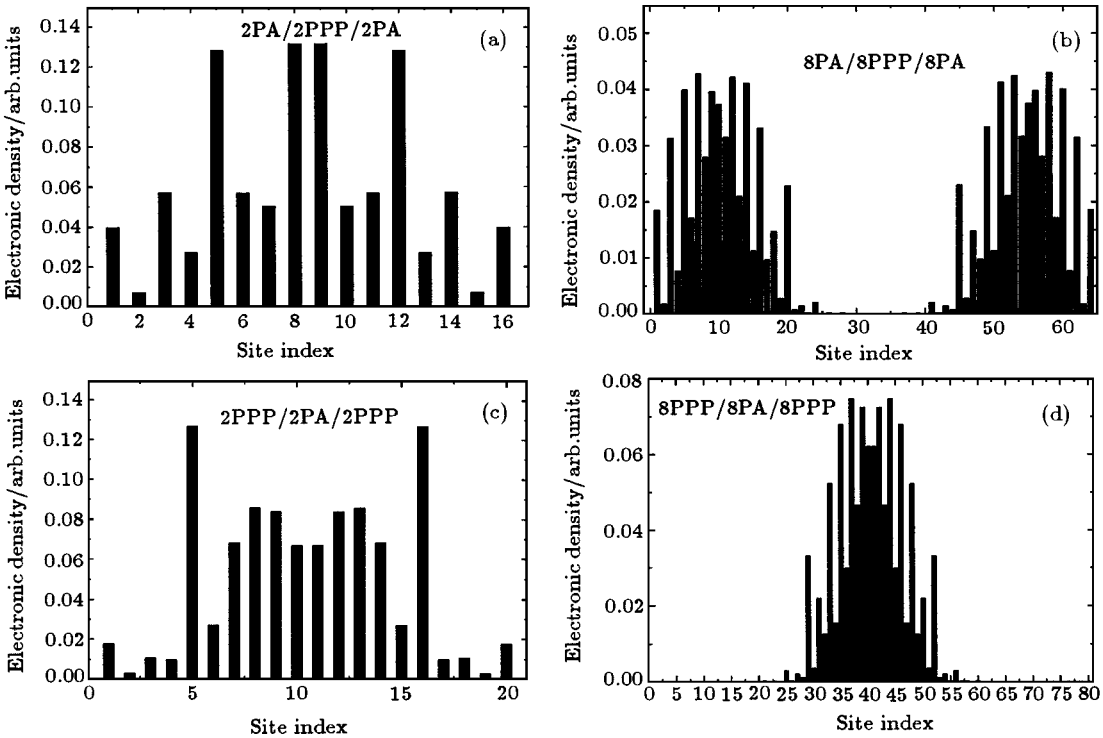


Fig.5. Distribution of the probability density of the lowest CB state in triblock copolymers (β=1). (a) 2PA/2PPP/2PA, (b) 8PA/8PPP/8PA, (c) 2PPP/2PA/2PPP, and (d) 8PPP/8PA/8PPP.

The relationship between the electron density and the unit x in 50PA/xPPP/50PA is shown in Fig.6. When x is large enough (e.g. x >11), the wavefunction is almost completely confined in one of the PA segments (left-hand side, for example). With decreasing x, it can be seen that some electrons are transferred to the right segment of PA with a high probability. When x reaches or is less than a critical value x'_c, each (right or left) PA segment has almost the same electron probability, i.e. each owns one half of the wavefunction. This shows that the electrons on the lowest conduction band (CB) level could tunnel through the spacer barrier from one (left) well to another (right) even without the external electrical bias. This interesting phenomenon in the quantum barrier structure of nPA/xPPP/nPA is the so-called "spontaneous tunnelling". The critical value x'_c depends upon the interfacial coupling β. It changes from 9 phenyl rings at β=1, 8 phenyl rings at β=0.5, to 7 phenyl rings at β=0.05. This may come from the fact that the interface between PA and PPP acts as an "energy barrier".[24,25] A strong interfacial coupling would restrain the barrier and be favourable for electrons tunnelling.

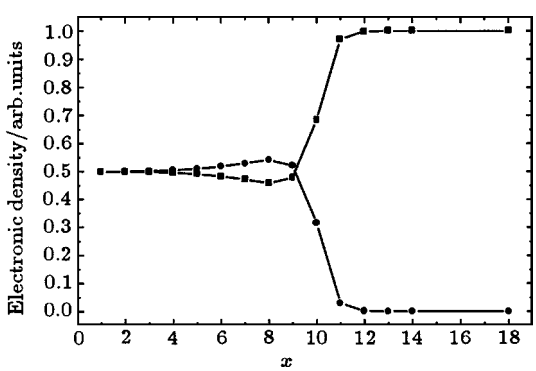


Fig.6. Dependence of the probability density of the lowest CB state in each segment of PA upon the lengths of PPP segment in 50PA/xPPP/50PA (β=1). ■: left segment; ●: right segment.

When doping an electron into the triblock copolymer nPA/xPPP/nPA, it is found that the doped electron is always localized in one of the PA segments and a polaron will be formed; and this is independent of the size of the PPP segment or the strength of the interfacial coupling. In addition, no spontaneous tunnelling is found. This kind of confinement will persist, even if the segment of PA is as small as 4 (CH) units. Therefore, in triblock well-barrier-well copolymers with strong electron-phonon interactions, the injected charges tend to be confined in one of the well parts of the copolymer, rather than to extend over the whole chain. This kind of confinement provides a larger recombination probability for opposite-charged carriers. Hence, it is expected that higher electroluminescence efficiency can be obtained by using such a triblock heterostructure copolymer than using homopolymers.

4. Conclusion

We have presented a tight-binding calculation to describe the triblock copolymers xPA/nPPP/yPA and xPPP/nPA/yPPP. Here the interfacial coupling between the homopolymer segments is attributed to the hopping of π-electrons and the coupling of σ-bonds. For xPA/xPPP/xPA structures, the interfacial coupling has a great influence on the band gap when x is small, but has little effect when $x \geq 20$. For nPPP/xPA/nPPP structures, the band gap varies with the PA segment length over a wide range, from 1.32 to 2.74eV, but for the nPA/xPPP/nPA, the band gap will not change with the PPP segment length. It is found that a spontaneous tunnelling phenomenon could take place in copolymer structures. Furthermore, the polaron caused by doping an electron into nPA/xPPP/nPA will tend to be confined in one of the well (PA) parts. This kind of confinement may lead to increasing electron–hole recombination probability. Referring to Refs.[26,27], the study of polarons transferring in copolymers under an applied electric field will be our future research work.

References

[1] Hu B, Zhang N and Karasz F E 1998 *J. Appl. Phys.* **83** 6002
[2] Wudl F, Kobayashi M and Heeger A J 1994 *J. Org. Chem.* **49** 3382
[3] Kyllo E M *et al* 2001 *Synth. Met.* **116** 189
[4] Zheng Q B *et al* 1998 *Synth. Met.* **97** 13
[5] Ma D *et al* 1999 *Synth. Met.* **112** 251
[6] Luzzati S, Panigoni M and Catellani M 2001 *Synth. Met.* **116** 171
[7] Terrill R H, Hutchison J E and Murry R W 1997 *J. Phys. Chem.* B **101** 1535
[8] Huang J S *et al* 1999 *J. Phys. D: Appl. Phys.* **32** 2841
[9] Hernández V *et al* 1994 *Synth. Met.* **84** 591
[10] Meyers F, Heeger A J and Brédas J L 1992 *J. Chem. Phys.* **97** 2750
[11] Liu D S *et al* 2001 *Acta Phys. Sin.* **50** 1763 (in Chinese)
Liu D S, Xie S J, Han S H 2000 *Acta Phys. Sin.* **49** 1556 (in Chinese)
[12] Kim S H and Jo W H 1998 *J. Chem. Phys.* **108** 4267
[13] Toussaint J M and Brédas J L 1991 *J. Chem. Phys.* **94** 8122
[14] Alemán C *et al* 1998 *J. Org. Chem.* **63** 1041
[15] He Y and Kanicki J 2000 *Appl. Phys. Lett.* **76** 661
[16] Quattrocchi C *et al* 1993 *Macromolecules* **26** 1260
[17] Mulazzi E *et al* 1992 *Phys. Rev.* B **45** 9439
[18] Ruckh R *et al* 1986 *J. Chem. Phys.* **85** 2797
Ruckh R *et al* 1987 *J. Chem. Phys.* **87** 5007
[19] Piaggi A, Tubino R and Colombo L 1995 *Phys. Rev.* B **51** 1624
[20] Moses D *et al* 1982 *Phys. Rev.* B **26** 3361
[21] Leising G, Pichler K and Stelzer F 1989 *Electronic Properties of Conjugated Polymers* III (Heidelberg: Springer) p100
[22] Xie S J *et al* 1995 *Phys. Rev.* B **51** 11928
[23] Su W P, Schriffer J R and Heeger A J 1979 *Phys. Rev. Lett.* **42** 1698
Su W P, Schriffer J R and Heeger A J 1980 *Phys. Rev.* B **22** 2099
[24] Xu C X *et al* 1999 *Appl. Phys. Lett.* **75** 1827
[25] Liu D S *et al* 2000 *J. Phys.: Condens. Matter* **12** 4333
[26] Fu R L *et al* 1998 *Acta Phys. Sin.* **47** 94 (in Chinese)
[27] Zhang C *et al* 1999 *Acta Phys. Sin.* **48** 917 (in Chinese)