Electronic structure of polyacetylene and poly(*p*-phenylene) diblock copolymers

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Abstract. The electronic structure of diblock copolymers consisting of poly(p-phenylene) and polyacetylene were studied in the framework of an inter-component coupling model. It was found that the band gaps could be tuned by the proportion of the homopolymers. The interfacial coupling between the components also affected the band gaps obviously. Localized states and hybridized states appeared in copolymers due to the interactions between the homopolymers. The doped charges accumulated in its one segment of a copolymer. The accumulation condition is discussed.

1. Introduction

The fabrication and potential applications of organic light emitting diodes (OLEDs) have excited great interest in the synthesis of organic polymers with a high migration of electron–holes, high radiative efficiency and the desired emission colour [1, 2]. Two common strategies for the organic materials could be applied to do this; one method is to attach electron donating or withdrawing side groups, another is to alternate conjugated and non-conjugated segments [3–6]. By mixing two or more homopolymers, one has the possibility of creating new organic materials that will combine some of the properties of each component. For example, poly(p-phenylene vinylene) (PPV), the first organic polymer used in OLEDs [2], could be seen as a copolymer consisting alternately of poly(p-phenylene) (PPP) and polyacetylene (PA). It could be expected that PPP and PA copolymer could emit light over the whole visible range by changing the extent of the block copolymer sequences. A copolymer of PPV and DMPPV (poly(2,5-dimethoxy-1,4-phenylene vinylene)) presents an enhanced efficiency with respect to PPV alone [6].

Up to now, two kinds of copolymers have been widely synthesized, diblock and multiblock copolymers. A diblock copolymer consists of two segments of homopolymers having a configuration $-(A_x)-(B_y)-$, a multiblock copolymer having a configuration such as $[-(A_x)-(B_y)-]_n$. To determine the evolution of the geometric structure and electronic properties, Meyers *et al* carried out the Austin-Model 1 (AM1) geometry optimization and valence effective Hamiltonian (VEH) band-structure calculations [7]. Jenekhe and Chen considered the

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copolymer chain as a one-dimensional quantum well system, the components having different well depths. By calculating the HOMO and LUMO the band structure of the copolymer was determined [8]. All the studies revealed that copolymers were similar to the homopolymers in structure and properties. In this paper, we extended the tight-binding model to the copolymers by supposing an interaction between the components. This model permits one to study a copolymer chain with any sizes and any boundary conditions. In section 2, the model Hamiltonian is established and the scheme of a self-consistent calculation is also outlined. In section 3 we describe the results of our numerical computation and discuss the effects of inter-component interactions. Finally, in section 4 our conclusions are summarized.

2. Model and formula

PPP and PA are well known organic conjugated polymers with quasi-one-dimensional chain structures. To distinguish them from copolymers, we call them 'homopolymers' hereafter. These homopolymers can be well modelled in the framework of the tight-binding approximation and have been widely studied [9–11]. Soliton theory found from the study on PA is the representative theory. Considering a diblock copolymer consisting of homopolymer PPP and PA, a $-(PPP_x)-(PA_y)-$ chain for the case of $x = y = 2$ is sketched in figure 1. It should be stressed that building a block copolymer with alternating sequences of precisely defined length was not a trivial synthesis to perform. However, novel polymerization schemes such as ring opening metathesis polymerization appears capable of opening the way to appropriate synthesis routes. Electrochemical synthesis of block conjugated copolymers via controlled cycling of electrochemical potential provides the possibility of synthesizing copolymers with varied block contents.
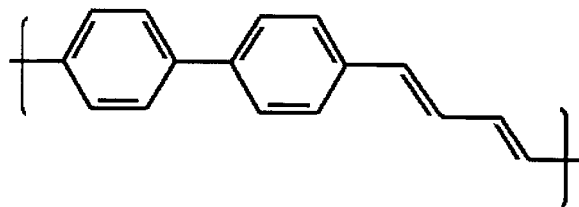

Figure 1. Molecular structure of 2PPP/2PA copolymer.

A diblock copolymer chain could be thought of as two homopolymer chains interacting via the ends. π-Electrons transfer along the homopolymer chains as well as transferring from one homopolymer to another through the connecting bond of the two blocks. The transition integral depends upon the connecting bond. In the tight-binding approximation, the Hamiltonian can be written as

$$H = -\sum_{n,s} t_{n,n+1}(c^+_{n+1,s}c_{n,s} + c^+_{n,s}c_{n+1,s}) + \sum_n \frac{1}{2}K_n(u_{n+1} - u_n)^2 \qquad (1)$$

where $t_{n,n+1}$ is the electron transition integral between site n and $n+1$ or between the end sites of the two components through the connecting bond, which was modulated due to the possible lattice distortion. For the PPP component we took $t_{n,n+1} = t_1 - \alpha_1(u_{n+1} - u_n) - t'_1\cos(n\pi/2)$ [12] and for PA we took $t_{n,n+1} = t_2 - \alpha_2(u_{n+1} - u_n)$ [9], u_n being the deviation of atoms. t_1 (or t_2) is the integral constant for a uniform structure and $\alpha_1(\alpha_2)$ the electron–phonon coupling parameter. t'_1 is a small value introduced to preserve the four-period structure of PPP. $c^+_{n,s}(c_{n,s})$ stands for the creation (annihilation) operator of electrons on site n with spin s. The distortion
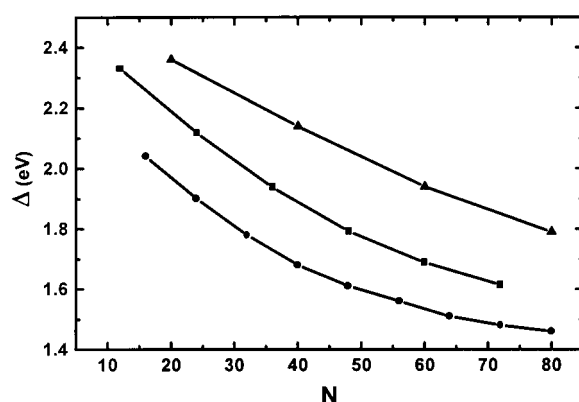
Figure 2. Evolutions of band gaps with the lengths of –(PPP$_x$)–(PA$_y$)– chains at different ratios x:y (▲, 2:1; ■, 1:1; and ●, 1:2).

of the lattice would result in an increase of the site potential energy, which was included in the second term of equation (1), and K_n (=K_1 in PPP and =K_2 in PA) is the spring constant.

Interactions between the components are described by a parameter β such that

$$t_{12} = \beta(t_1 + t_2)/2$$
$$\alpha_{12} = \beta(\alpha_1 + \alpha_2)/2$$
$$K_{12} = \beta(K_1 + K_2)/2 \qquad (2)$$

which gives the electronic transfer integral t_{12}, the electron–phonon coupling constant α_{12} and the spring constant K_{12} of the bond connecting the facing ends of the two components. If $\beta = 0$ the result is two isolated components.

The eigenvalue $\varepsilon_{\mu,s}$ and eigenstate $\psi_{\mu,s} = \sum_{n,s} Z_{\mu,n,s}|n\rangle$ were obtained by solving the eigenequation

$$-t_{n-1,n}Z_{\mu,n-1,s} - t_{n,n+1}Z_{\mu,n+1,s} = \varepsilon_{\mu,s}Z_{\mu,n,s} \qquad (3)$$

which depends upon the lattice configuration $\{u_n\}$. A stable lattice structure should have the minimum value of total energy

$$E = \sum_{\mu,s}{}' \varepsilon_{\mu,s} + \frac{1}{2}\sum_n K_n(u_{n+1} - u_n)^2. \qquad (4)$$

Through the perturbation theory we could obtain the static equilibrium condition of the lattice configuration determined inversely by the eigenstates. The deduction was trivial and can be found elsewhere.

The calculation procedure was as follows. For a given polymer chain, the electronic eigenequation was solved for an initial configuration. To find that whether the total energy was at a minimum the obtained eigenvalues were substituted into equation (4). If the energy was not at a minimum, we used the new configuration obtained from the static equilibrium condition to repeat the calculation until the difference between the total energy from two successive iterations was less than 10^{-8}. In the present calculation, a periodic boundary condition for the copolymer chain was adopted.

3. Results and discussion

For homopolymer PPP, we took the parameters, $t_1 = 2.5$ eV, $t'_1 = 1.0$ eV, $K_1 = 2100.0$ eV nm^{-2}, $\alpha_1 = 45.0$ eV nm^{-1}, which correspond to the band gap of PPP $E_g \approx 2.73$ eV.
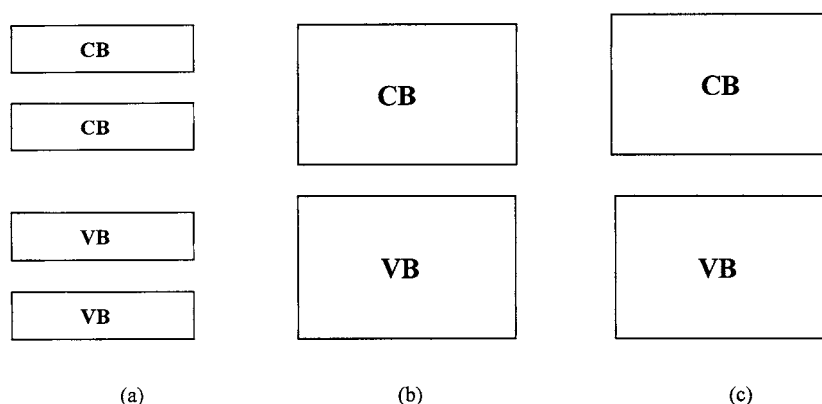
Figure 3. Band structures of PPP, PA and their copolymer $-(PPP_x)-(PA_y)-$: (a) PPP, (b) PA and (c) $-(PPP_{15})-(PA_{30})-$.

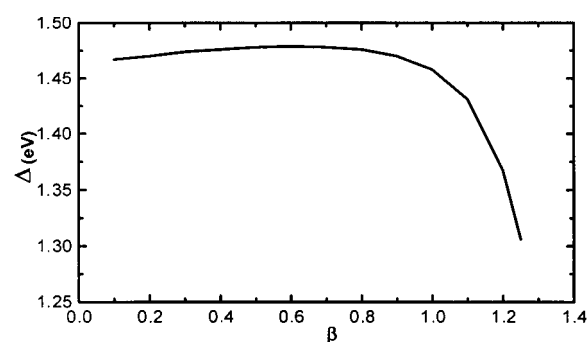**Figure 4.** Dependence of the band gap of copolymer $-(PPP_{10})-(PA_{20})-$ with the interfacial coupling β.

For component PA, we took $t_2 = 2.5$ eV, $K_2 = 2100.0$ eV nm^{-2}, $\alpha_2 = 41.0$ eV nm^{-1}, corresponding to $E_g \approx 1.30$ eV. The calculated band gaps of the two components were consistent with the experimental data [10, 13]. Defining the dimensionless parameter $\phi_n = (-1)^n (\alpha/t_0) u_n$ and $\lambda_j = 2\alpha_j^2/\pi K_j t_j$, we found that PPP had a stronger electron–phonon coupling ($\lambda_{PPP} = 0.246$) than PA ($\lambda_{PA} = 0.204$).

3.1. Band gaps

It has been predicted that the band gap of a copolymer can be tuned by the components. The present calculations showed that the band gap of the copolymer was not the simple arithmetic average of those of the component homopolymers. Two factors affect the band gap: the proportions of the components and interactions between the components. Figure 2 shows the dependence of the band gaps on the proportion of the components. It can be seen that the band gaps vary between the larger band gap of component PPP and the smaller one of PA. The band structures of the components and the diblock copolymer are sketched in figure 3. For a given proportion of the components, dependence of the band gap of the copolymer on the interactions between the components is shown in figure 4. The band gap Δ increases non-obviously with the increasing of the component coupling strength (β). At $\beta \approx 0.7$, Δ reaches its maximum.
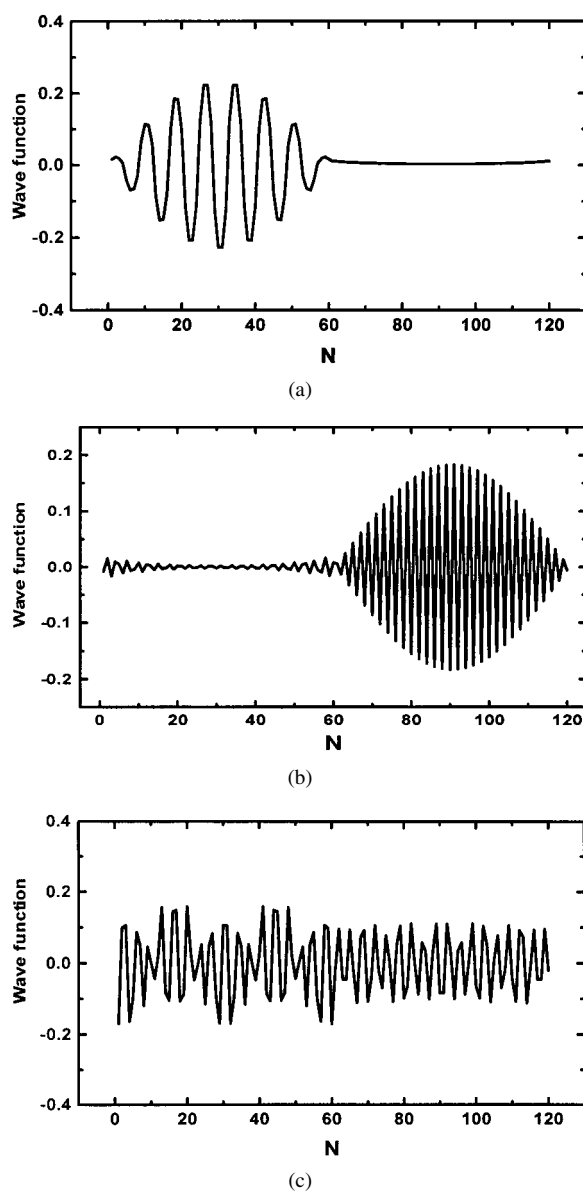
Figure 5. Electronic states in copolymer $-(PPP_{15})-(PA_{30})-$: (a) localized electronic states in PPP, (b) localized electronic states in PA and (c) hybridized electronic states.

With further strengthening of the component interactions Δ decreases rapidly. Band gaps of $-(PPP_x)-(PA_y)-$ copolymers can be decomposed into two terms

$$E_g = \Delta E^{1-4} + \Delta E^{\{u_n\}} \tag{5}$$

where ΔE^{1-4} corresponds to a contribution from the interaction between the both-side atoms in the aromatic rings of segment PPP; $\Delta E^{\{u_n\}}$ refers to a gap arising from bond-length alteration ($\{u_n\}$) along the conjugated carbon backbond. ΔE^{1-4} can be obtained by setting $u_n = 0$. It was found that the band gaps of $-(PPP_x)-(PA_y)-$ were mainly dominated by the bond-length

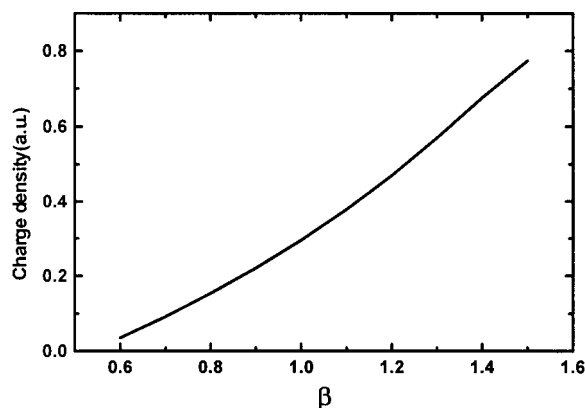**Figure 6.** Evolution of the bond charge densities on the connecting bond with the β in copolymer $-(PPP_{15})-(PA_{30})-$.

alternation. For example, at $\beta = 1.0$, the contribution of ΔE^{1-4} to the band gap was 0.178 eV, while the contribution coming from the bond-length alteration was $\Delta E^{\{u_n\}} = 1.280$ eV.

3.2. Hybridized electronic states

When homopolymers combined into a copolymer, the electronic states changed a great deal. Electrons could transfer from one component to another through the connecting bond. As shown in figure 5, two typical kinds of electronic states appeared in copolymers: 'localized' states and 'hybridized' states. Here 'localized states' means that the eigenstates were confined in one component. Hybridized states means that the eigenstates extended along the whole copolymer chain. If we checked the position of the hybridized states in the energy bands, it was found that the levels of the hybridized states had fallen into the overlapped range of the bands of the homopolymers. The non-overlapped range corresponded to the localized states. The coexistence of localized and hybridized states is characteristic of copolymers. It differs absolutely from homopolymers.

3.3. Interface potentials

We define the bond charge density as

$$G_{n,n+1} = \frac{1}{2}\langle c_{n+1,s}^+ c_{n,s} + c_{n,s}^+ c_{n+1,s}\rangle = \sum_{ooc} Z_{\mu,n,s} Z_{\mu,n+1,s}. \tag{6}$$

We calculated the charge on the connecting bond of the components. Its dependence on the coupling β is shown in figure 6. With the increasing of the component interactions, the charge density on the connecting bond increases. In the case of weak coupling, the charges on the connecting bond were less than the average bond charge within the components. It indicates that the interface of the components acted as a high energy barrier for electrons [14]. However, in the case of strong coupling, the charges on this bond were more than the average value and the interface acted as a low energy barrier. From this point of view, a weak coupling is unfavourable for the transfer of electrons.

3.4. Doping states

It is well known that electron or hole doping in conjugated polymers results in the formation of excitations called solitons, polarons and bipolarons. In homopolymer PA, all the three kinds of excitations could be excited. But in PPP, only polarons and bipolarons were possible due to its non-degenerate ground state. In this paper, we studied the doping states in diblock copolymer $-(PPP_x)-(PA_y)-$. It was found that the doped electrons or holes always accumulate in the PA segment when y is large enough. With the shortening of the PA segment, the electrons can transfer into the PPP part through the connecting bond. One-electron doping will excite a polaron, and two-electron doping will excite a soliton–antisoliton pair. A charged soliton can also be excited in the PA segment, but it requires that the PA segment consists of odd (CH) groups in order to meet the topological demand of a soliton. If the PA segment is short enough, $y = 8$, for example, it was found that the doped electrons accumulated either in segment PPP or in segment PA, depending upon the strength of the interface coupling β. When $\beta \geqslant 0.7$, they still accumulated in segment PA. However when $\beta < 0.7$, the doped electrons could accumulate either in the PPP segment or in PA, depending upon the initial doping condition. The reason for this was that as the interface acted as a high energy barrier in the case of small β, the doped electrons could not jump over the barrier.

4. Conclusion

Copolymers are in fact the one-dimensional organic heterojunctions or superlattices [8, 15]. They can store charges in their component parts [14, 16]. We have extended the tight-binding model to the $-(PPP_x)-(PA_y)-$ diblock copolymer by supposing an interfacial interaction between the homopolymers. The band gaps of copolymers come from the contribution of both the aromatic rings and the bond-length alternations. It predicts the possibility to operate a fine tuning of the band gap value over the whole visible range by changing the proportion of segments and the interface couplings. Coexistence of 'localized' and 'hybridized' electronic states is the prominent characteristic of copolymers, which obviously differ from the homopolymers. It was found that the interface of the components acted as either a high energy barrier or a low energy barrier, depending upon the strength of the interfacial coupling. Finally, the doping states of copolymer were studied. The doped electrons or holes always accumulated in the PA segment when the length of PA is long enough.

Acknowledgment

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