Transport of carriers in a semiconductor polymer random chain: a renormalization approach

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Abstract. We present a theoretical study for the quantum transport of carriers in a random semiconductor polymer poly(p-phenylene vinylene) (PPV) chain with the benzoid rings partially replaced by quinoid rings. A renormalization approach maps the polymeric chain into an effective one-dimensional lattice and the transmission coefficient as a function of energy is computed by transfer matrix techniques. In the case of randomly-distributed quinoid rings the spectrum shows narrow peaks in the conduction and the valence bands which indicate the presence of special resonant electron and holes states, lying within a larger fraction of localized states. The obtained density of states (DOS) shows a bandgap smaller than the transmission gap between the electron and the hole resonance peaks, which implies that an electric voltage larger than the band gap is required to inject electrons and holes into the polymer. This could explain why the operating voltage of PPV light-emitting diodes (LEDs) is larger than the semiconductor gap, in sharp contrast to conventional semiconducting LEDs.

1. Introduction

Although electroluminescence (EL) in organic semiconductors has been known for a considerable time [1–4], the interest has recently been revived by the observation of high efficiencies in several specially fabricated polymer films [5, 6]. It has been shown that conjugated polymers, in particular poly(p-phenylene vinylene) (PPV), can be used as emissive layers in light-emitting diodes (LEDs) exhibiting high solid-state photoluminescent efficiencies with emission in the visible part of the spectrum. In these materials, electrons and holes are injected from the contacts and subsequently undergo a radiative recombination. Thus, an appropriate description for the nature of the carrier mobility and the corresponding transport properties is of particular importance for understanding the EL mechanism. In many experimental studies of PPV both photoexcitation and transport properties are examined [7–10]. In the theoretical side a major point is still a controversy surrounding the understanding of the mechanism for the primary photoexcitation. In order to explain the recent experiments both band-based and exciton-based models have been proposed, with most of the debate centred at the Coulomb electron–hole binding energy of the system. If the binding energy is small then a band description may be appropriate while if electrons and holes are strongly bound the exciton-based model seems to be more reasonable [11].

A full quantum description for the dynamics of realistic polymers is prohibitively complicated due to the large number of lattice degrees of freedom for the coupled lattice–electron system. Thus, one is forced to apply a kind of adiabatic approximation, separating

the electronic from the lattice degrees of freedom. However, the remaining problem is still very difficult particularly if the 'quenched' structures caused by the electron–lattice coupling are considered. In this respect renormalization ideas can yield a simple powerful scheme for the treatment of the polymer electronic structure, as was originally applied for the polyacene [12, 13]. In this scheme all members of the quasi-one-dimensional polymers can be formally reduced to a polyacetylene structure and hence their electronic properties can be solved in a generic way. Recently, Galvao *et al* [14] with the same technique studied the decisive role of the disorder, due to the random distribution of quinoid and benzoid rings in a polyaniline chain. This method can be also used to study very long disordered chains of realistic size.

We use the renormalization method combined with the transfer-matrix technique in order to study electron and hole diffusion in a PPV chain with a portion of the benzoid rings randomly replaced by quinoid rings. We give results for the transmission spectrum which demonstrate sharp resonant peaks in both the conduction and the valence bands. The corresponding density of states (DOS) is also calculated via negative-factor-counting (NFC) methods. The comparison between the transmission and the corresponding DOS shows that the transmission peaks are much narrower than the corresponding DOS bands and the obtained transmission gap is wider than the band gap. The latter feature implies that the applied electric voltage for injecting electrons and holes into the polymer should be larger than the band gap. This presents a possible explanation for the experimental fact concerning the magnitude of the operating voltage in PPV LEDs, which is usually larger than the semiconductor gap in contrast to conventional semiconductor LEDs.

2. The renormalization formula for the random PPV chain

The basic chemical bond structure of a PPV chain is shown in figure 1(*a*), where the chain is shown to consist of benzoid rings. It has been experimentally established that the benzoid rings can be substituted by quinoid rings upon oxidation or doping of the material with impurities [15]. On the other hand, part of the injected electrons or holes can be trapped by the lattice distortions to form quenched bipolarons which also correspond to a quinoid structure, as previously suggested in polyaniline chains [14]. The substitution of a benzoid ring with a quinoid ring is illustrated in figure 1(*b*). After establishing the structure of the conjugated PPV chains our main aim is to study the influence of the randomly distributed quinoid substitutions on the diffusive properties of the itinerant electrons and holes. We describe the system of π electrons in the carbon backbone by introducing a tight-binding Hamiltonian scheme. It must be pointed out that the calculation of the transmission coefficient and the corresponding DOS requires a choice for the tight-binding parameters which can represent at best the family of PPVs (see table 1). It must also be noted that the carbon to which the ligands are attached is distinguished from the rest of the carbons in the rings by a different site energy [16].

We proceed by exploring the basic idea of the renormalization approach, which is a decimation procedure for certain degrees of freedom of the system [17] by keeping the relevant properties unchanged. This is illustrated in the simple example of a system which consists of three atoms with the middle one decimated. In this case we can easily obtain an effective two-atom system by equating the overall transfer matrices for the original three-atom and the resulting systems via

$$\begin{pmatrix} \frac{E-\epsilon_3}{t_{34}} & \frac{-t_{23}}{t_{34}} \\ 1 & 0 \end{pmatrix} \begin{pmatrix} \frac{E-\epsilon_2}{t_{23}} & \frac{-t_{12}}{t_{23}} \\ 1 & 0 \end{pmatrix} \begin{pmatrix} \frac{E-\epsilon_1}{t_{12}} & \frac{-t_{01}}{t_{12}} \\ 1 & 0 \end{pmatrix} = \begin{pmatrix} \frac{E-\epsilon_3^{(1)}}{t_{34}} & \frac{-t_{13}^{(1)}}{t_{34}} \\ 1 & 0 \end{pmatrix} \begin{pmatrix} \frac{E-\epsilon_1^{(1)}}{t_{13}^{(1)}} & \frac{-t_{01}}{t_{13}^{(1)}} \\ 1 & 0 \end{pmatrix} \quad (1)$$
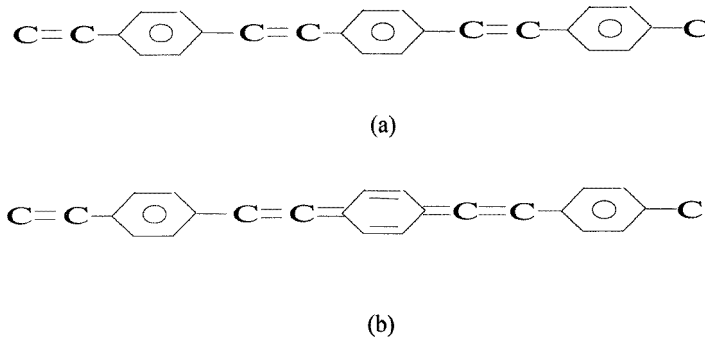
(a)

(b)

Figure 1. The possible configurations for the PPV chain: (a) a pure chain consisting of benzoid rings; (b) a chain with a bipolaron (substitution of a benzoid ring with a quinoid ring).

Table 1. Hückel parameters for substituted PPV chains, in units of $\beta = 2.5$ eV.

Carbon atoms	Site energies	Chemical bonds	Hoppings
Ring carbon with ligand	0.4	C–C in benzoid rings	−1.0
Ring carbon without ligand	0.0	C–C in quinoid rings	−0.76
Carbon outside the rings	0.0	C=C in quinoid rings	−1.24
		C–C outside the rings	−0.76
		C=C outside the rings	−1.24

where t_{ij} denotes the hopping between sites i and j, ϵ_i is the ith site energy and the original system consists of sites 1, 2, 3 with 0, 4 the outmost left and right boundary sites. The effective site energies and the hoppings of the renormalized two-atom system are easily obtained via

$$\epsilon_1^{(1)} = \epsilon_1 + \frac{t_{12}^2}{E - \epsilon_2} \tag{2}$$

$$\epsilon_3^{(1)} = \epsilon_3 + \frac{t_{23}^2}{E - \epsilon_2} \tag{3}$$

$$t_{13}^{(1)} = \frac{t_{12}t_{23}}{E - \epsilon_2}. \tag{4}$$

The corresponding renormalization steps of an eight-atom unit including a ring and two ligands for a realistic PPV system are shown in figure 2. In this procedure such an eight-atom unit also reduces to an effective two-atom cluster, so that the whole system eventually becomes a monoatomic chain. The corresponding site energies and the hoppings of the resulting two-atom cluster of figure 2(c) are

$$\epsilon_0^{eff} = a_0 + \frac{t_{01}^2}{E - \alpha - \tau^2/(E - \beta)} \tag{5}$$

$$\epsilon_7^{eff} = a_7 + \frac{t_{47}^2}{E - \beta - \tau^2/(E - \alpha)} \tag{6}$$

$$t^{eff} = \frac{t_{01}t_{47}}{(E - \alpha)(E - \beta) - \tau^2} \tag{7}$$

where a_i, $i = 0, 1, 2, \ldots, 7$, are the site energies of the carbon atoms shown in figure 2(a),
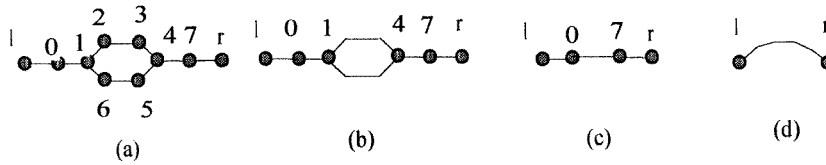
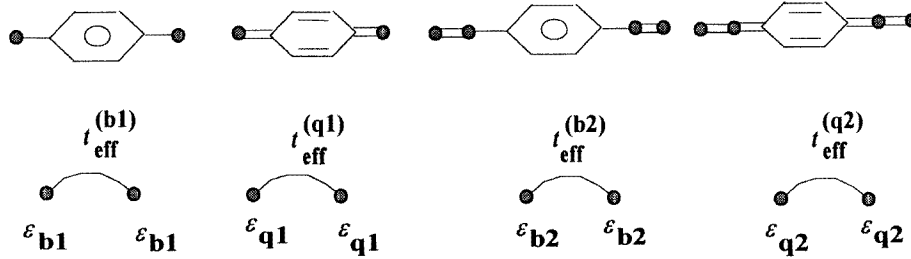**Figure 2.** The renormalization steps of the PPV chain into a monoatomic chain.

Figure 3. The effective two-atom clusters obtained by renormalization from benzoid and quinoid rings.

t_{ij} is the hopping strength between i and j and

$$\alpha = a_1 + \frac{t_{12}^2}{E - a_2} + \frac{t_{16}^2}{E - a_6} + \frac{t_{12}t_{23}}{(E - a_2)(E - a_3 - t_{23}^2/(E - a_2))}$$
$$+ \frac{t_{16}t_{56}}{(E - a_6)(E - a_5 - t_{56}^2/(E - a_6))} \tag{8}$$

$$\beta = a_4 + \frac{t_{34}^2}{E - a_3} + \frac{t_{45}^2}{E - a_5} + \frac{t_{23}t_{34}}{(E - a_3)(E - a_2 - t_{23}^2/(E - a_3))}$$
$$+ \frac{t_{16}t_{56}}{(E - a_5)(E - a_6 - t_{56}^2/(E - a_5))} \tag{9}$$

$$\tau = \frac{t_{12}t_{23}t_{34}}{(E - a_2)(E - a_3) - t_{23}^2} + \frac{t_{16}t_{45}t_{56}}{(E - a_5)(E - a_6) - t_{56}^2}. \tag{10}$$

For benzoid and quinoid rings, the obtained two-atom clusters are symmetric as shown in figure 3. Thus, the obtained effective monoatomic chain coincides with the random dimer model (RDM) proposed by Dunlap *et al* [18], apart from the fact that the site energies and the hopping integrals are now energy (E)-dependent.

On the basis of the obtained effective monoatomic lattice the transmission coefficient can be calculated via the transfer-matrix technique [19]. The Schrödinger equation written as

$$t_{n,n+1}^{eff}\psi_{n+1} + t_{n,n-1}^{eff}\psi_{n-1} = (E - \epsilon_n)\psi_n^{eff} \tag{11}$$

where ψ_n denotes the amplitude of the wavefunction on the nth site, $t_{n,n+1}^{eff}$ and ϵ_n^{eff} are the effective hopping and effective site energy, respectively, can be rewritten in terms of the transfer matrix

$$\begin{pmatrix} \psi_{n+1} \\ \psi_n \end{pmatrix} = A_n \begin{pmatrix} \psi_n \\ \psi_{n-1} \end{pmatrix} \tag{12}$$

with

$$A_n = \begin{pmatrix} \frac{E-\epsilon_n^{eff}}{t_{n,n+1}^{\text{eff}}} & \frac{-t_{n,n-1}^{eff}}{t_{n,n+1}^{eff}} \\ 1 & 0 \end{pmatrix}. \tag{13}$$

In the case of a finite $(N+1)$-site chain, the coefficients at the two ends are related to each other via

$$\begin{pmatrix} \psi_N \\ \psi_{N-1} \end{pmatrix} = A_{N-1} A_{N-2} \dots A_1 \begin{pmatrix} \psi_1 \\ \psi_0 \end{pmatrix} \equiv T \begin{pmatrix} \psi_1 \\ \psi_0 \end{pmatrix}. \tag{14}$$

In order to compute the transmission coefficient we insert the finite lattice in a pure chain and inject an electron from the left. The expansion coefficients of the scattered states can be written as $\psi_n = e^{ikn} + r e^{-ikn}$ for $n \leqslant 0$ and $\psi_n = t e^{ikn}$ for $n \geqslant N$, where k is the Bloch wavevector in the pure chain, and r and t are related to the reflected and transmitted amplitudes, respectively. The corresponding transmission coefficient can be directly obtained from the formula

$$|t|^2 = \frac{4 \sin^2(k)}{[T_{21} - T_{12} + (T_{22} - T_{11})\cos(k)]^2 + (T_{11} + T_{22})^2 \sin^2(k)} \tag{15}$$

where $T_{11}, T_{12}, T_{21}, T_{22}$ are the elements of the transfer matrix T.

3. Numerical results

3.1. The transmission coefficient

We have calculated the transmission coefficient as a function of the energy for the PPV chains with various densities of the quinoid-ring substitutions. The effective chain obtained from the renormalization scheme contains 2000 sites and the quinoid rings are randomly distributed in the host chain by taking averages over 100 random configurations to suppress the statistical fluctuations. The used Hückel parameters are shown in table 1.

The obtained effective chain from the renormalization process consists of four types of dimers, which are randomly mixed. This is due to the fact that within the renormalization scheme every group of one quinoid ring associated with two ligands on its sides reduces to a dimer of sites with energies denoted as ϵ_{q1}, while the site energies of the effective dimers for the groups of one quinoid ring with four ligands and one benzoid ring with two and four ligands are ϵ_{q2}, ϵ_{b1} and ϵ_{b2}, respectively (see figure 3). The effective hopping strengths for the four groups become t_{eff}^{q1}, t_{eff}^{q2}, t_{eff}^{b1} and t_{eff}^{b2}, respectively. It must be noted that the obtained disordered chain seems to have stronger spatial correlations than the RDM since it corresponds to a real polymer with randomly-distributed benzoid and quinoid rings. Thus, it is natural that in the PPV structure more complicated transmission resonances are expected. In the actual calculations the concentration of the quinoid rings is denoted by p, which varies from 0 to 50%, while the random positions of the quinoid rings are numerically generated.

The obtained transmission coefficients as a function of the energy for various concentrations p of the quinoid rings are plotted in figure 4. At $p = 0$ there is no disorder and the transmission spectrum shows a band structure with the conduction and the valence subbands separated by gaps. In the disordered case ($p > 0$) the transmission bands gradually reduce to two resonant peaks for higher p, one at the conduction band the other at the valence band. The situation is similar to the resonant tunnelling in the RDM, except that in the RDM only one such resonant level exists [18]. Obviously the
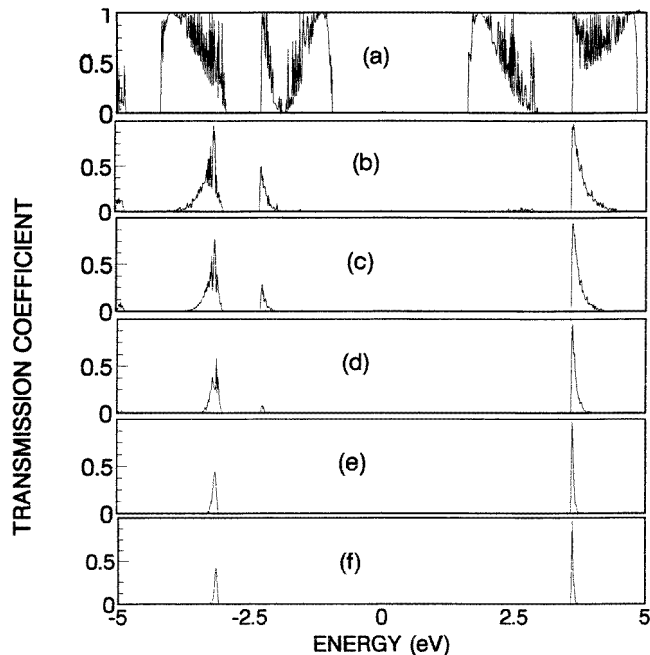
Figure 4. The transmission coefficients as a function of the energy for a PPV chain with 2000 rings. The concentration of the quinoid rings is (a) 0.0, (b) 0.01, (c) 0.02, (d) 0.05, (e) 0.25, and (f) 0.5.

peaks in figure 4 correspond to extended states in such a random structure but it must be remembered that the vast majority of states in the random case ($p > 0$) are localized, with a small transmission coefficient exponentially decaying with the size.

3.2. The density of states (DOS)

In order to specify the changes in the band structure due to the structural disorder which may be important for the luminescence properties, we have also calculated the DOS using a NFC scheme [20]. The results for systems with the same quinoid-ring concentrations corresponding to figure 4 are shown in figure 5. We observe that in contrast to the drastical change in the transmission coefficient the band structure for small p displayed via the DOS remains almost the same as that of the ordered case. If p is further increased several small peaks appear within the gaps, which correspond to 'impurity' levels produced by the random structure. This behaviour in the presence of disorder together with the sharpness of the transmission peaks implies that most of the electron and hole states localize due to randomness in the quinoid ring distribution, except for the states near the resonant levels which are extended. This is very important for understanding EL in PPV, especially since the obtained gap in the transmission spectrum is much wider than the gap in the band structure so that a larger applied electric field is needed for injecting holes and electrons in the system. Our results are in agreement with what is experimentally found, since in contrast to the inorganic semiconductor devices the polymer LEDs typically begin to generate light at voltages much greater than their bandgap [21]. This fact was previously explained by a suggestion about additional barriers at the contacts. As it is a necessary condition for the
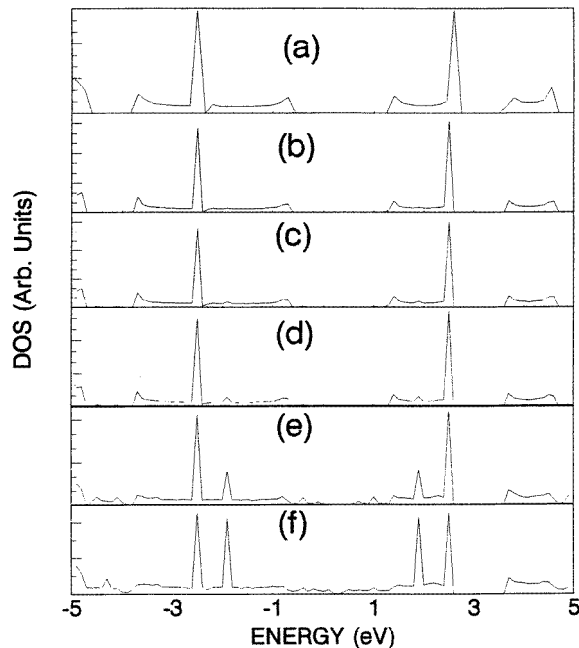
Figure 5. The DOS as a function of the energy of a PPV chain with 2000 rings. The concentration of quinoid rings is (a) 0.0, (b) 0.01, (c) 0.02, (d) 0.05, (e) 0.25, and (f) 0.5.

operation of a LED to inject mobile holes and electrons from the contacts, our results which show a transmission gap larger than the bandgap provide a possible natural explanation of the PPV experiments.

4. Discussion and conclusions

We have mapped, via the renormalization method, a PPV chain with quenched disorder into an effective one-dimensional lattice. Thus, we can study the diffusive properties of electrons and holes by calculating the transmission coefficient and the density of states (DOS) for systems at various concentrations of the quinoid-ring substitutions. In the presence of disorder the transmission bands reduce to sharp resonant peaks but the DOS structure remains almost unchanged for small quinoid-ring concentrations. Moreover, the two transmission resonant peaks which appear both in the conduction and the valence bands have a distance between them larger than the energy gap. These results can provide a natural explanation of the experimental fact concerning the operation voltage of a polymer LED which is larger than the bandgap of the material. It must also be pointed out that the introduced simplified model for PPV makes our calculation only a primary study, since many more factors other than the disorder must be introduced into the model. However, the calculated electronic structure clearly shows new resonant features for the semiconducting polymers which may shed light on our understanding of the EL mechanism.

PPV opens a new chapter in polymer material science since it is a very promising light-emitting semiconductor-like device, which has been studied, so far, mostly experimentally. There have not been many studies on the theoretical understanding of PPV and in this paper we have addressed the effect of disorder in the electronic structure. It must be

noted, however, that various kinds of disorder may exist in conjugated polymer systems, for example winding of the chains, random coupling between chains and random breaking points owing to the polymer finite lengths. In the present work we have only studied the influence of randomly-distributed substitutions by quinoid rings, and from the renormalization scheme it is revealed that both the benzoid and quinoid rings associated with the ligands reduce to dimers. Thus, one expects the existence of a correlated disorder structure, as in the RDM, to be a common feature for the PPV family. As a consequence, sharp resonant levels exist in both the conduction and the valence bands. It may also be expected that most of the non-resonant states are localized if the disorder level is high. These facts could have important implications on the exciton, polaron and other elementary excitation features, particularly if the Coulomb and electron–phonon interaction are included.

Acknowledgments

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