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Reverse polarization in conjugated heterocycle polythiophene*

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Reverse polarization in polythiophene under an applied electric field has been studied in the framework of the tight-binding model. It is found that the applied electronic field has a great influence on the excited states of polythiophene. The effect of the heteroatoms on the polarization has been calculated and analysed carefully. It is indicated that a reverse polarization of biexcitons in polythiophene will be observed more easily. The heteroatoms increase this reversed polarization strength apparently.

Keywords: reverse polarization, self-trapping exciton, heterocycle polymer
PACC: 7135, 6320, 3390

1. Introduction

In recent years, intensive research work[1−6] has been focused on the electroluminescence (EL) in organic polymers since the first light-emitting device (LED) based on poly(*p*-phenylenevinylene) (PPV) was demonstrated.[7] For application of electronic devices, the key research point is to study the behaviours of polymeric molecules under an applied electric field. Sun *et al*[8,9] have found that, in the nondegenerate *cis*-polyacetylene (*cis*-PA), an applied electric field induces a separation of positive and negative charges in the self-trapping excited states. The polarization of the self-trapping single-excited state is normal, but the polarity of this self-trapping biexcited state shows a reverse character. This means that when an excited polymeric molecule absorbs another photon, its electric dipole will be reversed. This phenomenon is called photoinduced polarization inversion (PIPI).[8] Wang *et al* have indicated that PIPI should be stable at least to some extent even when the effects of temperature and impurities are included.[10] Reverse polarization in ferroelectric materials including ferroelectric polymers has been studied for many years,[11−14] but in conducting polymers it is a new phenomenon. PIPI is an ultrafast process. Such a switching effect is very important not only for fundamental study, but also for possible technological applications. Investigation into the nature of PIPI will be instructive for developing novel functional materials with negative polarization and quantum switch devices.

The calculations for studying PIPI until now have been carried out in a *cis*-PA chain,[8,9] one of the simplest nondegenerate polymers. In fact, *cis*-PA is thermodynamically unstable, for it can be converted to trans-PA by being heated above 150°C.[15] Of all the other polymers with nondegenerate ground states, polythiophene (PT) as well as its oligomers have been widely used in the study of EL, PL (photoluminescence)[16−18] and spin transport.[19] The high chemical stability, solubility, and the low oxidation potentials[20] render these materials very attractive in the development of new molecular electronic devices.[1] A thiophene ring consists of a heteroatom sulfur, which represents a different series of compounds containing additional heteroatoms. A PT molecule can be regarded as a chain of sp^2 hybridized

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carbon atoms. The existence of heteroatoms can destroy the electron–hole symmetry, even there is not any e–e interaction. The effect of heteroatoms on the electronic structure and the vibrational properties of this kind of polymer has been carefully studied and some new phenomena resulting from the heteroatoms have been predicted.[21–24] In this paper, we study the relevant polarization phenomena in PT when an external electric field is applied. In Section 2 the theoretical formulation is presented. In Section 3 the calculation is carried out and the results are discussed. Finally in Section 4 a summary is given.

2. Theoretical formulation

A polythiophene molecule can be regarded as a chain of sp^2 hybridized carbon atoms analogous to that of *cis*-polyacetylene, and it is stabilized by a heteroatom which bonds covalently with neighbouring carbons to form the heterocycle. In the bulk of polythiophene, electron–hole interactions are considered to be significant for the binding of excitons and biexcitons.[25] For low-dimensional excitons and biexcitons, their binding energies are bigger than those of three dimensional ones. Interaction of electron–lattice can dominate the binding of an exciton and biexciton. So the polyene chain can be described in terms of an extended SSH model by lifting the degeneracy.[23,24] In the presence of an applied electric field with the strength E, the Hamiltonian can be written as

$$H = H_{\mathrm{e-p}} + H_{\mathrm{elastic}} + H_E + H_{\mathrm{b}} + H_{\mathrm{e-e}}, \quad (1)$$

$$\begin{aligned} H_{\mathrm{e-p}} = &-\sum_{n,s}\left[t_0 - \alpha\left(u_{n+1}-u_n\right) + (-1)^n t_1 \cos\frac{n\pi}{2}\right] \\ &\times \left(C^+_{n+1,s}C_{n,s} + \mathrm{h.c.}\right) \\ &-\sum_{n,s} t_2\left(C^+_{4n-3,s}C_{4n,s} + \mathrm{h.c.}\right) \\ &-\sum_{n,s} t_3\left(C^+_{4n,s}C_{4n,s} + C^+_{4n-3,s}C_{4n-3,s}\right), \end{aligned} \quad (2)$$

$$\begin{aligned} H_{\mathrm{elastic}} = &\frac{1}{2}K\sum_l (u_{l+1}-u_l)^2 \\ &+ \sum_l K'(u_{l+1}-u_l), \end{aligned} \quad (3)$$

$$H_E = \sum_{n,s} eE\,(na+u_n)C^+_{n,s}C_{n,s}, \quad (4)$$

$$H_{\mathrm{b}} = -qE\sum_l u_l, \quad (5)$$

$$\begin{aligned} H_{\mathrm{e-e}} = &U\sum_{n,s} C^+_{n,s}C_{n,s}C^+_{n,-s}C_{n,-s} \\ &+ V\sum_{n,s,s'} C^+_{n,s}C_{n,s}C^+_{n+1,s'}C_{n+1,s'}, \end{aligned} \quad (6)$$

where $H_{\mathrm{e-p}}$ describes the electron–lattice interaction of PT, in which the electron hopping between sites $4n-3$ and $4n$ via the heteroatom is given by the second term, where t_2 is the carbon–sulfur (C–S) coupling constant, and the third term represents the effective confinement of π electrons to the heteroatom (as shown in Fig.1). Taking the carbon binding energy to be the zero point, t_2 and t_3 (confinement parameters) will be approximately equal. We assume $t_2 = t_3$ in a numerical computation for simplicity. H_{elastic} expresses the elastic energy due to the displacement of carbon atoms, in which the second term is introduced in order to stabilize the free ends of the chain. H_{E} is the interaction of the electrons with the electric field E, whose direction is from the left to the right along the chain. H_{b} depicts the potential energy variation with the displacement of positive ions, and it will make the whole system remain stable in the electric field. In a neutral chain without doping, $q = e$. $H_{\mathrm{e-e}}$ is the e–e interaction, which is described by the extended Hubbard model and will be treated in an unrestricted Hartree–Fock approximation.[26] U is the usual on-site Hubbard energy and V represents the site–site interaction. The Hamilton describing *cis*-PA can be derived from the above equation by simply setting $t_2 = t_3 = 0$ and the cosine term is replaced with $\cos(n\pi)$.[8]

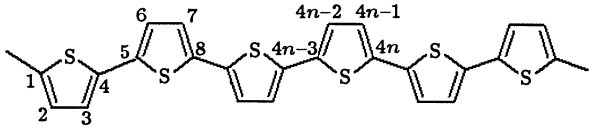


Fig.1. Schematic diagram of the structure of polythiophene. The constants t_0 and t_1 describe the hopping between the nearest-neighbouring carbon atoms such as $4n-3$ and $4n-2$, $4n-2$ and $4n-1$ or $4n-1$ and $4n$; t_2 describes the electron hopping between sites $4n-3$ and $4n$ via the heteroatom; t_3 describes the site energy in $4n-3$ and $4n$, which comes from the effective confinement of π electrons due to the heteroatom.

With a small deviation from the equilibrium configuration $\{u_n\}$, the static condition for the lattice can be derived by minimizing the total energy of the system which is characterized by the wavefunction

$$\psi_{\mu,s} = \sum_n Z_{\mu,n,s} |n\rangle,$$

$$F(n) + eE\left(\sum_{\mu,s}{}' Z_{\mu,n,s} Z_{\mu,n,s} - 1\right) = F(n-1), \quad (7)$$

where

$$F(n) = -K(u_{n+1} - u_n) - 2\alpha \sum_{\mu,s}{}' Z_{\mu,n,s} Z_{\mu,n+1,s} - \frac{4\alpha}{\pi}.$$

Here the prime means sum over all the occupied states only. Electronic eigenstate $Z_{\mu,n,s}$ corresponding to the eigenvalue $\varepsilon_{u,s}$ is determined by a single-particle eigen equation, through treating the e–e interaction by the mean-field method:

$$\begin{aligned} &-\left[t_0 - \alpha(u_n - u_{n-1}) - t_1 \cos\frac{(n-1)\pi}{2}\right] Z_{\mu,n-1,s} \\ &-\left[t_0 - \alpha(u_{n+1} - u_n) - t_1 \cos\frac{n\pi}{2}\right] Z_{\mu,n+1,s} \\ &-(t_2 Z_{\mu,n-3,s} + t_3 Z_{\mu,n,s})\,\Delta\left(\frac{n}{4}, \text{int}\right) \\ &-(t_2 Z_{\mu,n+3,s} + t_3 Z_{\mu,n,s})\,\Delta\left(\frac{n+3}{4}, \text{int}\right) \\ &+eE(na + u_n) Z_{\mu,n,s} = \varepsilon_{\mu,s} Z_{\mu,n,s}, \end{aligned} \quad (8)$$

where

$$\Delta(i, \text{int}) = \begin{cases} 1, & i = \text{integer}, \\ 0, & \text{otherwise}, \end{cases}$$

and the charge density distribution is given by

$$\rho_n = \sum_{\mu,s}{}' |Z_{\mu,n,s}|^2 - 1. \quad (9)$$

Equations (7) and (8) can be solved numerically in an iteration method to find the energy levels, charge density distribution and so on.

3. Results and discussion

Selecting parameters a=0.122nm, t_0=2.5eV, K=2100.0eV/nm^2, α=4.5eV/nm, t_1=0.27t_0, $t_2 = t_3 = 0.05t_0$,[23,24,27] the energy band gap of PT is calculated to be 2.15eV, which is very close to the experimental data.[28,29] The variation of bond-length of the ground state is shown in Fig.2 as the dash-dotted curve, from which the $4a$ periodic structure character of PT chains can be seen clearly. This result is also consistent with that obtained from the STO-3G optimized geometry.[30]

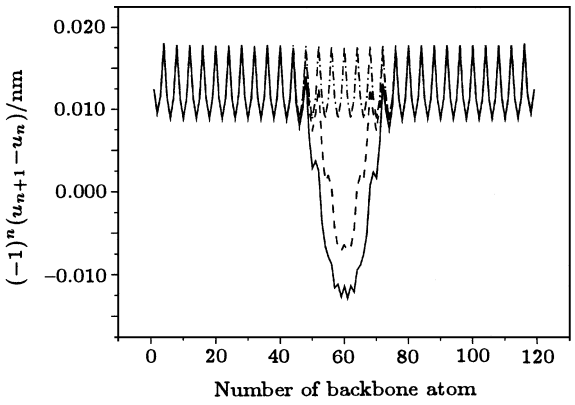


Fig.2. Lattice configurations of ground state, self-trapping exciton and self-trapping biexciton in a PT chain. The dash-dotted curve is the lattice configuration of ground state, and the dashed and solid curves are those of self-trapping exciton and self-trapping biexciton, respectively. In the case of excited states, the applied electric field is 10^{-2}V/nm.

By using femtosecond spectroscopy, it has been verified that in polymers the primary photoexcitations are intrachain excitons.[31] And very recently, a biexciton, which is sequential re-excitation of intrachain excitons, has also been observed.[32] Assuming that photoexcited electrons transfer into the lowest empty levels from the highest occupied states, we shall obtain the self-trapping excitons or self-trapping biexcitons in a PT chain. As shown in Fig.2, the dashed curve is the lattice configuration of a self-trapping exciton, and the solid curve is that of a biexciton. Figure 2 shows that the extra electrons and holes induce the local deformation of the lattice, leading to a strained field. In the meantime, they are trapped by the strain field. When electrons are photoexcited to the lowest empty level, holes will be left at the valence levels. When an electric field is applied, this system will be polarized. We define the induced charge Q as[33]

$$Q = \sum_{N/2=1}^{N} \rho_n, \quad (10)$$

where N is the chain length. In this paper, $N = 120$ sites. Its dependence on the applied field is shown in Fig.3. With the strengthening of the electric field, three plateaus appear. When the electric field is weaker than the first critical E_{c1}=0.1V/nm, i.e. on the first plateau, there is no electron–hole separation. In this region, if we photoexcite one electron from the highest occupied molecular orbital (HOMO) into the lowest unoccupied molecular orbital (LUMO), an exciton forms in the PT chain. The charge density distribution of exciton in this plateau region is displayed

in Fig.4(a). It shows a positive polarity. If two electrons are photoexcited to the LUMO, a biexciton will be found, but it is stable only when the applied field is weaker than 0.65×10^{-1}V/nm. The charge density distribution of this biexciton is shown in Fig.4(b). It can be seen that the polarization direction is opposite to that of the applied electric field. Since the biexciton is a sequential re-excitation of intrachain exciton,[32] it is possible to observe the PIPI in PT if the applied electric field is not too high.

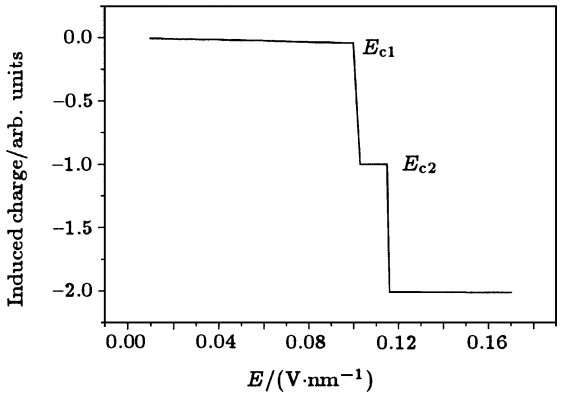


Fig.3. Amount of induced charge Q of self-trapping exciton versus the applied electric field E.

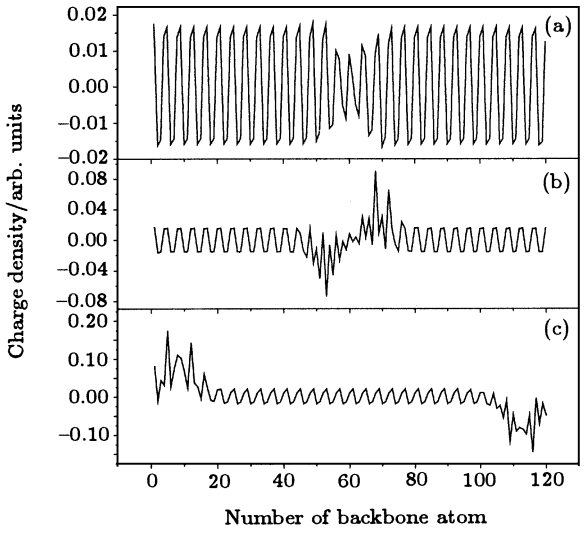


Fig.4. Charge density distributions of (a) self-trapping exciton (the applied electric field is $E = 3 \times 10^{-2}$V/nm), (b) self-trapping biexciton ($E = 10^{-2}$V/nm) and (c) a pair of polarons ($E = 1.05 \times 10^{-1}$V/nm).

With further increase of the electric field, the electron–hole will be separated due to the external field, and the self-trapped exciton begins to decay into a pair of polarons. The positively charged hole polaron moves along the direction of electric field, while the negatively charged electronic polaron moves in the opposite direction. The charge density distribution in the second plateau region is presented in Fig.4(c). It is a typical distribution of a pair of polarons.

However, if the electric field is stronger than a certain value $E_{c2} = 1.16 \times 10^{-1}$V/nm, it is found that the polarons are no longer stable. In this region, the electron–electric field (e–E) interaction will dominate over the electron–phonon (e–ph) interaction, and the system will become disordered. The corresponding lattice configuration will also not be that typical of one of the nonlinear excitations, such as exciton or polaron. Considering the effect of length, we have calculated several PT chains with various lengths and found that this phenomenon still emerges. So we conclude that neither polarons nor excitons could exist in the high electric field region.

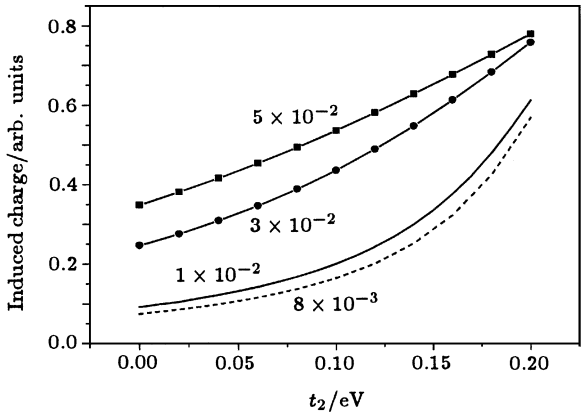


Fig.5. Amount of induced charge Q of self-trapping biexciton as a function of t_2 (t_3) with different applied electric fields. The applied electric fields are 8×10^{-3}V/nm (dashed curve), 10^{-2}V/nm (solid curve), 3×10^{-2}V/nm (full circles) and 5×10^{-2}V/nm (squares), respectively.

The existence of heteroatoms makes PT-like polymers completely different from those polymers without heteroatoms such as polyacetylene. We have studied the effect of heteroatoms on the reverse polarization theoretically by changing the carbon–sulfur coupling parameter t_2 and confinement parameter t_3. The results with different applied electric fields are shown in Fig.5. The heteroatoms apparently raise the reverse polarization. For example, when the external field is 3×10^{-2}V/nm, the reverse induced charges will increase from 0.247e to 0.579e with $t_2 = t_3$ going from 0 to 0.15eV. Compared to the carbon–carbon coupling strength t_0=2.5eV in the backbone of the PT chain,

an observable effect of the heteroatoms should always be present. Therefore, our calculations show that the PIPI will be more easily observed in heterocycle polymers than in *cis*-PA. From Fig.5, it can also be seen that for a certain value of $t_2\,(t_3)$, the higher the applied electric field, the more prominent the reverse polarization.

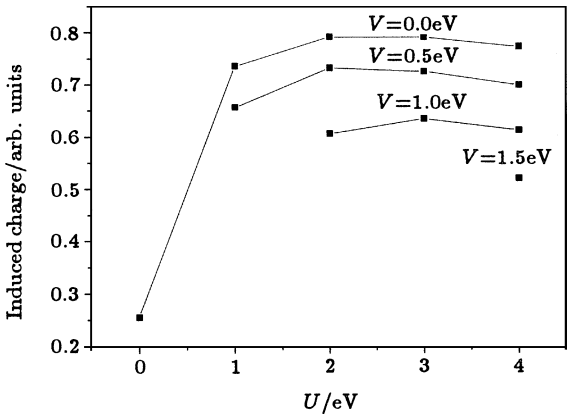


Fig.6. Amount of induced charge Q of self-trapping biexciton as a function of on-site e–e interaction U, with various site–site e–e interactions V, the applied electric field is 1.0×10^{-2}V/nm.

Electron–electron (e–e) interaction is another factor that affects the polarization. For a biexciton, the calculated induced charge versus the on-site Hubbard energy U with different nearest-neighbour Coulomb interactions V is depicted in Fig.6. In the case of $V = 0$, i.e. only the on-site term is included, reverse induced charges increase dramatically as soon as the e–e interaction is switched on. But the site–site e–e interaction decreases the induced charges. As we know, a biexciton is a confined state of electrons and holes. The attraction between the electrons and holes in a biexciton will increase further with the site–site interaction. It will thus lead to the decrease in the induced charges. Therefore, the long range Coulomb e–e interaction will diminish the reverse polarization.

4. Summary

Reverse polarization in heterocycle polymers and its behaviour have been studied by considering the effect of heteroatoms. It has been found that biexcitons, excitons or polarons can be formed in polythiophene separately under different applied electric field strengths. The polarization around a biexciton is a reverse one. The heteroatom has a strict effect on the polarization, apparently increasing the reverse induced charges. Therefore it is expected that PIPI will be observed more easily in heterocycle polymers, such as polythiophene, polypyrrole (PPy), than in *cis*-polyacetylene. In addition, it was found that a long range Coulomb e–e interaction tends to suppress the reverse polarization

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