

Polarons and Bipolarons in a Model Tetrahedrally Bonded Homopolymer

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A coupled electron-lattice model of a saturated homopolymer, such as a poly(organosilylene), is introduced. It shows that the states available in the polymer for the addition or excitation of electrons, or holes, are localized intragap states that are spontaneously generated by bond-order polaron formation.

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One-electron-theory models¹ that stress electron-lattice coupling have been successful in interpreting the observed solid-state properties of conjugated polymers such as polyacetylene.² In this Letter we report on an extension of this type of model to describe a *saturated* polymer. Specifically, we have constructed a microscopic model of a tetrahedrally bonded polymer with formula $(-AR_2-)_n$, where A denotes a Group IVA atom and R an organic side group. This type of saturated homopolymer includes the polysilylenes³ and the polygermylenes⁴ as well as, of course, the wide class of carbon-based polymers. They have band gaps in the ultraviolet (UV).

Very interestingly, the model shows that, provided the electron-lattice interaction is not so strong that scission

of the polymer occurs, the saturated polymer can support polaron states with localized gap-state and infrared vibrational characteristics similar to those found in models of conjugated polymers with nondegenerate ground states.^{5,6} In particular, there is a paramagnetic *polaron*, a diamagnetic *bipolaron*, and a charge-neutral polaron *excitation* that is the relaxed photoexcitation of the polymer. They involve localized regions of reduced *bond order* and, hence, of weakened bonds. For the UV-sensitive *polyorganosilylenes*,^{3,7} we estimate that the width of the neutral polaron is only a few bond lengths, thus providing a specific mechanism for energy localization.

The microscopic model is defined by the Hamiltonian

$$H = 2\Delta_0 N + \sum_j (Br_j^{-l} + \frac{1}{2} MR_j^2) - \Delta \sum_{j,\sigma} (a_{j,\sigma}^\dagger b_{j,\sigma} + \text{H.c.}) - \sum_{j,\sigma} V_{j,j-1} (a_{j,\sigma}^\dagger b_{j-1,\sigma} + \text{H.c.}) \quad (1)$$

It describes N ($N \rightarrow \infty$) A atoms of mass M whose instantaneous positions and velocities in a *trans* chain backbone (lying along the x axis) are denoted by \mathbf{R}_j and $\dot{\mathbf{R}}_j$, respectively ($j=1,2,\dots,N$). It is assumed that the electronic states of the backbone are derived from interaction of atomic- A sp^3 -like orbitals, $\psi_a(\mathbf{x}-\mathbf{R}_j)$ and $\psi_b(\mathbf{x}-\mathbf{R}_{j-1})$, which point along the same $A-A$ bond (see Fig. 1). The other atomic hybrid orbitals, pointing along the $A-R$ bonds, are supposed to be *effectively* decoupled from the a and b orbitals on account of strong bonding with the side groups R . The matrix element describing the interaction of the a and b orbitals is denoted by $V_{j,j-1}$ and taken to have the specific form^{8,9} $V_{j,j-1} = Dr_j^{-2}$, where D is a constant and $r_j \equiv |\mathbf{R}_j - \mathbf{R}_{j-1}|$. At the same time, a repulsive interaction $U_j = Br_j^{-l}$ is assumed to exist between the same pair of atoms, j and $j-1$, where B and l are constants. Together, $V_{j,j-1}$ and U_j microscopically define the electron-lattice interaction. $a_{j,\sigma}^\dagger$ and $b_{j,\sigma}^\dagger$ are fermion operators which create, respectively, an electron with spin σ in the a and b orbitals of the atom j . Δ denotes the matrix element between a and b orbitals on the same atomic site and $4\Delta_0$ denotes the atomic sp^3 promotion energy. The energies in (1) are measured relative to the atomic energies and there is one electron per orbital.

The ground state of (1) is that of a covalent semiconductor¹⁰ with bonds of equal length r and an electron en-

ergy spectrum, \mathcal{E}_κ , given by

$$\mathcal{E}_\kappa - \Delta_0 = \pm [V^2(r) + \Delta^2 + 2V(r)\Delta \cos(\kappa a)]^{1/2} \equiv \pm E_\kappa \quad (2)$$

Here, $V(r) = D/r^2$, $2a = 2r \sin \theta$ is the period of the *trans* chain, 2θ is the tetrahedral bond angle, and the allowed wave vectors, κ , are defined in the extended zone $-\pi \leq \kappa a < \pi$. The covalent energy gap, E_g , is just $2[V(r) - \Delta] \equiv 2a$. If $\Delta = 0$, the polymer consists of $N-1$ independent bonds in which the electronic energy levels are at $\Delta_0 \pm V(r)$. If $\Delta \neq 0$, the bonds become coupled and the charge delocalizes from them toward the atomic sites. Minimization of the total energy per bond $E(r)$ with respect to r fixes the equilibrium bond length r_0 ac-

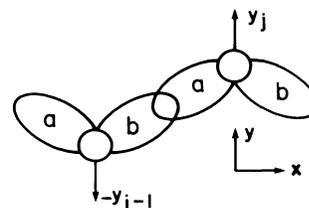


FIG. 1. The *trans* polymer model.

ording to

$$B/r_0^2 = [4V/l(N-1)] \sum_{\kappa} (W_{\kappa}/E_{\kappa}), \quad (3a)$$

and leads to the result

$$E_b = 2\Delta_0 - [2/(N-1)] \sum_{\kappa} E_{\kappa} [1 - (2VW_{\kappa}/l)E_{\kappa}^{-2}] \quad (3b)$$

for the binding energy per bond, $E_b = E(r_0)$, where $W_{\kappa} = V + \Delta \cos(\kappa a)$ and $V \equiv V(r_0)$. Similarly, $K(r) = \partial^2 E / \partial r^2$ may be evaluated to give

$$K = \frac{2(l-2)\beta}{3(N-1)} \sum_{\kappa} W_{\kappa} E_{\kappa}^{-1} - \frac{2\gamma^2}{(N-1)} \sum_{\kappa} \Delta_{\kappa}^2 E_{\kappa}^{-3}, \quad (4)$$

the bond stretch force constant, $K = K(r_0)$, where $\Delta_{\kappa} = \Delta \sin(\kappa a)$, and $-\gamma$ and β are respectively the first and second derivatives of $V(r)$ evaluated at r_0 . The frequency of the transverse optical (TO) phonon of the polymer is $\omega_{\text{TO}} = (4K/M)^{1/2} \cos\theta$. The sums in (3a), (3b), and (4) are easily evaluated in terms of elliptic functions. Together with the formula for E_g they may be used, in principle, to determine the four microscopic parameters B , l , D , and Δ from the experimentally observed values of r_0 , E_b , K , and E_g .

We now consider the states available in the polymer for the addition or excitation of electrons or holes. Because of the nature of the ground state we anticipate polaron formation that involves bond-length relaxation. If we require the latter to leave the length of the polymer unchanged, we are led to consider a static displacement pattern of the form of a TO phonon, i.e., $y_j = (-1)^j (u_j/2 \cos\theta)$, where y_j denotes the displacement in the y direction of the j th atom from its ground-state equilibrium position \mathbf{R}_j^0 (see Fig. 1). If the bond relaxation (elongation) amplitude u_j is sufficiently small and only slowly varying over interatomic distances, we may expand (1) about $\{\mathbf{R}_j^0\}$ and express the orbital amplitudes for electronic states with levels ε_n close to the gap edges as $a_{j,n} = (-1)^j A_n(x)$ and $b_{n,j} = -(-1)^j B_n(x)$, where x denotes an arbitrary point along the polymer axis in a continuum description, $ja \rightarrow x$. The electronic states and $u_j = u(x)$ are then found to be determined by the simultaneous solution of

$$\varepsilon_n A_n(x) = Q_-(x) B_n(x), \quad (5a)$$

$$\varepsilon_n B_n(x) = Q_+(x) A_n(x), \quad (5b)$$

$$v(x) = -(2\gamma^2/K_0) \sum_n [p_n(x) - p_n(\infty)] v_n, \quad (5c)$$

where $Q_{\pm}(x)$ are the operators

$$Q_{\pm}(x) = -\alpha - (a^2/2) V \nabla_x^2 + v(x) \pm V a \nabla_x,$$

and $p_n(x)$ the local bond orders

$$p_n(x) = [A_n^*(x) B_n(x) + \text{c.c.}] / 2.$$

(5c) is the potential $v(x) = \gamma u(x)$ felt by the electrons as

a result of $u(x)$, v_n is the occupation of the n th level, and K_0 is the *unscreened* force constant given by the first term of (4). A_n and B_n are normalized according to

$$\int (dx/a) [|A_n(x)|^2 + |B_n(x)|^2] = 1, \quad (6)$$

and the total energy of the polymer is

$$E = \sum_n v_n \varepsilon_n + (K_0/2) \int (dx/a) u(x)^2, \quad (7)$$

where in (6) and (7) the integral extends over $L = N/a \rightarrow \infty$, and the levels ε_n are measured relative to Δ_0 .

We have derived polaron solutions of (5) which have the form $u(x) = (\varepsilon^2/\alpha\gamma) \text{sech}^2(x/\xi_p)$, where $\varepsilon = (\Delta V)^{1/2} \times (a/\xi_p)$, and are accurate to order $(a/\xi_p)^2 (V/2\alpha)^2 \equiv \lambda^2$. The corresponding spectrum of electronic states consists of the following: (a) A pair of localized *intra-gap* levels with energies $\pm (\alpha^2 - \varepsilon^2)^{1/2} \equiv \pm \varepsilon_p$, and wave functions $A_{\pm}(x) = f_0(x + x_0)$ and $B_{\pm}(x) = \mp f_0(x - x_0)$, where $f_0(x) = (a/4\xi_p)^{1/2} \text{sech}(x/\xi_p)$ and $x_0 = (V/2\alpha)a$. The polaron half-width, ξ_p , is

$$\xi_p = \xi_p(v) = (2K_0 \Delta V / \alpha \gamma^2) (a/v). \quad (8)$$

We have introduced $v = v_+ + 2 - v_-$, where v_+ and v_- are the electronic occupations of the upper and lower intragap levels, respectively. Note that ε is proportional to v . (b) Conduction- (+) and valence- (-) band states with energies $\varepsilon_{\pm}(k) = \pm [\alpha^2 + \Delta V (ka)^2]^{1/2}$ ($k \neq 0$), and wave functions $A_{\pm,k}(x) = f_k(x + x_0)$, $B_{\pm,k}(x) = \mp f_k(x - x_0)$, where

$$f_k(x) = (a/2L_k)^{1/2} \exp(-ikx) [k\xi_p + i \tanh(x/\xi_p)] \quad (9)$$

and $L_k = L [1 + (k\xi_p)^2] + 2\xi_p$. The wave vectors k are obtained from $kL = 2\pi\tau + \theta_k$, where $\tau = 0, \pm 1, \pm 2, \dots$, and $\theta_k = 2 \tan^{-1}(1/k\xi_p)$ is the phase shift experienced by the band states in their transmission through the region of the polaron.

The quantity $\lambda = v(\gamma^2/4K_0\Delta) \sim v[V/4\Delta(l-2)]$ is a measure of the strength of the electron-lattice interaction. We note that, formally, if $\lambda \rightarrow (V/4\Delta)^{1/2} \lesssim 1$, $\varepsilon_p \rightarrow 0$, the energy of an unpaired orbital. This suggests that if $\lambda \approx 1$, the addition or excitation of an electron or hole will cause *scission* of the polymer.

The presence of the polaron removes precisely one state per spin from the occupied valence band. Consequently [and as may be directly verified from Eq. (9)], there is a valence-band *charge deficit* in the region of the polaron that is equal to the charge of two electrons.¹ The total charge, Q , of the polaron is thus found to be $Q = e(v_+ + v_- - 2)$, where e denotes the charge on an electron. Since either intragap level may accommodate zero, one, or two electrons, it follows that there is a paramagnetic *polaron* ($v=1$) with charge $\pm e$, a spinless *bipolaron* ($v=2$) with charge $\pm 2e$, and a *charge-*

neutral polaron ($\nu=2$). The occupancies of the intragap levels, the spin states, and the stable excited ($\nu=3,4$) states of these polarons are depicted in Table I. The neutral polaron corresponds to a relaxed electron-hole pair *excitation* and may be photogenerated in the polymer. Free charges are not, therefore, directly created by photoexcitation. In calculating the polaron formation energy, $E_p(\nu)$, from Eq. (7), we find that the (downward) shifts of $\mathcal{E}_-(k)$ relative to their ground-state values (due to θ_k) sum *precisely* to ϵ_p per spin, thus, remarkably, exactly canceling the energy of the lower intragap level $-\epsilon_p$. In consequence $E_p(\nu)$ is just

$$E_p(\nu) = (\nu/3\alpha)\epsilon^2(\nu) + \nu[\alpha^2 - \epsilon^2(\nu)]^{1/2}, \quad (10)$$

from which the polaron binding energy, $\epsilon_B(\nu) \approx -\nu\epsilon^2(\nu)/6\alpha$, is seen to vary as ν^3 . There is, therefore, a strong tendency for two polarons on the same chain to form a bipolaron.

An *approximate* calculation of the vibrational modes of the polarons may be carried out by the introduction of bonding and antibonding states, $\sqrt{2}\psi_n \pm(x) = A_n(x) \pm B_n(x)$, for the electrons and then, in the consideration of their response to small oscillations about the static polaron solutions, neglect of the coupling between ψ_n^+ and ψ_n^- . The problem may then be mapped on to the corresponding problem for the Holstein *large* polaron,¹¹ with the result that the frequencies, Ω_s , of the odd-parity (infrared) modes are

$$\Omega_s^2 = \omega_{\text{TO}}^2(s+5)/(s^2+5s+4), \quad (11)$$

where $s=0,2,4,\dots$. This spectrum consists of a zero-frequency translational mode ($s=0$) and a quasiband of localized modes beginning at $0.88\omega_{\text{TO}}$ and extending up to just below ω_{TO} . It implies a quantum correction to $E_p(\nu)$ of order $-\hbar\omega_{\text{TO}}/2$. If we denote by m the mass of an electron, the *adiabatic* translational masses of the

TABLE I. Characteristics of the polaron states of the saturated homopolymer.

charge	gap-state occupancy ^a	spin states	stable excited state
2e		S = 0	
e		S = 1/2	
0		S = 0,1	
-e		S = 1/2	
-2e		S = 0	

^aEach solid circle denotes an electron. The gap states are "screened" by a valence band charge deficit of two electrons.

polarons are

$$m_p(\nu) = |Q| \frac{m}{e} + \frac{4\epsilon^5(\nu)M}{15(\alpha\gamma a)^2(\Delta V)^{1/2}}, \quad (12)$$

where the second term has been obtained by boosting the static polaron solution and calculating the resulting kinetic energy of the lattice from (1).

For the poly(organosilylenes) (PS's) the observed energy, $E_g(N)$, of maximum UV absorption (~ 4 eV for $N \rightarrow \infty$) exhibits a striking dependence on polymer length, aN .^{7,12} This is consistent with the electronic transitions occurring between delocalized bonding and antibonding states of the Si backbone.¹³ For *finite* N , (2) leads to the result $E_g(N) = 2\{\alpha^2 + 2V\Delta[1 - \cos(\pi/N)]\}^{1/2}$ for the energy gap, and is able to account for the N dependence observed¹² for poly(dimethylsilylene) for $N=3$ to 24 if $V=3.3$ eV and $\Delta=1.3$ eV. Further, with the experimental values¹⁴ $r_0=2.34$ Å and $K=9.5$ eV Å⁻², we obtain $\gamma=2V/r_0=2.8$ eV Å⁻¹ and, from (4), $K_0=9.9$ eV Å⁻². These values lead to the estimates of ξ_p/a , $u(0)/r_0$, ϵ_B , m_p/m , and $\Delta\epsilon_s=2(\alpha-\epsilon_p)$ that are presented in Table II. In the calculation of m_p from (12), M was taken to be the mass of the dimethylsilylene unit. It is seen that the polaron ($\xi_p \sim 5a$) is estimated to be weakly bound. For adiabatic motion, i.e., for temperatures $T \ll \sim m_p v_0^2/2k_B \sim 600$ K, where $v_0=4\xi_p\omega_{\text{TO}}$, it would behave like a free electron or hole. This is consistent with the observations that the PS's support hole transport.^{15,16} On the other hand, the narrow width $\xi_p \sim 2.5a$ found for either the bipolaron or neutral polaron suggests that formation of the latter excitation would be a very effective mechanism for energy localization and may well be the precursor of polymer scission. The estimate $\Delta\epsilon_s \approx 0.32$ eV for the corresponding Stokes shift is in agreement with the values observed¹⁷ for the UV-sensitive (alkyl) PS's. Numerical minimization of the energy of the discrete model (1) with a $\text{sech}^2[(j-j_0)(a/\xi_p)]$ Ansatz for u_j , and with B and l determined¹⁸ from (3a) and (4), confirms the results of Table II for the polaron but indicates a significantly narrower width, $\xi_p \sim 1.65a$, for the neutral polaron. (Narrower widths for the charged polarons also can be expected if the electronic polarizability of the polymer medium is taken into account.)

Photoinduced absorption measurements on the PS's should be able to detect the intragap levels of the neutral polaron. While photoexcitation of a single chain does

TABLE II. Polaron parameters for poly(dimethylsilylene).

	$\nu=1$	$\nu=2$
ξ_p/a	5.3	2.6
$u(0)/r_0$	1.0×10^{-2}	4.1×10^{-2}
$-\epsilon_B$ (eV)	1.3×10^{-2}	0.10
m_p/m	1.7	24
$\Delta\epsilon_s$ (eV)	7.8×10^{-2}	0.32

not create free charges, *interchain* photoexcitation in the presence of an electric field would lead to the generation of free polarons on different chains and, hence, to a photocurrent. Also, light acceptor or donor doping of the polymers should lead to a system of infrared-active, paramagnetic, *dopant-pinned* polarons. At a higher dopant concentration this system could exhibit a transition to a diamagnetic bipolaron lattice or liquid.

We are currently extending (1) to include the effects of the side groups R and, hence, of full ground-state band structures for particular group *IVA* homopolymers.

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