Statistical Model for Intermolecular Adhesion in π-Conjugated Polymers

Jeremy D. Schmit*
Materials Research Laboratory, University of California, Santa Barbara, California 93106, USA

Alex J. Levine
Department of Chemistry & Biochemistry and The California Nanosystems Institute, UCLA, Los Angeles, California 90095-1596, USA

(Received 31 October 2006; revised manuscript received 10 September 2007; published 14 May 2008)

We propose an interchain binding mechanism in π-conjugated polymers based on the intermolecular tunneling of the delocalized electrons occurring at points where the polymers cross. This mechanism predicts specific bound structures of chains that depend on whether they are semiconducting or metallic. Semiconducting chains should form polyacenelike states exhibiting binding at every other site, while (doped) metallic chains can bind at each site. We also show that solitons colocalize with the intermolecular binding sites thereby strengthening the binding effect and investigate the conformational statistics of the resulting bimolecular aggregates.

DOI: 10.1103/PhysRevLett.100.198303 PACS numbers: 82.35.Cd, 61.25.H−, 83.80.Rs

Conjugated polymers are exotic, low-dimensional semiconductors [1] with applications to a variety of optical [2] and electronic [3] devices as well as biosensors [4,5]. While exploring these applications [5] researchers discovered the surprising tendency of the polymers to aggregate into multimolecular filaments even in the presence of significant electrostatic repulsion. The understanding of these attractive interactions is critical to controlling aggregation as well as the morphology of blends, such as those in organic photovoltaic cells [6].

There are many potential aggregation mechanisms, including electrostatic [7] and dispersion [8] forces. In this Letter, we point out another mechanism available to π-conjugated systems. Based on quantum chemical calculations [9], we propose that intermolecular tunneling between extended π states made possible where two such polymers cross creates a weak binding interaction (of order k_BT) leading to the formation of supramolecular aggregates.

Intermolecular tunneling creates spatially localized states energetically far from the Fermi level that are analogs of traditional bonding or antibonding orbitals [see Fig. 1(a)]. These states lead to a binding energy on the order of thermal energy at room temperature, approximately 10^3 times weaker than a typical covalent bond. Because of this, the formation of supramolecular aggregates requires many bonds so aggregation relies on the subtle interplay of attraction due to the reorganization of the electronic degrees of freedom and repulsion due to loss of chain conformational entropy. This interplay between electronic structure and chain configurations also leads to important differences between the energetic ground states of aggregates of doped, metallic (M) or undoped, semiconducting (SC) polymers. For SC polymers, the ground state is a polyacenelike conformation (see Fig. 2) with binding at every other site. For M chains the interchain electronic interaction favors the formation of a configuration where there is electronic tunneling at every site (see Fig. 2). Additionally, for SC polymers, the coupling of electronic and conformational degrees of freedom leads to an interaction between solitonic excitations on the chains with the binding sites that can enhance the binding energy.

One may detect these intermolecular bonds via their effect on the conformational statistics of bound pairs primarily by modifying their effective persistence length. As the binding strength increases, the dominant deformation mode of the polymers goes from bond rotations in the free chains to localized bending at defects in the intermolecular bonding pattern for weakly bound chains, and finally to the elastic bending of stiff polymer bundles.

We use the Su-Schrieffer-Heeger (SSH) Hamiltonian [1] to describe the electronic degrees of freedom on each chain. Although it is based on the highly symmetric structure of polyacetylene, this model has proved a useful description of more complex π-conjugated systems [10]. At a specific set of sites α (i.e., the crossing points between

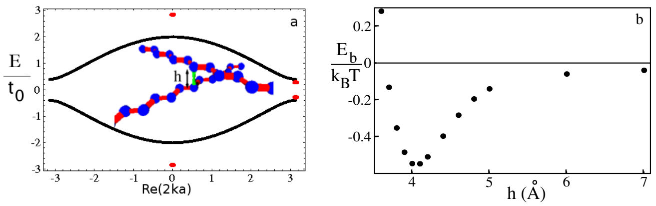

FIG. 1 (color online). (a) The spectrum of electron states (SC chains) resulting from electronic intermolecular tunneling at the crossing point. The bound states (red or gray dots) are at $\mathrm{Re}(k) = 0, \pi$. The schematic figure in the center represents such a single intermolecular overlap (green or light gray) between tight-binding sites (blue or dark gray) on two crossing polymers. (b) HF calculations of the binding energy between two polyacetylene chains ($N = 20$) separated at a distance h at their single crossing point.

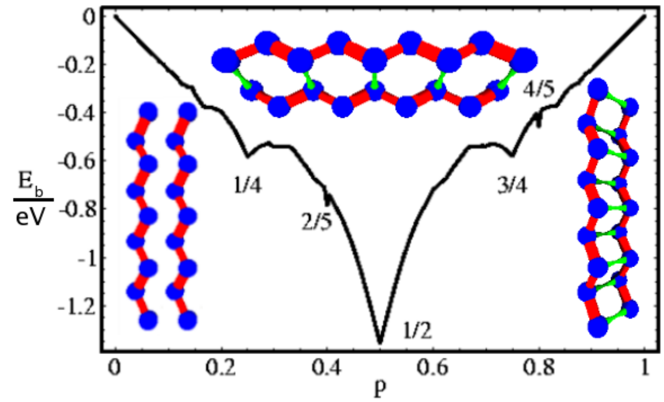

FIG. 2 (color online). The energy of the bound undoped chains as a function of the fraction p of (equally spaced) binding sites for $t' = 0.25$ eV. The insets show (left to right) two free chains ($p = 0$), and the expected forms of the maximally bound SC chains at $p = 1/2$ and M (doped) chains at $p = 1$ using the same color or shading scheme as in Fig. 1. The former structure is similar to polyacene except the binding results from the hybridization of the π_z orbitals.

chains) we allow interchain tunneling with the overlap integral $t' \simeq 0.2$ eV [9]. Thus, we write the system Hamiltonian as

$$H = \sum_{\ell,n}[-t_{\ell,\ell+1}(|\ell,n\rangle\langle\ell+1,n| + |\ell+1,n\rangle\langle\ell,n|)] - t'\sum_{\{\alpha\}}[|\alpha,1\rangle\langle\alpha,2| + |\alpha,2\rangle\langle\alpha,1|]. \quad (1)$$

Here the $|\ell, n\rangle$ represents an electron on the ℓth tight-binding site of the nth chain where the sum $\ell = 1, \ldots, N$ extends over all sites, N is the polymerization index, and $n = 1, 2$ labels the two chains. In the case of the undoped, homogeneously dimerized chain $t_{\ell,\ell+1} = t_0 + (-1)^{\ell}\frac{\Delta}{2}$. We expect $t \simeq 2.5$ eV and $\Delta \simeq 0.5$ eV [1]. M chains (i.e., without the Peierls distortion) have $\Delta = 0$.

To explore intermolecular binding via electronic tunneling, we consider a single crossing point between two infinite, undoped chains (SC) using a transfer matrix approach [11]—see the inset in Fig. 1(a). Intermolecular tunneling produces four localized states at energies

$$E_b = \pm\sqrt{t_1^2 + t_2^2 + \frac{t'^2}{2} \pm \sqrt{4t_1^2t_2^2 + t'^2(t_1^2 + t_2^2) + \frac{t'^4}{4}}}, \quad (2)$$

where we have defined: $t_{1,2} = t_0 \pm \frac{\Delta}{2}$; these are shown as red circles in the band structure diagram, Fig. 1. The two ultraband [12] states above and below the valance and conduction bands are split from the band edges by $2t[\sqrt{1 + t'^2/(4t^2)} - 1]$ and spatially localized over a distance of $\mathcal{O}(at_0/t')$ where a is the undimerized lattice spacing. These states are identical to those appearing in M chains ($\Delta = 0$). For SC chains there are two additional localized states that appear symmetrically in the gap at the edge of the Brillouin zone. For both SC and M chains, however, the dominant contribution to the binding energy comes from the occupation of the lower ultraband state; the effect of the gap states and the shift in the continuum states can be neglected [13]. Thus, for both the M and SC chains the appearance of a single localized state centered at the crossing point of two polymers reduces the system's energy by ~10 meV. We confirmed this result numerically using Hartree Fock (HF) calculations [14] on two polyacetylene chains of 40 carbons [Fig. 1(b)]. While HF cannot account for electron correlations such as those that give rise to dispersion forces, its simplicity makes it useful for larger molecules. These calculations give a maximum binding energy of −14 meV at an interchain separation of $d \simeq 4.0$ Å [11] agreeing with our analytic calculation where $t' \sim 0.26$ eV. This is consistent with its value found from Ref. [9].

Although the single tunneling site energetics of SC and M chains is nearly identical, most energetically favorable (ground state) configurations of pairs of M and SC chain are dramatically different. M polymers have maximal interchain binding (in the absence of chain electrostatic repulsion) in the parallel chain configuration as shown on the right side of Fig. 2. In this configuration the localized low energy ultraband states hybridize into a new filled band. As this seems intuitively reasonable, it is surprising to find that for SC chains the parallel configuration results in *no binding energy* at all. In the parallel configuration the interchain interaction symmetrically splits the filled valance band of the SC polymer. Since the band remains well separated from the similarly split conduction band there is no net energy reduction upon splitting [9]. For strong enough interchain tunneling ($t' \simeq \Delta$) where the valance and conduction bands interact, the Peierls distortion of the chains breaks down and returns the system to the case of M polymers.

The minimum energy configuration of SC chains is a polyacenelike structure with binding at every other site (middle cartoon of Fig. 2). To understand this we compute the binding energy as a function of the density of (equally spaced) tunneling sites by direct diagonalization of the two-chain Hamiltonian with 200 tight-binding sites on each; the results are shown in Fig. 2. The energy is symmetric about its minimum at $p = 1/2$ tunneling site density. The symmetry between binding site densities p and $1 - p$ can be understood if we realize that removing a single binding site from the fully linked chains creates the same set of localized states as adding a binding site to unbound chains. This is due to the symmetry $t' \rightarrow -t'$ in Eq. (2) and applies to any set of bound or unbound sites. The effect of quenched spatial randomness in the distribution of the (non-)tunneling sites on these energies is minimal [13].

The absence of an attractive interaction in the maximally overlapped configuration is consistent with the scarcity of this configuration observed in crystal structures of aromatic compounds. Furthermore, *ab initio* calculations on benzene and thiophene oligomers show that the cofacial orientation is a high energy state with the interaction between molecules becoming more favorable as one of the molecules is either displaced laterally [15] or rotated along the conjugation axis [16] such that the intermolecular overlap is removed from some of the carbon atoms. Our HF calculations on polyacetylene show that the polyacene (or antiparallel) configuration is favored over the parallel alignment consistent with Fig. 2; however, interactions not accounted for in our tight-binding model push the energy minimum away from precisely antiparallel chains for chains of finite length [11].

Low-dimensional systems typically exhibit strong electron phonon coupling. Polyacetylene, in particular, admits solitonic excitations associated with localized defects in the dimerization pattern. Complex excitations such as polarons may be thought of as superpositions of solitons [1,17]. To gain insight into the general interaction of these conjugational defects with tunneling sites, we study the interaction of solitons and tunneling sites. We consider two chains linked at one tunneling site and examine their binding energy as a function of the distance between the solitons and the tunneling site.

First, we place one soliton symmetrically on each chain and vary the position of the interchain tunneling site with respect to the positions of the soliton—see the inset of Fig. 3(a). While moving the tunneling site, we require it to remain on equivalent sites on the two chains. Here we approximate the soliton as a single-site shift in the dimerization. Below we consider a physical, spatially extended soliton, but this simplified model captures the basic effect of the solitons in an analytically tractable manner.

A single-site soliton at the binding site introduces new localized states at energies E given by the roots of

$$0 = E^3 - E(4[t_0^2 + \Delta^2] + t'^2) \pm 4t'\Delta, \qquad (3)$$

where the upper (lower) sign applies to the chain antisymmetrized (symmetrized) states. For large E the bound states occur at $E \simeq (4[t_0^2 + \Delta^2] + t'^2)^{1/2}$ similar to the previously discussed ultraband states. At small E, however, we find another pair of midgap states with energy $E \simeq \pm t'\Delta/t_0$. These are remnants of the usual soliton associated midgap states of the two chains split by the tunneling matrix element t'. The midgap state associated with an uncharged soliton on the chain is singly occupied so that the splitting of these states allows for the double occupancy of the lower state resulting in a net reduction of the system's energy and interchain binding. The localization of an uncharged soliton on each chain at their crossing point further lowers their electronic energy by $\Delta/t' \simeq 2.5$ enhancing the binding energy at that site. In contrast, for the case of charged solitons (as would occur on lightly doped, SC polymers) both midgap states on each chain are filled; there is no further energy reduction due to the colocalization of the charged solitons with the binding site. We expect that this result reflects general properties of the interaction of interchain tunneling with lattice distortions; if the midgap states associated with these defects are not full, their splitting by interchain tunneling increases the binding energy and leads to the colocalizating of defects and tunneling sites.

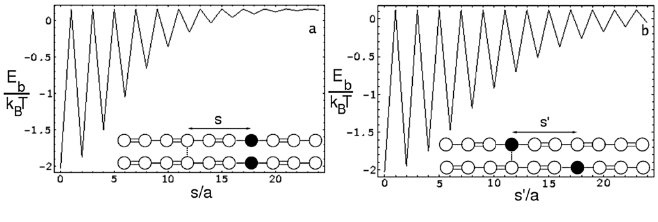

FIG. 3. (a) The interaction energy of a pair of symmetrically placed solitons displaced from the binding site by s. (b) The interaction energy of two solitons where one remains at the binding site while the other is displaced from the binding site by s'.

To extend this result to more physical solitons we put one SSH soliton (width $7a$) at the center of each $N = 199$ chain and numerically calculate the binding energy. The interaction energy between the SSH solitons and the tunneling site is shown in Fig. 3. The solitons are attracted to the interchain tunneling site in a cooperative manner due to the overlap of the midgap states. The unperturbed midgap states have nodes on alternating sites leading to the oscillations in the interaction.

The formation of these bimolecular assemblies will affect the photophysics of the system [18] and the conformational statistics of the polymers in solution. As the site binding energy E_b is increased there is an abrupt condensation of the polymers in dilute solution into bimolecular filaments. See the inset of Fig. 4. We do not consider aggregation into larger supramolecular assemblies. The persistence length of the bimolecular filaments has three distinct regimes as a function of E_b. In the limit of a vanishing E_b, conformations of the free chains may be approximated as a freely jointed chain with a Kuhn length

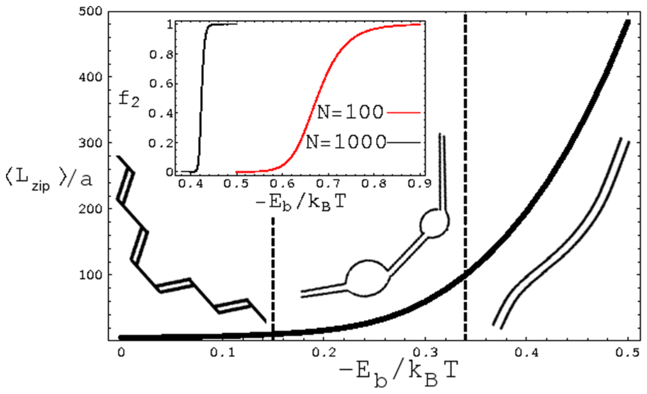

FIG. 4 (color online). The mean length $\langle L_{zip} \rangle$ of the bound regions versus the binding E_b energy between tunneling sites on the two chains. The vertical lines and associated cartoon depict the three persistence length regimes discussed in the text. The inset shows the fraction f_2 of bound chains as a function of E_b in dilute solution.

of $l_{\min} \sim 10a$ [19]. For $E_b \gg k_B T$ the bimolecular filaments saturate their available binding sites, and the intermolecular bonds hinder bond rotations so that the softest deformation mode involves bending in the conjugation plane. Using known bond bending and stretching constants [1,20], we estimate that the persistence length is $\ell_{\max} \sim 100a$. Between these extremes, where defects in the intermolecular binding are typically separated by less than $\ell_{\max}$, the chain tangents decorrelate primarily due to the essentially free rotations at those defects. Thus the bimolecular filaments will have a continuously varying persistence length ℓ_P, $\ell_{\min} < \ell_P < \ell_{\max}$ and their effective persistence length is determined by the mean length of the fully bound chain segments $\langle L_{\text{zip}} \rangle$.

We determine the mean length $\langle L_{\text{zip}} \rangle$ using a modified Poland-Scheraga (PS) model [21]. The partition function for the partially bound pair of chains each containing N sites may be written as

$$Z(N) = \sum_{p} \sum_{\{i_\pi^{(1)}, i_\pi^{(2)}, j_\pi\}} \prod_{\pi=0}^{p} u(i_\pi^{(1)}, i_\pi^{(2)}) v(j_\pi), \qquad (4)$$

where $u(i_\pi^{(1)}, i_\pi^{(2)})$ $[v(j_\pi)]$ is the Boltzmann weight of the πth unbound (bound) region consisting of $i_\pi^{(1)} + i_\pi^{(2)}$ (j_π) consecutive tight-binding sites where the superscript indexes the two chains. The total number of tight-binding sites is fixed in the sum. We relax this constraint using the grand canonical ensemble and, from the PS technique we compute the free energy $F = -k_B T N \ln(x_1)$, where x_1 is the root of

$$\frac{x(x - v)}{xv - v^2(1 - \sigma)} = \sum_{n=1}^{\infty} e^{-\pi \ell_{\min}/n} \left(\frac{u}{x}\right)^n \left(\frac{n}{2}\right)^{-c}. \qquad (5)$$

Here $u \simeq \exp(a/\ell_p) \approx 1$ is the exponentiated entropy of a segment of unbound chain, while $v = \exp(-E_b/k_B T)$ is the Boltzmann weight of a single binding site. The effect of electrostatic and dispersion interactions, not explicitly accounted for here, may be included in the weight v. The exponent $c \simeq 2.1$ reflects the loss of entropy in these unbound regions due to self-avoidance and the loop closure condition [22]. Finally, $-k_B T \ln\sigma$ is the domain wall energy between bound and unbound regions accounting for local chain bending energy. The approximation of using a single E_b for all binding sites is supported by our HF calculations showing insensitivity of the binding energy to the precise alignment of the chains [11].

The fraction of binding sites is given by $\theta = \partial \ln x_1 / \partial \ln v$, and the mean length of bound regions $\langle L_{\text{zip}} \rangle$ may be computed from the ratio of θ to the fraction of sites at the boundary of bound and unbound regions, θ_b. The results are shown in Fig. 4. For $E_b < 0.4 k_B T$, $\langle L_{\text{zip}} \rangle < \ell_{\max}$, so for $N > 10^3$ chains will aggregate in dilute solution (10^{-5}M) into the intermediate state where the persistence length is continuously controlled by E_b. Measurements of the persistence length will test the estimates of E_b, which combine the electrostatic or dispersion forces between the chains in solution and the tunneling effect.

More direct tests require measurements on chemically simpler π-conjugated systems (e.g., polyacetylene) in index matched solvents to minimize the effect of dispersion forces. In addition, the mechanism discussed here makes definite predictions for differences in the bound-state structure of molecular dimers between M and SC chains (Fig. 2). Such differences may help to distinguish the effect of this mechanism from that of other attractive interactions.

This work was supported by the MRSEC Program of the National Science Foundation under Award No. DMR00-80034. The authors thank Fyl Pincus for enjoyable discussions.

---

[*] Present address: Department of Pharmaceutical Chemistry, UCSF, San Francisco, CA 94158, USA.

[1] W. P. Su *et al.*, Phys. Rev. Lett. **42**, 1698 (1979); W. P. Su *et al.*, Phys. Rev. B **22**, 2099 (1980); H. Takayama *et al.*, Phys. Rev. B **21**, 2388 (1980); A. J. Heeger *et al.*, Rev. Mod. Phys. **60**, 781 (1988).

[2] B. J. Schwartz, Annu. Rev. Phys. Chem. **54**, 141 (2003); R. H. Friend *et al.*, Nature (London) **397**, 121 (1999).

[3] F. Garnier *et al.*, Science **265**, 1684 (1994).

[4] L. H. Chen *et al.*, Proc. Natl. Acad. Sci. U.S.A. **96**, 12 287 (1999).

[5] D. L. Wang *et al.*, Chem. Phys. Lett. **348**, 411 (2001).

[6] G. Yu *et al.*, Science **270**, 1789 (1995).

[7] C. A. Hunter *et al.*, J. Chem. Soc. Perkin Trans. 2 **5**, 651 (2001).

[8] T. Sato *et al.*, J. Chem. Phys. **123**, 104307 (2005); E. C. Lee *et al.*, J. Phys. Chem. A **111**, 3446 (2007); S. Grimme, J. Comput. Chem. **25**, 1463 (2004).

[9] J. L. Brédas *et al.*, Proc. Natl. Acad. Sci. U.S.A. **99**, 5804 (2002).

[10] F. Guo *et al.*, Phys. Rev. Lett. **74**, 2086 (1995).

[11] J. D. Schmit and A. J. Levine (to be published).

[12] S. R. Phillpot *et al.*, Phys. Rev. B **35**, 7533 (1987).

[13] J. D. Schmit and A. J. Levine, Phys. Rev. E **71**, 051802 (2005).

[14] M. J. Frisch *et al.*, Gaussian, Inc., Pittsburgh PA, 2003.

[15] M. O. Sinnokrot and C. D. Sherrill, J. Phys. Chem. A **110**, 10 656 (2006).

[16] G. R. Hutchinson *et al.*, J. Am. Chem. Soc. **127**, 16 866 (2005).

[17] S. Roth and H. Bleier, Adv. Phys. **36**, 385 (1987).

[18] C. Daniel *et al.*, J. Chem. Phys. **123**, 084902 (2005).

[19] C. L. Gettinger *et al.*, J. Chem. Phys. **101**, 1673 (1994).

[20] M. Canales and G. Sesé, J. Chem. Phys. **118**, 4237 (2003).

[21] D. Poland and H. A. Scheraga, *Theory of Helix-Coil Transistions in Biopolymers* (Academic Press, New York, 1970).

[22] Y. Kafri, D. Mukamel, and L. Peliti, Phys. Rev. Lett. **85**, 4988 (2000).