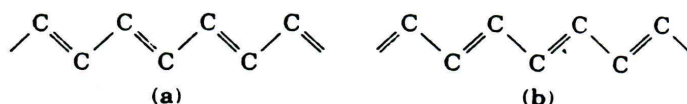
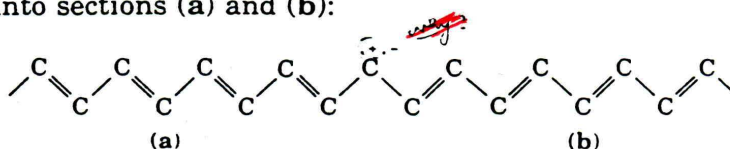


Theory

Charged Defects in Conjugated Polymers. The theoretical work on conducting polymers has been mainly concerned with radical and ionic sites, referred to as neutral and charged defects, respectively (8,19–25). Most of these studies are carried out on *trans*-polyacetylene because of its unusual ground-state geometry. The two energetically equivalent representations for the *trans*-polyacetylene backbone are (a) and (b):



These two structures are degenerate in energy for infinite chain length or for cyclic model molecules; the degeneracy is lifted for finite chains or conjugation lengths. A radical, cation, or anion defect on a polyacetylene backbone divides the polymer into sections (a) and (b):



Since the defect provides a boundary between two equal-energy moieties, it can move in either direction without affecting the energy of the backbone, assuming a highly idealized situation of infinite chain and conjugation length. The movement of the defect can be described mathematically as a solitary wave, or "soliton" in the language of field theory (8,19–22). The radical defect is referred to as a neutral soliton; the anion and cation defects are charged solitons. Theoretical work on these defects dates back to an early quantum chemical description of the system which recognized many of the interesting physical characteristics of solitons (11). This concept was extended and incorporated into a field-theory description of solitons in *trans*-polyacetylene (8). Both the field theory and the quantum chemical treatments of these defects employ a Hückel-type description of the π -electrons with inclusion of an estimate of the energy associated with distortion of the sigma-bond framework of the polyacetylene backbone. Both treatments yield nearly identical results for the energetics of soliton formation and for the geometry of solitons (24).

As noted earlier, charged solitons (anions or cations) have been suggested as an explanation for the experimental observation of spinless transport, since they carry charge but no spin (8). This idea lost some of its appeal with the observation of spinless transport in other systems, poly(*p*-phenylene) (140) and polypyrrole (174), which do not have the two energetically equivalent ground-state structures theoretically required for mobile solitons. This situation is illustrated in Figure 8 where positively charged defects on poly(*p*-phenylene) are compared with those on *trans*-polyacetylene. The two structures on either side of the cation defect on poly(*p*-phenylene) do not have the same energy; the benzenoid structure on the left of the defect (with the aromatic stabilization energy contributed by the intact benzene rings) is significantly more stable than the quinoid structure to the right of the defect (32). Substantial energy is therefore

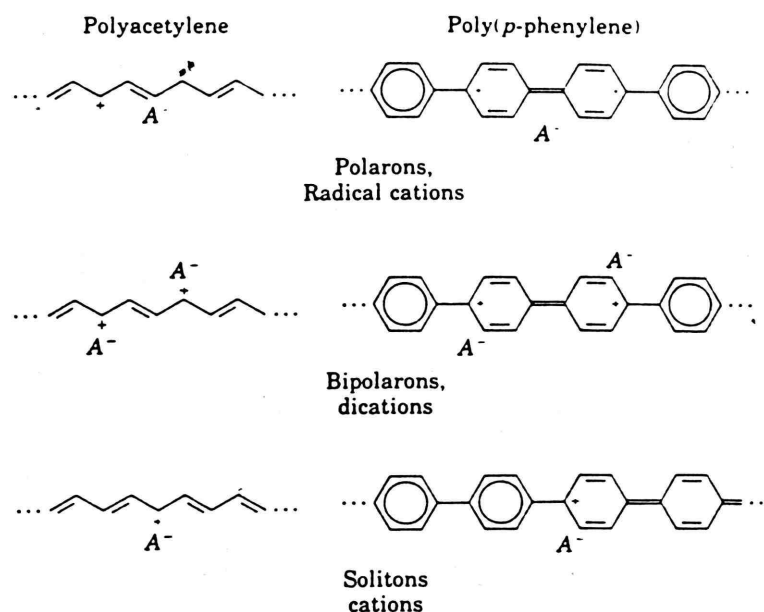


Fig. 8. Positively charged defects (cations, radical-cations, and dications) on *trans*-polyacetylene and poly(*p*-phenylene); the acceptor radical ion is indicated as A^+ . The negatively charged defects (donor doping) may be radical anions, dianions, and anions.

associated with the motion of this defect, i.e., an energy gain moving right in the figure (on creating more aromatic rings) or an energy loss moving left (on creating more quinoidal rings). As illustrated in this example, a general transport theory based specifically on charged soliton migration does not have universal applicability to all conducting polymers, since most conducting polymers do not possess degenerate ground states.

The initial species formed on ionization of a conjugated polymer is a radical ion which possesses both spin and charge (24,25). In the language of solid-state physics, the radical ion is referred to as a polaron. A polaron is either a positively charged hole site (radical cation) or a negatively charged electron site (radical anion), plus a lattice relaxation (distortion) around the charge. The radical cation in poly(*p*-phenylene), depicted in Figure 8, is a bound species, i.e., the radical and the cation are bound together by the high energy of the quinoid structure, since an increased separation between the two defects would require creation of additional high energy quinoid units. The radical cation in *trans*-polyacetylene is also bound; although not pictorially obvious, the motions of the neutral soliton and the charged soliton making up the radical ion are strongly correlated according to model calculations (24). Theoretical models (24) demonstrate that two radical ions (polarons) on the same chain react exothermically to produce a dication or dianion (bipolaron), as illustrated in Figure 9. In poly(*p*-phenylene), the dication is a bound species; in *trans*-polyacetylene the dication is not bound since breakup into two independent cations (charged solitons) is energetically feasible. Dications have been observed spectroscopically in several doped polymers, including poly(*p*-phenylene) (158), polypyrrole (156), polythiophene (157), and poly(*p*-phenylene sulfide) (159). It has not been established whether these doubly

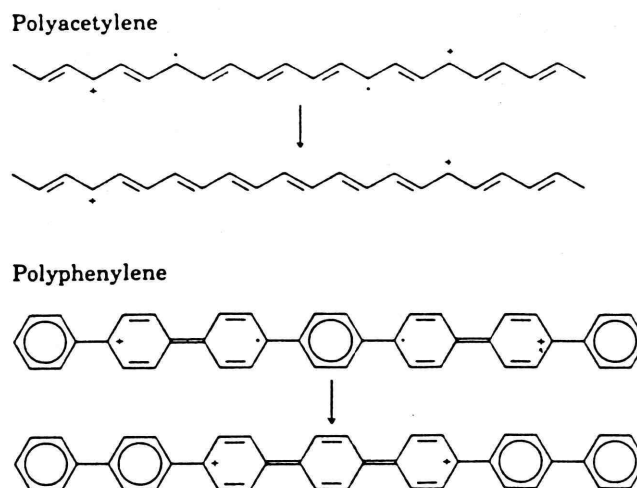


Fig. 9. Reaction of two polarons (radical-cations) to produce a bipolaron (dication) on *trans*-polyacetylene and poly(*p*-phenylene).

charged defects originate from the combination of two radical ions or from a second ionization of one radical ion. It is possible that dication or dianion migration is responsible for spinless conductivity in these polymers and in polyacetylene (139).

The above description of neutral and charged defects in conjugated polymers is based on quantum mechanical Hückel calculations which are well known to have quantitative limitations (175). More sophisticated treatments of neutral and charged defects in various conjugated polymers have been carried out (176,177), including *ab initio* calculations (178); they differ from the Hückel description in quantitative but not in qualitative conclusions. For example, a Hückel treatment of a radical defect on a polyacetylene backbone yields a distortion of the lattice extending about seven carbon atoms on either side from the defect (8,24). More detailed calculations yield a more localized entity with an extension of about three carbon atoms (177). This difference does not have important consequences in the application of these theories to the qualitative description of defect formation and transport in polyacetylene.

trans-Polyacetylene has provided a convenient experimental system for extensive theoretical study of soliton excitations. The field-theory approach has been extended to describe polarons, bipolarons, photoexcitations, and the dynamics of soliton motion (179). Though this work is important in its contributions to the fundamental study of soliton mechanisms, disorder in *trans*-polyacetylene limits the applicability of the soliton model. Disorder produces finite conjugation lengths (44) and a lifting of the degeneracy of the ground-state structure of the polymer due to end-group effects. This requires modification of soliton models of *trans*-polyacetylene which assume infinite chain length and degenerate ground-state structures.

Recent theoretical work (139) dealing with bipolaron (dication or dianion) transport in conjugated polymers suggests that charged solitons cannot contribute to interchain transport in *trans*-polyacetylene as isolated moieties. A schematic

illustration of interchain transport is given in Figure 10. A charged soliton on a *trans*-polyacetylene chain cannot hop to an adjacent, defect-free chain because of the high energy barrier associated with the accompanying geometrical reorganization (139). A pair of charged solitons can hop to an adjacent chain, as illustrated in Figure 10, for *trans*-polyacetylene and poly(*p*-phenylene), with only a modest geometrical reorganization. This mode of "spinless" transport does not require degenerate ground states and would remain operative even with the substantial disorder known to be present in *trans*-polyacetylene, poly(*p*-phenylene), and other conjugated polymers.

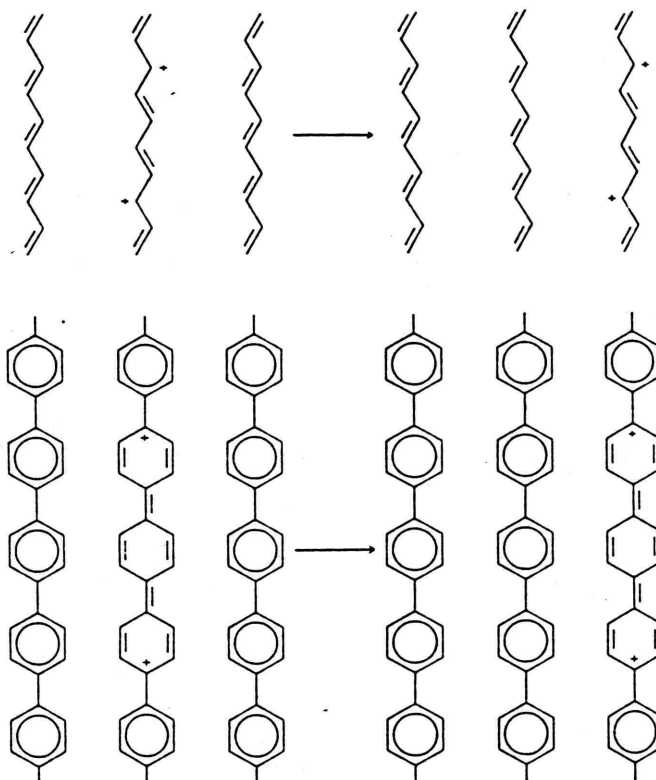


Fig. 10. Interchain transport of bipolarons (dications) in *trans*-polyacetylene and poly(*p*-phenylene).

Electronic Structure Calculations for Conjugated Polymers. Calculations of the electronic structure of conjugated polymers contribute to the understanding of ionization of existing materials (126) and to the prediction of new conducting polymer structures (180). The key properties of a conjugated polymer in relation to its potential as a precursor to a conducting composition are ionization potential, electron affinity, band gap, and band width. The relationship of these electronic parameters to the polymer band structure is illustrated in Figure 11. The ionization potential IP, ie, the energy required to remove an electron from the polymer into vacuum, is the fundamental measure of the polymer's aptitude for acceptor doping. A small value for the ionization potential indicates a polymer which is

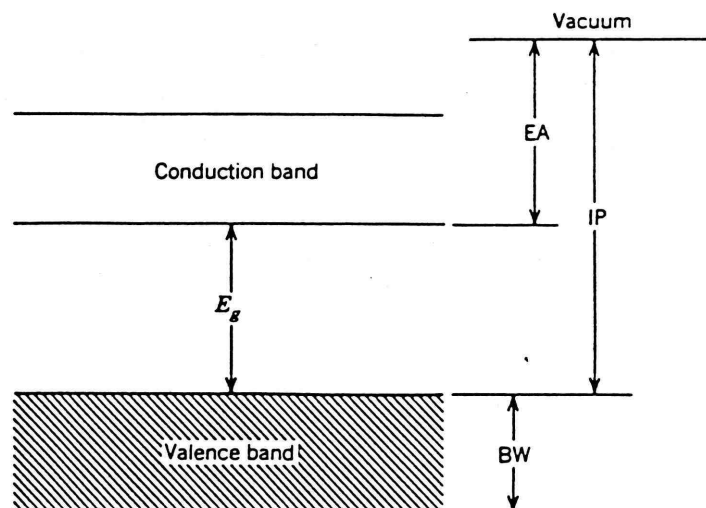


Fig. 11. Relationship of polymer π -electron band structure to vacuum and various energetic parameters. E_g is the optical band gap; BW is band width of the fully occupied valence band; EA is the electron affinity and is measured from the bottom of the conduction band to vacuum; IP is the ionization potential and is measured from the top of the valence band to the vacuum.

easily oxidized. The electron affinity, EA, reflects the relative ease of addition of an electron to the polymer (donor doping); it is a measure of the energy gain on addition of an electron from vacuum to the bottom of the conduction band (Fig. 11). A large value for the electron affinity indicates a polymer which is easily reduced. The band gap, E_g , is the difference between the ionization potential and the electron affinity and correlates with the optical-absorption threshold. The band width, BW, is the width of a particular band, which for conjugated polymers is usually the highest occupied band of states with π -electron character. Strong interactions among the π -electrons of the conjugated backbone result in a large band width indicative of a highly delocalized electronic structure. The band width is correlated to the carrier mobility; a large band width suggests a high intrachain mobility which favors high conductivity. For example, *trans*-polyacetylene has a band width theoretically estimated (8,126) to be in the 6–10 eV range reflecting a high degree of electron delocalization. Poly(*p*-phenylene sulfide), which has less potential for electron delocalization because of the non-planar structure of its backbone, has a band width estimated to be only about 1 eV (181). These band widths imply a higher intrachain carrier mobility in polyacetylene than in poly(*p*-phenylene sulfide). However, as noted earlier the intrachain mobility is, in general, not the limiting factor in determining the conductivity of a doped polymer. Facile intrachain transport is probably best viewed as a necessary, but not sufficient, condition for conductivity. For this reason, correlation between observed conductivities and theoretically calculated band widths can be expected to be qualitative at best (126). Thus, ionization potential and electron affinity indicate the relative ease of ionization, whereas the band width indicates whether or not the ionized material is conducive to intrachain charge transport.