Defect States in Poly(*p*-Phenylene Methine) and Similar Materials

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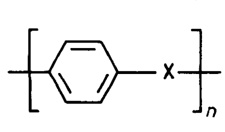
The electronic structure of poly(*p*-phenylene methine), PPM, obtained using a Hückel model with a bond–order bond–length relationship is degenerate and capable of supporting soliton defects, PPM thus being the parent of a class of π-conjugated polymer characterised by a repeat unit consisting of a ring sequence symmetrically interconnected by an odd-alternant group; an unusual structural relaxation about the polaron defect for PPM is described.

Much interest has centred on electronically conducting polymers since the discovery by Shirakawa that thin films of polyacetylene could be prepared by a Ziegler–Natta route.[1] Effort has been focused on the fundamental characteristics of these materials, the way charge is accommodated by the structure, the mechanisms of charge transport and so on, and also possible applications based on a favourable combination of the properties of polymers with those of traditional semiconductors or metals. *trans*-Polyacetylene is the archetypal material and considerable excitement has been aroused in the physics community stemming from the fact that the polymer possesses a degenerate ground state dependent on the phase of the carbon–carbon bond length alternation; this permits the formation of soliton defects occupying states at the Fermi level, mid-way between the π-electron valence and conduction bands. For other polymers having extended π-conjugation sequences, for example poly(*p*-phenylene), PPP,[2] and poly(*p*-phenylene sulphide), PPS,[3] this is not possible and for oxidative doping polaron (radical-cation) states are formed which coalesce on further reaction to generate bipolaron (dication) states of higher binding energy. Associated bonding and antibonding levels appear distributed about the band-gap centre and a local benzenoid to quinonoid structural distortion occurs throughout the length of the defect (Figures 1 and 2). There are complementary processes for n-doping. Here a class of polymer is described, based on inter-connected ring structures with poly(*p*-phenylene methine) as the parent, for which a degenerate ground state is predicted.

The *trans*-polyacetylene soliton forms a domain wall



X = S, poly(*p*-phenylene sulphide)
X = CH=CH, poly(*p*-phenylene vinylene)

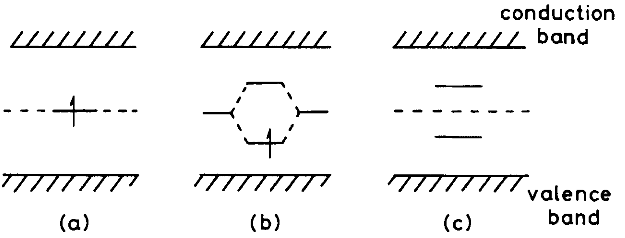


Figure 1. Schematic representation of the energy levels present between the valence and conduction bands for (a) a soliton, (b) a single positively charged polaron, and (c) a positively charged bipolaron.

between the two phases of bond length alternation and in molecular orbital terms it consists of a non-bonding orbital delocalised over approximately 15 carbon atoms, defining the length of chain in which the sense of alternation changes. This topological defect has particle-like properties and as it separates only degenerate structures is mobile along the polymer lattice. For a chain with an odd number of carbon atoms, prior to doping at least one soliton containing an unpaired electron must be present, otherwise the defects must be created in pairs (labelled soliton–antisoliton or kink–antikink to denote the phase relations). The driving force for the bond length alternation is a lowering of the total π-electron energy opening up a gap at the Fermi level and so giving a metal-to-semiconductor transition. This is accounted for within molecular orbital theory[4] and is equivalent to the Peierls distortion[5] for a one-dimensional metal. The electronic structure is well described using a modified Hückel theory; the Hamiltonian employed includes the σ-bond lattice elastic energy and a bond–order bond–length relationship introduced using an electron–phonon coupling constant in the expression for the transfer or resonance integral.[6] It is thought that when *trans*-polyacetylene is oxidatively doped, necessarily single charge injection occurs leading to the formation of polaron states. Charge may also be removed from any neutral soliton defects present to leave positively charged solitons with no associated spin. As the level of doping increases polaron pairs combine to generate two mid-gap states, soliton and antisoliton.

We now consider poly(*p*-phenylene methine), PPM, and initially assume an idealised structure where all the benzene rings adopt a planar conformation allowing maximum overlap with the $2p_z$ orbital of the sp^2 methine carbon, the $CC_{methine}H$ angle is 120°, and *cis*- and *trans*-conformations are of equal energy. Thus the ring π-systems can interact through the methine groups and an extended band structure is possible. Using a simple Hückel formalism a description of the developing band structure may be obtained. As for PPP there are two occupied π-bands which may be considered as derived from the a_{2u} and e_{1g} orbitals of benzene with non-zero coefficients at the 1- and 4-positions, which are directly bonded to the methine groups. There is also a dispersionless band leading to a maximum in the density of states formed from the benzene e_{1g} orbitals with a node at the 1- and 4-positions. Most importantly the p_z orbitals of the methine groups can be considered as interacting through the ring framework leading to the formation of a band, centred at energy $E = \alpha$, which can be equated with the valence-state ionisation energy for a carbon $2p_z$ orbital. By analogy with *trans*-polyacetylene, a bond length distortion along the chain which gives alternate rings a quinonoid character lowers the energies of the highest occupied states. This may be determined from the nature of the frontier levels and by applying a bond–order bond–length relationship. The polymer lattice may be represented in valence bond terms by the structures of Figure 3(a) and it can be seen that a degenerate ground state is created, dependent on the phase of the benzenoid–quinonoid alternation.

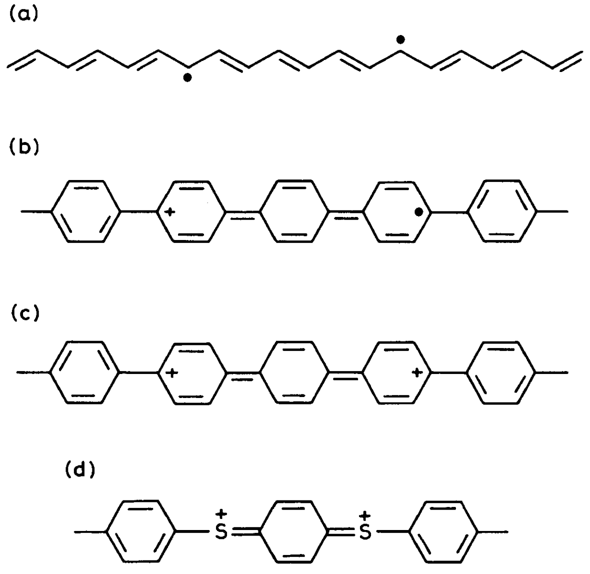


Figure 2. Valence bond descriptions of the defect states formed: (a) a soliton–antisoliton pair on a section of a *trans*-polyacetylene chain (the defects are drawn as occupying only single carbon atom sites, but each defect should extend over approximately 15 atoms); (b) a positively charged polaron state on PPP showing the quinonoid form adopted; (c) a positively charged bipolaron state on PPP; (d) a bipolaron defect occupying a segment of a PPS chain.

If there is an odd number of methine groups along the polymer chain then there must be a non-bonding molecular orbital (NBMO) present of energy α and thus situated at mid-gap. This NBMO is singly occupied in the undoped polymer and forms a domain wall between the degenerate phases; consequently it has soliton properties [Figure 3(b)]. As the soliton forms a boundary between the degenerate phases the lattice must relax about the defect; as drawn it extends over two rings centred on a methine carbon. Again, as the soliton separates only degenerate phases it should be mobile along the chain. The state may contain no electrons (positively charged, spin 0), one (neutral, spin $\frac{1}{2}$), or two electrons (negatively charged, spin 0) and is expected to be the stable charge-carrying defect. This is in contrast to other phenylene containing polymers, PPP, PPS, and poly(*p*-phenylene vinylene) where bipolaron states are predicted to be the stable, mobile defects formed on doping.[2,3]

If we consider a fully dimerised chain of PPM, that is having an even number of methine groups, then the soliton states must be created in pairs in order that the boundary conditions are maintained. If we now remove a single electron from the

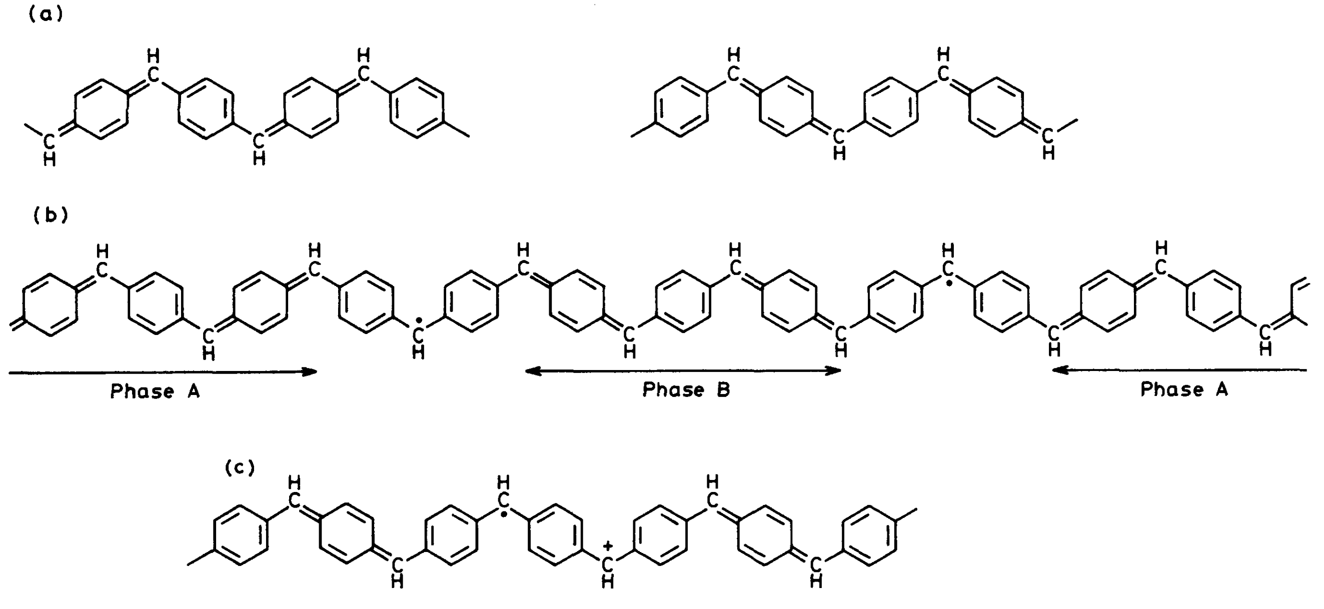


Figure 3. (a) The two equal-energy structures of PPM characterised by the phase of alternation of the quinonoid and benzenoid forms of the phenylene rings; (b) a valence bond representation of a soliton–antisoliton pair on a section of PPM demonstrating the change of phase about the defects; (c) a valence bond representation of a positively charged polaron on a PPM chain, showing a local structural relaxation to the benzenoid form for the extent of the defect.

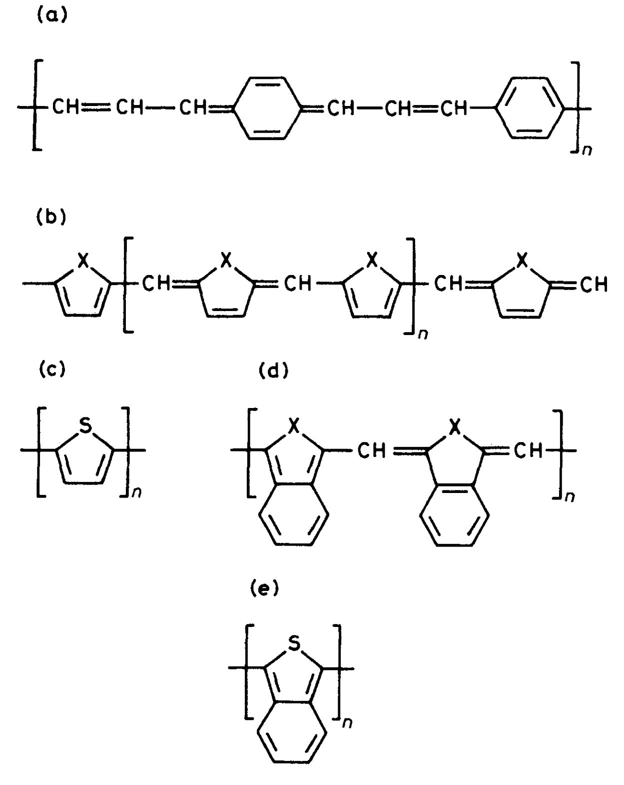


Figure 4. Other examples where a degenerate ground-state is expected, (a), (b), and (d) (X = NH or S); related conducting polymers are, polythiophene (c) and poly(benzo[*c*]thiophene) (e).

chain we generate a polaron state; spin ½, singly charged. This defect may be considered to be a correlated soliton–antisoliton pair interacting to produce bonding and antibonding levels centred about mid-gap, Figure 1(b). The levels originate one each from the valence and conduction band-edges and move into the gap, offsetting the ionisation energy requirement, permitted by the electron–phonon coupling and lattice relaxation. Here the structural relaxation is *quinonoid* to *benzenoid,* the molecular orbitals at the upper edge of the valence band and lower edge of the conduction band having the appropriate form. The structural modification weakens or reverses the ground-state quinonoid–benzenoid alternation over the length of the defect generated [Figure 3(c)]. This situation is most unusual and is a direct reversal of the lattice relaxation found for PPP where a *benzenoid* to *quinonoid* distortion occurs on formation of a polaron defect, Figure 2(b). As a consequence of the nature of the defect states formed for PPM the behaviour on doping is expected to mirror that of *trans*-polyacetylene.

PPM may not be the best example of this interesting class of polymer as a steric effect between adjacent phenylene groups will tend to decrease the extent of π-orbital overlap and so reduce the width of the highest occupied band; however the band-gap should also decrease. Another example from this group would include that given in Figure 4(a), and here steric problems should be less important. In principle, other odd-alternant aliphatic sequences may be used and so lead to formation of a polymer with a degenerate ground state. Similarly the ring moiety may be varied and interesting examples are given in Figures 4(b) and (d); they may be considered to be derived from either, for example, polythiophene[7] [Figure 4(c)] or from poly(benzo[*c*]thiophene)[8] [Figure 4(e)]. The rings now no longer have a plane of symmetry passing through the atoms bonded to the aliphatic segments, so long-range effects, and again steric effects, may be important, most particularly so for (d) of Figure 4.

In summary, a group of π-conjugated polymers has been described, characterised by an interconnected ring sequence in the repeat unit and yet they possess degenerate ground-states and should also be able to support soliton defects. There is a close analogy with *trans*-polyacetylene and the group of materials may be taken to represent an additional class of electronically conducting polymer. In order to test the predictions presented here synthesis of relevant polymers and spectroscopic[3,9] investigation, including the use of electron spin resonance, is required.

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