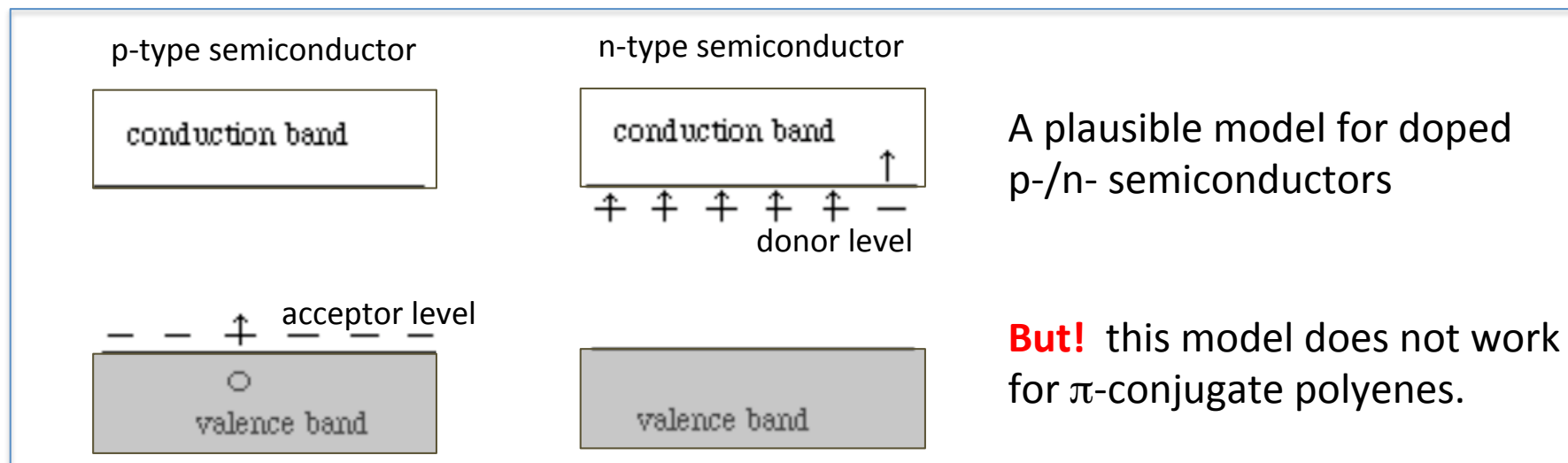


From the textbook of “Chemistry and Biotechnology Laboratory II” for the 3rd year students.

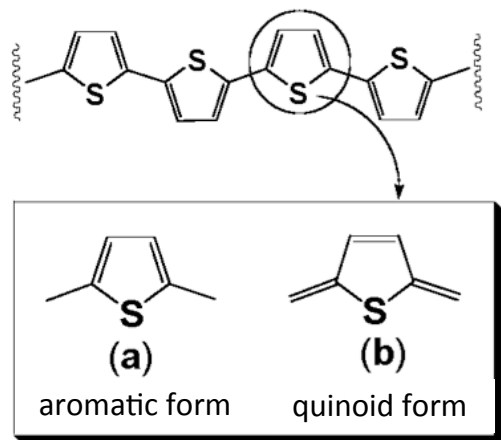
Conjugate polymers like polythiophenes have a through-conjugation π -electron system in a polymer backbone. General organic compounds like a corresponding monomer or a repeating unit carry the electrons satisfying the [(a)] principle; namely, each molecular orbital is occupied with two electrons, up and down each. When filled from bottom to top, the highest orbital of the occupied orbitals is called [(b)], and the lowest orbital of the unoccupied ones is called [(c)]. After polymerization, the band theory tells us that the [(b)] and [(c)] in the monomeric form construct [(d)] and [(e)] bands, respectively, after polymerized. In organic conjugate polymers, there is a [(f)] between the [(d)] and [(e)] bands, owing to the strong chemical bonding nature of the π -electrons. The [(d)] band is entirely filled by electrons, while the [(e)] band is completely empty. Under such conditions, the material has no carrier and accordingly behaves as an insulator.

When an electron [(g)] is doped, or in other words the polymer is oxidized, holes will be generated in the [(d)] band. On the other hand, when an electron [(h)] is doped, electrons are injected into the [(e)] band. This model actually works in inorganic semiconductors. But it does not explain the metallic behavior of organic polymers.

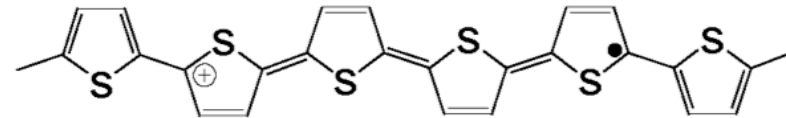


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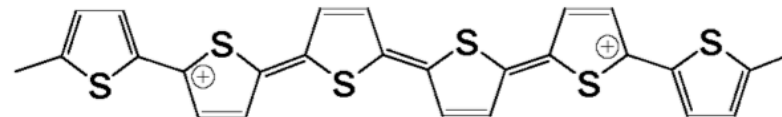
Let us take polythiophenes for example. We can imagine two canonical forms for polythiophenes: [(i)] form and [(j)] form. The former is more stable than the latter. After the polythiophene is oxidized, the regular aromatic structure is broken to form a partial quinoid structure. Such a radical cation portion with a lattice deformation is named a [(k)]. Since the partial quinoid structure is unstable, it is ready to be oxidized again, giving a dicationic portion upon further oxidation. Such a dicationic structure is named a [(l)].



(c) polaron structure



(d) bipolaron structure



A plausible polaron model is as follows.

The energy levels of the quinoid bonding and antibonding orbitals are located within the [(f)]. It is because the π -bonding nature of the quinoids is weaker than that of the aromatics. After the polymer is oxidized, a half-filled [(b)] of the polaron is located just above the top of the [(d)] band, and a vacant [(c)] of the polaron is located just below the bottom of the [(e)] band. The counter anion must be present near the cation due to the Coulombic interaction, which is the origin of the naming polaron.

Further doping leads to the formation of a [(l)] instead of another [(k)]. Much further doping produces many [(l)] levels to form the [(l)] bands. When a newly formed band is connected to the host [(d)] bands, the gapless band structure is realized. Consequently, the material becomes to be metallic.

