Nonclassical Conducting Polymers: New Approaches to Organic Metals?

Martin Baumgarten* and Nikolai Tyutyulkov

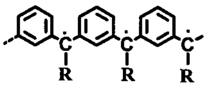
Abstract: J. A. Berson recently described new *meta*-phenylene bridged dimethylenethiophenes, -pyrroles, and -furans and suggested them as building blocks for conducting materials. The structural principles determining the presence or absence of magnetic ordering in such linear conjugated polymers with narrow, partially filled bands are discussed here on the basis of topological criteria and former work in solid-state theory, with major concern about the practicability of the suggested models. It seems that the suggested molecules rather are models in which the nature of spin–spin interaction in and between the subunits is controlled, but that conducting properties will still be difficult to achieve.

Keywords: conducting materials • electronic structure • nonclassical polymers • polymers • spin multiplicity

Introduction

Nonclassical conducting polymers have recently been suggested by Berson et al.[1, 2] but nonclassical polymers (a) and conducting polymers (b) are normally very different molecular entities:

a) Nonclassical polymers (NCP)[3] are organic π-conjugated macromolecules which cannot be described by a valence-Kekulé formula (for example, polyphenylenemethines **1**). They usually serve as a basis for the search for purely organic high-spin materials with ferromagnetic ordering.[4–6]



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b) Conducting polymers are usually π-conjugated macromolecules that exhibit semiconducting or conducting properties; here investigations are focused mainly on two groups,[7–9] namely, doped polymers (oxidised or reduced forms), such as doped polyacetylene (**2**), polyparaphenylenes (**3**), polypyroles (**4**), etc., and low-band-gap polymers with extended π-systems: polycondensed rings (ladder polymers) **5**,[10] graphitic ribbons **6**,[11] and donor acceptor moieties in the chain **7**.[12, 13]

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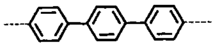

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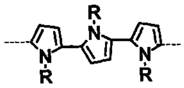

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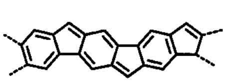

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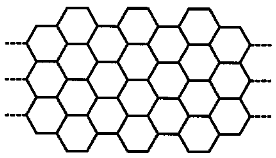

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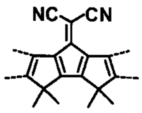

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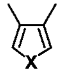
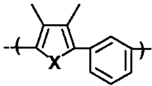
Discussion

Linear polyconjugated polymers with a metallic ground state, that is, with a zero energy gap ΔE between the valence and conduction bands are unknown, although in one-electron approximations there are many theoretical models for such one-dimensional (1D) organic polymers with a metallic ground state. However, when the electron correlation (Mott–Hubbard metal–dielectric transition[14, 15]) or the geometrical corrections (Peierls semiconductors[16]) are taken into account the metal becomes dielectric and the energy gaps have a nonzero value.

An idea for a new class of linear organic conducting polymers with metallic ground state is proposed in recent papers by Berson et al.,[1, 2] namely the quasialternant nonclassical polymers. The authors thus try to combine two very different approaches to organic molecules for materials science. Illustrations of the heteronuclear quasialternant radicals with nonbonding MOs and their corresponding *meta*-phenylene-bridged polymers suggested by Berson are provided by structures **8a–c** (X = S (**a**), O (**b**), NR (**c**); R = H, alkyl, tosyl, or brosyl) and **9a–c**, respectively. As demonstrated experimentally by Berson, the ground states of **8a–c** (X = O, S, or NCH_3) are certainly singlets in the accessible temperature range, but compounds **8c** with R = tosyl or brosyl persist in *both*



8a–c



9a–c

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singlet and triplet states[2, 17, 18] and the experimental results are in good agreement with ab initio calculations.[19, 20]

The basic idea of Berson's approach can be traced back to Whangbo[21] and Hubbard[14] (see also the paper by Slater[22]), who described qualitative theoretical conditions for enabling a simple determination of the relative stability of localised high-spin (magnetic) versus low-spin metallic (nonmagnetic) states in conjugated (organic) polymers. Whangbo and Hubbard, however, described no definite molecular structures of conjugated polymers for the determination of the ground state of the partially or half filled bands (HFB). It follows from the Whangbo–Hubbard conditions [Expression (1), $k \approx 1$] that if the HFB width $\Delta\varepsilon$ is small compared to the one-site Coulomb repulsion U, the magnetic high-spin state is favored, while the opposite relation should hold for conducting properties.

$$\Delta\varepsilon < kU \qquad (1)$$

Now Berson believes that one should just tune the bandwidth of the half-filled bands by substitution to obtain either type of material properties. There remains a basic problem, however: trying to tune this bandgap from one to the other state given by the spin-pairing energy, especially when using biradicals in each subunit combined through *meta*-phenylene bridging. This is demonstrated in Figure 1, since as long as the biradical state of the subunit prevails, magnetic ordering through intramolecular ferromagnetic interactions should occur, which may only be overcome by intermolecular interactions. If the subunit, on the other hand, possesses a singlet ground state, the gap between the partially occupied orbitals is 1–1.6 eV or larger[23] and can not be diminished easily, not even through *meta*-phenylene bridging, which is known to act as a conjugation barrier[24] (see Figure 1).

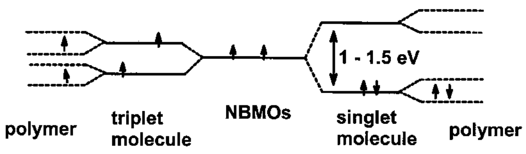
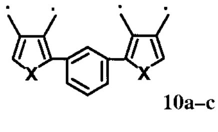


Figure 1. Splitting of the degenerate nonbonding (NB) MOs in a perturbed biradical and indication of the small band widening in *meta*-phenylene-bridged polymers.

Even worse, all the model compounds prepared so far (**8a–c, 10a–c**) decompose above 77 K, that is, they are kinetically very unstable and do not permit the determination of their electronic structure (e.g. thermal activation) at higher temperatures; this same behavior has to be anticipated for the polymers **9a–c**.



10a–c

In a more general description of the energetic situation of solid-state properties, it follows that if the degeneracy of a band is removed, then the widening of the nonperturbed (**NP**) band depends on the degree of perturbation, classified as weak (**WP**), moderate (**MP**), or strong (**SP**) (Figure 2), and it is of major scientific interest to obtain the low-spin metallic state (MP) or the high-spin magnetic state (NP, WP).

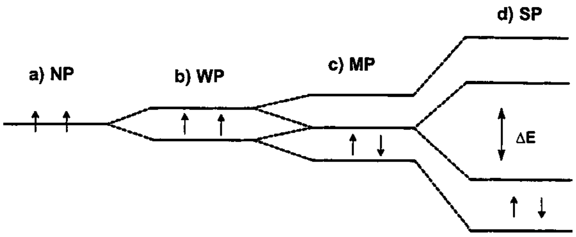


Figure 2. Energy-level diagrams showing increasing perturbation of non-classical polymers with half-filled orbitals. **NP** nonperturbed, **WP** weakly perturbed, **MP** moderately perturbed, and **SP** strongly perturbed.

π systems in which a carbon atom has bee replaced by a heteroatom or heteroatomic group in a NCP can be considered to be perturbed. In the terminology introduced by Longuet-Higgins,[25] a NBMO (in an alternant or QA system[26]) will be perturbed by substitution of a carbon atom only in those positions (active positions) for whose AO the coefficients (C) in the NBMO are nonzero. The active positions in the monomers of NCP **1** and QANCP **9** are shown in Figure 3. The polyphenylenemethines (**1**) have a nonmetallic (high-spin) ground state with ferromagnetically coupled electrons within the half-filled band—case **NP** in Figure 2.[3, 27, 28] Substitution of the exocyclic $C^{\bullet}H$ group with -$N^{\bullet}$- or -$HN^{\bullet +}$- results in the polymer **11** (dehydrogenated and cationic forms of poly(*meta*-aniline)) which have the *same topology* as **1**; however, the NBMO band splits and the width corresponds to the case **WP** in Figure 2. The ground state also remains a high-spin one.[27,28]

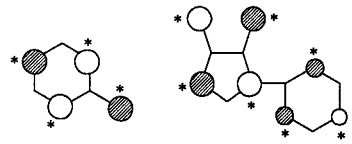
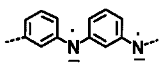


Figure 3. The active positions in structures **8**, **9**.



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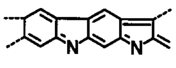

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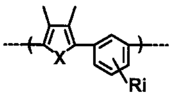
The case **SP** may be created by changing the *topology*. An example is the isoelectronic polymer of the dehydrogenated form of poly(*meta*-aniline), **12**. In this case, the ground state is nonmagnetic dielectric with a band gap $\Delta E > 1.5$ eV.[27]

The type **MP** may be anticipated by substitution of two or more carbon π-centers. A nonmetallic (high-spin) to metallic (low-spin) transition may be probably achieved by substitution of the active π-centers in polymer **9** with different substituents R_i within the *meta*-phenylene rings as indicated in **13**.



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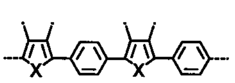

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If the topology of polymer **9** were changed, for example to the *para*-phenylene-bridged case **14**, the π system would probably no longer be nonclassical. In this case there arises a doubling of the elementary unit with 26 π electrons per 26 π centers, where the *para*-phenylene now allows a much greater narrowing of the bandwidth, which should at least lead to very low-band-gap polymers, probably even conducting ones.The thermal and kinetic stability, on the other hand, would still be a problem.

In this report we have considered only the possibility of a transition from high-spin magnetic to low-spin metallic states. Any study of electrical conductivity requires a knowledge not only of the band structure (energy spectrum) of a linear polymer but also of the mobility of the electrons. It is well-known that *meta*-phenylene units are conjugation barriers[24] in linear polymers, that is, for synthesised nonclassical polymers, electrical conductivity depends on the charge carrier mobility and, even if achieved, cannot reach high levels.

In conclusion, we can claim that the physical idea for the existence of nonclassical conducting polymers with metallic ground state as in Figure 2b (**WP**) is correct. The models presented so far, however, are in their initial stages. The discovery of a reliable structure requires additional, more extensive theoretical and experimental investigations, including also thermally and kinetically stable polymers; this will certainly be difficult to achieve, but is necessary. Finally it seems that the suggested structures rather are models to control and tune the low-spin to high-spin transition and the interaction between the subunits (see ref. [18]), but that conducting properties will still be difficult to achieve.

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