Macromolecules 1991, *24*, 3723-3724

Electronic Structure of Conducting Polymers with Nonconjugated Backbones: 1,4-Polybutadiene and 1,4-Polyisoprene

Highly conducting polymers form an important class of novel materials that combine outstanding electronic, optical, and mechanical properties.[1-3] Since the pioneering work of Shirakawa, Heeger, and MacDiarmid on poly(acetylene), a whole series of polymers has been discovered, which display electrical conductivities in excess of 100 S/cm.[1-3] Besides poly(acetylenes), the currently most studied systems include poly(thiophenes), poly(anilines), poly(pyrroles), poly(p-phenylenevinylenes), and their derivatives. The common feature of all these polymers is to present a fully conjugated backbone with highly delocalized π electrons.

Therefore, the report by Thakur and co-workers[4-6] that polymers with nonconjugated backbones can be doped by iodine to reach moderately high levels of conductivity (up to ca. 0.1 S/cm) did come as a surprise.[7] The systems investigated by Thakur and (i) 1,4-poly(buta-1,3-diene) $[-\mathrm{CH_2CH{=}CHCH_2}-]_x$, hereafter denoted PBD, and (ii) 1,4-poly(2-methylbuta-1,3-diene), i.e., 1,4-polyisoprene $[-\mathrm{CH_2CCH_3{=}CHCH_2}-]_x$, denoted PIP. For the most part, the conductivity results of Thakur and co-workers have been reproduced by Shang et al.,[8] and Suh and Wnek.[9] However, the mechanism of conduction remains very controversial.[8-10] Thakur proposes that ethylenic radical-cation polarons are formed during the doping process and constitute the charge carriers moving through intra- and interchain hops.[4] On the contrary, Shang et al.[8] favor a mechanism by which iodonium $\mathrm{I^+}$ π complexes are formed with the double bonds; conductivity would then arise from hopping of such cationic iodine complexes along and between chains. Suh and Wnek suggest that either the polyiodide counteranion chains are responsible for the conductivity (this has, however, to be reconciled with the experimental indication that the charge carriers are p-type[4]) or there occurs an iodine-catalyzed isomerization yielding separate polyethylene and polyacetylene segments, the latter becoming doped in the usual way.

In order to contribute to a better understanding of the electronic properties of 1,4-polybutadiene and 1,4-polyisoprene, we report in this paper the results of quantum-chemical calculations, dealing with geometry optimizations and band-structure determinations on the cis and trans conformations of both PBD and PIP in the undoped state. Note that, from the conducting polymer standpoint, the backbones of PBD and PIP can be viewed simply as deriving from a polyacetylene backbone $[-\mathrm{CH{=}CH}-]_x$, through saturation of every other double bond. In other words, along the backbones of these nonconjugated polymers, two sp^2 carbons are followed by two sp^3 carbons.

The geometric structures of the various compounds are optimized with the MNDO (modified neglect of diatomic overlap) Hartree-Fock semiempirical approach[11] on oligomers containing at least 16 carbons. MNDO is known to provide reliable geometries (bond lengths and bond angles) of organic molecules. The backbone conformations are taken as reported in the literature.[12] They are as follows: among the polymers investigated here, only the conformation of *cis*-PBD is fully coplanar; the other polymers present skewed conformations: TST$\bar{\mathrm{S}}$ for *trans*-PBD and *trans*-PIP and CST$\bar{\mathrm{S}}$–C$\bar{\mathrm{S}}$TS for *cis*-PIP (where T stands for trans, C for cis, and S and $\bar{\mathrm{S}}$ for +120° and −120° torsion angles, respectively).[12]

Table I
VEH Electronic Properties of the Four Nonconjugated Polymers Investigated in This Work: Band Gap (E_g); Bandwidth (BW) for the Highest Occupied Valence Band; and Solid-State Ionization Potential (IP)

	E_g, eV	BW, eV	IP, eV
cis-PBD	6.85	0.10	6.95
trans-PBD	6.30	0.93	6.65
cis-PIP	5.84	0.79	6.29
trans-PIP	6.23	0.82	6.41

The geometries of the central part of the oligomers are then taken to build the polymer unit cells, which serve as input for VEH (valence effective Hamiltonian)[13] band-structure calculations. The VEH technique has an outstanding record of providing accurate valence electronic structures and in particular very good estimates for ionization potentials, bandwidths, and band gaps in a wide variety of organic polymers.[14]

The MNDO optimizations lead to very reasonable geometries. The C–C double bonds are calculated to be ca. 1.35–1.36 Å, the sp^2–sp^3 single bonds, ca. 1.51–1.52 Å, and the sp^3–sp^3 single bonds, ca. 1.545 Å. The backbone C–C–C bond angles around sp^3 carbons are on the order of 114°; those around sp^2 carbons range between 125° and 127°.

The main results of the VEH band-structure calculations are collected in Table I. The band structure for *trans*-PBD taken as an example is displayed in Figure 1. The major observations drawn from Table I and Figure 1 are the following.

(i) As expected, the band-gap values for the pristine materials are very large, >5.8 eV. This is in agreement with the optical spectra indicating no absorption in the wavelength region 200–800 nm.[4,5]

(ii) The widths of the highest occupied valence band (HOVB) dramatically depend on the polymer conformation. The fully coplanar structure of *cis*-PBD leads to an almost complete localization of the π electrons on the sp^2 carbons and an HOVB width of about 0.10 eV. *Bandwidths almost 1 order of magnitude larger are obtained for the polymers with skewed conformations*, 0.79–0.93 eV. In that case, there is strong σ–π mixing, and the HOVB has contributions not only from the π atomic orbitals on the sp^2 carbons but also from all other 2p atomic orbitals on the sp^2 and sp^3 carbons.

(iii) The solid-state ionization potentials are in all cases calculated to be on the order of, or larger than, 6.3 eV, i.e., a value that corresponds to the ionization potential experimentally and theoretically determined in poly(p-phenylene sulfide), PPS.[15] This result is especially important since it confirms that *iodine is too weak an acceptor to dope PBD or PIP to any significant extent.* Indeed, even in the case of poly(p-phenylene), which has an ionization potential of ca. 5.5 eV, stronger acceptors are required, such as $\mathrm{AsF_5}$.[15] The formation of ethylenic radical cations through oxidation by iodine, as suggested by Thakur,[4] is thus not possible.

In summary, through MNDO geometry optimizations and VEH band-structure calculations on both *cis*- and *trans*-PBD and -PIP, we have shown that the polymers with skewed conformations possess an HOVB width on the order of 0.79–0.93 eV. Holes in that band should therefore present a significant intrachain mobility. (Note that bandwidths in conducting charge-transfer molecular crystals such as TTF–TCNQ are about 0.5 eV.[16]) The solid-state ionization potentials are found to be too large to allow for oxidation by iodine and formation of ethylenic

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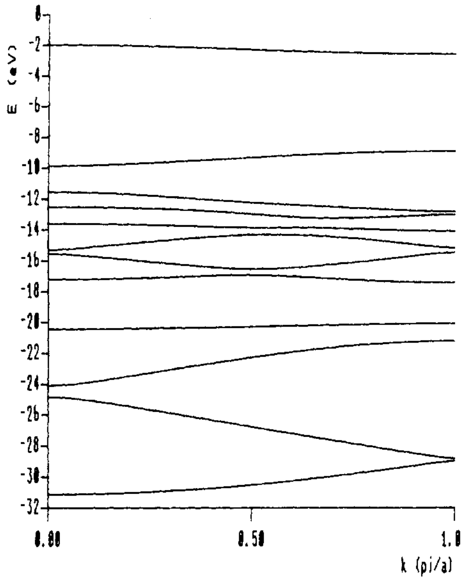

Figure 1. VEH band structure of *trans*-1,4-poly(buta-1,3-diene). All the valence bands and the lowest unoccupied conduction band are displayed.

radical cations. If iodine does not catalyze polymer isomerization, the conduction mechanism could thus be based on the mobility of iodonium π complexes with somewhat delocalized double bonds or on polyiodide chains. Finally, we note that *trans*-PBD has ionization potential and HOVB width values similar to those of PPS. It might thus be worthwhile to investigate the doping of this polymer with strong oxidants; the doping of PPS with AsF_5 leads, in the absence of backbone chemistry, to conductivities of about 0.1 S/cm.[15]

Acknowledgment. We thank the CCI Computer Center at the University of Mons, as well as SPPS (Programme d'Impulsion en Technologie de l'Information, IT/SC/22), FNRS, and IBM-Belgium for the use of the supercomputer facilities at KU Leuven, FNDP Namur, and the University of Liège. Ths work is partly supported by the Belgian "Pôle d'Attraction Interuniversitaire: Chimie Supramoléculaire et Catalyse".

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Received February 13, 1991

Registry No. PBD (homopolymer), 9003-17-2; PIP (homopolymer), 9003-31-0.