Density-Functional Study of *cis-* and *trans-*1,4-Polybutadiene

Heiko Meider and Michael Springborg*

Fakultät für Chemie, Universität Konstanz, D-78457 Konstanz, Germany

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Results of density-functional calculations on *cis-* and *trans-*1,4-polybutadiene are presented. The resulting band structures are compared with those of polyethylene and *trans-*polyacetylene. Charge-density plots of the highest occupied π band show that the results are in accordance with the intuitive concept of localized π bonds. Tight-binding fits of the band structure show that polybutadiene can be regarded as a copolymer between polyethylene and polyacetylene. A detailed study of the single-particle energies of polybutadiene, polyethylene, polyacetylene, and ethylene allows finally a determination of some of the parameters for an extended Hubbard model that can describe the π electrons of extended hydrocarbons. It is shown that the nearest-neighbor Hubbard parameters are small, indicating that further interactions are effectively screened.

1. Introduction

Conjugated polymers (e.g., *trans-*polyacetylene) have been at the center of research for nearly 2 decades. During this period this class of materials has reached a more mature state where also technological applications are emerging. Despite this impressive development, a number of more fundamental questions about the basic properties of these materials remain partly unsolved. One of those, the importance of correlation effects for the electrons, shall be indirectly addressed here.

Most conjugated polymers contain an essentially planar backbone consisting of carbon atoms with alternating shorter double and longer single bonds. The π orbitals formed by carbon *p* functions perpendicular to the plane of the backbone are those that appear closest to the Fermi level, and the electrons occupying those are responsible for most of the properties that make these materials interesting. Therefore, many models that have been developed to describe these properties concentrate on the π electrons.

Of these models, the one developed by Su et al.[1] explicitly for *trans-*polyacetylene, is the most well-known. Within this model the total energy is written as a sum of two terms of which one is a single-particle tight-binding term for the π electrons and the other remaining term is a simple analytic function of the nearest-neighbor bond lengths. The tight-binding part assumes that the on-site energies are constant and that the nearest-neighbor hopping integrals depend linearly on the corresponding bond lengths whereas all other hopping integrals are neglected. For a quantitatively more accurate agreement between theory and experiment, the inclusion of many-body effects seems inevitable (for example, see ref 2). This is even more clearly seen when studying the finite oligomers corresponding to *trans-*polyacetylene, especially as far as excited states are concerned.[3] The fact that the electrons for these oligomers are confined to a finite system makes electron−electron interactions more important.

Polybutadiene (throughout this paper we will refer to 1,4-polybutadiene simply as polybutadiene) is an interesting intermediate system being infinite on the one hand, but having similarties to the finite ethylene molecule on the other. The structure of the two isomers of polybutadiene $[(CH_2)_2(CH)_2]_x$ is shown in Figure 1b,c. Intuitively, one would expect that the π electrons are essentially localized to the C═C bonds between
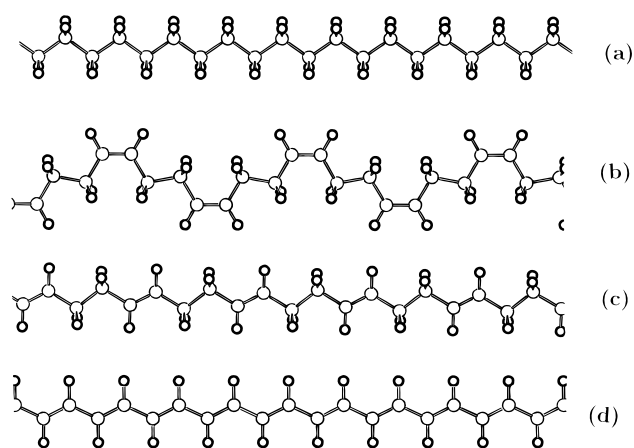
Figure 1. Structure of (a) polyethylene, (b) *cis-*polybutadiene, (c) *trans-*polybutadiene, and (d) *trans-*polyacetylene.

the CH units. Although this is to some extent the case for polyacetylene too [Figure 1d], the probability that the π electrons will hop from a C═C bond to the next in polybutadiene is significantly reduced compared to *trans-*polyacetylene. Thus, equivalently to the case for the finite oligomers, we would expect the π electrons of polybutadiene to show more pronounced many-body effects than those of *trans-*polyacetylene. However in contrast to the finite oligomers, polybudatiene and polyacetylene are both infinite systems.

In the present study (of which a small part was published in ref 4) we shall use parameter-free density-functional calculations on the two polybutadiene isomers of Figure 1b,c and on polyethylene [Figure 1a] and *trans-*polyacetylene [Figure 1d] to explore the role of correlation effects for the π electrons. To the knowledge of the present authors this work represents the first parameter-free study of the electronic properties of 1,4-polybutadiene.

In order to obtain a complete description of the π electrons of the hydrocarbons, additional calculations of ethylene (C_2H_4) were performed. We stress, however, that the purpose here is not to present new results for ethylene but that we merely have included this system for practical reasons to be discussed in section 4. In section 2 we briefly describe our computational method and in section 3 we present the first-principles results. The analysis of the π electrons is presented in section 4 and we give our conclusions in section 5.

2. Computational Method

Our computational method has been described in detail in ref 5, and only a brief account is given here. It is based on the density-functional formalism of Hohenberg and Kohn[6] in the single-particle formulation of Kohn and Sham.[7] The resulting Kohn−Sham single-particle equations

$$\left[-\frac{\hbar^2}{2m}\nabla + V_{\text{eff}}(\vec{r})\right]\psi_i(\vec{r}) = \epsilon_i\psi_i(\vec{r}) \tag{1}$$

are solved by expanding ψ_i in a basis of linearized muffin-tin orbitals (LMTOs). The LMTOs are of the form

$$h_1^{(1)}(\kappa|\vec{r} - \vec{R}_i|)Y_L(r\,\widehat{-\,R_i}) \tag{2}$$

augmented inside nonoverlapping atom-centered spheres with numerical functions obtained from eq 1 by replacing $V_{\text{eff}}(\vec{r})$ by its spherically symmetric part. In eq 2, $L = (l, m)$ describes the angular momentum, $\vec{R}_i$ is the position of the ith atom, κ is a purely imaginary number whose absolute value is a decay constant, and $h_1^{(1)}$ is a spherical Hankel function. It shall be stressed that we use the full potential and not only its muffin-tin part in the calculations, but that the basis functions are eigenfunctions of a muffin-tin potential. In eq 1, the exact form of the exchange-correlation part of the potential V_{eff} is not known, but in the present work we use the local approximation of von Barth and Hedin.[8]

Our specific method is constructed for calculations on infinite periodical helical polymers. The helical symmetry is used in constructing Bloch waves from equivalent basis functions of different unit cells, whereby the (atom-centered) basis functions are defined in local atom-centered right-handed coordinate systems with the z-axes parallel to the polymer axis and the x-axes pointing away from it. For the present study only the translational and the zigzag symmetry will be relevant as special cases of the helical symmetry. Thus from the jth basis function of the nth unit cell χ_{jn}, we define Bloch waves as

$$\chi_j^k = \lim_{N\to\infty}\frac{1}{\sqrt{2N+1}}\sum_{n=-N}^{N}\chi_{jn}e^{ikn\pi} \tag{3}$$

j describes the different atoms per unit cell, the angular dependence of the basis function, as well as any other dependence that distinguishes the basis functions. By using that the Hamilton operator of eq 1, $\hat{H}_{\text{KS}}$, possesses the full symmetry of the system, we obtain

$$\langle\chi_{j1}^k|\chi_{j2}^k\rangle = \lim_{N\to\infty}\frac{1}{2N+1}\sum_{n_1,n_2=-N}^{N}e^{ik\pi(n_2-n_1)}\langle\chi_{j_1n_1}|\chi_{j_2n_2}\rangle$$

$$= \lim_{N\to\infty}\sum_{n=-N}^{N}e^{ik\pi n}\langle\chi_{j_10}|\chi_{j_2n}\rangle \tag{4}$$

and

$$\langle\chi_{j1}^k|\hat{H}_{\text{KS}}|\chi_{j2}^k\rangle = \lim_{N\to\infty}\sum_{n=-N}^{N}e^{ik\pi n}\langle\chi_{j_10}|\hat{H}_{\text{KS}}|\chi_{j_2n}\rangle \tag{5}$$

In the actual calculations, the infinite summations in eqs 4 and 5 are carried through with an N high enough such that the summations can be considered converged.

We shall add that π functions of neighboring unit cells will be parallel for translational and antiparallel for zigzag symmetry (thus for π bands the roles of $k = 0$ and $k = 1$ are interchanged

for those two symmetries). In discussing the band structures, two further aspects will be important. First, density-functional calculations produce most often valence bands that agree well with experimental results (see, for example, ref 9 for a discussion of the case of polymers), whereas the gap between occupied and unoccupied orbitals is underestimated, and the unoccupied bands may be less accurate. Second, with the present approach, all bands may move slightly up or down (with the same shift) when changing various internal parameters of the calculations. This will become important when comparing different systems of Figure 1.

The carbon backbones of all four polymers were taken to be planar (cf. Figure 1). For polyethylene, and *cis*- and *trans*-polybutadiene we used the following geometric parameters:[10] The C−C distance was taken to be 2.90 au for a single bond and 2.53 au for a double bond. The C−H distance was taken to be 2.08 au for an aliphatic C-atom and 2.05 au for an olefinic C-atom. All bond angles were taken to be 109.5° and 120° for an aliphatic and an olefinic C-atom, respectively. For polyacetylene we used the optimized parameters found in ref 11, (i.e., C−C bond lengths of 2.58 and 2.76 au). Here, the C−H distance was set equal to 2.10 au, and the C−C−C bond angle was equal to 128°.

For polyethylene, *trans*-polybutadiene, and polyacetylene we used translational symmetry, whereas for *cis*-polybutadiene we used zigzag symmetry, which allowed us to restrict the number of atoms in the unit cell to 10 atoms, which is the same value as that in case of *trans*-polybutadiene. For polyethylene and polyacetylene we used unit cells with six and four atoms, respectively.

3. First-Principles Results

Our calculated band structures of polyethylene, *cis*- and *trans*-polybutadiene, and polyacetylene are shown in Figure 2. Since polybutadiene may be considered a copolymer of polyethylene and polyacetylene, we shall start with discussing the bands of the latter two systems. The interatomic bonds of polyethylene are essentially due to sp^3 hybrids of carbon and s functions of hydrogen. The bands between −15 and −10 eV stem from the bonds between carbon and hydrogen [Figure 2a], whereas the bonds between the carbon atoms lead to orbitals in the whole valence-band range. For the C−H bonds, the symmetric and antisymmetric combinations with respect to the plane of the backbone give rise to two σ and two π bands. The σ bands have an avoided crossing with the σ bands arising from C−C σ bonds. Without this avoided crossing, the C−C σ-bonds would form two bands ranging in total from −23 to −8 eV.

For *trans*-polyacetylene [Figure 2d], the C−C and C−H σ bands are due to sp^2 hybrids on the C atoms and s functions on the H atoms. They form four bands between −22 and −9 eV in Figure 2d. Neglecting an avoided crossing, the C−C σ bonds would produce two broad bands between −22 and −9 eV. Finally, the C−C π bonds give rise to a filled band, which in Figure 2d is found between −10 eV and −5 eV, and an empty band. There is a gap (at $k = 0$) between this band and the lowest unoccupied band which is due to dimerization (i.e., the Peierls distortion).

The band structures of the polybutadienes [Figure 2b,c] are to some extent a mixture of the other two. Thus, the lowest bands are in all cases of σ symmetry and are formed by C−C bonding orbitals. Furthermore, we observe two π bands around −12 to −9 eV, which are due to orbitals of the CH_2 units and thus are found at positions in good agreement with those for polyethylene. Finally, the lowest unoccupied band as well as the highest π valence band are generated from π orbitals of the CH units.

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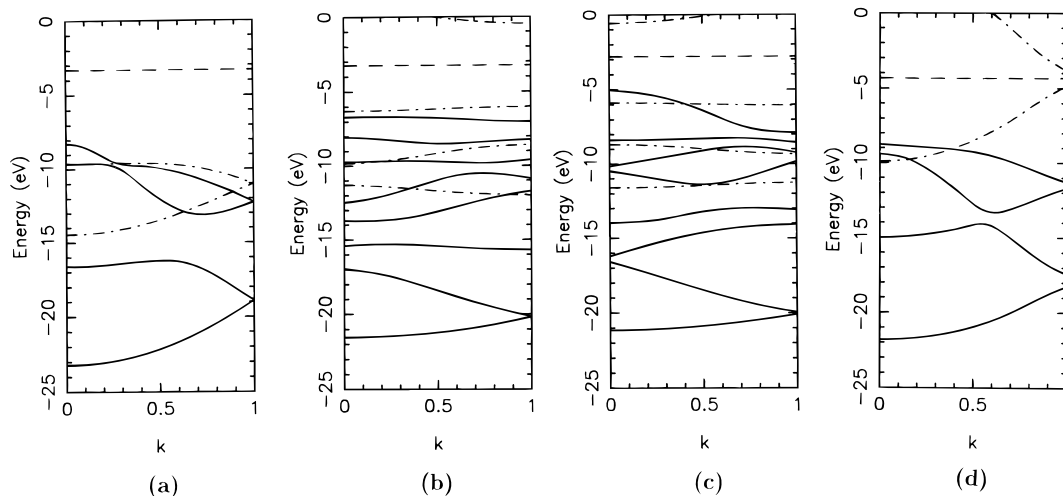*J. Phys. Chem. B, Vol. 101, No. 35, 1997* **6951**

Figure 2. Band structures of (a) polyethylene, (b) *cis*-, and (c) *trans*-polybutadiene, and (d) polyacetylene. The dashed lines mark the Fermi levels, and $k = 0$ and $k = 1$ are the center and the edge of the Brillouin zone, respectively. The π-bands are depicted as dashed–dotted lines.

To the best of our knowledge, the only other study of the band structures of polybutadiene is due to Shuai and Brédas.[12] They used the VEH (valence effective Hamiltonian) method, which is based on the Hartree–Fock approximation. They found the total valence-band width to be around 20 eV, whereas ours is around 15 eV. Experience has shown, however, that the bandwidths of density-functional calculations agree well with experiments, whereas those of Hartree–Fock calculations are overestimated (for example, see ref 13 for a discussion of polyethylene). With this difference in mind, the agreement between our bands of Figure 2 and those of Shuai and Brédas is good.

The Mulliken gross populations may give some qualitative insight into charge redistributions upon bonding. It turns out, however, that for the present systems there is only a very small redistribution. The total numbers of valence electrons remain close (within 1%) to five and six for the CH and CH_2 units, respectively, when passing from polyethylene and polyacetylene to polybutadiene. A more detailed information can be provided by the Mulliken overlap populations. In order to compare the strength of the C–C double bonds in the polybutadienes to that of polyacetylene, we performed a calculation on polyacetylene with a unit cell which was doubled (i.e., contained eight atoms). This made it possible to separate the overlap population of the shorter C–C bond from that of the longer C–C bond (for a more detailed discussion of this technical point, see ref 11). The net/overlap populations of the olefinic carbon atoms were 2.45/1.24 for polyacetylene, 2.52/1.41 for *cis*-polybutadiene, and 2.51/1.40 for *trans*-polybutadiene. This suggests that the bond order between the olefinic carbons is roughly constant in both polybutadienes and greater than the bond order of the double bond in polyacetylene (i.e., that the π electrons of polybutadiene are more localized than are those of polyacetylene).

For *cis*-polybutadiene [Figure 2b] the highest occupied band is a π band (width: 0.27 eV) whereas for *trans*-polybutadiene (Figure 2c) a broader σ band (width: 2.8 eV) crosses the highest occupied π band (width: 0.17 eV). These bandwidths suggest that the π electrons are rather localized. This is further supported by contour plots of the charge density of the highest occupied π band at $k = 0.5$ (midway between zone center and zone boundary), which are shown in Figure 3. Contour plots at other k values are very similar.

We find that the *cis* form is lower in energy (0.2 eV/10 atoms) than the *trans* form. But we stress that this difference is so small that it easily could change sign for optimized geometries.
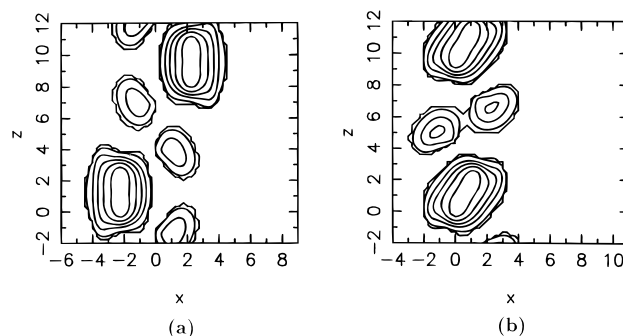

Figure 3. Contour plot of the electron density of the highest occupied π-band of (a) *cis*- and (b) *trans*-polybutadiene for $k = 0.5$. The contour values are 0.001, 0.002, 0.005, 0.010, 0.020, and 0.040 au.

In our calculations we assumed that the macromolecules have a planar backbone. This is the case for crystalline *cis*-polybutadiene, but not for crystalline *trans*-polybutadiene. The true geometry is, however, TSTS̄,[12,14] where T, S, and S̄ stand for torsion angles of the carbon backbone of 180°, 120°, and −120°, respectively (The T torsion angles are those that are found when looking along C–C bond between both CH or between both CH_2 units). Using this geometry, Shuai and Brédas[12] found from VEH calculations on *trans*-polybutadiene that the highest occupied valence band has a width of 0.93 eV as compared to 0.10 eV for the planar structure of *cis*-polybutadiene. This enlarged band width is ascribed to σ–π mixing. σ–π mixing should also have an effect on our band structure for *trans*-polybutadiene, especially because the highest occupied π band is crossed by a σ band.

cis- and *trans*-Polybutadiene have aroused interest because I_2 doping of *trans*-polybutadiene leads to a conducting polymer, while *cis*-polybutadiene does not become conducting under I_2 doping. A mechanism for this was proposed by Dai et al.[15] According to this, the conductivity in *trans*-polybutadiene stems from the formation of conjugated sequences through addition of I_2 to the double bonds and subsequent elimination of HI. In case of *cis*-polybutadiene the HI elimination is hindered because of an unfavorable conformation. Shuai and Brédas[12] found ionization potentials of 6.95 eV and 6.65 eV for *cis*- and *trans*-polybutadiene, respectively. From this they inferred that iodine is too weak an acceptor to dope polybutadiene to any significant extent by noting that even for poly(*p*-phenylene) with an ionization potential of about 5.5 eV stronger acceptors (e.g., AsF_5) are required. Having in mind that density-functional methods generally yield to low ionization potentials, our

ionization potentials of 6.02 eV for *cis*- and 5.04 eV for *trans*-polybutadiene support those same conclusions.

In total, all these results demonstrate that our results are accurate and in agreement with those of other studies wherever a comparison is possible.

4. The π Electrons

Having established that our first-principles method provides accurate information about the electronic orbitals and band structures, we can now turn to our central question, namely how does the localization of the π electrons affect their properties.

Of the four π bands in Figure 2b,c three are occupied. To a first approximation, the two lowest ones are mainly due to orbitals of the CH_2 units whereas the orbitals of the π bands around the Fermi level are formed predominantly by functions of the CH units. The Mulliken net populations can be used to explore this further. Thus for *cis*-polybutadiene the two lowest π orbitals have at the zone center ($k = 0$) net populations around 0.1 (the sum of all contributions, including overlap populations, normalized to 1) on each of the C and H atoms of the CH_2 units, and much smaller for the atoms of the CH units. The uppermost two π bands have dominating components on the C atoms of the CH-units, which are 0.25 and 0.35 for the lower and the upper π band, respectively. For $k = 1$ (at the zone boundary) similar results are found, and also the results for the *trans* isomer differ only marginally from these.

We shall now model the π bands using the following single-particle (sp) Hamiltonian

$$\hat{H}_{\pi,\text{sp}} = \sum_n \tilde{\epsilon}_n \hat{c}_n^\dagger \hat{c}_n + \sum_n t_{n,n+1}(\hat{c}_{n+1}^\dagger \hat{c}_n + \hat{c}_n^\dagger \hat{c}_{n+1}) \qquad (6)$$

Here, n numbers the sites along the polymer with each site being either a CH_2 or a CH unit. $\hat{c}_n$ and $\hat{c}_n^\dagger$ are the corresponding annihilation and creation operators for the π electrons; $\tilde{\epsilon}_n$ is an effective on-site energy which depends only on whether the site is a CH_2 or a CH unit. $\tilde{\epsilon}_n$ does, however, include effects that depend on the nearest environment of the site in question. The hopping integral $t_{n,n+1}$ depends on the type of both site n and site $n + 1$. Note that when choosing all basis functions such that their overlap is positive, $t_{n,n+1}$ should be negative. Furthermore, we have neglected an explicit spin dependence.

We fitted our first-principles π bands with those for the model of eq 6. (Note that, within a tight-binding model only considering nearest-neighbor interactions, there is no difference between zigzag and translational symmetry. In the case of *cis*-polyacetylene we only have to exchange the roles of $k = 0$ and $k = 1$ in the band structure and can then fit the band structure in exactly the same way as in case of *trans*-polybutadiene.).

For *cis*-/*trans*-polybutadiene we obtained thereby the following parameter values: aliphatic on-site energy $\tilde{\epsilon}_a = -9.8/-9.9$ eV, olefinic on-site energy $\tilde{\epsilon}_b = -3.7/-3.3$ eV, aliphatic hopping integral $t_{aa} = -1.4/-1.3$ eV, mixed hopping integral $t_{ab} = -1.7/-1.2$ eV, olefinic hopping integral $t_{bb} = -3.4/-3.1$ eV. For polyethylene we got as on-site energy $\tilde{\epsilon}_a = -11.5$ eV and as hopping integral $t_{aa} = -1.3$ eV. For polyacetylene we got $\tilde{\epsilon}_b = -3.9$ eV as on-site energy and $\tilde{t}_{bb} = -2.9$ eV, $t_{bb} = -3.5$ eV as hopping integrals for the single and double bonds, respectively.

We shall now use these parameter values in studying how the properties of the π electrons change when passing from polyacetylene or polyethylene to polybutadiene. However, one problem shows up as indicated in section 2. Thus, slightly different calculations for the same system may give band structures that are shifted rigidly with respect to each other.

Therefore, also the different sets of band structures in Figure 2 may suffer from such shifts. But since these shifts are essentially rigid, they will not lead to any modifications in the hopping integrals but merely in the on-site energies. We therefore start with a discussion of the hopping integrals.

The absolute values of the hopping integrals for polyethylene and the equivalent ones for the two isomers of polybutadiene are all significantly smaller than those for polyacetylene (about 2 eV). This implies that the π electrons of polyethylene and of the CH_2 units of polybutadiene are much more localized than are those of polyacetylene or of the CH units of polybutadiene. This is fully in accord with the fact that these orbitals are deeper in energy.

t_{bb} of polybutadiene is smaller than that of the double bonds of polyacetylene (-3.5 eV) but larger than that of the single bonds (-2.9 eV), which may mean that the corresponding bonds in polybutadiene have less double-bond character than the equivalent bonds of polyacetylene. This is further supported by the fact that the hopping integrals t_{ab} of polybutadiene are relatively large. But due to the large difference in the on-site energies of the CH_2 and the CH units, these larger hopping integrals (t_{ab}) do not lead to a noteworthy mixing of π functions from the CH and CH_2 units. This finding may first of all be taken as an indication that the Mulliken populations are not accurate when fine details shall be compared, especially for different systems. But it may also indicate that the difference in the double bonds between polyacetylene and the two isomers of polybutadiene is minor.

In order to arrive at a common energy scale for all compounds that allows us to compare the on-site energies we notice that the bottom-most orbital of the lowest valence band (of σ symmetry) for all four systems is formed mainly by 2s functions from *all* carbon atoms. We may thus assume that this orbital will have the same energy for all four compounds and can thereby obtain a common energy scale. When the on-site energies for polyacetylene are left unchanged, this results in $\tilde{\epsilon}_a = -10.1$ eV and $\tilde{\epsilon}_b = -3.9$ eV for *cis*-polybutadiene, $\tilde{\epsilon}_a = -10.5$ eV and $\tilde{\epsilon}_b = -3.9$ eV for *trans*-polybutadiene, $\tilde{\epsilon}_a = -10.1$ eV for polyethylene, and $\tilde{\epsilon}_b = -3.9$ eV unchanged for polyacetylene. Due to the uncertainties related to this shift we may estimate that these values are accurate to within ± 0.2 eV. With this approach we find accordingly that those electrons that for practical applications are the most interesting (i.e., the energetically upper-most electrons), are to be ascribed essentially the same on-site energies for all compounds, whereas $\tilde{\epsilon}_a$ shows some variations. The first result is the most important one, as we now shall argue.

By focusing on the π electrons, we can define the following many-body model Hamiltonian,

$$\hat{H} = \sum_n \sum_\sigma \epsilon_n \hat{c}_{n,\sigma}^\dagger c_{n,\sigma} + \sum_{n,m} \sum_\sigma t_{n,m}[\hat{c}_{n,\sigma}^\dagger \hat{c}_{m,\sigma} + \hat{c}_{m,\sigma}^\dagger \hat{c}_{n,\sigma}] +$$
$$\tfrac{1}{2} \sum_{n,m} \sum_{\sigma_1,\sigma_2} (1 + \delta_{n,m}) V_{n,m} \hat{c}_{n,\sigma_1}^\dagger \hat{c}_{n,\sigma_1} \hat{c}_{m,\sigma_2}^\dagger \hat{c}_{m,\sigma_2} \quad (7)$$

Here, $\hat{c}_{n,\sigma}$ and $\hat{c}_{n,\sigma}^\dagger$ is the annihilation and creation operator, respectively, of a π electron on site n with spin σ. ϵ_n and $t_{n,m}$ are on-site energies and hopping integrals, respectively, and $V_{n,m}$ are correlation parameters. The factors $\tfrac{1}{2}$ and $(1 + \delta_{n,m})$ have been included in order to avoid double-counting. Compared with the operator of eq 6 we have here explicitly included many-body effects through the parameters $V_{n,m}$.

The parameters we have determined above are not directly those of the model, but related to them. Thus, our first-principles calculations do not give any direct information on

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$V_{n,m}$. Within the Hartree−Fock approximation we will, however, set

$$\sum_n \sum_\sigma \{\epsilon_n \hat{c}_{n,\sigma}^\dagger \hat{c}_{n,\sigma} + {}^1/_2 \sum_m \sum_{\sigma_2} (1+\delta_{n,m}) V_{n,m} \hat{c}_{n,\sigma}^\dagger \hat{c}_{n,\sigma} \hat{c}_{m,\sigma_2}^\dagger \hat{c}_{m,\sigma_2} \}$$

$$\simeq \sum_n \sum_\sigma \{\epsilon_n \hat{c}_{n,\sigma}^\dagger \hat{c}_{n,\sigma} + + {}^1/_2 \sum_m \sum_{\sigma_2} (1+\delta_{n,m}) V_{n,m} [\hat{c}_{n,\sigma}^\dagger \hat{c}_{n,\sigma} \times$$
$$\langle \hat{c}_{m,\sigma_2}^\dagger \hat{c}_{m,\sigma_2} \rangle + \langle \hat{c}_{n,\sigma}^\dagger \hat{c}_{n,\sigma} \rangle \hat{c}_{m,\sigma_2}^\dagger \hat{c}_{m,\sigma_2} - \langle \hat{c}_{n,\sigma}^\dagger \hat{c}_{n,\sigma} \rangle \langle \hat{c}_{m,\sigma_2}^\dagger \hat{c}_{m,\sigma_2} \rangle]\}$$

$$= \sum_n \sum_\sigma \{[\epsilon_n + {}^1/_2 \sum_m \sum_{\sigma_2} \langle \hat{c}_{m,\sigma_2}^\dagger \hat{c}_{m,\sigma_2} \rangle (V_{n,m} + V_{m,n})] \hat{c}_{n,\sigma}^\dagger \hat{c}_{n,\sigma} -$$
$$ {}^1/_2 \sum_m \sum_{\sigma_2} (1+\delta_{n,m}) V_{n,m} \langle \hat{c}_{n,\sigma}^\dagger \hat{c}_{n,\sigma} \rangle \langle \hat{c}_{m,\sigma_2}^\dagger \hat{c}_{m,\sigma_2} \rangle \}$$

$$\equiv \sum_n \sum_\sigma \{\tilde{\epsilon}_n \hat{c}_{n,\sigma}^\dagger \hat{c}_{n,\sigma} - {}^1/_2 \sum_m \sum_{\sigma_2} V_{n,m} \langle \hat{c}_{n,\sigma}^\dagger \hat{c}_{n,\sigma} \rangle \langle \hat{c}_{m,\sigma_2}^\dagger \hat{c}_{m,\sigma_2} \rangle \}$$

$$(8)$$

with $\sum_{\sigma_2} \langle \hat{c}_{m,\sigma_2}^\dagger \hat{c}_{m,\sigma_2} \rangle$ being the number of electrons on site m. The tight-binding fits above have given the values of $\tilde{\epsilon}_n$ that are seen to depend both on the "real" on-site energies ϵ_n as well as on the Hubbard parameters $V_{n,m}$ together with the numbers of electrons on the different sites.

We may use the Mulliken gross populations in estimating the numbers of π electrons of the individual sites. For polybutadiene, there are three valence bands of π symmetry. For the *trans* isomer the lowest π band has populations corresponding to 0.90 electrons on each CH_2 unit, whereas the second-lowest one has 0.85 electrons on each CH_2 unit. On the other hand, the highest occupied π band has only 0.24 electrons on the CH_2 units. Since there are two CH_2 and two CH units per unit cell, these numbers correspond obviously to 0.10, 0.15, and 0.76 π electrons per CH unit for the three bands, respectively. For the *cis* isomer the numbers on the CH_2 units are equivalently 0.90, 0.89, and 0.20, respectively, giving 0.10, 0.11, and 0.80 for the CH units.

For pure *trans*-polyacetylene, there is one π electron per CH unit, and for pure polyethylene there are two π electrons per CH_2 unit. These numbers are thus only marginally modified when passing to polybutadiene, when taking *all* three π valence bands into account. Then we find 1.99 π electrons per CH_2 unit and 1.01 π electrons/CH unit.

We now assume that only those $V_{n,m}$ with $|n-m| \le 1$ are nonvanishing (i.e., we neglect long-range interactions), and that they take the values U_a and U_b for $n = m$ for CH_2 and CH units, respectively, and V_{aa}, V_{ab}, and V_{bb} for $|n-m| = 1$ for n and m both corresponding to CH_2 units, one to a CH_2 unit and one to a CH unit, and both to CH units, respectively. Moreover, we shall for simplicity assume that we have two and one π electrons on the CH_2 and the CH units, respectively. By finally assuming that the fitted on-site energies $\tilde{\epsilon}_a$ and $\tilde{\epsilon}_b$ are constants independent on the system (which is a good approximation according to the discussion above), we arrive at the following four equations

$$\epsilon_b + U_b + V_{bb} + 2V_{ab} = \tilde{\epsilon}_b$$

$$\epsilon_a + U_a + 2V_{aa} + V_{ab} = \tilde{\epsilon}_a$$

$$\epsilon_b + U_b + 2V_{bb} = \tilde{\epsilon}_b$$

$$\epsilon_a + U_a + 4V_{aa} = \tilde{\epsilon}_a \qquad (9)$$

where the first two equations are those for polybutadiene and the last two for polyacetylene and polyethylene, respectively.

These equations lead to

$$V_{bb} = 2V_{ab} = 4V_{aa} \qquad (10)$$

(i.e., the Hubbard parameters for nearest-neighbor interactions are four times larger between CH units than between CH_2 units and twice that between CH and CH_2 units). Due to the larger localization of the π electrons of the CH_2 units than those of the CH units, this result appears to be reasonable.

In order to arrive at absolute values for the Hubbard parameters V and U we consider an isolated ethylene molecule, C_2H_4, for which we performed calculations similar to those reported above. The purpose here is not to study that molecule in detail and we shall therefore solely focus on those results that are relevant for the polymers.

The energetically lowest two valence orbitals of ethylene are to a good approximation the bonding and antibonding linear combination of the carbon 2s functions. With $\tilde{\epsilon}_s$ and t_s being the effective on-site energies and hopping integrals for those, the energies of the two orbitals will be $\tilde{\epsilon}_s \pm t_s$. Assuming that these parameter values are the same for the polymers (this is a reasonable assumption since these orbitals are fairly localized and thus less sensitive to the long-range interactions), the bottom of the valence bands will be at $\tilde{\epsilon}_s - 2|t_s|$, and by using the same approximations as above for the polymers this value will fix our energy scale. The calculated orbital energies for ethylene are accordingly shifted *en bloc* such that the estimated band energy agrees with that calculated for polyacetylene.

Ethylene has one occupied π orbital which appears at $\tilde{\epsilon}_e - |t_{bb}|$, where we have assumed that the hopping integral t_{bb} is as that for polyacetylene. Moreover, the on-site energy obeys

$$\tilde{\epsilon}_e = \epsilon_b + U_b + V_{bb} \qquad (11)$$

The orbital energy from the density-functional calculations predict $\tilde{\epsilon}_e = -4.7$ eV, which then immediately leads to $V_{bb} = 0.8$ eV, when using the models of eqs 7 and 8 for the finite ethylene molecule. Since each of $\tilde{\epsilon}_s$, ϵ_b, and U_b is given by an uncertainty of ≈ 0.2 eV we will estimate the uncertainty of V_{bb} to be ± 0.5 eV. V_{bb} describes how much energy it will cost to change the number of π electrons on one site due to the electrons on a neighboring site. It does take into account that such a change leads to a redistribution of all electrons (i.e., screening effects). Intuitively, we will expect that these screening effects are almost exclusively located to the electrons at the two sites involved, and therefore that studying the ethylene molecule instead of the whole polymer is an acceptable approximation.

In order to estimate U_b we have to change the populations ascribed to the individual atoms. So far the symmetry of our systems has defined these uniquely, but the on-site Hubbard parameter U_b can only be determined by lowering the symmetry. When lowering the symmetry for the ethylene molecule, such that there will be more electrons around one C atom than around the other, we enter the problem that we have to split the total (π) electron distribution into distinct atomic components. Furthermore, the screening effects discussed above are expected to occur not only at the site whose population is changed but at least also at the nearest neighboring sites. For the ethylene molecule, any site has only one neighboring site and the screening becomes less effective, which in turn results in too large values for U_b. In fact, applying so-called constrained density-functional calculations on the ethylene molecule (this

procedure will be described in detail elsewhere[16]) leads to values of U_b well above 10 eV which we consider much too large and due to the lacking screening.

5. Conclusions

We have presented results of the first parameter-free study of the electronic properties of polybutadiene. The calculations were performed with a density-functional method that has been developed explicitly for treating polymeric systems. In the present work we considered two isomers, a *trans* and a *cis* isomer, of polybutadiene. This polymer consists of repeated units of two CH_2 and two CH groups and may thus be considered a copolymer of polyethylene and polyacetylene. In order to study the effects of each type of groups separately and those that are special for the complete system we also studied polyethylene and *trans*-polyacetylene.

Our calculated band structures agreed reasonably with those obtained previously using the VEH method. Since the VEH method represents a parametrisation of *ab initio* Hartree−Fock calculations, it suffers from the overestimate of bandwidths inherent to such methods, and with this in mind most of the differences between the results of our calculations and those based on the VEH method could be explained.

It turned out that the band structures of the polybutadiene isomers to a large extent could be considered as a superposition of those of polyethylene and of *trans*-polyacetylene. There were no significant shifts when passing from the "parent" polymers to the copolymer, and the Mulliken populations gave only marginal changes in the electronic distributions. Since neither polyethylene nor *trans*-polyacetylene consists of highly polarized units, the formation of the copolymers does not lead to the occurrence of extra electrostatic potentials which could lead to band shifts. Thus, we suggest that in order to obtain a copolymer of the polybutadiene type with properties that are more specific for the copolymer one should replace (parts of) the hydrogen atoms with (e.g., halogen atoms, cyano groups, or hydroxy groups).

Since our band structures agreed with those found earlier, the explanation of Dai et al. for why the *trans* but not the *cis* isomer becomes conducting upon I_2 doping remains valid also when basing it on our results.

Considering polybutadiene as an example of the conducting polymers the π orbitals closest to the Fermi level become the most important ones. These are for polybutadiene largely localized to the CH units and are very similar to those of the *trans*-polyacetylene parent polymer. By studying the occupied π bands in detail we found that the hopping integrals and Hubbard parameters for the interactions between the CH_2 units were considerably smaller than those for the CH units. This is in accordance with the larger localization of the CH_2-centered π electrons than of the CH-centered ones. By finally including also ethylene in the general discussion we were able to estimate the nearest-neighbor Hubbard parameters. We found that these were small, indicating that the electronic screening in these materials is very effective. Thus, within models of the form of eq 4, only terms with $|n - m| \leq 1$ need to be included.

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References and Notes

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