anionic species. This supports the possibility of a reaction product formed between sodium and the tungsten species.

Depth profiling shows (Figures 4 and 5) the reduction of Nb_2O_5 to Nb^{4+} and Nb^{2+}. Preferential sputtering leads to the presence of a steady-state mixture of niobium oxidation states. The presence of sodium is also confirmed (Figure 6) by depth profiling. This is expected if sodium and tungsten are associated in the form of a precipitation product.

Calculations based on the RBS data suggest an average stoichiometric formula of NbO_2 for the oxide layer. This is unexpected based on other studies of anodically grown niobium films which predict the presence of Nb_2O_5. Also, the RBS data (Figures 7 and 8) show evenly spaced precipitation bands, as would be expected for a precipitation reaction occurring under the influence of an electric field. In addition, it was noted that increased voltage (100 V as compared to 72 V) allowed the formation of a more extensive layering structure (five peaks as opposed to three peaks) within the oxide film. This is useful for those materials where maximum incorporation of anions would be beneficial.

The anodic oxidation of niobium and the incorporation of anions into forming anodic films are important areas of research. With increased understanding of how these processes operate, steps can be made to control and adapt these processes to our needs.

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Electronic Transmission Coefficient as a Tool for the Analysis of the Effect of Impurities and Defects on the Electronic Structure of Polymers

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The effect of impurities and defects on the electronic structure of some polymeric chains has been approached by considering a model infinite chain ···AAAABAAAA···, where B is an impurity or defect embedded in an infinite chain ···AAAAA···. The transmission coefficient $t(E)$ and differential density of states $\Delta DOS(E)$ curves have been used to characterize the different types of interactions between an impurity/defect level and an energy band. When the energy band can interact with more than one level of the impurity/defect, interference effects have to be considered. A rule to predict the constructive/destructive nature of these interferences is given. The use of the transmission coefficient as an analytical tool and the connection with the usual orbital interaction analysis of the electronic structure of molecules and solids are illustrated. The effect of several C=X impurities (X = O, S, CH_2) and sp^3 defects as well as donor and acceptor pendant groups on the electronic structure of polyacetylene chains has been considered.

1. Introduction

Impurities and defects have a strong influence on the electronic structure of polymeric materials. Hence, several theoretical approaches have been recently developed[1] with the aim of understanding the consequences of this rupture of translational invariance. Important tools to analyze the phenomenon, like the density of states or the charge–bond order matrix for several imperfect polymers have thus been evaluated.[1] Sometimes, the problem has been faced from a different methodological perspective, by using standard quantum chemical methods to perform calculations on discrete molecular species aiming to represent the local effect of such impurities.[2-5] Although both approaches have been very important in providing a basis for the understanding of the chemistry of these imperfect polymers, they seem to be less well suited to face one of the most exciting problems in the field, i.e., the control of

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[†] The Laboratoire de Chimie Théorique is associated with the CNRS (UA 506) and is a member of ICMO and IPCM (Orsay).

(1) For some leading references see: (a) Ladik, J.; Seel, M. *Phys. Rev. B* **1976**, *13*, 5338. (b) Del Re, G.; Ladik, J. *Chem. Phys.* **1980**, *49*, 321. (c) Seel, M.; Ladik, J. *Phys. Rev. B* **1985**, *32*, 5124. (d) Seel, M.; Del Re, G.; Ladik, J. *J. Comp. Chem.* **1982**, *3*, 451. (e) Seel, M. *Int. J. Quantum Chem.* **1984**, *26*, 753. (f) Gies, M.; Seel, M.; Ladik, J. *J. Mol. Struct. (THEOCHEM)* **1987**, *150*, 267. (g) Hennico, G.; Delhalle, J.; André, J.-M.; Seel, M.; Ladik, J. *Solid State Commun.* **1987**, *64*, 1257. (h) Biczo, G. *Can. J. Chem.* **1985**, *63*, 1992, and references therein. (i) The case of an impurity B embedded in an infinite linear chain ···AABAA··· has also been briefly considered by using the moments method: Burdett, J. K.; Lee, S.; Sha, W. C. *Croat. Chem. Acta* **1984**, *57*, 1193.

(2) Jeyadev, S.; Conwell, E. M. *Phys. Rev. B* **1988**, *37*, 8262.

(3) Tanaka, S.; Yamanaka, S.; Koike, T.; Yamabe, S. *Phys. Rev. B* **1985**, *32*, 2731.

(4) Surjan, P. R.; Kuzmany, H. *Phys. Rev. B* **1986**, *33*, 2615.

(5) Navarrete, J. T. L.; Zerbi, G. *Solid State Commun.* **1987**, *64*, 1183.

0897-4756/89/2801-0225$01.50/0

electronic transmission by an impurity embedded in a polymeric chain and its possible response to external changes. In our opinion, a rational approach to this problem should rely on a method able to directly assess the electronic transmission properties of the chain through the impurity.[6,7] In addition, the method should be easily amenable to a *chemical understanding* of the consequences of structural and/or chemical modifications in the impurity.

A useful step toward this end is the calculation of the transmission coefficient, $t(E)$, which is directly related to the chain low-voltage conductance.[8-10] An important tool in this process is the building of the so-called scattering matrix, $\mathbf{S}(E)$, which relates the amplitudes of the outgoing waves to the incoming waves on the impurity. This approach is well-known in solid-state physics,[11-13] but, to our knowledge, has not yet been applied to the discussion of chemical systems. Sautet and Joachim[14,15] have recently developed a method based on these ideas. Although it was initially presented with the restriction of a single orbital per site,[14] it was later generalized to a many orbitals per site formulation.[15] Several applications, such as the effect of benzene or *N*-salicylideneaniline embedded in polyacetylene, have been considered.[16,17] The original reports on this method were mainly concerned either with the technical aspects of the procedure or with the numerical results obtained for several systems. Thus, a presentation showing how these results can be analyzed from the viewpoint of the orbital interaction analysis,[18] which has proved to be so fruitful in rationalizing the electronic structure of both molecules and crystalline materials,[19] is still lacking. This we will try to remedy in this contribution.

The paper is organized as follows. In the next section, we briefly recall the main points of the method and outline the different steps needed to analyze the transmission coefficient and differential density of states as a function of the energy. As an illustration, in section 3 we consider in detail the case of several impurities in a polyacetylene chain. Finally, the relevance of these results in understanding some recent reports concerning the ability of sp^3 defects[20,21] or C=O units[22] to interrupt the conjugation in polyacetylene is discussed in section 4. Let us point out, however, that in spite of the interest of the last problem by itself, our main present concern is in showing how the results concerning the transmission coefficient can be understood on quite a simple basis. It is hoped that extension of this type of analysis to other impurities or defects will lead to a series of simple ideas useful for molecular electronics.

2. Relation between the Transmission Coefficient and the Nature of the Impurity via the Scattering Matrix Approach

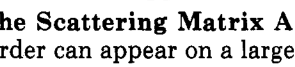
Outline of the Scattering Matrix Approach. Although the disorder can appear on a large scale, and despite the fact that the dimensionality of the problem can have a substantial influence, a first step toward the chemical understanding of the role of impurities and defects in polymers is the study of a chain **1**, built from a

···AAABAAA···

1

one-dimensional chain with repeat unit A where a single impurity B has been inserted. The overall system is therefore nonperiodic, and band theory is not valid anymore. However, this system is not random, and the periodic nature of the chain "ends" can be fully exploited in the study of the electronic structure of **1**. The periodic portions of the chain (···AAAAA···) are characterized by a set of continuous energy bands. For each allowed energy, the wave function has an extended nature and appears as a combination of two modulated plane waves propagating in each direction. System **1** can then be approached from a scattering theoretical viewpoint; i.e., how are the plane waves characteristic of the periodic chain affected by the presence of B?

If chain **1** is represented by **2**, where α, β (γ, δ) are the amplitudes of the Bloch waves on the left (right) side of the impurity, the transmission coefficient $t(E)$ (i.e., the elastic transmission coefficient of an electron with energy E coming from one of the periodic chains) will be defined as $t(E) = |\gamma|^2/|\alpha|^2$ if $\delta = 0$. In the periodic case (B = A in **1**), the plane waves are of course not affected and $t(E)$ is 1 for each allowed energy. On the other hand, a complete rupture in the chain will be associated with the total reflection of the waves, i.e., $t(E) = 0$. When a molecular impurity (B) is inserted in the chain, the transmission coefficient indicates how strongly the extended nature of the wave function is interrupted. It quantifies how the left and right semichains are electronically connected (or disconnected) *at the energy E*. This energy-dependent coefficient can give a direct insight into the conducting properties of the chain **1** via the Landauer formula.[8]



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As mentioned above, a procedure for the calculation of the transmission coefficient $t(E)$ and the associated differential density of states ΔDOS(E) (i.e., the change of the chain density of states due to the introduction of B into the chain) has been developed.[14,15] It involves the calculation of $t(E)$ from the scattering matrix $\mathbf{S}(E)$ through the relation[23]

$$t(E) = N^{-1}\ \mathrm{Tr}\ [\Gamma^{+}(E)\ \Gamma(E)]$$

where $\Gamma(E)$ is the diagonal block of $\mathbf{S}(E)$ and N the number of electronic channels considered. In turn, $\mathbf{S}(E)$ can be obtained from the transfer matrix $\mathbf{T}(E)$.[7] Essentially, this transfer matrix allows the determination of the amplitude of the wave function corresponding to an energy

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(6) (a) Joachim, C. *J. Mol. Electron.* **1988**, *4*, 125. (b) Sautet, P.; Joachim, C. *J. Phys. C* **1988**, *21*, 3939.

(7) For a recent review about electron transfer in solids see: Mikkelsen, K. V.; Ratner, M. A. *Chem. Rev.* **1987**, *87*, 113.

(8) Landauer, R. *Philos. Mag.* **1970**, *21*, 863.

(9) Azbel, M. Ya. *Phys. Lett. A* **1980**, *78*, 410; *Solid State Commun.* **1983**, *45*, 527.

(10) Fisher, D. S.; Lee, P. A. *Phys. Rev. B* **1981**, *23*, 6851.

(11) Stone, A. D.; Joannopoulos, J. D.; Chadi, D. J. *Phys. Rev. B* **1981**, *24*, 5583.

(12) Anderson, P. W.; Thouless, D. J.; Abraham, E.; Fischer, D. S. *Phys. Rev. B* **1980**, *22*, 3519.

(13) Liu, Y. Y.; Riklund, R.; Chao, K. A. *Phys. Rev. B* **1985**, *32*, 8387.

(14) Sautet, P.; Joachim, C. *Phys. Rev. B* **1988**, *38*, 12238.

(15) Sautet, P.; Joachim, C., to be published.

(16) Sautet, P.; Joachim, C. *Chem. Phys. Lett.* **1988**, *153*, 511.

(17) Sautet, P.; Joachim, C. *Chem. Phys.*, submitted for publication.

(18) Hoffmann, R. *Acc. Chem. Res.* **1971**, *4*, 1.

(19) Albright, T. A.; Burdett, J. K.; Whangbo, M.-H. *Orbital Interactions in Chemistry*; Wiley: New York, 1985.

(20) Yang, X. Q.; Tanner, D. B.; Arbuckle, G.; MacDiarmid, A. G.; Epstein, A. J. *Synth. Met.* **1987**, *17*, 277.

(21) Zuo, F.; Epstein, A. J.; Yang, X. Q.; Tanner, D. B.; Arbuckle, G.; MacDiarmid, A. G. *Synth. Met.* **1987**, *17*, 433.

(22) Chien, J. C. W.; Babu, G. N. *J. Chem. Phys.* **1985**, *82*, 441.

(23) Washburn, S.; Webb, R. A. *Adv. Phys.* **1986**, *35*, 375.

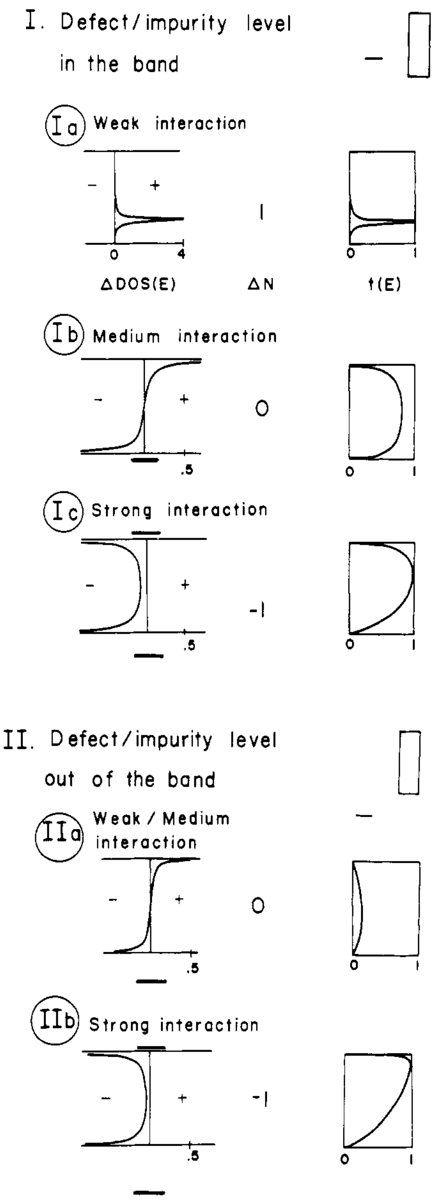


Figure 1. Different types of ΔDOS(E) and $t(E)$ curves for a single level impurity/defect (B) embedded in an infinite chain (i.e., ···AAABAAA···). The strength of the impurity/defect–chain interaction is given relative to the intercell interaction in the chain ···AAAAAA···. ΔN represents the impurity/defect induced change of the number of states within the band energy range.

E for any unit of 1, once the amplitudes in two successive units are chosen. Since a version of the formalism with many orbitals per site has been developed, the chemical nature of A and B can be explicitly introduced in the calculation. The actual version of the method makes use of the extended Hückel type approximations.[24]

The analysis of the computed $t(E)$ involves three main steps: (a) determination of the fragment molecular orbitals (FMO) of B and the band structure of ···AAAAAAAA···; (b) determination of the individual contributions to the transmission coefficient from every FMO of B; (c) mixing these contributions to obtain $t(E)$. The first step is straightforward. In the next two subsections we will consider steps b and c, respectively.

Qualitative Transmission Coefficient Curves for an Impurity Level Interacting with a Single Band. There are two factors to consider when looking at the coupling of a fragment molecular orbital (FMO) of an impurity (B) with a single band of the chain (···AAAA···): (a) the overlap factor, which will be proportional to the overlap integral between the pertinent atomic orbitals of the chain and the impurity; (b) the energy factor, which depends on the position of the FMO energy level with respect to the energy levels of the band. Not only does this relative energy contribute to the mixing coefficients between the levels of the chain and the impurity, but the relative position with respect to the band as a whole (i.e., within or outside the band energy range) can also have a strong influence on the shapes of the ΔDOS(E) and $t(E)$ curves.

Chart I

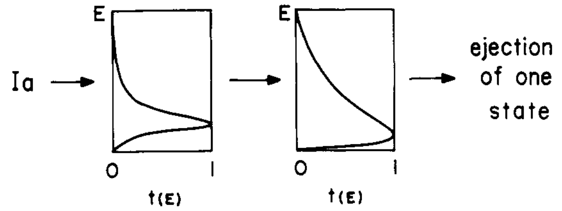
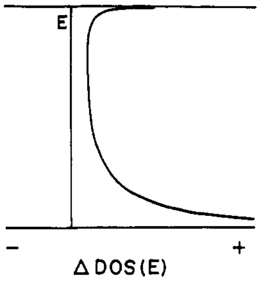


Chart II



On the basis of an analytic model study for a one-level impurity embedded in a one-band chain[14] and of the actual analysis of several many orbitals per site calculations, several types of interaction between an impurity level and a band can be distinguished. The ΔDOS(E) and $t(E)$ curves for some typical cases are schematically presented in Figure 1, where the impurity level has been considered to be either in the lower half of the band energy range or below outside it. The impurity–polymer interaction strengths (B–A type) in this figure are given relative to those corresponding to the intercell interactions in the polymer (A–A type).

In weak interaction cases (Ia and IIa in Figure 1) the transmission coefficient is of course small in average. However, if the level lies within the band (case Ia), a resonance in $t(E)$ is found around the impurity energy level: a tunnel effect occurs through the impurity level. High $t(E)$ values can thus be found on a *narrow* energy range even in the case of small coupling. Such a phenomenon is of course not found if the impurity level lies outside the band. A study of how to control the energy range where these peaks in $t(E)$ appear, through chemical or structural modifications of the impurity, could lead to some useful ideas to delineate current switching systems.

When the strength of the interaction increases, the peak in the $t(E)$ curve is progressively broadened and shifted down in energy (Chart I). Eventually, one state is ejected out of the band energy range. The broadening of the resonance is an obvious result of the increase of the interaction, and the shifting down results from the fact that the impurity level (which, recall, was chosen to be in the lower part of the band energy range) is subject to the action of more stabilizing interactions with upper states of the band than destabilizing ones with lower band states.

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(24) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397.

Concerning the ΔDOS(E) evolution, the narrow peak in Ia (Chart I) broadens and shifts down but at the same time there is also some accumulation of states at the top of the band. A typical situation just before the ejection of the level is shown in Chart II. Worthy of mention is that the states in the lowest part of the band are mainly "chain"-type initially, but when the interaction increases these states become more and more "impurity"-type. This is the result of the appreciable interaction (recall interactions are relative to those in the polymer chain) and of the asymmetry of the impurity level with respect to the band energy range. In other words, except for very small interactions, when many levels of one fragment interact with a single level of another fragment whose energy level is asymmetrically located with respect to the energy range of the many-levels system, the many upper levels pushing down the single level dominate over the fewer lower levels pushing up the same single level. It is also easily understandable that small "bits" of the single level go to the many higher energy states although less to the highest ones, and consequently, $t(E)$ curves such those at the right in Chart I result. Finally, a further increase of the interaction results in a state being ejected out of the band at lower energies. Although the function corresponding to this state will have important tails in the chain, it is fundamentally "impurity"-type. When this state is ejected, the number of states in ΔDOS(E) decreases by one, the lower part of the band being the most affected. The curve then has a typical S shape (see Figure 1, case Ib). Simultaneously, $t(E)$ decreases in the lower part of the band: the maximum value of 1 is not reached anymore.

A further increase of the interaction results in an increase of $t(E)$ in the medium and higher energy values simply because of the stronger mixing. Although $t(E)$ can never reach the value of 1, it can have very sizeable values (typically of the order of 0.7). There is also an increase of the above-mentioned mainly "chain" states near the top of the band. A typical situation is that of case Ib in Figure 1. When the interaction is strong, a second state is pushed out of the band to higher energies. This state is fundamentally "chain"-type. The ΔDOS(E) curve will thus present a second strongly negative zone (recall the curve should have an integrated value of -1) to give a U-shape curve. The ejection of the "chain"-type state increases the weight of the impurity in the band, and $t(E)$ can again reach values as high as 1 (case Ic in Figure 1). Usually the $t(E)$ curve is very broad due to the strong interaction.

A similar description could be done for the case where the impurity level lies out of the band. However, as sketched in Figure 1, the transmission coefficient never reaches high values for the case of weak or medium interactions. Although analytically one can also find the ejection of a "chain"-type state in the case of strong interaction (with a corresponding high transmission coefficient), this would most often correspond to unrealistically high interaction strengths once the "chemical" nature of these interactions is considered. To summarize, for defect/impurity levels lying within the band energy range, important transmission coefficients can be found (in different energy intervals) for almost any type of interaction strength. In contrast, when the state is out of the band energy range, sizeable values of $t(E)$ can only be found for relatively strong interactions (IIa < interaction < IIb).

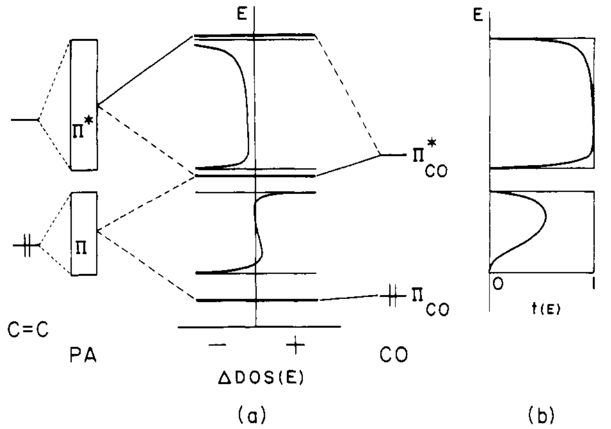

Figure 2. Interaction diagram (a) and transmission coefficient curves (b) for a C=O group impurity embedded in a polyacetylene (PA) chain, 3. In (a), band edges and discrete levels are represented by thin and heavy lines, respectively.

Interferences. Once the individual impurity level contributions have been estimated, one needs to combine them to determine the qualitative shape of the *total* $t(E)$ curve. According to the scattering matrix approach,[14,15] the individual contributions are not additive. Destructive/constructive interferences can occur. We then need to establish a qualitative rule to know the constructive or destructive nature of these interferences when trying to analyze a calculated $t(E)$ curve. An important point is that the nature of the interference is very energy dependent.[16]

A simple rule can be given once the following two criteria characterizing each of the impurity levels are determined: (a) the relative energy position of the impurity level with respect to the band level in question (i.e., upper or lower); (b) the phase relationship between the atomic sites connected to the chains for the impurity level (i.e., in-phase or out-of-phase). If two impurity levels interact with a band level, the interference is destructive if the two impurity levels coincide in *one and only one* of the two criteria above. Otherwise the interference is constructive. For instance, if we consider two impurity levels with the same phase relationship between the connected sites, interferences will be destructive for energy values between the two levels but constructive outside this energy range, where the energy position factor is identical. An interference hole ($t(E) = 0$) appears between the two levels, and it can be shown that it lies closer to the impurity level with the smallest coupling with the chain. The above-mentioned rule can be proved in the case of a simple single orbital per site band model.[25] For the many orbitals per site case it is only approximate but still generally holds. Although the meaning of the term "destructive interference" will be clearer after the examples of the next section, let us point out that it means not that the two individual $t(E)$ contributions should be exactly substracted but that there is a decrease with respect to the strongest contribution.

3. Application to Polyacetylene Chains

In this section we analyze the origin of the $t(E)$ and ΔDOS(E) curves for some polyacetylene chains containing defects or impurities. An extended Hückel type Hamiltonian[24] and a modified Wolfsberg–Helmholz formula[26] to calculate the nondiagonal elements H_{ij} were used. The exponents and parameters for H, C, N, O, and S were taken from previous work.[27,28]

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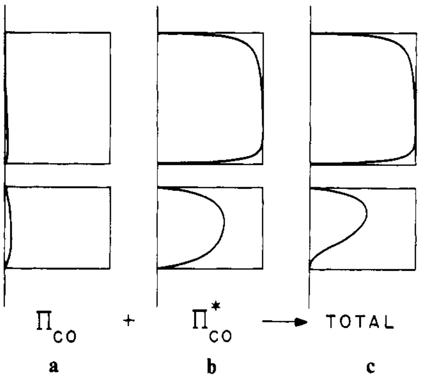
(25) The specific case of two degenerate defect states interacting with a band energy state was considered in ref 6a. The treatment has recently been generalized: Sautet, P.; Joachim, C., to be published.

(26) Ammeter, J. H.; Bürgi, H.-B.; Thibeault, J.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 3686.

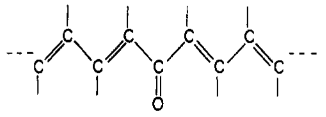
(27) Summerville, R. H.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 7240.

(28) Hughbanks, T.; Hoffmann, R. *J. Am. Chem. Soc.* **1983**, *105*, 1150.

Chart III



A. C=O Groups. The interaction diagram and $t(E)$ curves appropriate for chain **3** are reported in Figure 2, parts a and b, respectively. Shown in Figure 2a are the discrete π levels of the C=O group at right, the π and π^* bands of the polyacetylene chain at left, and the calculated ΔDOS(E) for **3** in the middle. This ΔDOS(E) consists of two continuous parts, corresponding to the polyacetylene energy bands, and three discrete levels appearing in the forbidden energy region.



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The curves corresponding to the π^* band are easy to understand. From the two levels of C=O, the $\pi_{C=O}$ is concentrated on the oxygen and very far from the band energy range, whereas the $\pi^*_{C=O}$ is strongly concentrated on the carbon and lies within the band energy range. It is the latter orbital that almost completely determines the ΔDOS(E) and $t(E)$. The interaction is good in both energy and overlap terms, and, consequently, it is a typical type Ic one. The $\pi^*_{C=O}$ level is thus ejected into the interband gap, and a chain state is pushed up out of the band. According to our preceding discussion, the $t(E)$ curve presents very high values along a broad energy range.

The situation is quite different for the π band. In that case, both the $\pi_{C=O}$ and $\pi^*_{C=O}$ levels play a role. Because the $\pi_{C=O}$ is strongly centered on the oxygen, the interaction is weaker and additionally, since the level lies out of the band, it is a type IIa interaction. The ΔDOS(E) has the typical S shape with a negative contribution in the lower part of the band and a positive contribution in the upper part. The transmission coefficient is small all along the band (Chart III, a). $\pi^*_{C=O}$ has a very good overlap coupling but is nevertheless out of the band. The interaction is somewhat between types IIa and IIb: the $t(E)$ curve is broad and reaches values of 0.63 (Chart III, b). The competition of the two contributions is clearly seen in the ΔDOS(E) of Figure 2a, where the curve retains the S shape but with a significant portion of the positive upper part shifted to the lower part of the band. In other words, the destabilizing effect resulting from the interaction with the $\pi_{C=O}$ is considerably relieved by the interaction with the $\pi^*_{C=O}$. The next step is to look for the possible interference effect concerning this π band. Since the same atom is linked to the right and left chains, there is no phase change in any of the two orbitals of the impurity ($\pi_{C=O}$ and $\pi^*_{C=O}$). We can conclude from the qualitative rule that the interference will be destructive in the region between the levels, i.e., in the whole energy range of the π band. As mentioned, an interference hole should be produced near the state with the smaller coupling, which is the $\pi_{C=O}$. This is clearly illustrated in Chart III where the calculated separate contributions to $t(E)$ and the total curve are reported. The maximum values of the total curve are ~0.5.

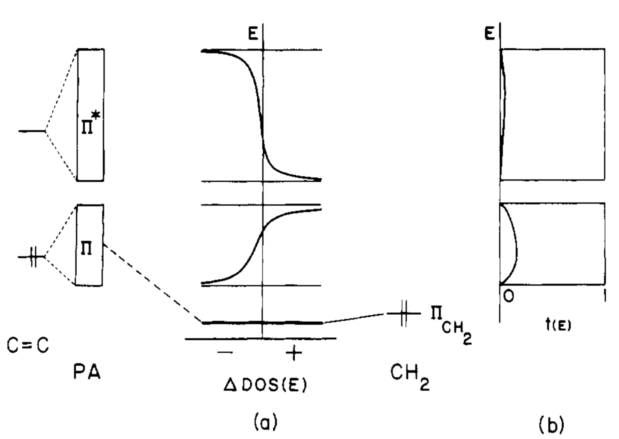


Figure 3. Interaction diagram (a) and transmission coefficient curves (b) for an sp^3 defect embedded in a polyacetylene (PA) chain. The $\pi^*_{CH_2}$ level is out of the energy range of the figure. In (a), band edges and discrete levels are represented by thin and heavy lines, respectively.

Concerning the discrete states in Figure 2a, the lowest one is a "$\pi_{C=O}$" state very strongly localized on the impurity (i.e., the coefficients on the chain decrease very fastly, being already very small on the third carbon atom near the impurity), and the highest one is "chain" type. The middle one is an impurity state (i.e., a $\pi^*_{C=O}$ one), which nevertheless has long and sizeable tails on the polyacetylene chains. One should thus expect noticeable interactions between this last type of levels in polymers with a high concentration of CO groups.

B. sp^3 Defects. The interaction diagram and $t(E)$ curves for an sp^3 defect in polyacetylene are reported in Figure 3. The important difference with the previous case is that now the two defect levels are out of the band energy range. In addition, the $\pi^*_{CH_2}$ is well out of the energy range of the π^* band, which means that the interaction is very weak. For the π_{CH_2} level, although the overlap is somewhat better than for $\pi_{C=O}$ the interaction is still relatively weak. Thus, in both cases the interaction type is IIa, and consequently small transmission coefficients should be expected. Because of the energy factor, those associated with the π band should be better, as is indeed found (see Figure 3). The interactions are nevertheless small enough so that no detectable interference effects are found. The maximum in the $t(E)$ curve for the π band is 0.16, which clearly proves that sp^3 defects severely break the conjugation in polyacetylene. We note that this time no discrete level appears in the gap between the π and π^* bands.

C. C=X (X = O, S, CH$_2$) Groups as Impurities. In subsection A, where the C=O impurity was considered, it was shown how the $t(E)$ curve for the π band was related to the $\pi_{C=O}$ and $\pi^*_{C=O}$ contributions. In that case the $\pi^*_{C=O}$ contribution was dominant. As an example of how the $t(E)$ curves can be modified by chemical substitution, we compare here the results for C=X groups (X = O, S, CH$_2$) as impurities. The results are reported in Figure 4. As could be expected, there is a clear change for the π band and a very minor change for the π^*.

The logic behind the results concerning the $t(E)$ curves for the π band is simple. As X changes from O to S, the polarization of both $\pi_{C=X}$ and $\pi^*_{C=X}$ decreases. At the same time, the $\pi_{C=X}$ level is raised in energy, while the

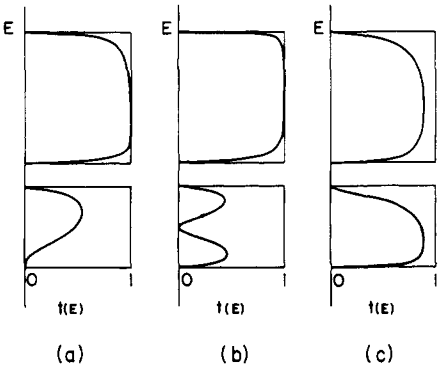
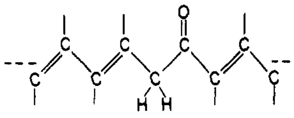


Figure 4. Transmission coefficient curves for a C=X group impurity in a polyacetylene chain: (a) X = O, (b) X = S, and (c) X = CH_2.

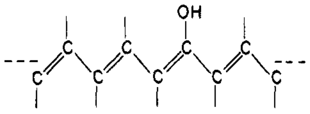
$\pi^*_{\mathrm{C=X}}$ is slightly lowered. Globally, these changes lead to an increase in the coupling of the π-band states with $\pi_{\mathrm{C=X}}$ and to a decrease with $\pi^*_{\mathrm{C=X}}$. The interference hole should appear at higher energies. Since the $\pi_{\mathrm{C=X}}$ contribution has considerably increased (in fact we are entering into the Ib category because $\pi_{\mathrm{C=S}}$ lies at the bottom of the band), the interference effect is even stronger and a minimum is clearly visible in the middle of the π band (see Figure 4b).

When X is CH_2, the above-mentioned effects are considerably enhanced, especially because the $\pi^*_{\mathrm{C=X}}$ is now definitely high in energy and its contribution to the π band $t(E)$ curve is small. The interaction of the $\pi_{\mathrm{C=X}}$ level and the π band is now a typical Ib one. The destructive interference is small and affects only the top of the band. In consequence, the $t(E)$ curve does not present a double maxima but an asymmetry even less marked than in the case of X = O. As could be expected, the transmission of the conjugation is very good.

D. Donor and Acceptor "Pendant" Groups. Let us consider a C=O and an adjacent CH_2 group as the impurity. These groups are found in some polyacetylene samples prepared by Roth and co-workers.[29] Two different forms, **4** and **5**, can be considered. **4** represents another type of impurity, i.e., a "pendant" group. Chemical intuition would associate **4** with a rupture of conjugation but not at all for **5**. The calculated $t(E)$ curves confirm this expectation. The $t(E)$ values are never greater than 0.10 for **4**, so that a C=O group adjacent to an sp^3 defect even increases the degree of interruption of the conjugation. More interesting is **5**, for which $t(E)$ is close to 1 in both the π and π^* bands (see Figure 5). Let us fragment system **5** as shown in **6**; the impurity is then a three-level system. The $t(E)$ curve for the π band is mainly determined by the interaction with the π_2 orbital (see Figure 5), which is a good type Ib interaction, but the interference due to π_1 should also be considered. This interference should be destructive, i.e., should introduce an interference hole near the region of the π_1 level. Except for the greater numerical values, the curve is very similar to that shown in Chart III, c, although a combination of different types of interactions is at work.



4



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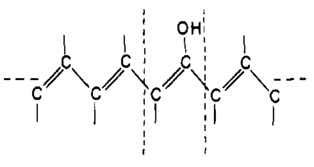

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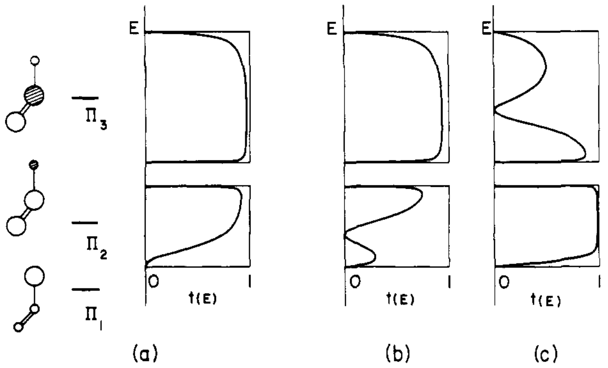

Figure 5. Transmission coefficient curves for different pendant groups in a polyacetylene chain: (a) OH, (b) NH_2, and (c) C≡N. The three impurity levels corresponding to the OH case (π_1, π_2, and π_3) are also shown in (a).

If NH_2 is used as a pendant group, the scheme is qualitatively similar, but since π_1 is higher in energy because of the smaller electronegativity of nitrogen, the destructive interference will be stronger and shifted toward higher values. As happened in the C=S case, a curve with a double maxima results, although now the higher coefficients occur near the top of the π band. In short, the nature of the donor group can significantly change the shape of the $t(E)$ curves. In a similar vein, it can be shown that π acceptors as pendant groups appreciably change the $t(E)$ curve for the π^* band (see Figure 5c for C≡N as an example). Therefore, the introduction of the pendant group levels may result in significant interference effects which can annihilate the electronic transmission within restricted energy intervals.

The previous series of examples was mostly chosen to highlight the use of the transmission coefficient as a tool for the analysis of the effects of the presence of impurities and defects in polymers. The principles needed to analyze more involved (and also more "realistic") impurities do not differ from those used here. Let us point out that when bigger impurities are used, the possibility arises of creating different types of interferences by changing the branching mode of the impurity. The case of benzene has been considered in detail.[16] Substituents and branching modes can then be used to modulate the type of $t(E)$ curves.[16,17]

4. Electronic Delocalization in Polyacetylene Chains Containing sp^3 Defects or C=O Groups

The degree of interruption of the conjugation in modified polyacetylene chains is a topic of current interest. Several techniques have been used to study this problem.[20-23,29-31] The recent report by Zuo et al.,[21] suggesting that sp^3 defects have only a moderate effect on the conjugation of the π band of polyacetylene, has stimulated some theoretical work.[2,5,32] There has also been the suggestion by Roth et al.[29] that sp^3 defects do not limit the

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(29) Schäfer-Siebert, D.; Roth, S.; Budrowski, C.; Kuzmany, H. *Synth. Met.* **1987**, *21*, 285.

(30) Kuzmany, H.; Kürti, J. *Synth. Met.* **1987**, *21*, 95.

(31) Budrowski, C.; Przylusky, J.; Roth, S.; Kuzmany, H. *Synth. Met.* **1986**, *16*, 291.

(32) Tanaka, K.; Yamanaka, S.; Oiji, M.; Yamabe, T. *Synth. Met.* **1988**, *22*, 247.

resistivity of polyacetylene. Nevertheless, this result seems to be in conflict with the recent results of Naarmann et al.[33] on polyacetylene with very few sp^3 defects.

The results of Figure 3 clearly show that sp^3 defects almost completely break the conjugation in polyacetylene chains. This result agrees with the recent theoretical results reported by Conwell et al.,[2] Brédas et al.,[34] and Zerbi et al.,[5] although these authors used a very different technique. However, we disagree with an early theoretical study by Surjan and Kuzmany,[4] where, on the basis of CNDO/S computations of the transition energies for some small conjugated systems, it was concluded that sp^3 defects only partially interrupt the conjugation. The reason for this disagreement is that the "molecules" used to model the conjugated backbone were too small, and consequently the hyperconjugating ability of an sp^3 group was exaggerated. Our results also show that C=O groups adjacent to sp^3 defects even increase the interruption of conjugation, a result in agreement with a recent report by Kuzmany and Kürti.[30] It seems to us that the optical results of Yang et al.[20] and Zuo et al.[21] concerning the role of these sp^3 defects in breaking the conjugation can be best explained by assuming a strongly nonuniform distribution of sp^3 defects in the samples studied by these authors. This "clustering" of defects was also recently suggested by Brédas et al.[34] and Lefrant et al.[35] on the basis of SCF calculations on model chains and Raman spectra, respectively. The small shift on the valence to conduction band absorption, the decrease of the oscillator strength, and the broadening of the absorption are consistent with this hypothesis. We then conclude that from the two hypotheses advanced by Zuo et al.,[21] (a) uniform distribution of defects and moderate rupture of conjugation and (b) nonuniform distribution of defects, that the second hypothesis is appropriate.[36]

Chien et al.[22] have recently reported the synthesis of several acetylene–carbon monoxide copolymers with different (CH=CH)/CO content ratios. Several features of the X-ray photoelectron and ultraviolet photoelectron spectra should be sensitive to the degree of disorder, so that Hennico et al.[1g] have studied several model acetylene–carbon monoxide copolymers. The density of valence-one-electron states was computed for copolymers with a (CH=CH)/CO ratio of 13% and a total of 200 units by the negative factor counting technique. The authors concluded that "the predicted reduction in energy gap, 2.59 eV, from polacetylene (3.81 eV) to the most irregular system (1.22 eV) is quite puzzling". This reduction of the energy gap is obviously related to the occurrence of the discrete state in between the π and π^* bands reported in Figure 2a. Since this state is "impurity"-type but has important tails on the CH=CH backbone, it is clear that when many of these states are created, they will interact, except when they stay very far apart. This will decrease still more the "energy gap". The decrease will be greater when *several* CO groups are separated by short sequences of CH=CH groups. This is indeed what happens when the detailed distribution of the copolymers studied by Hennico et al.[1g] is taken into account. A detailed analysis of both absorption energies and oscilator strengths should then be very useful to characterize the monomer sequences in these copolymers.

Concerning the π band of these copolymers, let us point that according to the present model calculations, the transmission coefficient, although smaller than in polyacetylene itself, is nevertheless sizeable (see Figure 2b). This suggests that *if* a metallic band regime is actually reached for heavily doped polyacetylenes, the presence of C=O groups in the chain should only moderately decrease the conductivity. Recent results by Chien and Babu[22] could be interpreted in this vein, but in the absence of a more careful characterization of the highly doped level conductivity regime this would be premature.

5. Concluding Remarks

The transmission coefficient is an energy-dependent tool that can be calculated through the scattering matrix technique and can be chemically analyzed. Several different types of interactions between an impurity/defect level and an energy band can be distinguished and characterized through their corresponding $\Delta\mathrm{DOS}(E)$ and $t(E)$ curves. When the impurity/defect has more than one level that can interact with a band, interference effects have to be considered. A qualitative rule to predict their constructive/destructive nature has been given. The usefulness of this conceptual scheme to control the transmission coefficient curves by chemical means has been illustrated by considering the effect of different C=X impurities (X = O, S, CH_2), sp^3 defects, and donor/acceptor pendant groups on the electronic structure of polyacetylene chains. In connection with recent speculations concerning the degree of interruption of the conjugation by sp^3 defects in polyacetylene chains, it is suggested that these defects severely break the conjugation and that a very nonuniform distribution of the defects offers a more likely explanation of the experimental results. By contrast, the introduction of C=O impurities results in only a moderate interruption of the conjugation. The corresponding transmission coefficients are high, especially for the π^* band.

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(33) Naarmann, H. *Synth. Met.* **1987**, *17*, 223. Naarmann, H.; Theophilou, N. *Synth. Met.* **1987**, *22*, 1. Basescu, N.; Liu, Z.-X.; Moses, D.; Heeger, A. J.; Naarmann, H.; Theophilou, N. *Nature* **1987**, *327*, 403.

(34) Brédas, J. L.; Toussaint, J. M.; Hennico, G.; Delhalle, J.; André, J. M.; Epstein, A. J.; MacDiarmid, A. G. *Springer Ser. Solid State Sci.* **1987**, *76*, 48.

(35) Lefrant, S.; Arbuckle, G.; Faulques, E.; Perrin, E.; Pron, A.; Mulazzi, E. *Springer Ser. Solid State Sci.* **1987**, *76*, 54.

(36) After submission of this work, experimental evidence in favor of this interpretation was reported: Wan, M. X.; Arbuckle, G. A.; MacDiarmid, A. G.; Epstein, A. J. *Synth. Met.* **1988**, *24*, 283.