EFFECT OF OXYGEN IMPURITIES ON THE IONIZATION POTENTIAL AND ELECTRONIC EXCITATIONS OF POLYETHYLENE

M. RÉVÉSZ

Research Laboratory for Inorganic Chemistry
of the Hungarian Academy of Sciences, Budapest

Summary

We have compared the applicability of the CNDO/S, EHT and HAM/3 semiempirical quantum chemical methods for studying the ionization potentials and energy gaps in systems $-(CH_2)_x-O-(CH_2)_x-$, as functions of the relative etheric oxygen content as well as the change of these quantities with the number of carbon atoms in a regular paraffinic chain.

Introduction

The physical and chemical properties of polymers, among them polyethylene, as well as the relations between these properties and different practical applications of these materials are surveyed in the literature quite in detail [1]. One of the important fields of applying polyethylene is connected with its insulating properties, so one can get additional information from assessing the changes in the electronic structure of polyethylene, taking place in the range of the conduction band. Accordingly, our aim was a theoretical study of the structure of polyethylene.

In the course of processing the material, it is customary to use peroxides (often dicumilleperoxide) as cross-linking agents [2], so the polymer contains some amount of oxygen already when getting its final structure. Oxygen can be built into the chains during the ageing of the polymer, as well [3, 4], modifying its structure and thereby, its physical and chemical properties. For this very reason the effects exhibited on the electronic structure of the polymer by oxygen atoms forming different types of bonds (etheric, carbonylic, peroxide) has been studied by quantum chemical methods.

Nowadays the ESCA method of X-ray photoelectron spectroscopy is gaining more and more widespread use. As to our problem, it can give experimental information on the structure of the internal and external shells of the different components, and so on the binding situation in which the latter exist, in the outermost few atomic layers of solid samples. Åsbrink et al. [5, 6] have developed the semiempirical quantum chemical method HAM/3 for the

interpretation of the photoelectron spectra of molecules studied by this method; it permits to calculate the changes in the ionization potentials and electronic transitions, primarily in the vicinity of the conduction band.

Effect of ether-type oxygen

At first we have studied the effect of ether-type oxygen atoms built in the chains $CH_3—(CH_2)_x—O—(CH_2)_x—CH_3$, where x is uniformly 1, 3 or 4. Clark et al. [9] have considered the same molecules, but unlike us they calculated the 1s energetic levels of the C atoms. We have taken as reference the paraffinic chain n-$C_{13}H_{28}$ which already does simulate well the polymeric one [3]; see Fig. 1. It may be seen how the number of energetic levels increases with that of the C atoms and how the discrete energetic levels merge to form the bands.

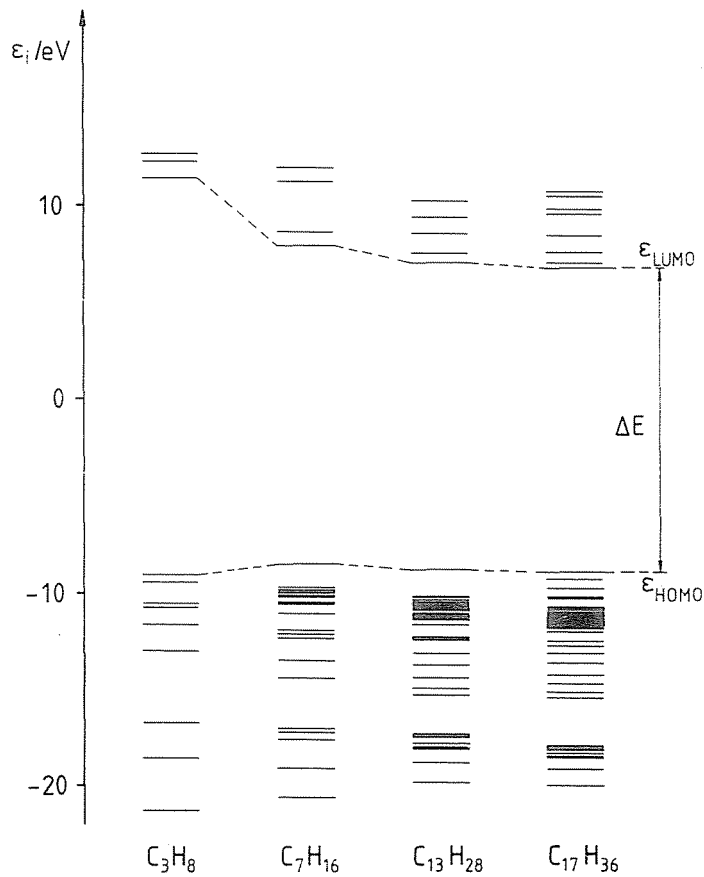

Fig. 1. Dependence of the energy levels on the C atoms

There are no significant changes in the LUMO (lowest unoccupied molecular orbital) and HOMO (highest occupied molecular orbital) energy values already for the chains containing 13 and 17 carbon atoms, so it is expected that no significant error will be caused by drawing conclusions for the properties of polymer chains from the results obtained in the calculations performed for the systems with 13 C atoms.

For the purposes of testing the HAM/3 program, comparative calculations have also been performed with the aid of EHT and CNDO/S programs, as well.

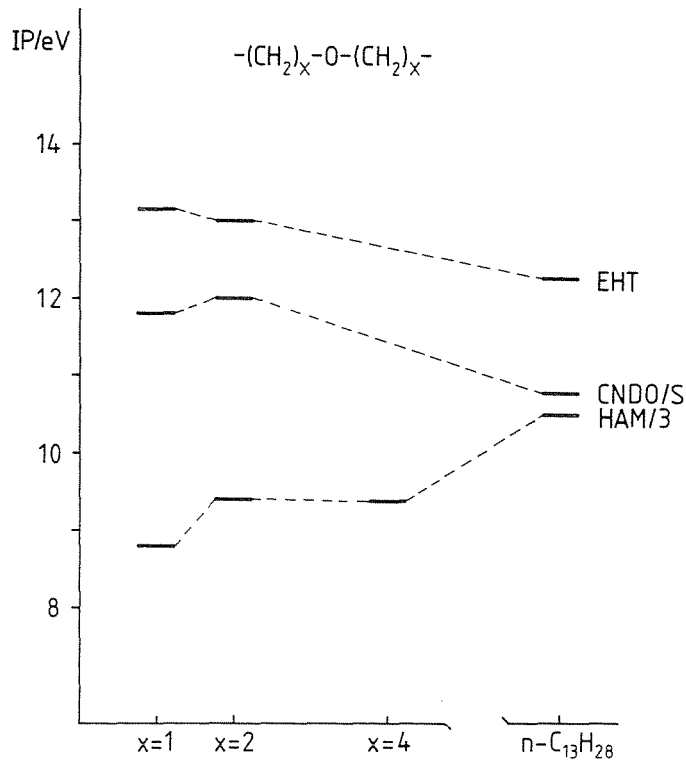

Fig. 2. Dependence of the ionization potential on the relative O content

EHT is one of the earliest semiempirical methods involving the most severe approximations; it appears well applicable for chains containing a great number of C atoms and, especially, for performing comparative calculations on series of related systems. The method is less reliable for molecules containing heteroatoms. CNDO/S is a method parametrized for calculating electronic excitations.

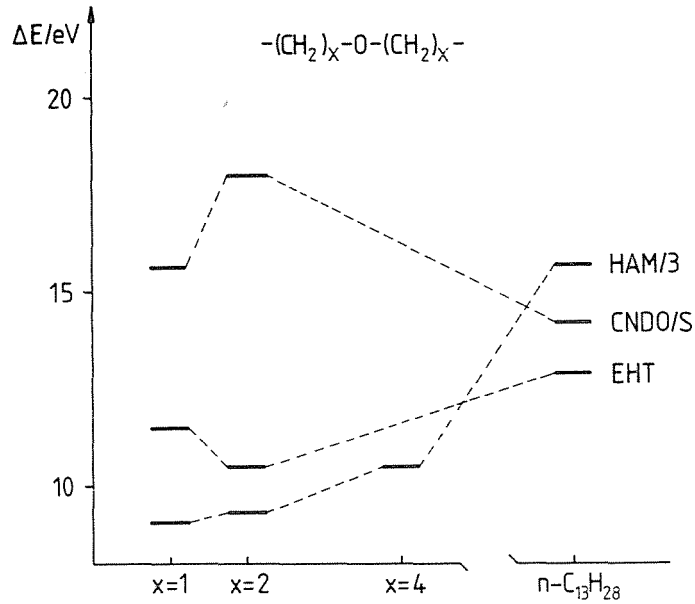

Fig. 3. Dependence of the energy gap on the O content

Figure 2 displays the changes in the ionization potentials as functions of the concentration of the etheric oxygen atoms. The following definitions have been applied IP = ionization potential:

$$IP = -\varepsilon_{HOMO} \text{ (EHT; CNDO/S)}$$

$$IP = \varepsilon_i \text{ (HAM/3, option "PES")}$$

When oxygen is built in the chain, the ionization potential increases, although only to a small extent, according to the results obtained by the EHT and CNDO/S methods. However, method HAM/3 predicts that the appearance of the etheric type oxigen atoms decreases the ionization potential.

Figure 3 shows the comparison of the gaps between the valence and conduction bands. According to the EHT method, the gap $E = \varepsilon_{LUMO} - \varepsilon_{HOMO}$ decreases under the influence of the oxygen, while CNDO/S indicates a significant increase. The results obtained by using the HAM/3 method indicate that the gap becomes narrower with the increase of the oxygen content. This is the most realistic picture, agreeing with the different results in the literature; so the HAM/3 method seems to be the most appropriate one for such type of studies. Although the LUMO energies are overestimated, the tendencies are reflected well. The etheric type oxygen has an important role in forming both the highest occupied and the lowest unoccupied orbitals. With the increase of

the relative oxygen concentration the contribution of the atomic orbitals of the oxygen to the HOMO also increases, and simultaneously the energy necessary to remove or excite an electron from the highest molecular orbital decreases. This leads to a decrease of the ionization potential as well as to a narrowing of the interband gap with the increase of the oxygen content, as compared with the pure polyethylene.

Therefore the etheric type oxygen atoms built in the polymer chains deteriorate the insulating properties of polyethylene.

The author should express her gratitude to dr A. Tóth for raising the problem and to Dr I. Mayer for useful discussions.

References

1. ANDRE, J. M.–DELHALLE, J.–DELHALLE, S.–CAUDANO, R.–PIREAUX, J. J.–VERBIST, J. J.: Chem. Phys. Lett. Ed. *23*, 206 (1973).
2. KUNERT, K. A.: J. Polym. Sci. Polym. Lett. Ed. *19*, 479 (1981)
3. PIREAUX, J. J.–RIGA, J.–CAUDANO, R.–VERBIST, J.: Photon, Electron and Ion probes. ACS Symposium Ser. No. 162 (169–201) 1981.
4. DILKS, A.: J. Polym. Sci. Polym. Lett. Ed. *19*, 1319–1327 (1981)
5. ÅSBRINK, L.–FRIDH, C.–LINDHOLM, E.: Chem. Phys. Lett. a) *52*, 63 (1977), b) *52*, 69 (1977), c) *52*, 72 (1977)
6. ÅSBRINK, L.–FRIDH, C.–LINDHOLM, E.: Int. J. Quant. Chem. *19*, 1203 (1981)

Márta RÉVÉSZ H-1502 Budapest POB 132