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Qualitative Evaluation of the Band Gap in Polymers with Extended π Systems

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ABSTRACT: Hückel calculations combined with C_m-symmetry transformations have been used for a qualitative evaluation of the frontier orbital gap (band gap) in a series of hypothetical polymers containing a polyacetylene skeleton. Similarly, the band gaps in polymers with pyrrole rings and related species have been calculated.

Recently we demonstrated a facile method based on Hückel theory and symmetry properties for the evaluation of a lower limit for the band gap (energy difference between filled and empty MO:s) in a series of polyarenes and poly(vinylarenes).[1] The linear polymer chains are regarded as being similar to a large cyclic polymer, and a C_m-symmetry transformation of the total Hückel determinant results in a series of smaller ones, the majority of which represent degenerate MO:s. However, the series also includes a determinant that can be derived from the smallest repetitive unit closed upon itself to form a ring of Hückel topology and, if n is even, another determinant that can be derived from the same ring but with Möbius topology. The important frontier orbitals that correspond to the band gap in the polymer can usually be found within either of the two subsets of MO energies derived from the two smallest rings of different topology. This result is shown schematically in Figure 1.

In this paper the scheme for the evaluation of the lower limit of the frontier orbital gap (band gap) has been applied to a series of hypothetical and idealized polymers with special emphasis on modified polyacetylenes and nitrogen-containing species with the aim to identify polymers with small band gaps, a property of prime importance for possible applications of the polymers as organic conductors.

Results and Discussion

Polyacetylene (PA) is by far the most studied organic conductor with a large delocalized π system.[2] By the simple Hückel approximation the band gap should ideally be zero; i.e., the frontier orbitals are two degenerate nonbonding orbitals with two electrons, as in the case of [4n]annulenes. However, bond alternation raises the degeneracy of the frontier orbitals to give a finite value for the band gap, $2|\beta_1 - \beta_2|$, where β_1 and β_2 are the resonance integrals for the double and single bonds.[3] By use of bond lengths for [4n]annulenes and a β value of 2.2 eV calculated from electrochemical data, a lower limit for the band gap in PA of 1.0 eV (exptl 1.4 eV, ref 2e) was calculated.[1b] To make the calculations as simple as possible here I have assumed a constant resonance integral for the hydrocarbons and slightly modified coloumb and resonance integrals for the heteroatoms and their bonds to carbon atoms.[4a]

The calculated lower limits of the band gap relative to that of PA for a series of polymers and some related ring compounds are collected in Table I.

Hydrocarbon Chains. If α-, β-, and γ-bridging vinylene groups are introduced into the carbon chain in polyacetylene, three new polymers, **3**, **4**, and **5**, respectively, will result. Of these, the poly(3,4′-fulvalene) (**4**) has the same small band gap ($\Delta = 0.0\beta$) as PA by this method, whereas the band gaps in the hypothetical poly(1,2-cyclobutadienylene) and the well-known poly(p-phenylene)[2c,d] are much larger ($\Delta = 0.76\beta$ and 0.83β, respectively). Upon incorporation of an increasing number of sp^2 carbon atoms between the five-membered rings in polymer **4** to give **6**, **7** and **8**, an interesting alternation of the band gap is revealed by the HMO calculations. For the series of β-bridged polyacetylenes **4**, **6**, **7**, and **8**, the first and the third have the same calculated band gap as PA, whereas the second and the fourth members have band gaps of $\Delta = 0.62\beta$ and 0.45β, respectively. A similar alternating behavior is observed for the three polymers **5**, **9**, and **14** with conjugated six-membered rings separated by none, one, and two sp^2 carbon atoms, respectively, although in this case the first and third members have the larger band gaps, $\Delta = 0.83\beta$ and 0.51β, respectively. The intermediate polymer **9** has the same band gap as PA. It

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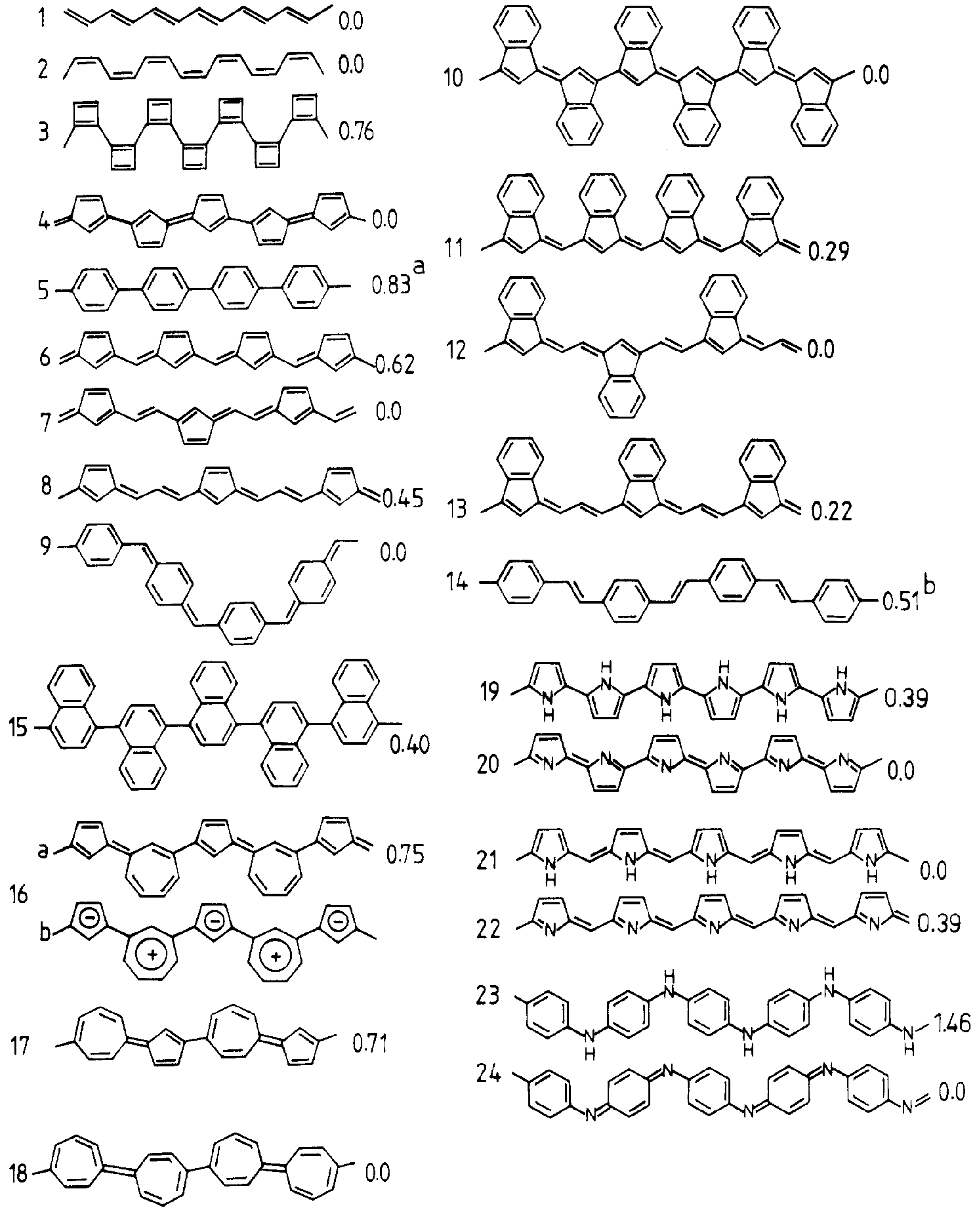
Table I

HMO Calculations of the Lower Limit of the Frontier Orbital Gap for a Series of Ideal Polymers with Extended π Systems Built from Simple Repeating Units

Compound Number, Compound, and Calculated Band Gap Difference from PA in β



[a] 1.8 eV with β = 2.2 eV, ref 1b; calcd to 1.8 eV in ref 2d. [b] 1.1 eV, ref 1b; calcd to 1.1 eV in ref 2d.

is also interesting to note that in a qualitative sense benzannelation has no effect. The two polymers **10** and **15** show the same trend as **4** and **5**. Similarly, the series **10**, **11**, **12**, and **13** shows alternating band gaps, as does the series **4**, **6**, **7**, and **8**, but benzannelation tends to decrease the calculated band gap. With the increased stability of the indene system over that of cyclopentadiene in mind, the two polymers **10** and **12** are interesting candidates for synthetic efforts. The combination of a five- and seven-membered ring, as in the polymer **16**, leads to an unexpectedly large band gap from the HMO calculations. The resonance form of the polymer with charge separation as depicted in **16b** looks more interesting than the calculations reveal it to be. The change in substitution pattern, as in **17**, has only a slight effect on the band gap. The combination of two conjugated seven-membered rings, as in the poly(heptafulvalene) **18**, leads to small band gaps for all symmetrically linked polymers, i.e., the 2,2′ or 2,7′, 3,3′ or 3,6′, and 4,4′ or 4,5′ (**18**) linked isomers. This is a consequence of the symmetry properties of the determinants for the large ring built from the repeating unit of Möbius topology, as will be discussed below.

Polymers with Nitrogen Atoms in the Chain. Pyrrole and aniline can be oxidatively polymerized to polypyrrole and polyaniline, and recent investigations on these relatively stable and highly conducting polymers have demonstrated their extraordinary properties.[2a,c,5] We have tested the Hückel theory by using slightly modified Couloumb and resonance integrals for the nitrogen atoms (two types)[4a] combined with the Möbius ring concept to

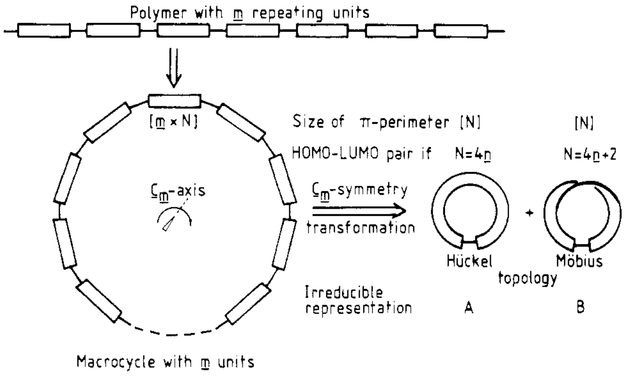


Figure 1. Schematic representation of the evaluation of the HOMO-LUMO energies (frontier orbitals) for a polymer with a repeating unit and a conjugated π system by use of rotational symmetry transformation of the HMO determinant.

calculate the band gaps in the ideal polymers. Two extreme structures of both polymers have been used. In the first, all nitrogens are of the pyrrole type (=C—NH—C=), which corresponds to the fully reduced polymer, while in the second, all nitrogens are of the imine type (=C—N=C—), which corresponds to the oxidized forms of the polymer. For comparison, we have also considered polypyrrole with an extra sp^2 carbon atom between the pyrrole rings. For polypyrrole and polyaniline, the reduced forms show relatively large calculated band gaps ($\Delta = 0.39\beta$ and 1.46β, respectively), whereas the band gap in poly(pyrrolylmethylidyne) is the same as in PA. The oxidized forms of the three polymers show the opposite results, with small band gaps for polypyrrole and polyaniline, while poly(pyrrolemethylene) now has a relatively large band gap. In practice, both polypyrrole[2a,c] and polyaniline[5] are prepared under oxidative conditions, and the conducting polymers are partly oxidized and charged species.

Symmetry Consequences. The calculated frontier orbitals for several of the polymers discussed here are degenerate, and thus the band gap is regarded as the same as in PA. In real polymers the situation is different, with several factors other than bond alternation causing the band gap to increase (deviations from planarity, interchain conductivity, etc.), and more sophisticated MO theories will reveal these effects on the band gaps.[2d] Nevertheless, the simple HMO theory gives small band gaps for a number of polymers. This can be shown to be a consequence of the symmetry properties of the π-systems, and thus there is reason to believe that the polymers do indeed have small band gaps if geometrical factors allow this.

Consider a cyclooligomer with four identical units and a C_4 axis of symmetry as shown in Figure 2. A C_2-symmetry transformation of the total Hückel determinant will result in two new determinants that correspond to rings of half the size with Hückel and Möbius topology, respectively.[1] A second C_2-symmetry transformation of the new ring with Hückel topology will result in determinants from the repeating unit closed onto itself in a Hückel and Möbius sense (see Figure 2). Alternatively, a direct C_4-symmetry transformation of the original cyclooligomer yields determinants from the small rings of Hückel and Möbius topology and a determinant of the order of $|2N \times 2N|$ that has degenerate solutions (E-type irreducible representation).[4b] The latter is the determinant from the Möbius topology ring with a $2N$ π-perimeter (see Figure 2). Now, if $2N$ equals $(4n + 2)$, which means that the frontier orbitals of the original macrocycle are found among the solutions of the Möbius topology ring of size $2N$,[1] the frontier orbitals are then degenerate and thus the theoretical band gap is zero for symmetry reasons. (When the $4n + 2$ π electrons are distributed between degenerate orbitals, the last two electrons have two degenerate orbitals to choose between.) Thus, polymers that theoretically should have zero band gaps for reasons of symmetry are recognized by a repeating unit with $4n + 2$ π electrons in conjugation between the ends and a C_2 axis of symmetry perpendicular to the π system. Examples of such polymers are found in Table I, i.e., the polyfulvalenes **4** and **7** and the corresponding indene derivatives **10** and **12**, poly(phenylenemethylene) (**9**), the oxidized polypyrrole **20** and polyaniline **24**, and the reduced form of poly(pyrrolylmethylidyne) (**21**). It is particularly interesting that the presence of heteroatoms as in, for example, polypyrrole and polyaniline does not invalidate the symmetry arguments, and thus the problem with the relevant coloumb and resonance integrals is of no great consequence.

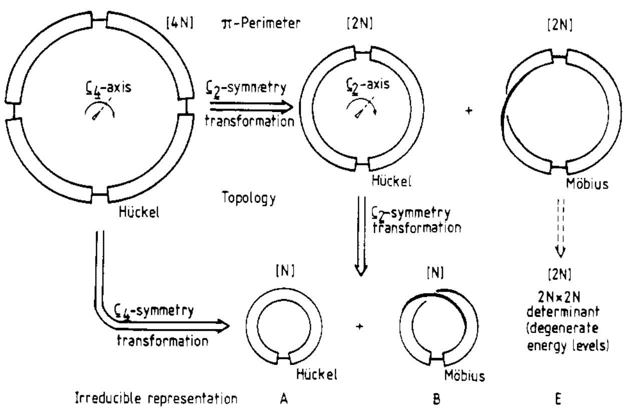


Figure 2. Schematic representation of a C_4-symmetry transformation of the HMO determinant for a cyclooligomer with a π-perimeter and the alternative twofold C_2-symmetry transformations which shows that the $2N \times 2N$ determinant for the Möbius ring with a $2N$ π-perimeter gives degenerate energy levels.

Conclusions

Hückel theory combined with C_m-symmetry transformations of the Hückel determinant provides an extremely simple method for the qualitative evaluation of the lower limit of the band gap in linear polymers with simple repeating units and an extended π system. Several polymers derived from polyacetylene and polyimines by introduction of various bridging groups should have small band gaps according to the calculations, and a simple scheme to recognize such polymers has been found.

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Registry No. **1**, 73589-68-1; **2**, 74373-36-7; **3**, 98170-18-4; **4**, 98170-19-5; **5**, 25190-62-9; **6**, 98170-20-8; **7**, 98170-21-9; **8**, 98170-22-0; **9**, 93473-55-3; **10**, 98170-23-1; **11**, 98170-24-2; **12**, 98170-25-3; **13**, 98170-26-4; **14**, 26009-24-5; **15**, 25322-48-9; **16**, 98170-27-5; **17**, 98170-28-6; **18**, 98170-29-7; **19**, 51325-03-2; **20**, 98170-30-0; **21**, 98170-31-1; **22**, 98170-32-2; **23**, 32036-19-4; **24**, 91885-56-2.

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Effects of Annealing and Prior History on Enthalpy Relaxation in Glassy Polymers. 5. Mathematical Modeling of Nonthermal Preaging Perturbations

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ABSTRACT: Computer simulation studies of the effects of hydrostatic pressure, tensile stress, and vapor-induced swelling on the physical aging of glass poly(vinyl chloride) (PVC) are presented. Published data indicate that application and rapid release of these nonthermal perturbations before aging produce glasses with elevated enthalpies and increased aging rates compared with those of unstressed glasses. These experimental observations are well described by a modified version of a phenomenological model which gives a good account of purely thermal history effects (Hodge, I. M.; Berens, A. R. *Macromolecules* 1982, *15*, 762).

1. Introduction

In earlier papers of this series[1-4] it was shown that the effects of physical aging on enthalpy relaxation in polymers are described with good accuracy by a four-parameter phenomenological model based on the work of Tool,[5] Narayanaswamy,[6] Mazurin et al.,[7] and DeBolt et al.[8] This model reproduces the effects of cooling rate, aging time, aging temperature, and heating rate on the temperature and magnitude of heat capacity maxima observed in many aged polymers[2] and can be fitted to experimental data by standard optimization procedures.[3,4] In this paper we extend the model to include the effects on physical aging of hydrostatic pressure, tensile stress, and vapor-induced swelling, applied and released before aging. Our goal is to reproduce, qualitatively, experimental data with a calculation procedure which is computationally efficient and convenient.

We first review published experimental data that are relevant to our modeling studies. The effects of hydrostatic pressure on enthalpy relaxation in polymers have been studied experimentally by several investigators. Weitz and Wunderlich[9] observed isobaric heat capacity maxima in DSC scans, at 5 K min^{-1} and atmospheric pressure, of polystyrene (PS) and poly(methyl methacrylate) (PMMA) glasses formed by cooling at 5 K h^{-1} under hydrostatic pressures ranging from 0 to 345 MPa (0–3.45 kbar). At low pressure (69 MPa) the large heat capacity overshoot near T_g, characteristic of slowly cooled and rapidly heated glasses, was diminished compared with that of the glass formed at atmospheric pressure. At intermediate pressure (207 MPa) the heat capacity maximum moved to a lower temperature, $T_{\max}$, to appear as a sub-T_g peak (magnitude $C_{p,\max}$), similar to those observed by Illers[10] and others[1,11-13] in aged PVC glasses formed at atmospheric pressure. At the highest pressure (345 MPa) a broad exothermic heat capacity minimum developed between $T_{\max}$ and T_g. Similar results were observed by Yourtee and Cooper,[14] Dale and Rogers,[15] and Wetton and co-workers[16,17] for PS and by Kimmel and Uhlmann[18] and Price[19] for PMMA. For nonpolymeric glasses [phenolphthalein, sucrose, $KNO_3/Ca(NO_3)_2$] Weitz and Wunderlich observed only a decrease in overshoot near T_g with increasing pressure.[9] Prest and co-workers[12,13] reported heat capacity data obtained during heating at 20 K min^{-1} for PVC formed by cooling at 20 K min^{-1} under hydrostatic pressures ranging from 100 to 600 MPa and aged at room temperature and atmospheric pressure for 110 days. The sub-T_g heat capacity peak moved to slightly lower temperatures and became more asymmetric with increasing pressure. Berens and Hodge[1,11] observed that cold drawing, powder compaction, and vapor-induced swelling of glassy PVC accelerated the rate of sub-T_g peak development with aging time but noted that $T_{\max}$ was a weak function of the type and magnitude of the nonthermal perturbation. Similar findings were reported by Shultz and Young[20] for freeze-dried PS and PMMA and by Prest and Roberts[12] for mechanically compacted PS powder.

2. Modeling Studies

Before describing the introduction of nonthermal perturbations, we first review the model and calculation procedure described in detail elsewhere[2] for purely thermal histories.

2.1. Thermal Histories. The calculation procedure treats cooling and heating as a series of temperature steps and isothermal holds whose relative magnitudes are determined by the cooling and heating rates. Aging is introduced as an isothermal hold during cooling. The response of enthalpy to each temperature step is described by a response function $\phi(t)$, which for convenience and good accuracy is chosen to be of the form

$$\phi(t) = \exp[-(t/\tau_0)^{\beta}] \tag{1}$$

The ratio t/τ_0 is the reduced time

$$t_r = t/\tau_0 \tag{2}$$

The relaxation time τ_0 depends on temperature T and fictive temperature T_f according to the empirical Narayanaswamy expression[6]

$$\tau_0 = A \exp\left[\frac{x\Delta h^*}{RT} + \frac{(1-x)\Delta h^*}{RT_f}\right] \tag{3}$$

where x is a numerical measure of nonlinearity ($1 \geq x >$

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