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On the high-resolution X-ray photoelectron spectrum of poly(ethylene terephthalate): the sensitivity to *trans–gauche* conformation

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A recently suggested dependence of the C 1*s* core-level binding energy shift on the conformation of the glycol unit in PET is confirmed on the basis of *ab initio* calculations. The joint result shows that core-level X.p.s. spectroscopy may be employed to study polymer conformational properties. © 1997 Elsevier Science Ltd.

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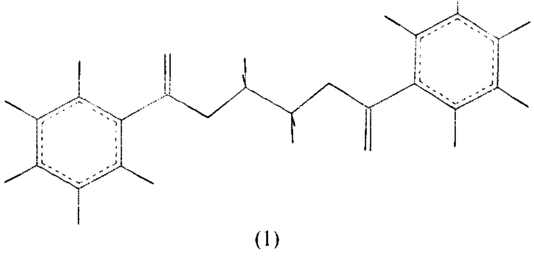
INTRODUCTION

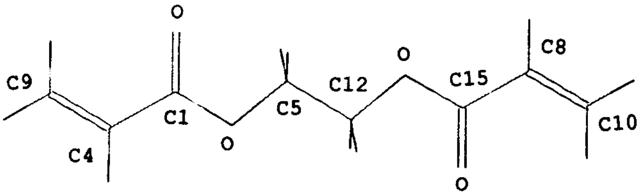
Very recently Beamson *et al.*[1] reported on the high-resolution X-ray photoelectron spectra of crystalline and amorphous poly(ethylene terephthalate) in biaxially oriented form, spin cast film, and polymer melt. This work very interestingly suggested the capability of core-level X.p.s. spectroscopy to discriminate various conformations of the poly(ethylene terephthalate) chain. They concluded that 'The differences in the valence band between crystalline and amorphous PET are subtle and lack the clarity of the C 1*s* glycol shift.... Hence in terms of monitoring polymer chain conformation at the surface of PET, measurement of the C 1*s* glycol shift seems to be the method of choice'. The assignment of a small shift of about 0.1 eV by Beamson *et al.* to the *trans–gauche* difference of the glycol fragment was based on a similar shift in poly(acrylic acid) we predicted seven years ago[2]. This prediction was based on *ab initio* calculations. Beamson *et al.* therefore noted that 'Calculations specifically on PET are required to fully confirm this'. It is evident that we could not withstand the temptation to perform the necessary calculations.

The structure of poly(ethylene terephthalate) is



(1)

Whereas the computational effort for *ab initio* calculations rises considerably with the number of basis functions involved, and therefore implicitly with the number of atoms involved, and because X.p.s. core-electron shifts are only determined by the atoms up to the next-nearest-neighbour shell, we may simplify the PET structure to a fragment which still retains the glycol fragment for which the conformational dependence of the core-electron C 1*s* shift was claimed. However, a reference level is required, e.g. the carboxyl C 1*s* binding energy. In addition, in order to mimic the effect of the phenyl ring we have substituted that ring by an ethylene group. Taking into account all these considerations, we decided to subject the following species to *ab initio* calculations



(2)

This species was studied with the glycol fragment in the *trans* (180°) conformation as well as in the *gauche* (60°) conformation. It was shown in ref. 2 that the 4-31G basis set was sufficient to recover the experimentally observed primary and secondary shifts in polyacrylic acid. We have therefore employed this basis set in the current study.

COMPUTATIONAL DETAILS

The *ab initio* calculations were performed using the Gaussian 94[3] suite of programs as installed on a CRAY YMP-4 at the Forschungszentrum Jülich. Geometries

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Table 1 Calculated C 1*s* binding energies for species **2**. The left-hand column containing numerical data comprises the binding energies obtained after applying Koopmans' theorem, while the right-hand column contains the shifts relative to the C9/C10 atoms

C atom in species **2** *trans* conformation	Binding energy (Koopmans) in eV	Relative binding energy in eV
C1/C15	309.78/309.78	4.03
C5/C12	307.13/307.12	1.375
C4/C8	305.94/305.94	0.19
C9/C10	305.75/305.75	0
C atom in species **2** *gauche* conformation		
C1/C15	309.70/309.70	4.02
C5/C12	307.17/307.16	1.485
C4/C8	305.87/305.87	0.19
C9/C10	305.68/305.68	0

were optimized until individual gradients were less than 4.5×10^{-4} Hartree/bohr and the root-mean-force less than 3×10^{-4} Hartree/bohr. The 4-31G basis set was employed.

RESULTS AND CONCLUSIONS

The calculated C 1*s* binding energies for the *trans* and *gauche* conformations of the aforementioned species (**2**) have been collected in *Table 1*. The difference between the carboxyl C 1*s* binding energy and the C 1*s* binding energy of the carbon atoms in the glycol fragment was experimentally determined as 2.36 eV (ref. 1), whereas our calculations revealed a value of about 2.5 (differences between *trans* and *gauche* conformers neglected). The difference between the C 1*s* binding energy for the phenyl carbons in species **1** and the ethylene carbons of species **2** will be small; the experimental shift between the phenyl C 1*s* binding energy and the carboxyl C 1*s* binding energy was established as 3.94 eV, whereas the calculated result is 4.025 eV. Experimental and calculated shifts thus agree quite well for the large shifts in the species considered. Let us therefore immediately turn to the *trans–gauche* difference. Taking the ethylene C9/C10 binding energies as the reference, the *trans* conformation of the glycol unit has a calculated C 1*s* shift of 1.375 eV, whereas the *gauche* conformation exhibits a calculated shift of 1.485 eV. In the experimental spectra reported by Beamson *et al.* the *gauche* rich polymer melt spectrum had a C 1*s* glycol unit band more close to the carboxyl C 1*s* in comparison to the corresponding band in the oriented film primarily comprising *trans* sequences. Taking into account the subtlety of the effects, the calculated difference of 0.11 eV is in very good agreement with the experimentally observed shifts ranging from 0.1–0.14 eV, thereby clearly supporting the interpretation given by Beamson *et al.* and also supporting our previous calculations[2] which suggested that conformational changes do influence core level C 1*s* binding energies in the 0.1 eV range.

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