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# Valence electronic structure of selected polyorganosiloxanes; x-ray photoelectron spectroscopy and quantum chemical studies

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**Abstract.** The valence electronic structures of poly(dimethylsiloxane) (PDMeSO), poly(methylsilsesquioxane) (PMeSSO), and poly(phenylsilsesquioxane) (PPhSSO) were calculated by the *ab initio* Hartree–Fock LCAO crystal orbital method and were studied experimentally by x-ray photoelectron spectroscopy. The basic features of the experimental spectra could be reproduced by the calculations, and thus the peaks could be assigned to structural elements. The electrons of the methyl side-groups of these polymers are basically localized. The aromatic electrons of the phenyl side-groups interact with the  $\sigma$ -bonds of the silsesquioxane skeleton. This skeleton–side-group interaction is similar to what has been reported for polyorganosilanes, though in PPhSSO these states are delocalized to a lesser extent as their smaller  $k$ -dispersion shows. The methyl side-groups of PDMeSO and PMeSSO contribute to the spectra only in the inner valence regions (between 16 eV and 28 eV), while the contribution of the phenyl groups in PPhSSO is important also in the outer valence region. These observations may facilitate the interpretation of chemical changes occurring during the transformation of these polymers into ceramic-like materials.

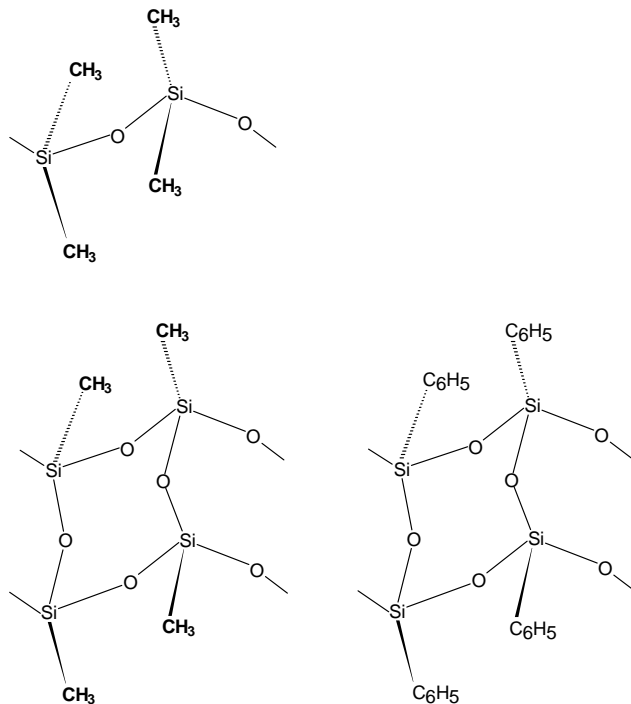
## 1. Introduction

Organosilicon polymers are gaining an increasing role in various fields of materials science and technology. Due to their advantageous dielectric and adhesive properties and crack resistance, they are widely used, for instance, in the microelectronics industry (see e.g. references [1–4]). Furthermore, they can be applied also as precursors for non-oxide advanced ceramics or ceramic coatings [5], where a possible way to transform them into a ceramic (or ceramic-like) state can be their treatment with energetic particles (ions or atoms) [6].

Obviously, during processing, compositional and structural changes may occur, many of which can be monitored experimentally, e.g. by x-ray photoelectron spectroscopy (XPS, or ESCA) [7–11]. The valence band region, in particular, is expected to be very sensitive to chemical alterations. However, while the valence band electronic structure of polysilanes has been studied relatively well [12], there are only few studies [13] on that of polysiloxanes and polysilsesquioxanes.

In this work the valence band regions of poly(dimethylsiloxane) (PDMeSO), poly(methylsilsesquioxane) (PMeSSO), and poly(phenylsilsesquioxane) (PPhSSO) (figure 1)

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**Figure 1.** Schematic representation of the unit cells of the polymers PDMeSO, PMeSSO, and PPhSSO.

were studied by XPS, and the corresponding interpretation is proposed on the basis of calculations performed by the *ab initio* Hartree–Fock LCAO crystal orbital method [14].

## 2. Experimental procedures

The PDMeSO sample studied was an LP-118 GE-SE30 silicon rubber (F & M Scientific, Division of Hewlett-Packard). The PMeSSO and PPhSSO samples were synthesized in the laboratory scale, according to known procedures [3].

The XPS measurements were performed by a Kratos XSAM800 spectrometer using Mg  $K\alpha_{1,2}$  radiation. The x-ray gun operated at 12 kV and 15 mA. The usual pressure in the sample analysis chamber was about  $3 \times 10^{-7}$  Pa. The spectra were recorded in the fixed-retardation-ratio mode. Data acquisition was performed with a Sun SPARC IPX workstation and the Kratos Vision 2000 data system. The spectra were referenced to the C 1s line at binding energy BE = 284.4 eV [15].

## 3. Hartree–Fock LCAO calculations

The electronic structures of the polymers were calculated using the *ab initio* Hartree–Fock LCAO crystal orbital method using the CRYSTAL 92 program [16]. The 3-21G basis set with d orbitals on the silicon atoms was selected as a compromise between accuracy and the available computer facilities. Using a split valence basis set with d functions on the

silicon atoms is expected to be essential to the correct description of the valence bands of the organosilicon polymers. The simulation of the photoelectron spectra was based on the Koopmans theorem [17]. The calculated density of states (DOS) was modulated with Scofield's photo-ionization cross-sections [18] using the Gelius model [19] extended to polymers [20]. According to this model, the photo-ionization intensity of a band,  $I_n(k)$ , is proportional to the Mulliken gross atomic population [21] and to the photo-ionization cross-sections of the atomic orbitals:

$$I_n(k) \propto \frac{1}{2} \sum_{pq} C_{np}(k) C_{nq}(k) S_{pq} (\sigma_p + \sigma_q) \quad (1)$$

where  $C_{np}(k)$  is the coefficient of the atomic orbital  $p$  in band  $n$ ,  $S_{pq}$  is an element of the atomic orbital overlap matrix, and  $\sigma_p$  is the relative photo-ionization cross-section for atomic orbital  $p$ .

A good reproduction of the experimental photoelectron spectra can be achieved if the energy scale of the calculated spectra is contracted by a factor of 1/1.2 and is shifted towards lower BEs by 2.0 eV. The need of such contraction is in line with the general experience that the Hartree–Fock method overestimates bandwidths. The energy shift accounts for the polarization effect occurring in the solid and missing from the model of the single polymer chain. Similar parameters were applied in studies using the valence effective-Hamiltonian approach to simulate valence photoelectron spectra [22]. The DOS diagram obtained after the above manipulation is convoluted with Gaussian functions:

$$G(E - E_i) = \frac{D_c(E_i)}{E_i} \exp\left[-\ln 2 \frac{(E_i - E)^2}{h(E_i)}\right]. \quad (2)$$

This form of the Gaussians was chosen following the suggestion of Endo *et al* [23] and corresponds to a linear dependence of the Gaussian half-width at half-maximum parameter  $h(E_i)$ , on the energy:

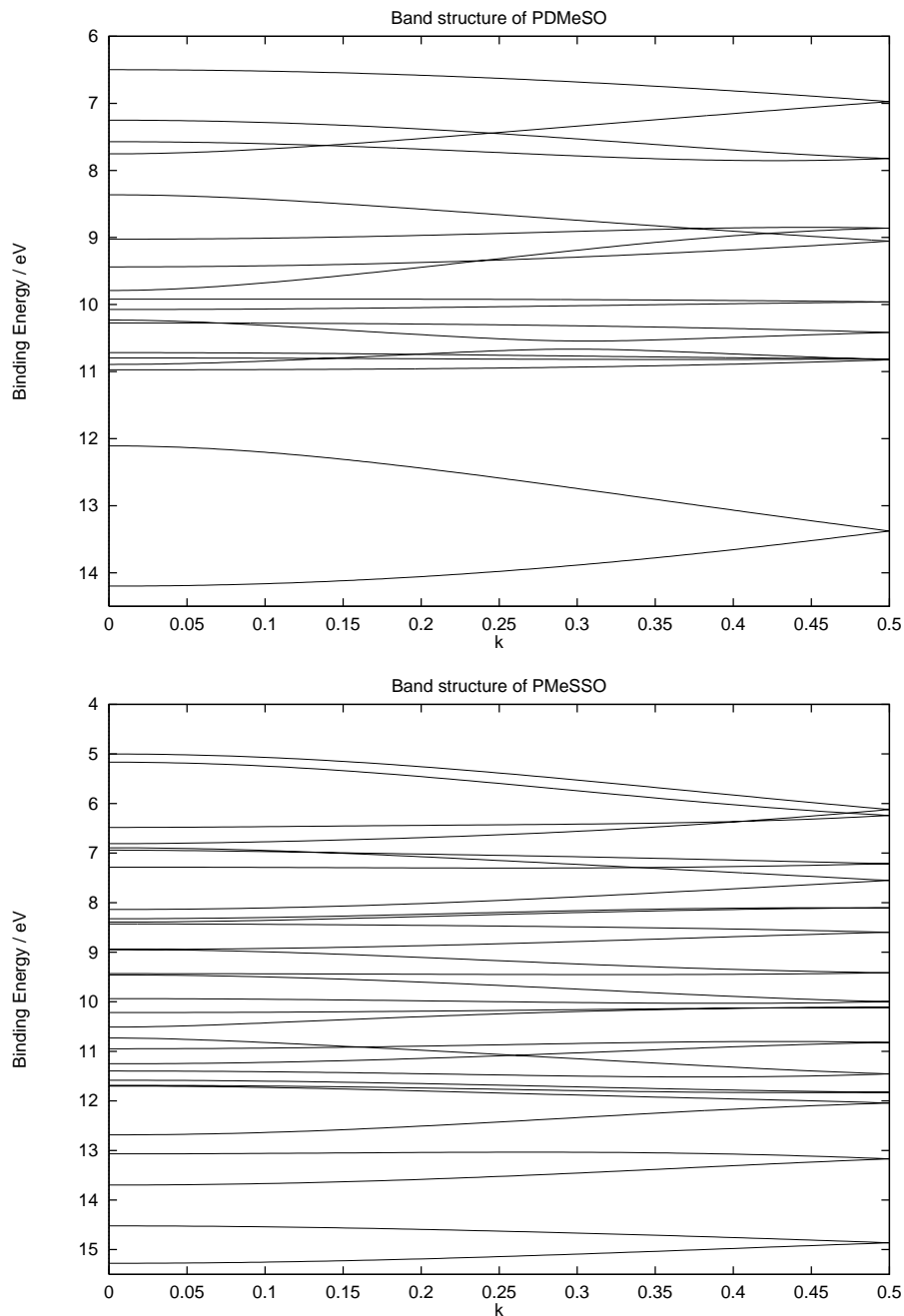
$$h(E_i) = gE_i \quad (3)$$

which results in the broadening of the peaks at higher BEs. Note, that the integral of such a Gaussian is proportional to  $D_c(E_i)$ , the calculated intensity, and does not depend explicitly on  $E_i$ .

The polymers studied were supposed to be linear with  $Pcm2_1$  symmetry. The geometry of a unit cell was obtained in the following way: a trimer was built and the dangling bonds were saturated with hydrogen atoms. Then a geometry optimization using the semi-empirical AM1 [24] method was performed with the constraint that the units of the trimer be appropriate to the unit cell of a crystal with  $Pcm2_1$  symmetry. The plane of the phenyl side-groups were taken to be orthogonal to the extension of the trimer 'backbone' and was not allowed to change orientation during the geometry optimization. The geometry of the middle unit of the trimer was accepted as the unit-cell geometry.

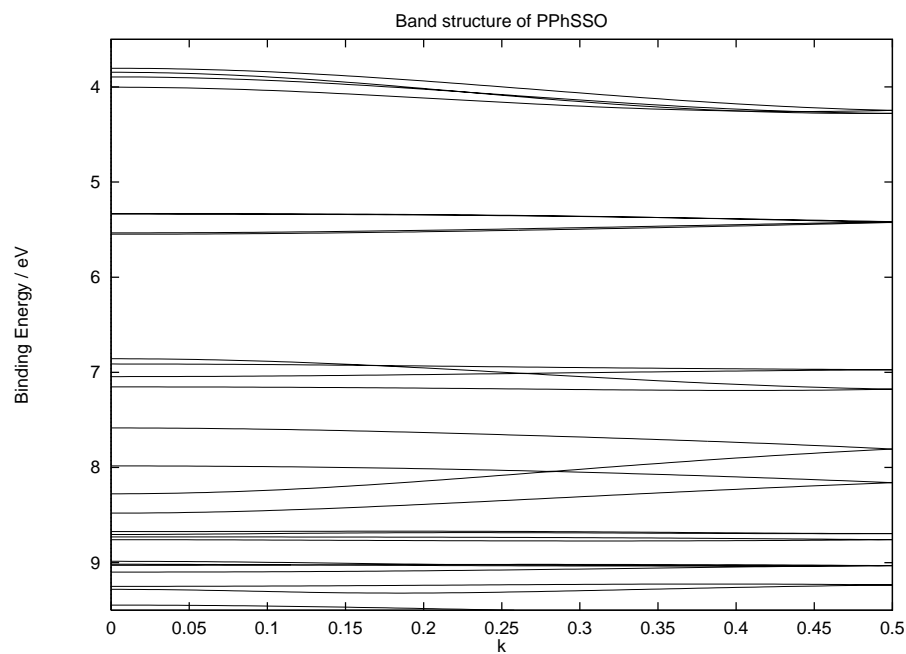
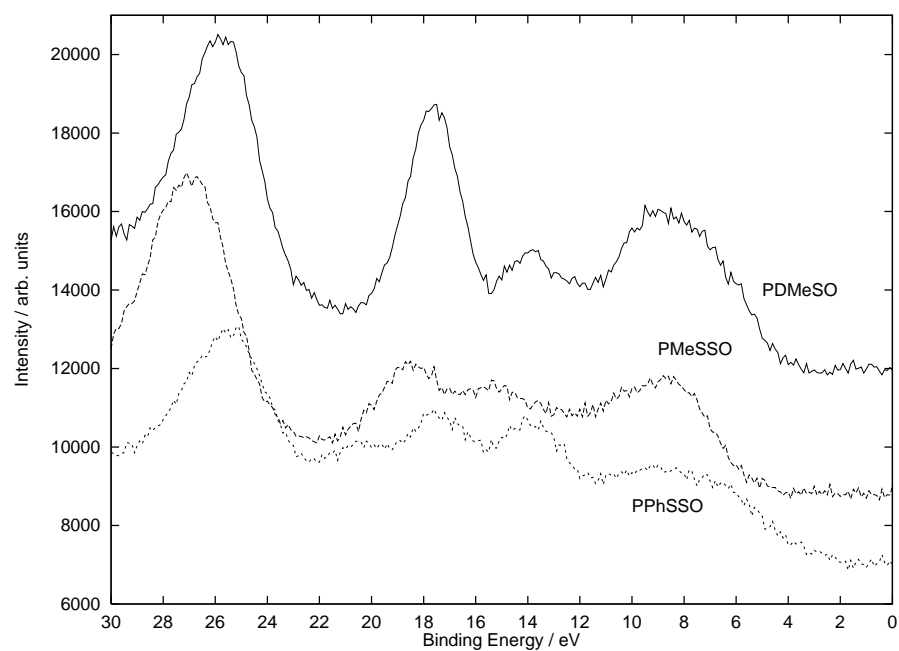
#### 4. Results and discussion

In the discussion of the electronic structure of the polymers, all energies refer to values obtained after the transformation described in the previous section. The low BE regions of the band structure of the polymers are presented in figure 2. Their examination reveals that most bands are narrow. According to an analysis of the Hartree–Fock eigenvectors the narrowest bands (bandwidth below 1 eV) contain contributions from both the polymer backbone and the side-groups, while wider bands (bandwidth between 1 eV and 2 eV) are



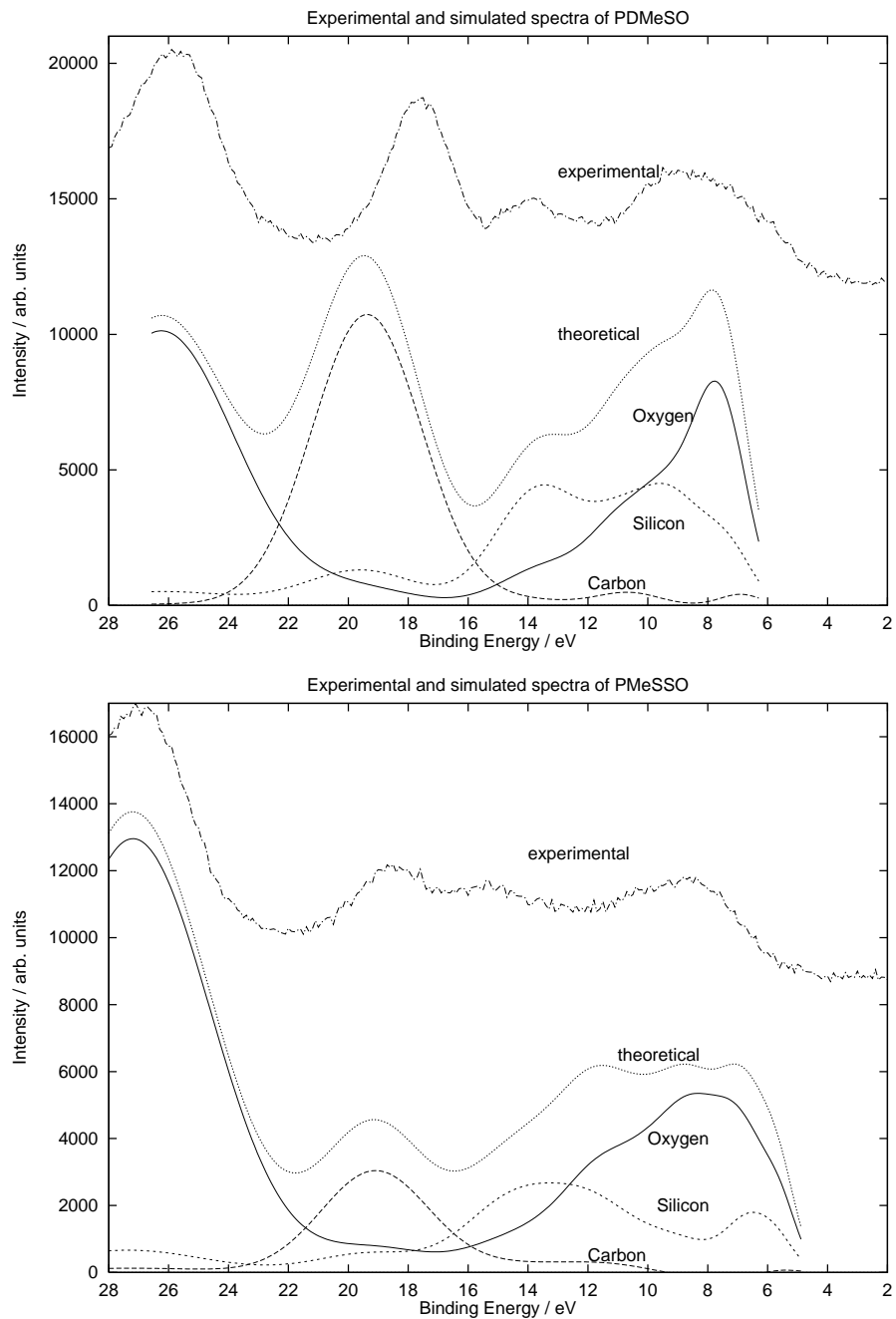
**Figure 2.** Band structures of polymers PDMeSO, PMeSSO, and PPhSSO.

dominated by orbitals of the polymer backbone. This observation suggests that the electrons of the side-groups are basically localized, while the larger  $k$ -dispersion in the  $E$ - $k$  relation of the backbone bands is a result of the interaction between the backbone bonds. This is most clearly exemplified by the wide band between 12 and 14 eV for PDMeSO, which

**Figure 2.** (Continued)**Figure 3.** X-ray photoelectron spectra of the polymers PDMeSO, PMeSSO, and PPhSSO.

belongs to the Si–O bonds of the polymer skeleton.

In PMeSSO and PPhSSO the considerable increase of the number of bands between 8



**Figure 4.** Experimental and simulated spectra of the polymers PDMeSO, PMeSSO, and PPhSSO.

and 12 eV with respect to that in PDMeSO is due to the presence of the extra oxygen atoms in the silsesquioxane skeleton. The oxygen orbitals give the most important contributions to these bands.

The band structure of PPhSSO near band edges differs from those of PDMeSO and

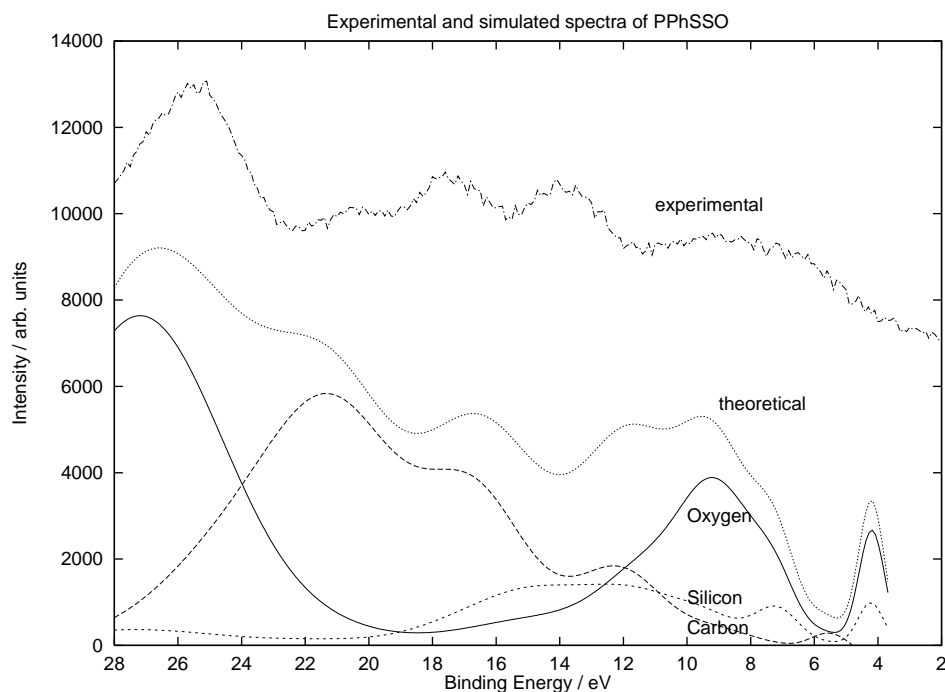


Figure 4. (Continued)

PMeSSO. There are two sets of bands, one near 4 eV and another between 5 and 6 eV; both are well separated from one another and from all other bands. The highest energy set contains four bands which arise from the interaction of the phenyl  $\pi$ -orbitals with the oxygen 2s and 2p<sub>z</sub> orbitals, the latter being parallel with the polymer skeleton.

The backbones of the three polymers investigated are formed by repeating Si–O bonds, and their band structures show important differences with respect to those of polyorganosilanes [12] whose skeleton is built from Si–Si bonds. In the latter type of polymer the delocalized backbone  $\sigma$ -electrons are the sources of special properties, like semiconductivity, and intense UV absorption. The electrons of the Si–O backbone are also, though to a lesser extent, delocalized, as their  $k$ -dispersion shows. Similarly to the case for polyorganosilanes, the highest occupied valence band (HOVB) of the skeleton of PPhSSO is able to mix with the  $\pi$ -electrons of the phenyl groups, resulting in a  $\sigma$ – $\pi$  interaction. In contrast to the case for polyorganosilanes, in PPhSSO the oxygen orbitals take part in this interaction, and the contribution of the Si 3p orbitals is unimportant. It is worth noting that the HOVB of PPhSSO exhibits considerably less  $k$ -dispersion, showing that these electrons are less delocalized than those of the HOVB of polyorganosilanes. It is interesting to see that both in PPhSSO and in polyorganosilanes, the highest energy band below the HOVB belongs to the phenyl  $\pi$ -electrons, and is localized in the individual phenyl groups [12].

The experimental spectra (figure 3) of the three polymers show the following common features: (i) appearance of an intense peak at around 26 eV; (ii) appearance of another less intense peak near 19 eV; and (iii) at least two further peaks can be distinguished at lower binding energies ( $\approx 14$  eV and  $\approx 9$  eV).

The simulated valence photoelectron spectra (figure 4) were calculated as described in the ‘Hartree–Fock LCAO calculation’ section, section 3. The simulated spectra were



decomposed into contributions coming from the Si, C, and O atoms, and these contributions together with the experimental spectra are also shown in figure 4.

Comparing the experimental spectra with the theoretical ones, it can be seen that the positions of the two high-BE peaks are reproduced to within less than  $\pm 2$  eV, and their relative intensities are also reasonably represented. The atomic decomposition of the spectra clearly shows that these peaks can be assigned to the inner valence electrons, namely to the O 2s ( $\approx 26$  eV) and to the C 2s ( $\approx 19$  eV) electrons.

In the experimental spectra of PDMeSO and PMeSSO, two further peaks ( $\approx 14$  eV;  $\approx 9$  eV) can be distinguished; they are less resolved in the spectrum of PMeSSO, while the higher-BE peak in the spectrum of the PDMeSO seems to show further details. In the theoretical spectra, the peak at 14 eV can be clearly identified for PDMeSO, while a shoulder appears for PMeSSO. Instead of a single wide peak near 9 eV in the experimental spectra, several sharper peaks appear near that position in the theoretical spectra of PDMeSO and PMeSSO. Considering the decomposition of the simulated spectra, the peaks near 14 eV and 9 eV can be attributed to Si–O bonds and to oxygen lone pairs, respectively. Although the C–H bonds also contribute to the DOS in these regions, they have no significant effect on the spectra due to their low photo-ionization cross sections.

The spectrum of the PPhSSO deserves a separate discussion. Its structure is more complex than those of the other two polymers, and the uncertainty in the peak positions makes it difficult to find an unequivocal correspondence between the experimental peaks and the theoretical ones.

In contrast to the case for the other two polymers, the contribution of the bonds formed by the carbon atoms dominates over a wide range between 12 and 24 eV. According to the analysis of the Hartree–Fock eigenvectors, these bonds are of C–Si and of C–C  $\sigma$ -type.

Instead of the very broad peak, extending from  $\approx 4$  eV to  $\approx 11$  eV in the experimental spectrum of PPhSSO, sharper peaks appear in the corresponding simulated spectrum. A similar observation, the appearance of several sharp peaks in the theoretical spectra near to the position of a wide peak in the experimental spectra, was also made in the case of the two other polymers. This may occur as a consequence of the conformational freedom of the polymers. The polymer chains, and especially the side-groups, are not strictly ordered, and this may be reflected in the experimental spectra by less resolved peaks in the outer valence region. Finally, the structures of the polymers studied may not strictly correspond to the idealized models shown in figure 1.

The HOVB arising from the  $\sigma$ – $\pi$  mixing in PPhSSO give rise to a small peak appearing near 4 eV in the simulated spectrum, which merges to a broad peak in the experimental one.

While in PDMeSO and PMeSSO the lowest-BE contribution of the side-groups to the spectra is in the inner-shell region ( $\approx 19$  eV), in PPhSSO important contributions arise from the phenyl groups also at lower BEs.

## 5. Conclusion

Summarizing the result of the analysis of the valence photoelectron spectra of the polymers studied, it can be concluded that the basic features of the experimental spectra could be reproduced by the calculations, making it possible to assign the peaks to structural elements. Calculated peak positions and relative intensities may somewhat differ from the experimental ones, and the lowest-binding-energy peak is broader in the experimental spectra than in the theoretical one for all three polymers. These differences are thought to arise from the approximate nature of both the computational (HF LCAO) and the geometrical (idealized

periodical) model used in the calculations.

The methyl side-groups of the polymers contain localized bonds. The  $\pi$ -orbitals of the phenyl groups are able to mix with the highest-energy  $\sigma$ -states of the silsesquioxane skeleton. This is similar to what is found for polyorganosilanes. The mixed  $\sigma$ - $\pi$  states are considerably less delocalized over the polymer skeleton formed by Si-O bonds, as their smaller  $k$ -dispersion shows.

The methyl side-groups of PDMeSO and PMeSSO contribute significantly to the spectra only in the inner valence region, while the phenyl group contributions of PPhSSO appear also in the outer valence region. The above observations may facilitate the interpretation of chemical changes of these polymers occurring during their transformation into ceramic-like materials.

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