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Fine structure of Auger electron spectra from hydrocarbon polymers

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For the surface chemical analysis of polymers X-ray photoelectron spectroscopy (XPS) has been one of the most favoured surface analytical techniques. Because of the small chemical shift of the C1*s* photoelectron line, however, various methods have been used to overcome this shortcoming. One of them is the X-ray induced Auger electron spectroscopy (XAES). The chemical shifts in Auger spectra are often larger than comparable shifts in XPS. In addition to energy shifts, it has been suggested that Auger line shapes may provide useful chemical information for the analyst. Till now, however, little attention has been given to the C *KVV* Auger line shape of polymers.

In the present work, we have studied the fine structure of Auger spectra of polyethylene (PE), polypropylene (PP), and polystyrene (PS). The polymers have been purchased from Charles Evans & Associates and their purity was guaranteed by means of static SIMS. The Auger spectra were obtained by a PHI-5400 ESCA system using monochromatic Al K $_{\alpha}$-ray excitation. For transitions where the initial hole lies in a core level and the two final holes are in the valence band, the line shape of the Auger transition approximately represents the self-convolution of the density of states in the valence band. The two Auger peaks at 263.8 eV and 257.4 eV on the C *KVV* Auger spectrum of PE can be attributed to the transitions from the antibonding and bonding molecular orbitals C2*s* in the valence band, respectively. In case of PP, additional contribution of the Auger transition from the methyl pendant group makes the Auger line shape in the region between 250 eV and 270 eV quite different from that of PE. In the energy loss peaks below 250 eV, however, no shape difference between PE and PP was observed. This can be explained with the postulate of modified radiationless transition in one dimensional system like polymers.