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## Effect of Spatial Confinement on the Radiolytic Efficiency of High-Energy Ions in Polymers

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In this work, the radiolytic efficiency of MeV-GeV heavy ions in polymer thin films has been quantified, following the induced chemical damage as the layer thickness  $h$  of the films is systematically reduced ( $2 < h < 200$  nm). X-ray photoelectron spectroscopy (XPS) was employed to evaluate bond-breaking in the polymer thin films after ion irradiation. We evaluated the rate of decrease of C-O and C-Cl XPS peaks in PMMA and PVC films as a function of the thickness of the polymer layers. Bond breaking cross sections, estimated from XPS data were found to be insensitive to thickness reductions, even in layers as thin as 5nm. The damage cross-sections for PMMA were  $\sim 1.5 \times 10^{-13}$  cm<sup>2</sup> (for O-C-O bonds) and  $\sim 2.3 \times 10^{-13}$  cm<sup>2</sup> (for C=O bonds) for the 2.2 GeV Bi irradiation, whilst for 2 MeV H irradiation the values were  $\sim 2.7 \times 10^{-16}$  cm<sup>2</sup> and  $\sim 4.4 \times 10^{-16}$  cm<sup>2</sup>, for O-C-O and C=O bonds, respectively. Meanwhile, PVC damage cross-sections for C-Cl bonds were estimated as  $\sim 1.5 \times 10^{-15}$  cm<sup>2</sup> for 2 MeV H irradiation. These findings indicate that most of the bond-breaking induced by the ions is related to short-range events close to the track core. Films thinner than  $\sim 5$  nm were difficult to analyse, because of the non-negligible influence of the adventitious carbon on the substrate, combined to changes caused by the ion beam (such as roughening and thinning). Our observations are also in contrast to recent studies showing that surface effects, such as mass transport and cratering formation, are substantially weakened, when individual ion tracks are confined into polymeric ultra-thin films due to the suppression of cooperative effects of excited atoms along the ion track. We will also show results on radial dose profile due to the delta rays in thin water layers obtained from Monte Carlo simulations with the GEANT-DNA toolkit. Such simulations provide a first approach to rationalize the impact of film thickness on the energy spread by the secondary electrons, which is directly coupled to the radiolytic efficiencies.

### Country/Organization invited to participate

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