

# Micrometer-long covalent organic fibres by photo-initiated radical polymerization on an alkali-halide surface

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We present a new concept for the fabrication of up to 1  $\mu\text{m}$  long polymer fibres on insulating alkali-halide substrates [1]. The novelty of our approach is that first, the chosen dimaleimide molecules (fig. a) perform a chain-like (and not a step-like) growth via a radical polymerization, second, that the polymerization is initiated from a two-dimensional gas phase rather than from an intermediate self-assembled structure, and third, that the cations of the chosen alkali-halide substrate interact with the molecule's oxygen atoms and facilitate a defect-free propagation of the polymer fibres along a preferred axis of the substrate.

We discuss the different initiation mechanisms of the polymer reaction at room-temperature that can either be spontaneous (fig. b), or induced by UV-light (fig. d). Once initiated, the chain-like polymerization proceeds easily and is only stopped by either defects on the surface or exhaustion of the precursor molecules. The propagation of this reaction on the surface, the involved reaction barriers as well as the structure and stability of the formed 1D polymer fibres (fig. c) are discussed by means of Density Functional Theory calculations, Climbing Image Nudged Elastic Band Calculations, and noncontact Atomic Force Microscopy imaging and manipulation at room temperature.

[1] F. Para *et al.*, under revision

