Characterisation of Polymerisation Defects in Rigid Rod Conjugated Polymers: Electrospray Deposition Combined with High-Resolution Scanning Tunnelling Microscopy

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Conjugated polymers (CPs) demonstrate unique electronic and optoelectronic properties, outstanding biocompatibility and mechanical flexibility, and have been implemented in a wide range of modern technologies [1]. The majority of CPs used in thermoelectrics, (bio)electronics and neuromorphic computing are based on complex chemical compositions and structures obtained through multi- and co-polymerisation techniques. The precise control of the microstructure in CPs is thus essential for understanding their behaviour in high-performance organic electronic devices and central for the development of CP based next-generation applications. However, traditional analytical techniques used in polymer science (XRD, NMR, mass spectrometry, chromatography) often struggle to precisely characterise modern CPs.

This work aims to solve this fundamental problem by using the ultimate spatial resolution of scanning probe microscopy and its ability to provide structural and local electronic properties of molecules with sub-nm scale precision. To this end, vacuum electrospray deposition (ESD), central to the ability of studying thermolabile macromolecules in ideally controlled conditions [2], was used to deposit rigid rod CPs, synthesised by an aldol condensation polymerisation, on Au(111) single crystalline surfaces in ultrahigh vacuum (UHV). The aldol condensation polymerisation is an important reaction frequently used in organic synthesis, and the resulting CPs show excellent electronic properties to be employed in advanced (bio)electronic devices [3]. The samples were analysed in situ by low temperature scanning tunnelling microscopy (LT-STM) in UHV to acquire sub-monomer resolved images, revealing the composition and structure of the CPs at a level that is impossible with any other present analytical technique [4,5].

Unexpected polymerisation defects were demonstrated, showing the occurrence of homocoupling reactions between co-monomers that had not been considered so far in the literature. The appearance of homocoupling could be explained by alternative reaction pathways that effectively “exchange the side-chains” between co-monomers. Moreover, stereodefects were also observed, resulting in kinks in the backbones with specific angles, which could be explained by possible coupling reactions at both carbonyl atoms of the monomers, as well as by *cis* instead of *trans* couplings. The results of this work bear a high potential impact for their implications in understanding the reaction mechanisms of aldol condensation polymerisation reactions at the molecular level.

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