Bisphenol A and diethylstilbestrol on Cu(111): On-surface polymerization initiated by hydroxy-directed ortho C-H bond activation

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The exploitation of surface-assisted covalent coupling and polymerization reactions is an appealing route toward bottom-up fabrication of robust low-dimensional networks relevant for technological applications. Fundamental atomic-level studies of these reactions on well-defined surfaces are crucial for the rational design of a wide range of functional nanostructured interfaces. In the present study, through a combination of X-ray photoelectron spectroscopy (XPS), temperature programmed XPS (TP-XPS), scanning tunneling microscopy (STM), temperature programmed desorption (TPD) and low-energy electron diffraction measurements, we shed light on the complex thermal evolution of bisphenol A (BPA) and diethylstilbestrol (DES) on Cu(111). Our findings provide evidence of a hydroxy-directed on-surface polymerization reaction, corroborating the recently reported ortho C-H bond activation in phenol derivatives [1]. Specifically, both BPA and DES undergo a remarkably similar series of chemical (XPS) and structural (STM) transformations (well-ordered overlayer \rightarrow "type A" chains \rightarrow "type B" chains [2] (cf. figure)), suggesting that for both species the same orthoortho coupling prevails. In agreement, the corresponding reaction steps are monitored via probing thermal desorption of the byproducts H₂ and H₂O (TPD). Such precise control over C-C bond formation between molecular precursors via directing OH groups can be highly relevant for the tailoring of robust covalent organic frameworks (COFs) [3] [4], and it extends the nanostructuring toolbox of interfacial covalent reactions, often relying on surface-assisted Ullmann coupling [5] [6].



References:

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