Revealing the structural detail of individual polymers using a combination of electrospray deposition and UHV-STM.

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Supporting Information

S1. Sample preparation

The absolute molecular masses of the polymer samples used in the current study were determined using GPC (Gel Permeation Chromatography) coupled to a MALS (multi angle light scattering) detector.

Stock solutions of PPV-TBDPS in toluene (Chromasolv Plus, Sigma Aldrich) were prepared by stirring a measured amount of PPV-TBDPS in toluene (0.5-1.0 mg/mL) overnight at 90 ℃ in a capped vial with an argon atmosphere in the dark. A volume of the polymer solution corresponding to 0.20 mg of dissolved polymer was then diluted to a volume of 6 mL in toluene. Finally, 2 mL of hot acetonitrile (Biotech grade, Sigma Aldrich) was added to the hot polymer solution. Adding acetonitrile without heating led to immediate precipitation of the polymers whereas solutions prepared using hot acetonitrile remained stable for weeks. Whenever possible, the polymer solutions were handled in darkness to avoid photo induced degradation of the polymers.

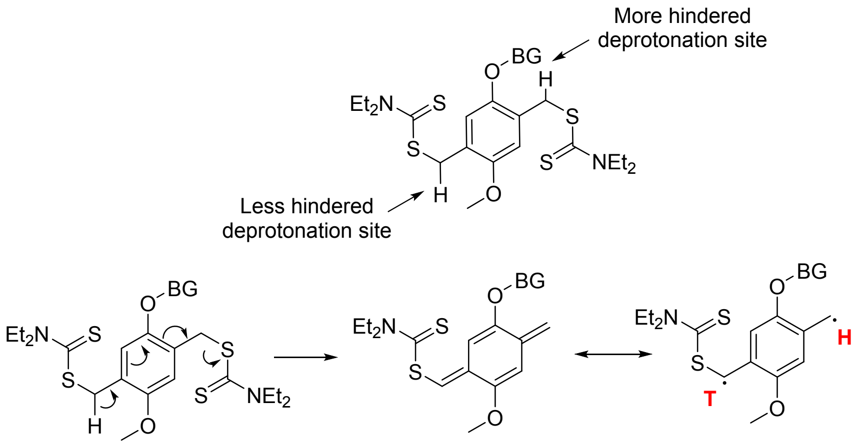
The Au(111) surface is cleaned using a series of cycles of Ar^+ ion sputtering at 2.00 keV followed by annealing to 800 K. The cleanliness of the surface is checked by scanning the surface with STM prior to performing experiments. Pt/Ir tips were used for STM measurements.

S2. Electrospray set-up

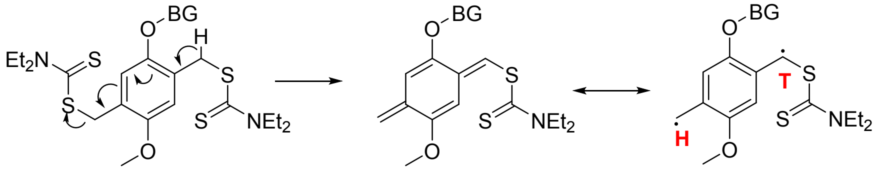
Commercial Electrospray Ionisation source available from MolecularSpray Ltd[1] was used for the deposition of PPV-TBDPS, and the equipment is fully described in reference [2]. The solution of PPV-TBDPS in 3:1 toluene/acetonitrile is pumped via a syringe into a stainless steel emitter, where it is subjected to around +2.2 kV bias. A fine spray is produced, which impinges on a stainless steel capillary (0.01 inch internal diameter). The charged droplets travel through 3 pumping stages (provided by 2 × scroll pumps and 1 × turbo pump) separated by apertures, where solvent from the droplets is gradually pumped away. This procedure results in a beam of gas-phase molecular ions travelling towards the crystal target, which is aligned approximately perpendicular to the incident beam. The base pressure in the chamber prior to electrospray of the PPV-TBDPS solutions is better than 1×10^{-10} mbar. During electrospray, the pressure fluctuates between 1×10^{-7} and 1×10^{-6} mbar. The pressure recovers rapidly to around 1×10^{-9} mbar once the gate-valve to the electrospray equipment is closed, while it may take up to 1 hour to drop to the original base pressure of the chamber. The overall distance between the emitter tip and the crystal target is approximately 60 cm resulting in a spot size of the incident molecular flux that is much smaller than the 28 mm^2 area of the Au(111) crystal. The required careful alignment of the crystal with the incident molecular beam is accomplished prior to the experiment, using a solution of C_{60} in 3:1 toluene/acetonitrile that is known to adsorb readily on the Au(111) surface.[3]

S3. Mechanistic insight for observation of regioregularity

As discussed by Vandenberg *et al.,*[4] the use of sterically hindered bases such as LiHMDS for formation of PPV polymers from asymmetric building blocks induces some degree of regioregularity in the final polymer product. The polymerisation is of radical nature, and it is initiated by deprotonation of a benzylic proton. Dependent on the nature of the monomer substituents, deprotonation at the least crowded benzylic position will to some extent be favoured. The site of deprotonation determines the isomerism of the final polymer product. If deprotonation was limited to one of the two benzylic positions and propagation occurred solely by Head to Tail couplings, a fully regioregular polymer would result. In the mechanistic discussions below, propagation solely by head to tail couplings is assumed. This assumption is not unreasonable, as polymerisations via the dithiocarbamate route proceeds almost exclusively by head to tail couplings. Only around 0.6 % H-H defects were reported[4,5] probably arising from H-H initiation. BG denotes big group, which is in our case the TBDPS-terminated triethylene glycol linker.



Deprotonation at least hindered benzylic position (H = Head, T = Tail)

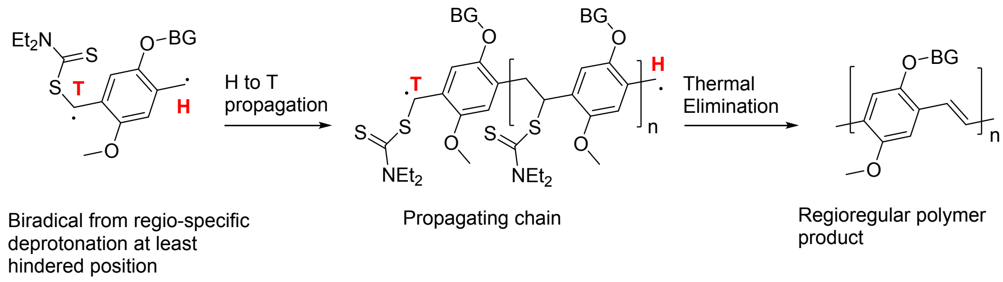


Deprotonation at most hindered benzylic position (H = Head, T = Tail)

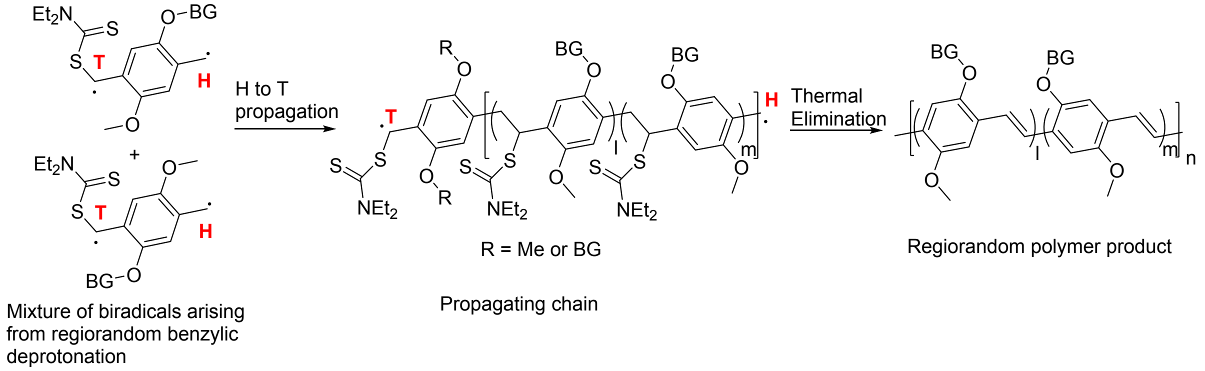
Scheme S1: Illustration of the initiation of polymerisation by formation of biradicals. Upper scheme depicts the biradical formation upon deprotonation at the least hindered site and the lower scheme illustrates biradical formation in the case of deprotonation at the most hindered site.

Upon deprotonation, the larger substituent (BG) will be attached to the carbon *ortho* to the Head position when deprotonation occurs at the least hindered site. In the opposite case, the methoxy group will be positioned *ortho* to the Head position, whereas the larger group will be positioned *meta* to the Head position. As the polymerisation occurs by H-T couplings, the deprotonation determines the regioisomerism of the polymer product.

The figure below serves to explain how the chain propagates in the case of initiation by regioselective deprotonation and regiorandom deprotonation respectively.



Regioregular polymerization



Regiorandom polymerization

Scheme S2: Explanation for formation of regioregularity in PPV products. Top scheme serves to illustrate the regioregular polymerization arising from site-specific deprotonation. The bottom scheme illustrates the situation when there is no regioselectivity in the deprotonation leading to the formation of regiorandom polymers. For simplicity, the possible Head-to-Head initiation of polymerization is not addressed in these schemes. BG denotes big group which is in our case the TBDPS terminated triethylene glycol linker.

S4. Additional Images of PPV-TBDPS on Au(111)

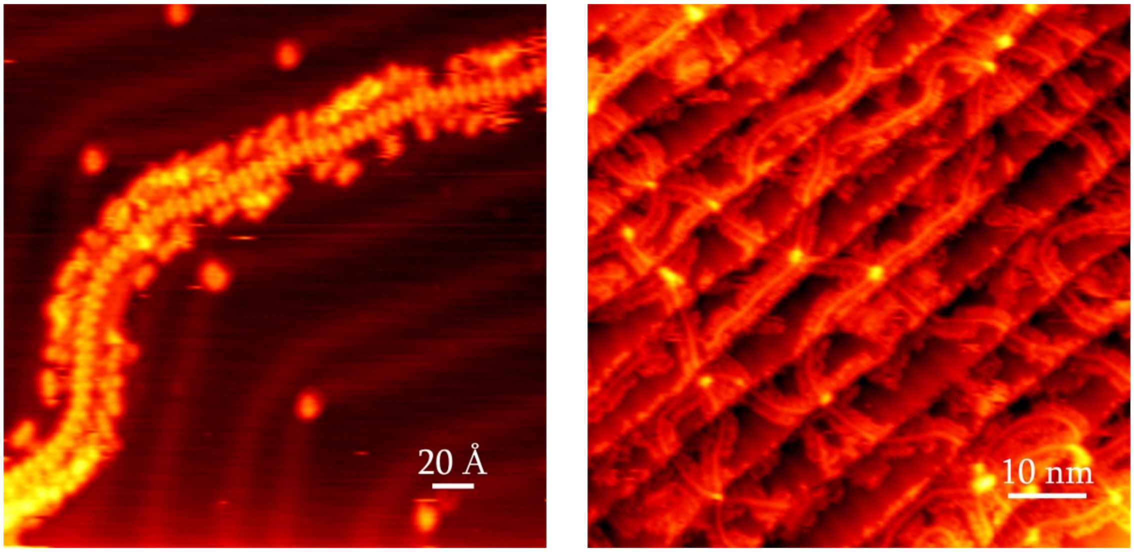


Figure S1 **(a)** Image showing clear alignment of PPV-TBDPS along the FCC regions of the Au(111) herringbone reconstruction **(b)** Multiple PPV-TBDPS strands adsorbed across multiple step-edges, inhibiting diffusion and highlighting the inhomogeneous coverage obtained with Electrospray Ionisation Deposition.

S6. REFERENCES (Supporting Information)

(1) http://www.molecularspray.co.uk/.
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(3) Satterley, C. J.; Perdigão, L. M.; Saywell, A.; Magnano, G.; Rienzo, A.; Mayor, L. C.; Dhanak, V. R.; Beton, P. H.; O'Shea, J. N. *Nanotechnology* **2007**, *18*, 455304.
(4) Vandenbergh, J.; Wouters, J.; Adriaensens, P. J.; Mens, R.; Cleij, T. J.; Lutsen, L.; Vanderzande, D. J. M. *Macromolecules* **2009**, *42*, 3661.
(5) Junkers, T.; Vandenbergh, J.; Adriaensens, P.; Lutsen, L.; Vanderzande, D. *Polymer Chemistry* **2012**, *3*, 275.