Title: Observing Polymerization in Two-Dimensional Dynamic Covalent Polymers

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The quality of crystalline two-dimensional polymers (2DPs)[1-6] is intimately related to the elusive polymerization and crystallization processes. Understanding the mechanism of such processes at the (sub)molecular level is crucial to improve predictive synthesis and to tailor material properties for applications in catalysis[7-10], and (opto)electronics[11, 12], among others[13-18]. We characterize a model boroxine 2D dynamic covalent polymer, by using *in situ* scanning tunneling microscopy, to unveil both qualitative and quantitative details in the nucleation-elongation processes in real time and under ambient conditions. Sequential data analysis allows for the observation of the amorphous-to-crystalline transition, the time-dependent evolution of nuclei, the existence of "nonclassical" crystallization pathways and importantly, the experimental determination of essential crystallization parameters including critical nucleus size, nucleation rate and growth rate with excellent accuracy. The experimental data has been further rationalized by atomistic computer models that altogether provide a detailed picture of the dynamic on-surface polymerization process. Furthermore, we show how two-dimensional crystal growth can be affected by abnormal grain growth (AGG). This finding provides support for the use of AGG - a typical phenomenon in metallic and ceramic systems - to convert a polycrystalline structure into a single crystal in organic and 2D material systems.

Two-dimensional polymers (2DPs) –covalently linked networks of monomers in orthogonal directions– can be found as individual monolayers, as part of few-layer stacks, or as part of multilayered crystals, the latter known as 2D covalent organic frameworks (2D COFs). Over the past decade, research has focused on exploring efficient and controlled synthetic strategies to produce highly crystalline 2DPs[19-26] and 2D COFs[27-29]. Yet little is known about the mechanistic and kinetic aspects of the dynamic processes involving bond formation/breakage, nucleation,

45   elongation and interplay between nuclei[30-36] because of the challenges associated with the

46   stochastic nature of nucleation events and requirements imposed by molecular level imaging.

47   Herein, we show a detailed picture of the different polymerization and crystallization steps for the

48   formation of a crystalline 2DP at the solid-liquid interface, by *in situ* scanning tunneling

49   microscopy (STM) under ambient conditions. The advantage of the solid-liquid interface is that

50   the 2D polymerization process can be decoupled from the stacking/destacking process that leads

51   to 2D COFs. Therefore, fundamental mechanistic parameters of the formation of 2DPs can be

52   obtained. For instance, the optimal resolution –in terms of space (molecular resolution) and time

53   (minute resolution)– of STM for this system enabled the observation and identification of the

54   different reactive monomeric, oligomeric, and crystalline species involved and their evolution over

55   time.

56   The self-condensation of pyrene-2,7-diboronic acid[37] (PDBA) has been studied as a model system

57   (Fig. 1a, e) since PDBA is known to form boroxine polycrystalline 2D COF powders[38], single-

58   crystalline 2D COF colloids[28], 2D COF thin films[39] and 2DPs[40] by dynamic covalent chemistry.

59   Here, a confined synthesis protocol[41] has been implemented for probing the polymerization and

60   crystallization of a PDBA 2DP on an atomically flat highly oriented pyrolytic graphite (HOPG)

61   surface, by *in-situ* STM with the scanning rate set at 1.5 minutes per frame. Dynamic on-surface

62   polymerization processes are clearly observed by *in-situ* STM when 5 µL of a 1-octanoic acid

63   solution of PDBA (50 µM) is drop-casted onto freshly cleaved HOPG surface. Initially, an apparent

64   disordered phase of PDBA was formed at the 1-octanoic acid/HOPG interface (Fig. 1b). The

65   amorphous nature of this phase is revealed by the halo feature of the fast Fourier transform (FFT,

66   inset Fig. 1b). Structural analysis of the amorphous phase revealed the co-existence of PDBA

67   monomers   and   oligomers   of   variable   sizes,   which   underwent   dynamic

polymerization/depolymerization processes on the surface, as supported by sequential data acquisition (Fig. 1a, Supplementary Fig. 1). After a period (*c.a.* 30-60 min) of structural fluctuation, honeycomb clusters with ordered 'cavities' emerged within the amorphous phase (Fig. 1c). Figure 1d displays the submolecular resolution STM image of this newly-formed phase, in which each pyrene unit appears as a six-lobed feature. FFT analysis (insert in Fig. 1c, Supplementary Text 1, Supplementary Fig. 2) of the honeycomb clusters reveals a hexagonal network with lattice parameters of $\mathbf{a}=\mathbf{b}=2 \pm 0.1$ nm and $\gamma = 60 \pm 2°$, which are in perfect agreement with the *ex-situ* synthesized PPy-COF and theoretical values[38, 40]. Computer models allow us to establish the on-surface reaction pathway (Fig. 1f) for the formation of a trimer. As shown in Fig. 1f, the activation energies for bond breaking (3-7 kcal/mol) are substantially lower than the forward reaction (10-12 kcal/mol), meaning that smaller 2D polymers are more likely to shrink than to grow. Figure 1g shows early-time snapshots of 2D crystalline clusters with their sizes ranging from 1 to 19 hexagonally ordered cavities. The nucleation pathway is clearly revealed by sequential imaging (Supplementary Fig. 3, Supplementary Video 1) that shows how the initial amorphous phase evolves into crystalline nuclei. In some rare cases (Supplementary Fig. 4), nucleation occurs via alternative pathways such as merging and division, *i.e.*, two smaller nuclei incorporate into a large one; or inversely, a large nucleus divides into two separate nuclei. The formation of well-structured oligomers from an amorphous phase, as well as the interconnection between them is consistent with a step-growth polymerization mechanism[24, 42]. The entropy penalty due to the covalent linking of many monomers into a larger entity and the confinement of the surface is balanced/overcome by the production of H_2O as a by-product.

As the system tends to equilibrate, the initial formation of oligomeric nuclei is entropically disfavored, but subsequent addition of monomer units to form larger polymeric structures becomes

energetically favorable for the crystallites to reach the critical nucleation size d_c (or critical diameter). We have experimentally determined d_c by means of the direct visualization of sub-, near- and super-critical nuclei at different timeframes. Real-time imaging by *in situ* STM enabled the unambiguous identification of the structure of individual nuclei, as well as their evolution over time (Fig. 2a-d, Supplementary Video 2). Noted that most of the nuclei have an irregular shape during the dynamic nucleation process, we use an equivalent diameter ($d_i = \sqrt{4A_i/\pi}$) derived from the area of nuclei (A_i) to specify the size of each individual nucleus (Supplementary Text 2, Supplementary Fig. 5). Upon statistical analysis of the time evolution of 2268 nuclei (Fig. 2e, Supplementary Text 3, Supplementary Fig. 6, Supplementary Data 1), we were able to determine the size dependence of the probability to grow (p_g) and the probability to shrink (p_s), shown in Supplementary Fig. 7. The critical size (d_c) lies in the range in which the difference ($p_g - p_s$) goes from negative to positive[43]. According to the plot of ($p_g - p_s$) against nuclei diameter (Fig. 2f), we found that d_c is ~ 9 nm, which corresponds to 54 ± 5 monomer units. Another important parameter that we have been able to establish and that provides information about the nucleation kinetics is the nucleation rate (J), which is defined as the total number (N_c) of 'mature' nuclei ($d \geq d_c$) created per time per unit area. A plot of N_c versus time t (Fig. 2g) gives a linear trend with a slope of 17.9 $\mu m^{-2} min^{-1}$ that corresponds to J. The growth rate is the second key factor in controlling the size of 2D crystals. By plotting the average nucleus size over time, we calculated an average growth rate of *c.a.* 0.05 nm/min (Fig. 2h). When considering the elongation at the *single-nucleus level,* the individual nucleus growth is rather complex since nucleus-nucleus interactions play an important role. Time-resolved *in situ* data revealed that the size of some nuclei increased continuously (Supplementary Fig. 8), whereas other nuclei underwent structural fluctuation or shrinkage (Supplementary Fig. 9, 10). The measured high nucleation rate and low growth rate can be used to

justify the lateral size of the generated 2DPs crystals. Consequently, when the coverage of 2DPs

reaches 30 % at time = 70 mins (insert, Fig. 2h), the average grain size is less than 14 nm. To

ensure that the observed 2D polymerization is not an effect of the tip[44, 45], the dynamic process has

been carefully analyzed (Supplementary Text 4, Supplementary Fig. 11-17), showing that the

observed 2D polymerization is not tip-induced.

When separate nuclei grew and approached one another, interface elimination takes place –in order

to reduce the total area of grain boundaries and thus decrease the free energy of the system–

generally via two possible pathways: either particle attachment or Ostwald ripening, of which

coalesce of grains is driven by attachment of aligned particles and monomer-by-monomer

reorientation, respectively.[46, 47]

Current understanding of the crystallization by particle attachment (CPA) process in 2DPs is

limited to theoretical predictions. Direct experimental evidence of CPA is still lacking despite of

the vital role of CPA in controlling crystal sizes, morphologies etc[45]. In Supplementary Fig. 18,

sequentially recorded data clearly reveal that when two adjacent nuclei (*I, II*) approach one another,

growth units are quickly added at their interface, thereby resulting in a perfect attached grain (*III*)

within 3 minutes. The two nuclei were perfectly aligned before attachment and their orientation

and relative location remained unchanged during the attachment process, arising from the 2D

confinement by the surface and trapping effect by surrounded nuclei. In order to understand if

small-sized nuclei of 2DPs are mobile due to reduced π-π interactions with the substrate, we

analyzed different sequences of cross-correlated STM images. The relative orientation or location

of nuclei is determined using reference points such as immobilized species and point defects.

Accordingly, we found that in-plane motion is never observed for nuclei larger than 6 nm

(Supplementary Video 3, Supplementary Fig. 19-20), and that translational or rotational motion is

possible for nuclei smaller than 3 nm (Supplementary Fig. 1, 21). This observation is consistent with theoretical calculations indicating that diffusion and rotation barriers increase as a function of the crystal size (Supplementary Figure 22). Such nuclei attachment events were not frequently observed as most often, we observed a mismatched interface followed by interface elimination.

Mismatched interface elimination is mainly driven by the Ostwald ripening process and two types of crystal evolution routes have been observed (Fig. 3d). The first type refers to 'continuous' or 'normal' grain growth (NGG), in which growth takes place in a uniform manner. In this case (Fig. 3e-g, Supplementary Video 4), nuclei of smaller size (*I, II, III* and *IV* in Fig. 3e) were gradually consumed. Total surface coverage of 2DPs is nearly constant after 75 min (Fig. 3g) and there is only a slight increase of the average grain size (Fig. 3h). All the nuclei are either aligned with respect to each other (green or blue domains), or rotated by an angle of 6°, suggesting that crystallization is a hetero-epitaxial process. Imaging of the underlying graphite lattice showed that the tilt angles between crystallographic orientations of 2DPs and main symmetry axes of the HOPG lattice [100] have opposite signs; that is, +27° for R_1-2DPs (blue) and -27° for S_1-2DPs (green), respectively (Fig. 3a-c).

The second type refers to 'discontinuous' or 'abnormal' grain growth (AGG), wherein a preferential growth of a few nuclei occurs at the expense of neighboring ones. In this particular case (Fig. 3b, c, j-l, Supplementary Video 5, Supplementary Fig. 23, 24), in addition to the primary type nuclei (R_1-2DPs, S_1-2DPs), another nucleus type is observed, of which the tilt angle with respect to the main axes of graphite lattice [100] is +19° for R_2-2DPs (pink) and -19° for S_2-2DPs (orange), respectively. In sharp contrast to the slow kinetics of the NGG process, a continuous increase of 2DPs coverage (Fig. 3m) is observed. More interestingly, a preferential growth (Fig. 3n) of nuclei of secondary type (S_2) occurs at the expense of the surrounding primary nuclei (R_1

and S_1), characteristic of AGG. In regions with all secondary nuclei (R_2 and S_2), the NGG behavior again dominates (Supplementary Fig. 25). In short, AGG process takes place only in presence of both nuclei of the primary and secondary type.

The two different growth modes (NGG/AGG) provide a new mean to control the size of crystals: secondary nuclei will continue to elongate laterally at the expense of surrounded primary nuclei or oligomeric species (within the amorphous phase) until reaching the interface of another secondary nucleus. If the purpose is to grow crystals to even larger sizes, the key factor lies in the fast generation of primary type nuclei, which on the one hand occupy the limited space on the surface (thus inhibiting the number of secondary nuclei) and on the other hand, serve as molecular sources for secondary nuclei to grow. This concept is demonstrated with the assistance of a STM tip. We show that if a domain of S_2 type is selectively 'scratched' by the STM tip, the surface will be quickly covered by an amorphous phase, followed by the formation of primary nuclei (R_1 and S_1), which in turn, allows for a further increase of crystal size through AGG (Supplementary Fig. 26). Indeed, when the number of secondary type nuclei is limited to one within the scanning region, the subsequent consumption of the primary type nuclei (R_1/S_1) results in the formation of a larger unidirectional domain (Supplementary Video 6).

To gain insight into the mechanistic aspects of the AGG processes, we considered both thermodynamic and kinetic aspects. Based on Ostwald's step rule that metastable phases often appear first, followed by the thermodynamically more stable phases, it is reasonable to assume that the on-surface generated secondary type nuclei (R_2/S_2) are more stable than the primary type (R_1/S_1), which is likely responsible for the gain in overall energy being the driving force for the growth of more stable phase at the expense of metastable ones. In order to validate our hypothesis, we carried out quantum calculations which indicate that the energetically favored phase will adopt

a specific orientation along a particular angle due to the mismatch of 2DPs and graphite surface periodic cells (Supplementary Fig. 27).

We then investigated the kinetic aspects of nuclei coalescence, up to single monomer level. When two nuclei share the same crystallographic orientations (R_1/R_1, R_2/R_2, S_1/S_1, and S_2/S_2), the grain boundary (GB) migration rate is measured to be less than 0.05 nm/min (Supplementary Fig. 28) due to slow kinetics of the building block exchange. Although the grain misorientation is 0° (GB-*I*), a slight lattice displacement (~0.6 nm) causes the separation of nuclei by nanometer-scale (~1.4 nm) distances (Fig. 4a). Other mismatch examples, both for NGG and AGG, involve those where two nuclei are not aligned with each other, therefore giving rise to the generation of tilt GBs. When both nuclei are of either primary type or secondary type (R_1/S_1, or R_2/S_2), a grain misorientation of 6° (GB-*II*, Fig. 4b) or 22° (GB-*III*, Fig. 4c) exists. The migration rates of GB-*II* and GB-*III* are measured to be lower than 0.1 nm/min (Fig. 4e-h, Supplementary Fig. 29). While for the mixture of primary and secondary type nuclei (R_1/S_2, R_2/S_1, R_1/R_2, or S_1/S_2), two additional types of grain misorientation, 8° (GB-*IV*) or 14° (GB-*V*), were identified (Fig. 4d). In this case, migration rates of GB-*IV* and GB-*V* are estimated to be 0.4 nm/min and 0.2 nm/min, respectively (Fig. 4i-l, Supplementary Fig. 30), which are at least two times faster than that of other types (GB-*I*, GB-*II* and GB-*III*). The measured anisotropic GB migration rate is in line with other systems[48, 49] showing that certain crystallographic grain boundaries have a higher mobility than others. Indeed, according to the Monte Carlo model established by Anderson and co-workers[50], if secondary grain (R_2 and S_2) shows *mobility advantage* compared to primary ones (R_1 and S_1), AGG is more likely.

Remarkably, this work illustrates our ability to establish experimentally the fundamental polymerization and crystallization parameters of 2D dynamic covalent polymers on a surface. Given the importance that the elucidation of reaction mechanisms has had on the synthesis of

precision polymers, this work paves the way for controlling 2D polymerization reactions directly on 2D materials of different nature, which in turn, will allow the development of novel 2D heterostructures with a level of precision similar to current state-of-the-art polymeric materials.

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Fig. 1 | Disorder to order transition. a, Schematic illustration of the dynamic nucleation process, from the monomer building block pyrene-2,7-diboronic acid (PDBA, left panel) towards the generation of 2D polymers nuclei (right panel), monitored by *in situ* STM at the 1-octanoic acid/HOPG interface. Four STM images reveal oligomers with variable sizes before forming a closed hexagonal unit. **b**, Amorphous phase formed on HOPG, insert: fast Fourier transform (FFT) image revealing the halo feature. **c**, Emergence of honeycomb clusters within the amorphous phase; insert: FFT of areas contoured with white dashed curve. **d**, High resolution STM image of the honeycomb cluster. White dotted square points out the unit three-armed pattern of 2D polymers with the chemical structure shown in **e**. **f**, Reaction pathway, representative structures and energies, for the on-surface polymerization of three monomers to give a trimer. The energies (in kcal/mol) are relative to isolated monomers on the surface. **g**, Snapshots of different images, showing individual nuclei with their sizes ranging from 1 to 19 hexagonally ordered cavities. Imaging conditions: **b-c**, 40 nm × 40 nm, I_{set} = 0.04 nA, V_{bias} = –0.2 V. **d**, 10 nm × 10 nm, I_{set} = 0.04 nA, V_{bias} = 0.5 V. **g**, 12 nm × 12 nm, I_{set} = 0.04 nA, V_{bias} = 0.5 V.

Fig. 2 | Nucleation-elongation processes. a-d, Large scale STM images obtained during the nucleation-growth processes. **e,** Growth rates plotted against the size of 2268 individual nuclei. **f**, Plot of the probability difference to grow (p_g) and the probability to shrink (p_s) against the nuclei diameter, allowing for the determination of critical nucleation size d_c. **g**, The evolution of the

number density (N_c. μm^{-2}) of 'matured' nuclei ($d \geq d_c$) over time. The nucleation rate (J) is

obtained from the slope of a linear fit. **h**, The evolution of the average nucleus size (mean value of

the diameter of 'matured' nuclei) over time, providing the average growth rate. Insert: plot of

surface coverage of 2DPs over time. Imaging conditions: **a-d**, 150 nm × 150 nm, I_{set} = 0.08 nA,

V_{bias} = 0.3 V.

Fig. 3 | Normal and abnormal 2D grain growth routes. a, Scheme illustrating the tilt angle θ

between the crystallographic orientation of 2DPs and the main axes of HOPG lattice [100]. **b**, STM

image revealing four possible orientations colored in orange, pink, blue, and green, respectively.

c, Scheme illustrating the four tilt angles with respect to graphite lattice: +27° (R_1) /-27° (S1) and

+19° (R_2) /-19° (S_2). **d**, Scheme illustrating the normal and abnormal grain growth processes. **e-g**,

STM images from Supplementary Video 4 at time = 0 min, 30 min and 75 min, respectively. **h**,

The evolution of 2DPs coverage (R_1 in blue and S_1 in green) over time. **i,** The evolution of average

grain size over time. **j-l**, STM images from Supplementary Video 5 at time = 0 min, 30 min and

75 min, respectively. **m**, The evolution of 2DPs coverage (R_1 in blue, S_1 in green and S_2 in orange)

over time. **n**, Bimodal evolution of average grain size over time, displaying the preferential growth

of S_2 type at the expense of R_1 and S_1. Imaging conditions: **b**, 80 nm × 80 nm, I_{set} = 0.1 nA, V_{bias} =

0.3 V. **e-g**, 60 nm × 60 nm, I_{set} = 0.08 nA, V_{bias} = 0.3 V. **j-l**, 100 nm × 100 nm, I_{set} = 0.08 nA, V_{bias}

= 0.3 V.

Fig. 4 | Identification of grain boundaries (GB) and their kinetic movement. a, STM image

showing the displacement of two nuclei sharing the same crystallographic orientations. **b-c**, Tilt

GBs of two nuclei of either primary or secondary type, of which a grain misorientation of 6° (R_1/S_1)

and 22° are identified, respectively. **d**, Tilt GB formed between a secondary type nucleus (R_2) and

the surrounded primary type (R_1 or S_1), leading to a grain misorientation of 8° and 14°. **e-h**, Sequential recorded images showing the kinetic movement of GB-*II* over time. **i-l**, Sequential recorded images showing the kinetic movement of GB-*V* over time. The white dashed circles in panel e-l indicate the immobilized point defects during the sequential imaging processes. Imaging conditions: **a-h**, 30 nm × 30 nm, I_{set} = 0.08 nA, V_{bias} = 0.3 V. **i-l**, 40 nm × 40 nm, I_{set} = 0.08 nA, V_{bias} = 0.3 V.

Methods

<u>Chemicals and sample preparation.</u>

Pyrene-2,7-diboronic acid (PDBA) was synthesized as reported in the literature[37]. 1-octanoic acid (Sigma-Aldrich ≥ 99%) and dimethylsulfoxide (Sigma-Aldrich ≥ 99%) were used without further purification. Solutions of PDBA were prepared by dissolving the solid sample in dimethylsulfoxide (1 mg/g) and further diluted with 1-octanoic acid to generate concentration series. For all STM measurements, we use commercially available solvent without further treatment. The ambient humidity was controlled to be in the range of 45% to 50%.

<u>*In situ* STM measurements.</u>

All experiments were performed at room temperature using a PicoLE (Agilent) machine operating in constant-current mode. STM tips were prepared by mechanical cutting from Pt/Ir wire (80/20, diameter 0.25 mm, Advent Research Materials). HOPG (grade ZYB, Momentive Performance Material Quartz Inc., Strongsville, OH, USA) was used as substrate for STM measurements at the solid-liquid interface under ambient conditions. Several samples were investigated, and for each sample, several locations were probed. The bias voltage refers to the substrate. STM images were processed using Scanning Probe Image Processor (SPIP, Image Metrology ApS) software.

388   Imaging parameters for the STM images are indicated in the figure captions and denoted by V_{bias}

389   for sample bias and I_{set} for tunneling current.

390   **Density Functional Theory (DFT) and Tight Binding (TB) calculations.**

391   DFT calculations were performed with the Fritz Haber Institute ab initio molecular simulations

392   package[51-53] using "light" numeric atomic orbitals, which approximately correspond to the TZVP

393   level of calculations. The PBE functional augmented with Many Body Dispersion (MBD)

394   corrections[54,55] was used for geometry optimization and energies. All presented data are

395   geometrically optimized minima obtained either with the FHI-aims internal optimizer or with the

396   FIRE optimizer[56] via the Atomic Simulation Environment (ASE)[57]. Tight Binding (TB)

397   calculations were benchmarked against DFT and used for the larger computations. For the study

398   of the motion of monomers, dimers and trimers and periodic 2DPs adsorbed on graphene the

399   Matsci parameter set with dispersion classical corrections from OPLSAA force-field

400   parametrization[58,59] was used within the DFTB+ program[60]. The polymerization pathway was

401   computed with the NEB-CI methodology with 8 images on a graphene 2D unit cell with 4 nm side

402   with 512 carbon atoms cut from a graphite crystal with a GFN1-xTB Hamiltonian[61] within the

403   DFTB module of the current version of the Amsterdam Modeling Suite[62]. The computation of the

404   larger systems presented, a finite 2DPs on a hexagonal graphene flake with 15780 atoms,

405   Supplementary Fig. S27, was performed with the XTB v6.4.1 software[63] with the GFN-FF

406   Hamiltonian[64].

407   **STM image calibration.**

408   For analysis purposes, recording of each series of images was followed by imaging the graphite

409   substrate underneath it under the same experimental conditions, except for increasing the current

410   and lowering the bias. Raw STM images were calibrated by using the STM images of the HOPG

lattice as a reference. This exercise removes the distortions in the STM images that arise due to thermal drift. The lattice parameters were then obtained from these calibrated images. SPIP software (Image Metrology ApS) was used for image calibration.

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448 **Data availability**

449 The main data supporting the findings of this study are available within the paper and its

450 Supplementary Information. Additional data are available from the corresponding authors upon

451 reasonable request.

452

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Author contributions

G.Z., Z.F.C., and S.D.F. conceived the idea and designed the experiments. G.Z., Z.F.C., L. Y. and N.H. carried out the *in situ* STM experiments and analyzed the data. K.S. and M.M.F carried out

the DFT and Tight-Binding calculation. M.M.A. carried out the synthesis of the monomer. The text was initially composed by G.Z., Z.F.C., A.M.A. and S.D.F., and all authors further contributed to the discussion of the experimental work and the final version of the manuscript.