On-water surface synthesis of crystalline, few-layer two-dimensional polymers assisted by surfactant monolayers

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Despite rapid progress in recent years, it has remained challenging to prepare crystalline two-dimensional polymers. Here, we report the controlled synthesis of few-layer two-dimensional polyimide crystals on the surface of water through reaction between anhydride and amine monomers, assisted by surfactant monolayers. We obtained polymers with high crystallinity, thickness of ~2 nm, and an average crystal domain size of ~3.5 µm². The molecular structure of the materials, their grain boundaries, and their edge structures were characterized using X-ray scattering and transmission electron microscopy techniques. These characterizations were supported by computations. The formation of crystalline polymers is attributed to the two-dimensional (2D) polymerization at the water–surfactant interface. The surfactant, depending on its polar head, promoted the arrangement of the monomers and in turn their polymerization—either horizontally or vertically with respect to the water surface. The latter was observed with a surfactant bearing a carboxylic acid group, which anchored amine monomers vertically through a condensation reaction. In both instances, micrometre-sized, few-layer two-dimensional polyamide crystals were grown.

Both synthetic and natural polymers play an essential and ubiquitous role in our daily lives. Typically, they can be described by a sequence of repeat units linearly connecting via covalent bonds according to the definition proposed by Hermann Staudinger in the early 1920s. There have been numerous impressive attempts to go beyond Staudinger's concept and synthesize sheet-like polymers with long-range order along two orthogonal directions that is, two-dimensional (2D) polymers), which can be dated back to Gee's experiments on interfacial polymerization in 1935. Blumstein's crosslinked polymer in the interlayer space of montmorillonite clay in 1958 and Stupp's bulk polymerization within a self-assembled crosslinked polymer in the interlayer space of montmorillonite clay in 1993. However, no real structurally defined 2D polymer was obtained until the successful isolation of a graphene layer from graphite, a prototype example of 2D polymers from nature.

The discovery of graphene has also inspired vigorous research efforts towards the rational synthesis of 2D polymers. For instance, pioneering works on 2D poly(m-phenylene) and covalent assemblies of porphyrin and thiophene have been reported via on-surface synthesis under ultrahigh vacuum. However, the mobility of monomers on the surface is limited and only small domain sizes (generally tens of nanometres) have been obtained. In addition, 2D polymers can also be achieved through solution exfoliation of van der Waals (vdW) layer-stacked 2D covalent–organic frameworks or polymer crystals synthesized by a solvothermal method and/or solid-state polymerization. Despite these successes, the exfoliation of defined thin-layer structures as well as precise control over their lateral sizes and thickness remain a challenge. Very recently, free-standing, crystalline, single- or few-layer films of 2D polymers have been developed via air/water and liquid/water interfacial synthesis by us and others. Nevertheless, the crystallinity of the resultant 2D polymers remains unsatisfactory and the crystalline domain sizes are small (typically tens of nanometres), posing a potential limitation to the development of reliable functions for this emerging class of organic 2D materials.

Under the SOS monolayer, 2DPA adopted a face-on configuration with a crystal domain size of ~0.3 \( \mu m^2 \). By unitizing an octadecanoic acid (stearic acid, SA) monolayer, we achieved edge-on-oriented 2DPA with significantly increased domain size (~121 \( \mu m^2 \)). The molecular structures, grain boundaries and edge structures of the polymers were investigated by grazing-incidence wide-angle X-ray scattering (GIWAXS) and aberration-corrected high-resolution transmission electron microscopy (AC-HRTEM) with the support of theoretical modelling. Our results indicate that the pre-organization of monomers under the surfactant monolayer contributes to the formation of 2D polymer crystals.

**Results and discussion**

**Synthesis of 2DPI on a water surface.** To synthesize 2DPI, we prepared a monolayer of SOS (Fig. 1a) on the water surface, and then added monomer 1 (1.5 \( \times 10^{-7} \) mol) into the water phase. The adsorption and subsequent pre-organization of monomer 1 under the surfactant monolayer was facilitated by electrostatic interactions and hydrogen bonding. Next, monomer 2 (3.0 \( \times 10^{-7} \) mol) was injected into the water phase and then diffused to the pre-organized monomer 1 where 2D polymerization was triggered on the water surface. The polycondensation reaction was kept at 20°C under ambient conditions for 7 d, affording the few-layer 2DPI crystals (Fig. 1b and...
The formation of imide bonds in 2DPI was confirmed using Fourier transform infrared spectroscopy (FTIR) by the appearance of the C=O characteristic peak (1,695 cm\(^{-1}\)) as well as the elimination of the N–H stretch (\(\nu_{\text{primary amino}}\), 3,350 cm\(^{-1}\)) of monomer 1 and the C=O vibration (\(\nu_{\text{carboxylic dianhydride}}\), 1,755 cm\(^{-1}\)) of monomer 2 (Supplementary Fig. 2). The UV–vis absorption spectrum of 2DPI exhibited the characteristic Soret (S) band at 437 nm and Q band at 748 nm, which correspond to the porphyrin structure in 2DPI (Supplementary Fig. 2)\(^{26}\).

Structural characterization of 2DPI. For structural characterizations, the 2DPI film was transferred horizontally onto SiO\(_2\)/Si substrates and holey copper TEM grids. After removing the surfactant with chloroform, the film remained stable and homogeneous (Fig. 1c). Atomic force microscopy (AFM) measurements on the SiO\(_2\)/Si wafer showed a film thickness of \(\approx 2\) nm, corresponding to approximately five layers (Fig. 1d, see height profiles). When transferred onto a holey copper grid, the film freely suspended over the hexagonal mesh with a side length of \(\approx 25\) \(\mu\)m (Supplementary Fig. 3). Bright-field TEM imaging showed that the polymer crystalline domains (dark) are bridged by amorphous areas (bright) in the thin film (Fig. 2a).

AFM measurements demonstrated step heights of 0.4 ± 0.10 and 0.7 ± 0.1 nm within different regions, which can be assigned to the thickness of a monolayer and bilayers, respectively.
Effect of surfactant monolayer on the crystallinity of 2DPI and model reaction. To investigate the key role of surfactant in the crystallization of 2DPI, we carried out control experiments without involving surfactants; only amorphous films were obtained (Supplementary Fig. 11). We also explored surfactants with different polar groups, including sodium 4-dodecylbenzenesulfonate (SDBS) and hexadecyl-trimethyl-ammonium bromide (CTAB). SDBS functions in a similar manner to SOS and can guide the self-assembly of monomer 1 via electrostatic interaction, leading to the formation of 2DPI crystals. In contrast, cationic surfactant CTAB only results in amorphous films (Supplementary Fig. 12), which can be attributed to the poor ordering of monomers under the surfactant monolayer due to the electrostatic repulsion between monomer 1 in the aqueous subphase and positively charged CTAB.

To gain insight into the polymerization mechanism, we characterized the thin films by GIWAXS before and after the addition of monomer 2. As shown in Fig. 3a (left), the self-assembly of monomer 1 under the SOS monolayer shows in-plane peaks at 0.40, 0.56 and 1.30 Å⁻¹, corresponding to a square lattice with \( a = b = 15.7 \) Å and \( \gamma = 90° \); this was further confirmed by SAED and AC-HRTEM investigations (Supplementary Fig. 13). A diffuse arc at 1.58 Å⁻¹ (Fig. 3b, left) suggests that monomers 1 stack face-to-face with a \( \pi-\pi \) stacking distance of 4.0 Å. Thus, before 2D polymerization, the self-assembled monomers 1 arrange horizontally (named pre-H) on the water surface. After polymerization and removal of the surfactants, 2DPI thin films show in-plane peaks at 0.20, 0.39 and 0.56 Å⁻¹, corresponding to the 010, 020 and 220 Bragg peaks of a square lattice with \( a = b = 31.4 \) Å and \( \gamma = 90° \) (Fig. 3a, right, and Supplementary Fig. 14), which agrees well with the DFTB, AC-HRTEM and SAED results. The out-of-plane stacking distance of 4.0 Å is maintained after polymerization (Fig. 3b, right). As shown in Fig. 3c, the lattice parameter of pre-H is around half that of 2DPI, favouring the growth of 2DPI along the \([100] \) and \([010] \) directions, probably because of lattice matching between the \((100)/(010)\) planes of pre-H (\( d_{100,\text{pre-H}} = 15.7 \) Å) and the \((200)/(020)\) planes of 2DPI.

With evidence from the GIWAXS, AC-HRTEM and SAED results, we have confirmed the pre-organization of monomers under the surfactant monolayer and the subsequent imidization reaction forming highly ordered 2D polymers on the water surface under ambient conditions. Despite the fact that the realization of the imidization reaction in solution generally requires elevated temperature (above 100 °C)22,34, its reaction rate could be significantly accelerated by on-water synthesis16-30. Here, a model reaction based on 5-(4-aminophenyl)-10,15,20-(triphenyl)porphyrin and monomer 2 was carried out on the water surface at room temperature; this readily provided the targeted imide compound (Supplementary Figs. 15 and 16). In contrast, the same imidization reaction failed to afford any products in aqueous solution. As illustrated by artificial force-induced reaction (AFIR) calculations37,38, the feasibility of the reaction under ambient conditions originates from the pre-organization of the monomers with self-assembled structures on the water surface (Supplementary Figs. 17 and 18), which accelerates the imidization condensation.

Synthesis of 2DPA on the water surface. To demonstrate the generality of the SMAIS approach, we explored the synthesis of 2DPA crystals by polymerization of monomers 1 and 3 at the SOS–water interface under similar synthesis conditions. As a result, we achieved a crystalline 2D polymer with a dual-pore structure (Fig. 1b and Supplementary Fig. 1) and a thickness of \( \sim 10 \) nm (Supplementary Fig. 19). FTIR results confirmed the formation of polyamide with the C=O amide stretch at 1,660 cm⁻¹ and N–H stretch at 1,335 cm⁻¹ (Supplementary Fig. 2). The UV–vis absorption spectrum of 2DPA also presented the characteristic Soret (S) and Q bands of porphyrin units at 485 nm and 847 nm, respectively (Supplementary Fig. 2). The AFIR calculation for the reaction...
pathway of polyamide (Supplementary Figs. 20 and 21) also indicates the same conclusion with the imidization reaction, that is, both the on-water effect and pre-organization of monomers can accelerate the polymerization rate.

The average crystalline domains of 2DPA exhibit a width of 0.1–0.2 µm and a length of up to 2 µm (Supplementary Fig. 22), revealing an anisotropic growth rate during polymerization (Fig. 4a). The areal ratio between the crystalline and amorphous region is ~1.9, suggesting that 66% of the polyamide film is crystalline. The edge of the crystal domain of 2DPA is shown in Supplementary Fig. 23 with its layer-by-layer stacking morphology. The SAED pattern shows first-order reflections at 0.52 nm⁻¹ and 0.65 nm⁻¹ (Fig. 4b), corresponding to a rectangular unit cell with lattice constants of $a = 15.4$ Å and $b = 19.2$ Å, respectively, which agrees with the DFTB calculations (Supplementary Fig. 24 and Supplementary Tables 4 and 5). The crystal structure was further confirmed by AC-HRTEM, where the darkest parts represent the larger pores of 2DPA (Fig. 4c and Supplementary Figs. 25 and 26). Similar to 2DPI, monomer 1 in the 2DPA crystal has a face-on orientation and extends horizontally on the water surface. As presented in Fig. 4d, the grain elongates in the [100] direction. The higher growth rate along the [100] axis has been attributed to the trivial mismatch between the lattice parameters of 2DPA ($a = 15.4$ Å) and pre-H (15.0 Å), which favours the crystal growth over that in the [010] direction.

**Control of growth orientation of 2DPA on water surface.** So far, we have illustrated that the SOS–water interface guided the face-on arrangement of monomer 1 and resulted in 2D polymer growth with layer-stacking direction perpendicular to the water surface. At this point, tuning of the growth direction becomes another appealing objective. To this end, we employed SA, whose carboxyl
group can react with one amine group in monomer 1, forming a covalent amide bond at the air–water interface (Supplementary Fig. 27). Consequently, monomer 1 could be vertically anchored under the SA monolayer as precursor (namely, pre-V). In contrast to pre-H (Fig. 3a, left), GIWAXS measurement of pre-V shows an intensive π–π stacking peak along the in-plane direction (Fig. 5a, left), which is also supported by SAED (Supplementary Fig. 13d,e), demonstrating the edge-on arrangement of monomer 1, which allows for 2D polymerization along the vertical direction (Fig. 5b and Supplementary Fig. 28). Compared with pre-H, the pre-V induced by SA could increase the polymerization rate between monomer 1 and monomer 3, as indicated by the rapid decrease in the concentration of monomer 1 in the water subphase during the reaction (Supplementary Figs. 29–31). As we expected, the GIWAXS pattern (Fig. 5a, right) confirms that we have successfully tuned the growth direction of 2DP A layers from horizontal to vertical (v2DP A, Supplementary Figs. 32 and 33 and Supplementary Table 5). The 001 reflection in the SAED pattern (Fig. 4c) and 001 lattice fringes in the AC-HRTEM image (Fig. 4f) further confirm the edge-on configuration of the 2DP A layers. AFM imaging reveals that v2DP A has a lamellar morphology and a layer step height of ~1.8 nm (Supplementary Fig. 19). The crystallinity of v2DP A is significantly higher than that of 2DP A. No amorphous fragments could be identified within v2DP A over 3 mm × 3 mm sized grids, and the crystal domain size of v2DP A is as large as ~121 μm² without significant variation of the in-plane crystallographic orientations (Supplementary Fig. 34).

Conclusions and outlook

We have developed the SMaIS strategy to synthesize 2D polymer crystals (2DP A and 2DP) under ambient conditions. The long-range ordering structures of both 2DP A and 2DP were elucidated by GIWAXS and SAED, respectively. The crystalline structures and grain boundaries were further visualized by AC-HRTEM, with molecular resolution. The surfactant monolayers were found to play a crucial role in facilitating the pre-organization of monomers, thus accelerating the polymerization rate on the water surface. Despite the current success in this on-water surface synthesis of 2D polymers, the remaining challenges are to reduce the amorphous area and prepare monolayer 2D polymers, as well as to increase the single-crystalline domain size, which will be of interest for the fabrication of molecular sieving membranes in the future. In addition, we hope that this synthetic strategy can be expanded to other 2D polymerizations including either reversible or irreversible covalent bonds.

Methods

Synthesis of 2DP A crystal. A 20 μl volume of SOS (1 mg ml⁻¹ in chloroform) was spread onto the surface of 100 ml Milli-Q water in a 200 ml beaker. The mean molecular area (mmu) was 24 Å², which can be calculated by

where A₁ = 25.12 cm² is the effective area, M_m = M_m,₃ = 370.5 g mol⁻¹ is the molecular weight of SOS, N_A = 6.02 × 10²³ mol⁻¹ is the Avogadro constant and m = m_m = 20 μg is the mass of surfactant. The mma of 24 Å² allows SOS molecules to form a monolayer, as proved by the π–A isotherm curve in Supplementary Fig. 35. The solvent was allowed to evaporate for 30 min, then monomer 1 (1 ml, 1 mg ml⁻¹ in 0.12 M HCl solution) was injected into the water. We waited 30 min for the dispersion of monomer 1 in water and then injected the solution of monomer 2 (2 molar equivalents to monomer 1) in 0.08 M LiOH aqueous solution beneath the water surface. After polymerization for 1 week, the formed 2DP A film was horizontally transferred onto substrates for characterization.

Synthesis of 2DP A crystal. A 100 ml volume of Milli-Q water was injected into a vial, forming a static air–water interface. Then, 3 ml 15% SOS (1 mg ml⁻¹ in chloroform) was spread onto the interface (monolayer, mma = 25 Å²). The solvent could evaporate for 30 min, then monomer 1 (100 μl, 1 mg ml⁻¹ in 0.12 M HCl solution) was injected into the water. A period of 5 min was allowed for the dispersion of monomer 1 in the water, and then monomer 3 solution was added (2 molar equivalents to monomer 1). Monomer 1 (1 ml, 1 mg ml⁻¹ in 0.12 M HCl solution) was added to the water subphase. We waited for 5 min for monomer 1 to disperse in the water, and then injected monomer 3 solution (2 molar equivalents to monomer 1, 0.64 ml, 1 mg ml⁻¹ monomer 3 in 0.04 M LiOH aqueous solution) into the water. The reaction was kept at room temperature for 1 week, or at 50 °C for 12 h.

Substrates. Single- and few-layer 2D polymers were deposited onto 300 nm SiO₂/Si substrate for optical microscopy and AFM, on quartz glass for UV–vis absorption spectroscopy, on copper foil for infrared spectroscopy and on copper grids for TEM characterizations.

Characterizations. Mass spectrometry analysis was performed on a Bruker Autoflex Speed MALDI TOF MS system (Bruker Daltonics) using dithanol as the matrix. Optical images were acquired in differential interference mode with an AxioScope A1 system (Zeiss). AFM was performed in air on a customized NTegra Aura/Spectra from NT-MDT with an SMENA head operated in contact mode. AC-HRTEM imaging and SAED were conducted on an image-side Cs-corrected FEI Titan 80-300 microscope operated at 300 kV. To reduce the electron irradiation damage on 2D polymers, the total electron dose for the acquisition of SAED patterns and HRTEM images was limited (effect of surfactant monolayer on the crystallinity of 2DP A and model 2.0 e⁻ Å⁻² (dose rate of 0.2 e⁻ Å⁻² s⁻¹) and 1.000 e⁻ Å⁻² (dose rate of 200 e⁻ Å⁻² s⁻¹), respectively. UV–vis absorption spectra were obtained on a UV–vis–NIR spectrophotometer Cary 5000 device at room temperature. FTIR was performed on a Tensor II system (Bruker) with an attenuated total reflection unit.

Computational methods. Details of the calculations are provided in the Supplementary Information.

Data availability

The data supporting the findings of this study are available within the Article and its Supplementary Information or from the corresponding author upon reasonable request.
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References