

Polymerization Order in the Synthesis of Two-Dimensional Block Supramolecular Copolymers

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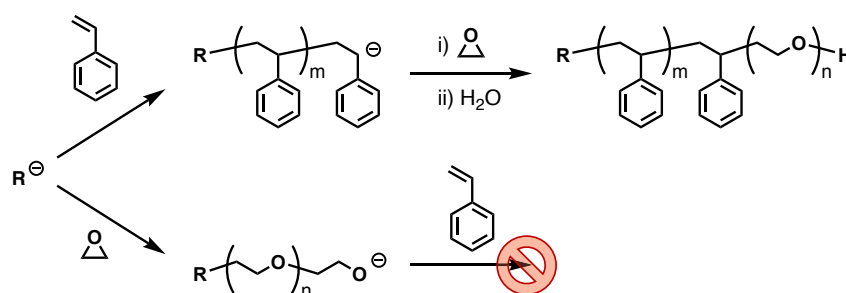
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Abstract: In the synthesis of block polymers through living polymerization, the order in which the monomers are copolymerized can have a critical effect on the polymerization efficacy. The same should hold true for the synthesis of block supramolecular polymers; however, this remains unexplored. We investigated the effect of the order of the polymerization of the monomers in two-dimensional seeded/living supramolecular block copolymerization of porphyrin-based monomers. Unlike one-dimensional living polymers, two-dimensional supramolecular polymers (or nanosheets) have two distinct propagation sites. We showed that inverting the order of polymerization can lead to distinct growth modes; importantly, secondary nucleation is involved in one of these cases. If secondary nucleation takes place at the edges of the seeds prior to two-dimensional growth, the resulting nanosheets tend to exhibit uncontrolled areas and edge roughness.

Introduction

Inspired by living polymerization^[1] and living crystallization-driven self-assembly (CDSA),^[2,3] living supramolecular polymerization (LSP) has seen significant progress in the last decade.^[4-9] Consequently, supramolecular polymers with narrow size distributions^[5] and block structures^[6,7] have become available. Furthermore, by using appropriately designed monomers, two-dimensional (2D) supramolecular polymers with controlled areas have been obtained.^[8,9] As illustrated by living CDSA,^[10] 2D structures are more attractive than 1D structures because of their rich variety of structural motifs, and their precise syntheses could lead to new functional materials. In this study, we investigated 2D LSP to produce block supramolecular nanosheets.

It is well known that to obtain a copolymer with a particular desired block structure, the order in which the monomers are polymerized needs to be considered carefully.^[11] For instance, to produce polystyrene-*block*-polyethylene oxide (PS-*b*-PEO) by living anionic polymerization, the PS block has to be synthesized before the PEO block (Scheme 1).^[11a] If the synthesis is attempted in the opposite order, the PEO block with an anionic chain terminus cannot efficiently initiate the polymerization of styrene as a result of its lower reactivity. Understanding of such “polymerization order” has contributed to the development of precision synthesis of covalent block polymers and other polymers with unique topologies;^[12] however, the effect of the polymerization order has scarcely been investigated for supramolecular counterparts. Ogi and Yamaguchi recently reported the one-dimensional (1D) seeded LSP of three distinct amino acid-based monomers.^[13] They found that, depending on the combination of seed and monomer used, either copolymerization or self-sorting occurred, thereby resulting in different products. The main determinant of the polymerization order was steric hindrance by the side residues of the amino acids. In this context, although several research groups,^[9] including ourselves,^[8] have reported 2D LSPs, the synthesis of 2D block supramolecular polymers remains challenging,^[8c] and the effect of the order of polymerization in two dimensions has yet to be investigated.



Scheme 1. Polymerization order in the synthesis of polystyrene-*block*-polyethylene oxide (PS-*b*-PEO) via living anionic polymerization.

Our 2D LSP has been established by using several porphyrin-based monomers (Scheme 2a). In terms of their mechanism, LSP has parallels with living CDSA, in that both methods rely on nucleation and growth processes and can be initiated by the external addition of seeds.^[2-4] For example, in the 2D LSP of monomer **6₁**,^[8a] spontaneous nucleation is kinetically prevented by a coupled equilibrium that temporarily forms the metastable nanoparticles (**NP-6₁**). Addition of a separately prepared thermodynamically stable 2D seed (**Seed-6₁**) to a solution of **NP-6₁** initiates 2D supramolecular polymerization to produce supramolecular nanosheets (**NS-6₁**) with a controlled area (Scheme 2b). The 2D growth is driven by hydrogen bonding of the amide groups and π -stacking of the porphyrin core in one axis (i.e., the *x*-axis) and by van der Waals interaction between the side chains (R groups) in another axis (the *y*-axis). In other words, 2D seeded growth involves two distinct propagation sites, an interesting characteristic not seen in 1D LSP. With these previous discoveries in mind, we investigated the effect of the order of polymerization of monomers in the synthesis of 2D block supramolecular copolymers.

Results and Discussion

Of the porphyrin derivatives investigated in our previous studies,^[8] monomers **62**, **63**, and **6N₃** were found to form stable 2D nanosheets (Scheme 2). We attributed the stability of these nanosheets in comparison with those of other porphyrin-based monomers such as **61** and **71** to an entropy factor that originates from the lower degree of conformational freedom of the unsaturated bonds in **62**, **63**, and **6N₃**.^[8b] In this study, we mainly used monomers **63** and **6N₃** to investigate block supramolecular copolymerization in two dimensions. Octadecyl chains are introduced to the gallic acid-based wedges so that agglomeration of nanosheets can be prevented (Scheme 2a).^[8f] Methyl cyclohexane (MCH) was used as a solvent.

First, we prepared 2D seeds consisting of **6N₃** or **63** by our previously established procedure [see the Supporting Information (SI)];^[8] hereafter, these 2D seeds are referred to as **Seed-6N₃** and **Seed-63**, respectively (Figures 1a). Number-average and weight-average areas (A_n and A_w , respectively) and the area distribution (A_w/A_n) were determined by atomic force microscopy (AFM) in conjunction with Image J software (SI, Figure S3). Reflecting a difference in the driving forces along the x - and y -axes (Scheme 2b), **Seed-6N₃** and **Seed-63** have distinct aspect ratios of 1.60 and 2.86, respectively. This result suggested that **6N₃** has a stronger propensity to self-assemble two dimensionally than **63**. The split Soret bands ($\lambda = 380\text{--}460$ nm) of **Seed-6N₃** and **Seed-63** indicated that the porphyrin molecules in the nanosheets are stacked in short slipping J-aggregates (Figure 1b), a porphyrin stacking mode with a medium offset between those of the J- and H-aggregates.^[8,14] Importantly, a small but significant difference in the absorption maxima between **NS-6N₃** ($\lambda = 444$ nm) and **NS-63** ($\lambda = 442$ nm) was observed (Figure 1b, inset), suggesting that these two monomers pack in slightly different structures. We assumed that this would affect the polymerization order in a subsequent seeded heteropolymerization (i.e., block copolymerization).

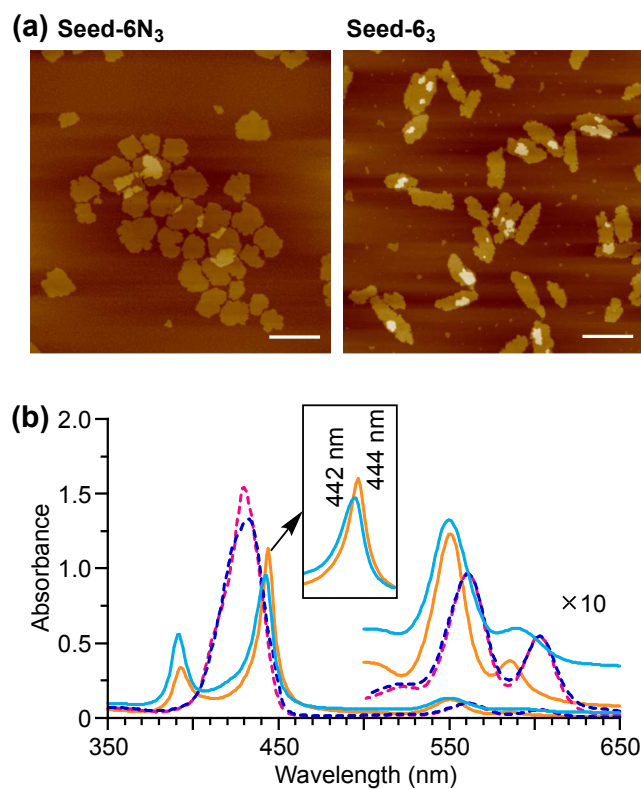


Figure 1. (a) AFM images of **Seed-6N₃** and **Seed-6₃** (bar = 500 nm): the preparations of these seeds are described in the SI. (b) Absorption spectra of **Seed-6N₃** (orange), **Seed-6₃** (sky blue), **NP-6N₃** (dashed pink), and **NP-6₃** (dashed blue): [Porphyrins] = 50 μ M.

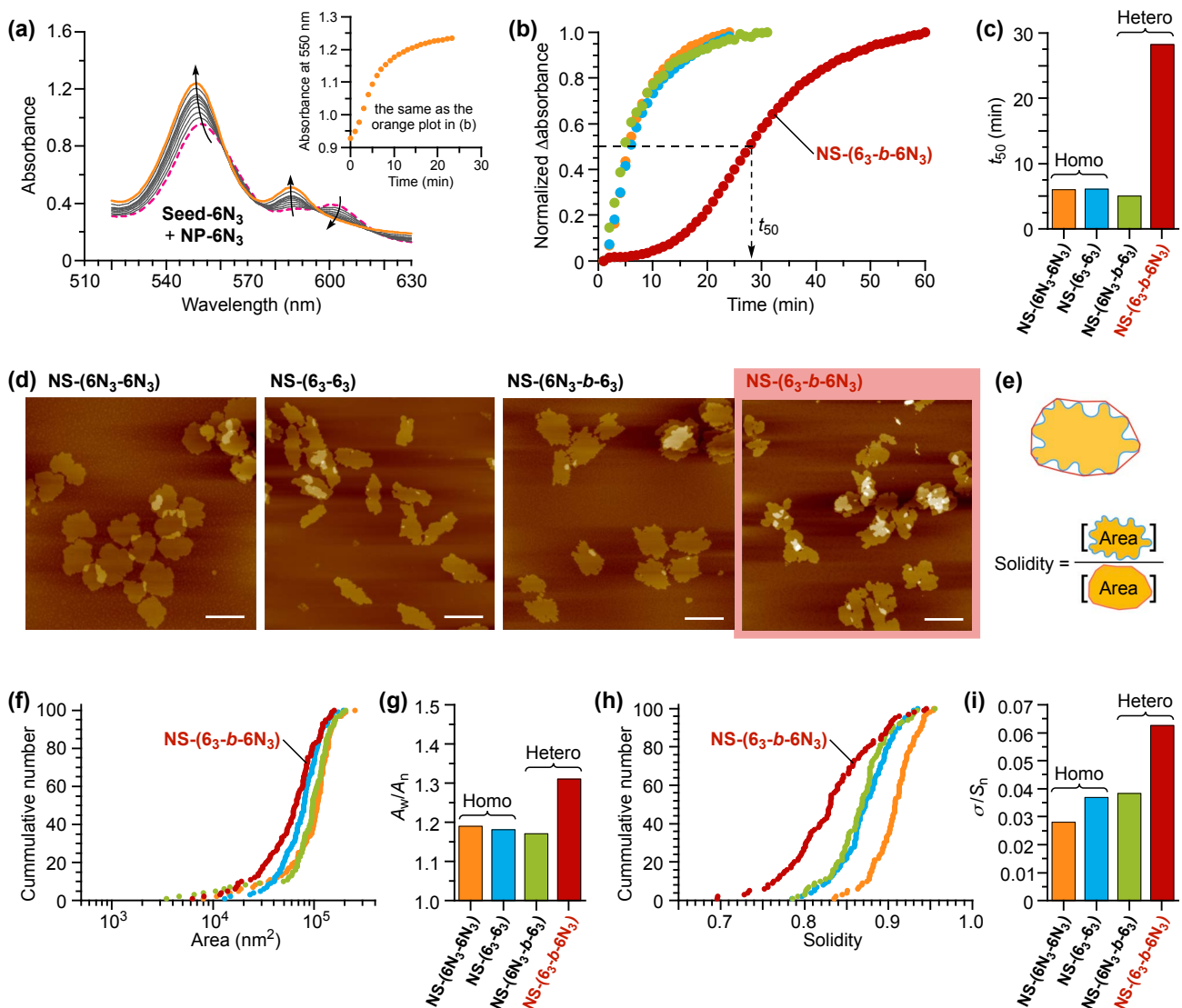


Figure 2. (a) Absorption spectral changes observed during seeded polymerization: the case conducted using **Seed-6N₃** and **NP-6N₃** are displayed: [**Seed-6N₃**] = [**NP-6N₃**] = 25 μ M in MCH, with respect to the concentration of **6N₃**. Note that the Soret band cannot be probed during this process because of the high molar-absorption coefficient. (Inset) Changes in the absorbance at 550 nm as a function of time. Spectral changes of other seeded growth are shown in the SI (Figures S4). (b) Kinetics of seeded/living 2D LSP, observed as changes in the absorbance at 550 nm during homo- and hetero-seeded polymerizations. (c) Values of t_{50} for the seeded growth process, determined from (b). (d) AFM images of **NS-(6N₃-6N₃)**, **NS-(6₃-6₃)**, **NS-(6N₃-b-6₃)**, and **NS-(6₃-b-6N₃)** (bar = 500 nm). (e) Illustration of the calculation of the solidity (S), (f) histograms of area, (g) A_w/A_n values, (h) histograms of solidity, and (i) σ/S_n values for the obtained nanosheets. Colours in Figures b, f, h correspond to those defined in Figures c, g, i, respectively.

Before investigating seeded heteropolymerization, seeded homopolymerization was conducted by mixing **Seed-6N₃** or **Seed-6₃** with metastable nanoparticles consisting of the corresponding monomers **NP-6N₃** and **NP-6₃**. The seeded growth process was monitored by examination of the changes in the absorbance as a function of time (Figure 2a and SI, Figure S4), confirming the consumption of the metastable nanoparticles (i.e., J-aggregates) and the growth of the nanosheets (short-slipping J-aggregates). Note that during this time frame (~ 60 min), self-nucleation from the metastable nanoparticles does not occur. As a result of this seeded growth process, we obtained supramolecular nanosheets with a controlled area and with relatively narrow A_w/A_n ratios (Figure 2d,f,g): these nanosheets are referred to as **NS-(6N₃-6N₃)** and **NS-(6₃-6₃)**, respectively.

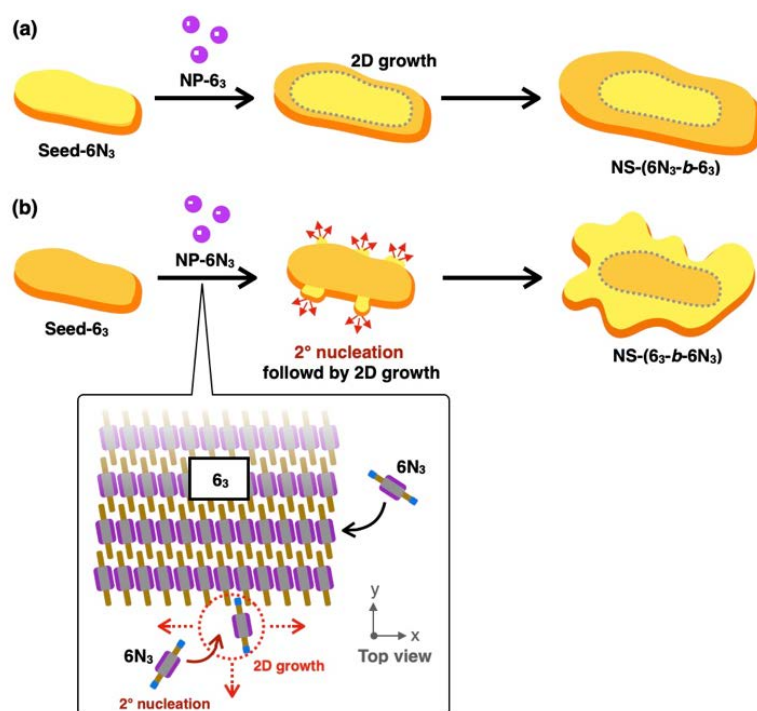
Next, we performed seeded heteropolymerization to produce 2D diblock supramolecular copolymers. Unlike covalent block copolymerization (see Scheme 1), in the 2D seeded heteropolymerization, the first block is surrounded by the second block. Accordingly, the polymerization orders of **6N₃-to-6₃** and **6₃-to-6N₃** result in distinct **6N₃⊂6₃** and **6₃⊂6N₃** diblock structures, respectively: these are referred to as **NS-(6N₃-*b*-6₃)** and **NS-(6₃-*b*-6N₃)**, respectively. Intriguingly, the shapes of **NS-(6N₃-*b*-6₃)** and **NS-(6₃-*b*-6N₃)** showed obvious difference (Figure 2d). We therefore used the solidity to evaluate the structures of the resulting nanosheets. In brief, solidity as defined by the equation shown in Figure 2e, quantifies the roughness of a shape, and its value approaches unity when the edge of the nanosheets is smooth.^[8f] The histogram of solidity for the obtained nanosheets are shown in Figure 2h, indicating that the values of **NS-(6₃-*b*-6N₃)** are broadly distributed in comparison with those of other nanosheets. Because each nanosheet can have distinct number-average solidity (S_n) depending on the structures of the monomer used,^[8f] we compared the dispersion of the distribution of solidity based on the coefficient of variation (CV): i.e., σ/S_n , where σ is the standard deviation.^[8c] Note that the value of σ/S_n for **NS-(6₃-*b*-6N₃)** was noticeably larger than those for the other nanosheets (Figure 2i). Moreover, the value of A_w/A_n for **NS-(6₃-*b*-6N₃)** was also larger than those for the other nanosheets (Figures 2f,g). These results indicate that seeded growth of **NS-(6₃-*b*-6N₃)** was not as well controlled as in the opposite case to produce **NS-(6N₃-*b*-6₃)**, suggesting that the order of polymerization is indeed important in 2D block supramolecular polymerization.

It is noteworthy that the kinetics of the seeded growth of **NS-(6₃-*b*-6N₃)** followed a sigmoidal curve, whereas the other copolymers showed concave profiles (Figure 2b). In addition, the half-time (t_{50}), defined as the time required for the consumption of 50% of the monomers (or, metastable nanoparticles, in this study), was significantly extended in this particular case (Figure 2c, the red bar). These results imply that secondary nucleation plays a pivotal role in the formation of **NS-(6₃-*b*-6N₃)**.^[15-17] In fact, like other supramolecular polymerizations involving secondary nucleation, the seeded growth kinetics of **NS-(6₃-*b*-6N₃)** showed a stronger concentration dependence in comparison with the other cases (SI; Figure S5d).

Taking the above observations into account, we propose that the 2D seeded heteropolymerization proceeds by the plausible mechanism shown in Scheme 3. In relation to this mechanism, we have to consider several determinants of the polymerization order observed in this study. First, the molecular packing structures of **6N₃** and **6₃** within nanosheets are slightly different, as suggested by the difference in the absorption maxima of the Soret band (Figure 1b). Secondly, the **6N₃** molecule is

slightly larger than $\mathbf{6_3}$; therefore, epitaxial growth of $\mathbf{6N_3}$ from **Seed- $\mathbf{6_3}$** is likely to be partially hindered. Thirdly, in the direction of the y -axis, the azide groups in $\mathbf{6N_3}$ should additionally enhance the van der Waals force due to their 1,3-dipole, as evidenced by the smaller aspect ratio of **Seed- $\mathbf{6N_3}$** (see above); therefore, $\mathbf{6N_3}$ (or **Seed- $\mathbf{6N_3}$**) could be regarded to be more “reactive” than $\mathbf{6_3}$ (or **Seed- $\mathbf{6_3}$**). A complex interplay of these determinants appears to cause the lattice mismatch during the block extension and increase the contribution of secondary nucleation of $\mathbf{6N_3}$ at the edge of **Seed- $\mathbf{6_3}$** (Scheme 3). This secondary nucleation occurs slowly and sporadically; but once it occurs, the growth of **NS- $\mathbf{6N_3}$** is initiated from that point (i.e., the secondary nuclei), which, in turn, leads to the formation of roughened edges. Because of the slow seeded growth kinetics, secondary nucleation would occur also at the surface of the nanosheets; we indeed observe smaller nanosheets piling up above some of the **NS- $(\mathbf{6_3-b-6N_3})$** (Figure 2d).

To verify the above mechanism, we investigated the formation of **NS- $\mathbf{6_2}$** , which showed an absorption maximum at 442 nm, a value similar to that of **NS- $\mathbf{6_3}$** (SI; Figure S4). Like the case of $\mathbf{6N_3}$ and $\mathbf{6_3}$ displayed in Figure 2, **NS- $(\mathbf{6N_3-b-6_2})$** was obtainable, whereas **NS- $(\mathbf{6_2-b-6N_3})$** had roughened edges. In addition, both orders of polymerization that produce **NS- $(\mathbf{6_2-b-6_3})$** and **NS- $(\mathbf{6_3-b-6_2})$** worked well, as evidenced by the lower values of A_w/A_n and σ/S_n and by the shorter t_{50} (SI; Figure S6). Hence, a subtle difference between $\mathbf{6N_3}$ and $\mathbf{6_3}$ (and $\mathbf{6_2}$) dictates the appropriate polymerization order in our 2D LSP (SI; Figure S6).



Scheme 3. Plausible mechanism for the observed polymerization order in the synthesis of 2D block supramolecular copolymers using $\mathbf{6N_3}$ and $\mathbf{6_3}$.

Although nanosheets with larger σ/S_n values, such as **NS-(6₃-*b*-6N₃)**, might be regarded as structurally ill-defined, their roughened edges are not necessarily a drawback when designing functional materials that require large circumferences (or roughened edges).^[18] We expect that the ability to control the edge roughness of nanosheets by altering the order of polymerization might be useful for this purpose. As a proof of concept, we used metastable nanoparticles consisting of a mixture of **6N₃** and **6₃** in various ratios: $a = [6N_3/(6N_3+6_3)] \times 100 = 10\text{--}90\%$. Mixing such metastable nanoparticles with **Seed-6N₃** should produce **NS-[6N₃-*b*-(6N₃+6₃)]-*a***. The sequence of the monomers in the second block can be either random or blocky,^[6] the characterization of which is beyond the scope of the present study. The comparative AFM images of the resulting nanosheets are shown in Figure 3a: the values of A_w/A_n , and σ/S_n remained similar on changing the ratio of **6₃** to **6N₃** (Figures 3c and 3d). We also confirmed that t_{50} remained unchanged (Figure 3b). These results suggest that block extensions using **Seed-6N₃** proceeded regardless of the monomer ratios in the second block.

The same experiments using **Seed-6₃** instead of **Seed-6N₃** were conducted to produce **NS-[6₃-*b*-(6N₃+6₃)]-*a***. It is obvious from the AFM images that the roughness of the edges of the resulting nanosheets increased on increasing the proportion of **6N₃** in the second block (Figure 3e). The values of σ/S_n increased markedly when the ratio of **6N₃** in the metastable nanoparticle was above 60% (Figure 3h). Under these conditions, the t_{50} values for the seeded growth kinetics were, indeed, significantly extended (Figure 3f). It is noteworthy that nanosheets, prepared with the same a value in the second block (for example, compare **NS-[6N₃-*b*-(6N₃+6₃)]-60** and **NS-[6₃-*b*-(6N₃+6₃)]-60**) in Figures 3a,e, have edges consisting of the same monomers but display different degrees of roughness. We believe that such structural variations at the mesoscopic scale in block copolymers created from the same molecular components through kinetically controlled self-assembly will pave the way to new functions and properties of supramolecular assemblies.^[17b]

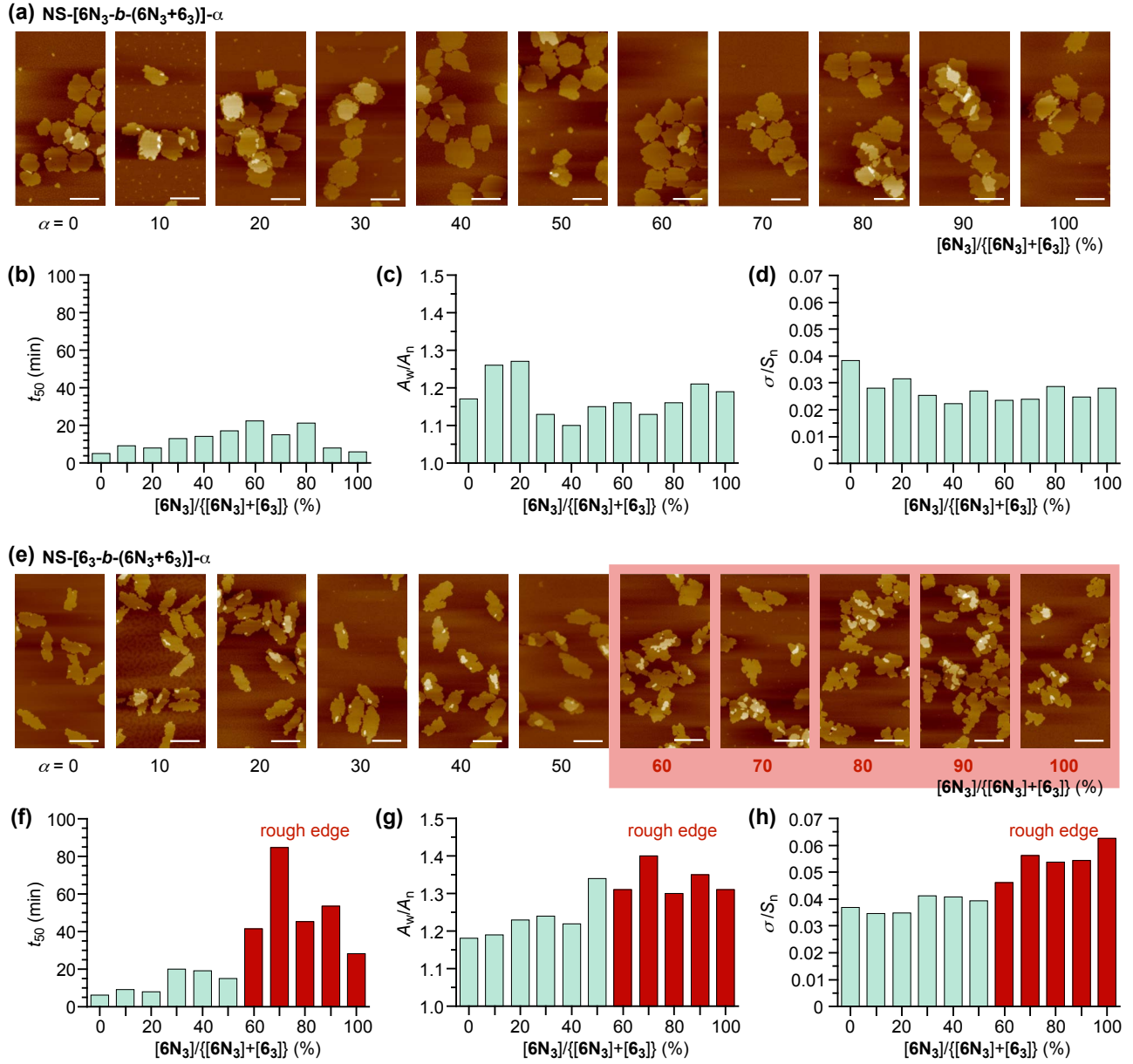


Figure 3. (a) AFM images of NS-[6N₃-*b*-(6N₃+6₃)] (bar = 500 nm): the proportions of 6N₃ in the second block are shown under each AFM image. (b) t_{50} , (c) A_w/A_n , (d) σ/S_n , for the NS-[6N₃-*b*-(6N₃+6₃)] nanosheets. [Seed-6N₃] = [NP-(6N₃+6₃)] = 25 mM. (e) AFM images of NS-[6₃-*b*-(6N₃+6₃)] (bar = 500 nm): the proportions of 6N₃ in the second block are shown under each AFM image. (f) t_{50} , (g) A_w/A_n , (h) σ/S_n , for the NS-[6₃-*b*-(6N₃+6₃)] nanosheets, [Seed-6₃] = [NP-(6N₃+6₃)] = 25 mM.

Conclusion

In conclusion, we have demonstrated that the order of polymerization affects the structure of 2D block supramolecular copolymers in a manner similar to that observed in syntheses of conventional covalent block copolymers. Unlike one-dimensional living polymers, two-dimensional supramolecular polymers (or nanosheets) have two distinct propagation sites. We showed that inverting the order of polymerization can lead to distinct growth modes; importantly, secondary nucleation is involved in one of these cases. This secondary nucleation occurs slowly and sporadically; but once it occurs, the subsequent block extension is initiated from that point (i.e., the secondary nuclei), which, in turn, leads to the formation of roughened edges.

From a different point of view, control over the shape (or edge roughness) of 2D nanosheets might be useful when designing functional materials that require large circumferences (or roughened edges). In addition, alkene (in **6₂**), alkyne (in **6₃**), and azide groups (in **6N₃**) introduced in our porphyrin-based monomers are well-known chemical handles for subsequent modifications of the products of supramolecular polymerization. For example, we previously demonstrated that azide groups on 2D supramolecular nanosheets can participate in click reactions in situ.^[8c] We therefore believe that this study suggests a new strategy for the synthesis of functional block supramolecular nanosheets.

Supporting Information

Supporting information for this article is available online at

Acknowledgements

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Keywords: s supramolecular polymerization • block copolymerization • polymerization order • two-dimensional materials

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