Two-Dimensional Living Supramolecular Polymerization:

Improvement in Edge Roughness of Supramolecular Nanosheets

by Using a Dummy Monomer

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Abstract: Supramolecular polymers are formed through nucleation (i.e., initiation) and polymerization processes, and kinetic control over the *nucleation process* has recently led to the realization of living supramolecular polymerization. Changing the viewpoint, herein we focus on controlling the *polymerization process*, which we expect to pave the way to further developments in controlled supramolecular polymerization. In our previous study, two-dimensional living supramolecular polymerization was used to produce supramolecular nanosheets with a controlled area; however, these had rough edges. In this study, the growth of the nanosheets was controlled by using a 'dummy' monomer to produce supramolecular nanosheets with smoothed edges.

Introduction

The recent development of living supramolecular polymerization (LSP) has permitted the synthesis of one-dimensional (1D) supramolecular polymers with a controlled length and a narrow length distribution.¹ It is noteworthy that LSP is based on a coupled equilibrium that is reminiscent of the reversible deactivation process in living radical polymerization (highlighted in blue in Schemes 1a and 1b). In LSP, a monomer has to be 'tamed' into a dormant state through a coupled equilibrium so that it does not immediately undergo supramolecular polymerization. To do so, several approaches, such as the formation of metastable aggregates,² intramonomer hydrogen bonds,³ and dynamic covalent bonds,⁴ or the exploitation of photoisomerization⁵ and additives⁶ have proven to be effective (Scheme 1c). Such dormant monomers polymerize upon the addition of seeds, i.e., short pieces of supramolecular polymer that act as 'initiators'. In this way, the length of the supramolecular polymer can be controlled by an appropriate choice of the ratio of the seeds to dormant monomers. In addition, LSP has led to the synthesis of block supramolecular polymers.⁷ Furthermore, this concept has recently been extended to two dimensions, permitting the formation of supramolecular nanosheets with controlled areas.⁸ In essence, these previous studies have lain the foundation for the kinetic control of the initiation (i.e., nucleation) process. On the other hand, little attention has been paid to the polymerization process, which is the subject of the present study. Specifically, herein we use a 'dummy monomer' to control the polymerization pathways to obtain the supramolecular nanosheets of better quality with respect to their shape.



Scheme 1. Schematic representation of (a) living radical polymerization (LRP) and (b) living supramolecular polymerization (LSP). Coupled equilibria (highlighted in blue) are key to controlling the kinetics of polymerizations. (c) To achieve LSP, an equilibrium that deactivates a monomer needs to be coupled with the polymerization process, several approaches to which have been reported. This study focuses on controlling the polymerization pathway for the further development of LSP. Previously, we achieved two-dimensional (2D) LSP by using the porphyrin-based monomers 6^{12} and $6N_3^{12}$ (Scheme 2): here, '6' and '6N₃' represent hexyl chains and azidohexyl chains, respectively, and the superscript '12' represents the dodecyl chains at the periphery of the porphyrin core.^{8a,e} 6^{12} (as well as $6N_3^{12}$) can form metastable nanoparticles (i.e., a dormant state) that, after a lag time, transform into thermodynamically more stable supramolecular nanosheets. Increasing the concentration of 6^{12} decreased the lag time, suggesting that the nanoparticles were on-pathway intermediates for the nucleation of the nanosheets.⁹



Scheme 2. Structures of the porphyrin-based monomers used in this study. The 2-phenylpropyl groups in **D** were used as a racemic mixture. Illustrations of the monomer structures (bottom right).

This unique kinetic behavior led to 2D LSP (Scheme 3). As in the case of its 1D counterpart, 2D supramolecular polymerization can be initiated by the addition of 2D seeds to a solution containing the metastable nanoparticles, thus producing supramolecular nanosheets with a controlled area. In the nanosheets, the porphyrin-based monomers self-assembled two-dimensionally through π -stacking of the porphyrin core in one axis (the *x*-axis) and van der Waals interactions between the hexyl chains of 6^{12} (or the azidohexyl chains of $6N_3^{12}$) in another axis (the *y*-axis) (Figure 3b). Intriguingly, reflecting the strength of these side-chain interactions in the *y*-axis (i.e., hexyl chains vs. azidohexyl chains) relative to that of the π -stacking in the *x*-axis, the aspect ratios of the supramolecular nanosheets of 6^{12} and $6N_3^{12}$ were distinct.^{8e} Such shape control remains challenging in noncovalent syntheses, and this finding

could pave the way to more-sophisticated self-assembled structures. In this context, however, we were not satisfied with the fact that the resulting supramolecular nanosheets of $6N_3^{12}$ had roughened edges (Scheme 3). To circumvent this shortcoming, we revisited the 2D LSP mechanism and realized that there was still room for improvement in the process. In brief, we presumed that the nanoparticles participated in *the polymerization process* (i.e., the particle-addition pathway: Scheme 3a), and hence, that the edge roughness reflected the size of the nanoparticles (~10 nm). Thus, suppression of the particle-addition pathways appears to be the key to this end. Herein, we show a method to control the polymerization pathways using an additive, a 'dummy monomer' (D) (Scheme 2),^{6a} which permits the synthesis of supramolecular nanosheets of better quality: i.e., improved edge roughness.



Scheme 3. Schematic representation of the most likely mechanism of 2D LSP of the porphyrin-based monomers. Note that not only the monomeric porphyrins but also the metastable nanoparticles take part in the 2D LSP.

Results and Discussion

Before addressing the problem of rough edges, we note that supramolecular nanosheets of $6N_3^{12}$ are prone to precipitate from solution over time, which would hinder the experiments that follow. We thus exploited a comonomer $6N_3^{18}$ bearing long octadecyl chains (Scheme 2): the superscript '18' represents octadecyl chains at the *para*-positions in the gallic acid-based wedges peripheral to the porphyrin core. We expected that copolymerization of $6N_3^{12}$ and $6N_3^{18}$ results in nanosheets with better dispersity, because the longer octadecyl chains disturb the surfaces of the supramolecular nanosheets and prevents their interlayer agglomeration [see Supplementary Information (SI), Figures S5 and S6].^{10,11} A relevant concept has recently been demonstrated to be effective in preventing 1D supramolecular polymers from bundling.¹⁰

First, we prepared 2D seeds consisting of $6N_3^{18}$ as reported previously.^{8a,e} The numberaverage and weight-average areas (A_n and A_w , respectively) of the obtained seeds are 10 800, and 18 500 nm², as determined by atomic-force microscopy (AFM), and therefore their ratio A_w/A_n was 1.71 (Figure 1a). Metastable nanoparticles consisting of $6N_3^{12}$ and $6N_3^{18}$ (4:1 molar ratio) were then mixed with the seeds in a ratio of 10:1, whereupon supramolecular polymerization was initiated (SI; Figure S7a). Compared with the homopolymerization of $6N_3^{12}$, copolymerization with $6N_3^{18}$ was indeed effective in preventing agglomeration and precipitation of the nanosheets (SI; Figure S6). The process was complete in 40 minutes, and an aliquot of the resultant solution was spin-coated onto a mica substrate for AFM measurements (Figure 1b). The areas of the resulting supramolecular nanosheets were consistent with the values expected from the ratio of the seeds to dormant monomers ($A_n =$ 127 800 nm²; $A_w/A_n = 1.13$), thus reproducing our previous results.^{8e} With such supramolecular nanosheets with better dispersity in hand, we evaluated the edge roughness of supramolecular nanosheets from the AFM images.

Figure 1. AFM images (scale bar = 600 nm, mica substrate) of (a) 2D seeds consisting of $6N_3^{18}$ and (b) supramolecular nanosheets consisting of $6N_3^{12}$ and $6N_3^{18}$ obtained through 2D LSP. 2D seeds were prepared by sonication. Conditions for 2D LSP: $[6N_3^{18}$ in seed] = 4.7 μ M, $[6N_3^{12} + 6N_3^{18}]$ in nanoparticles] = 47 μ M ($6N_3^{12}:6N_3^{18} = 4:1$), $[6N_3^{12} + 6N_3^{18}]$ in nanoparticles]/ $[6N_3^{18}]$ in seeds] = 10:1, in methylcyclohexane (MCH) at 298 K. (c) Solidity and convexity



are used to evaluate the roughness of the supramolecular nanosheets.

Solidity and convexity can be used to quantify the roughness of a shape. If we consider the convex perimeter that encloses the nanosheets, the solidity and convexity can then be defined as the ratios of actual area to convex area and convex perimeter to actual perimeter, respectively (Figure 1c).¹² These values approach unity when the edges of the nanosheets is smooth. The number-average solidity and convexity of the supramolecular nanosheets

obtained as above (Figure 1b) were determined from 100 objects in the AFM images to be 0.90 and 0.84, respectively (Figure S8).

As demonstrated previously,^{8a} the metastable nanoparticles are on-pathway intermediates for the nucleation of the supramolecular nanosheets. We therefore presume that not only the monomer but the nanoparticles can also participate in *the polymerization process* (i.e., the particle-addition pathway in Figure 3). Hence, the edge roughness is considered to reflect the size of the nanoparticles (~10 nm).^{2a,8a,13} If this is the case, suppression of the particle-addition pathways should result in nanosheets with smoother edges. This hypothesis prompted us to use a dummy monomer (D; Scheme 2) that is capable of co-assembling with $6N_3^{12}$ and $6N_3^{18}$ to form nanoparticles but is incapable of 2D supramolecular polymerization.^{6a,13} We envisioned that nanoparticles containing D would not participate in the particle-addition pathway and that the supramolecular nanosheets would propagate through the monomeraddition pathway exclusively (Scheme 4); consequently, nanosheets with smoother edges could be obtained. We prepared nanoparticles consisting of $6N_3^{12}$ and $6N_3^{18}$ ($[6N_3^{12}]/[6N_3^{18}]$ = 4:1, $[6N_{3}^{12} + 6N_{3}^{18}] = 47 \ \mu M$ in the presence of D (10-30 mol% with respect to $[6N_3^{12} + 6N_3^{18}]$). Addition of 2D seeds of $6N_3^{18}$ (see above) to a solution containing the nanoparticles of $6N_3^{12}/6N_3^{18}/D$ initiated 2D supramolecular polymerization. Importantly, increasing the concentration of **D** extended the time to completion of the 2D LSP, suggesting that the presence of **D** slowed down, but did not completely inhibit, the polymerization (Figure 2a,b). In all the cases, absorption spectral changes confirmed sigmoidal process kinetics, characteristic of 2D growth.^{8a,e} Absorption spectra of the solutions after the 2D LSP could be deconvoluted to those of nanosheets and nanoparticles (SI; Figures S7d,e). The proportions of nanoparticles, thus estimated, was consistent with the amount of the added **D**, which suggested that D was excluded from the polymerization process and remained as nanoparticles after the 2D LSP. In fact, AFM measurements confirmed the presence of nanoparticles together with nanosheets in samples prepared in the presence of D (shapeless aggregates coexisting around the nanosheets, Figure 3b-d. see also Figure S9). Accordingly, the area of the resulting nanosheets was independent of the amount of added D (Figure 3e). The values of A_w/A_n were as low as 1.09-1.15 in all the cases, suggesting that the supramolecular nanosheets propagated in a controlled manner.



Scheme 4. Schematic representation of a 2D LSP improved by using a dummy monomer (**D**), by which the particle-addition pathway is suppressed, and only the monomer-addition pathway is allowed. As a result, the roughness of the edge of supramolecular nanosheets becomes smooth. In this study, we used $6N_3^{18}$ in order to enhance the dispersity of the resulting supramolecular nanosheets (Figure S6).



Figure 2. (a) Changes in the absorption spectra observed during 2D LSP conducted in the presence of 10 mol% **D**. (b) Plots of changes in absorbance at 550 nm as a function of time in the absence (blue) and the presence of **D**: 10 mol% (gray), 20 mol% (orange), 30 mol% (red) with respect to $[6N_3^{12} + 6N_3^{18}$ in nanoparticles]. Conditions for 2D LSP: $[6N_3^{18} \text{ in seed}] = 4.7 \,\mu\text{M}$, $[6N_3^{12} + 6N_3^{18} \text{ in nanoparticles}]$ $= 47 \,\mu\text{M}$, $[D] = 4.7 \,\mu\text{M}$ (10 mol%), 9.4 μM (20 mol%), or 14.1 μM (30 mol%), MCH, 298 K.

Although the area and its dispersity were not affected by the presence of \mathbf{D} (Figure 3e), we noticed that the edge roughness decreased. Figures 3f,g show histograms of the solidity and convexity for 100 nanosheets observed in AFM images. Gratifyingly, the averages for both values increased with increasing amount of \mathbf{D} . For example, with 30 mol% of \mathbf{D} , the average solidity and convexity were 0.94 and 0.94 respectively. Remember that polymerization took longer in the presence of \mathbf{D} (Figure 2b), which might result in an improvement in the edge roughness due to a monomer-exchange process through equilibration. Importantly, however, this was not the case (SI; Figure S12), indicating that the extended polymerization time itself was not a factor in improving the edge roughness. We therefore inferred that the better

solidity and convexity were achieved as a result of controlling the polymerization pathways by using the dummy monomer in a manner illustrated in Scheme 4.



Figure 3. AFM images (scale bar = 600 nm, mica substrate) of supramolecular nanosheets consisting of $6N_3^{12}$ and $6N_3^{18}$ prepared (a) in the absence and (b–d) the presence of the dummy monomer **D**: (b) 10 mol%, (c) 20 mol%, (d) 30 mol% with respect to $[6N_3^{12} + 6N_3^{18}$ in nanoparticles]. Bottom images show magnified images of one of the representative nanosheets. Histograms of the (e) area, (f) solidity, and (g) convexity of the supramolecular nanosheets obtained after 2D LSP conducted in the absence (blue) and the presence of **D**: 10 mol% (gray), 20 mol% (orange), 30 mol% (red). Conditions for 2D LSP: $[6N_3^{18}$ in seed] = 4.7 μ M, $[6N_3^{12} + 6N_3^{18}$ in nanoparticles] = 47 μ M, $[D] = 4.7 \mu$ M (10 mol%), 9.4 μ M (20 mol%), or 14.1 μ M (30 mol%), MCH, 298 K.

Conclusion

In conclusion, this study has shown that there is still room for further development of controlled supramolecular polymerization, particularly in terms of the polymerization pathways. The presence of a dummy monomer controlled the polymerization pathway, leading to supramolecular nanosheets of better quality with respect to shape. In our previous study, the dummy monomer was also effective in controlling the kinetics of the nucleation process to achieve 1D LSP (Figure 1c).^{6a} As such, these two studies have demonstrated the concept

of using 'additives' in controlled supramolecular polymerizations. A recent example, reported by the Würthner group, is noteworthy as a sophisticated system in this direction, which was also achieved using additives: a molecular 'Chaperon' and a cofactor.^{6b}

In covalent synthesis, catalysts, additives, protecting groups, etc., that do not directly form the product can play important roles in controlling reaction pathways and improving reactivity and selectivity. We expect that noncovalent synthesis can further be developed through translation of these concepts into the supramolecular domain.

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