



Supramolecular Multiblock Copolymers Featuring Complex Secondary Structures

Elizabeth Elacqua,[®] Kylie B. Manning, Diane S. Lye, Scott K. Pomarico, Federica Morgia, and Marcus Weck^{*®}

Department of Chemistry and Molecular Design Institute, New York University, New York, New York 10003, United States

Supporting Information

ABSTRACT: This contribution introduces main-chain supramolecular ABC and ABB'A block copolymers sustained by orthogonal metal coordination and hydrogen bonding between telechelic polymers that feature distinct secondary structure motifs. Controlled polymerization techniques in combination with supramolecular assembly are used to engineer heterotelechelic π -sheets that undergo high-fidelity association with both helical and coil-forming synthetic polymers. Our design features multiple advances to achieve our targeted structures, in particular, those emulating sheet-like structural aspects using poly(*p*-phenylenevinylene)s (PPVs). To engineer heterotelechelic PPVs in a sheet-like design, we engineer an iterative one-pot cross metathesis-ring-opening metathesis polymer



ization (CM-ROMP) strategy that affords functionalized Grubbs-II initiators that subsequently polymerize a paracyclophanediene. Supramolecular assembly of two heterotelechelic PPVs is used to realize a parallel π -sheet, wherein further orthogonal assembly with helical motifs is possible. We also construct an antiparallel π -sheet, wherein terminal PPV blocks are adjacent to a flexible coil-like poly(norbornene) (PNB). The PNB is designed, through supramolecular chain collapse, to expose benzene and perfluorobenzene motifs that promote a hairpin turn via charge-transfer-aided folding. We demonstrate that targeted helix–(π sheet)–helix and helix–(π -sheet)–coil assemblies occur without compromising intrinsic helicity, while both parallel and antiparallel β -sheet-like structures are realized. Our main-chain orthogonal assembly approach allows the engineering of multiblock copolymer scaffolds featuring diverse secondary structures via the directional assembly of telechelic building blocks. The targeted assemblies, a mix of sequence-defined helix–sheet–coil and helix–sheet–helix architectures, are Nature-inspired synthetic mimics that expose α/β and $\alpha+\beta$ protein classes via *de novo* design and cooperative assembly strategies.

INTRODUCTION

The design of complex architecturally well-defined frameworks reminiscent of Nature necessitates a delicate synergy between covalent and noncovalent chemistries. Structures of biomolecules (e.g., enzymes and proteins) are orchestrated through an array of cooperative and orthogonal noncovalently driven processes that, as the result of hierarchical self-assembly, imbue long-range order across multiple domains. The engineering of well-defined structures reminiscent of Nature-in a sequencespecific and monodisperse manner¹⁻³—is currently beyond the realization of synthetic chemists. Strategies that achieve welldefined polymers capable of sustaining an orthogonal and directional self-assembly, as well as rendering compartmentalized domains of individual helices, coils, and sheets within synthetic frameworks, however, are substantive.^{4–18} Controlled polymerization routes allow for the fabrication of well-defined polymers with a high degree of control over both molecular weight and monomer placement, thus featuring the potential to sustain precision and sequence-specific materials.

To date, well-established routes to fabricate bio-inspired polymers are limited and rely mainly on single-chain polymer collapse, ^{5,16,19,20} which, although elegant in approach, is limited in the complexity of polymer backbones that can be integrated within the target scaffold. In this contribution, we exploit the controlled polymerization of structurally simple yet complex monomers to engineer polymers containing secondary structures such as helices, sheets, or random coils^{4,21} that are capable of further assembly into localized tertiary structures. Our strategy takes these elements and, through high-fidelity orthogonal molecular recognition processes, engineers threedimensional (3D) architectures from well-defined secondarystructure-containing building blocks.

Natural designs feature a vast array of structural motifs, arranged within discrete patterns that form tertiary structures upon self-assembly into compact, localized, and quasi-independent chains. Key structural facets include compartmentalized domains, intrastrand interactions, and binding pockets.^{5,20} Proteins and enzymes feature a large combination of α -helices and β -sheets, along with lesser-organized flexible regions

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Scheme 1. Schematic Representation of the Target Supramolecular Block Copolymers Comprising π -Sheets, Helices, and Coils via a Plug-and-Play Strategy Utilizing Orthogonal Metal Coordination and Hydrogen Bonding



comprised of random coils, in addition to supersecondary structures (e.g., β -hairpins and β -barrels). Bio-inspired synthetic polymers have achieved the construction of β -turn mimics²² as well as compartmentalized single-strand structures^{5,20} that feature small-molecule self-assembly into a dynamic helical pattern using side-chain-functionalized polymeric systems.^{11,23} Strategies that exploit the planarity of rigid backbones to drive the formation of secondary structures into foldamers are also prominent.^{24–30} Other approaches feature supramolecular motifs that fold via high-fidelity molecular recognition processes between polymer chains and/or pendant units, affording $helical^{31-35}$ and sheet-like oligomers^{36,37} and polymers predicated upon single supramolecular interactions. For example, poly(acrylate)s featuring helical benzene-1,3,5tricarboxamide and either self-associating 2-ureido-4[1H]pyrimidinone moieties¹³ or complementary cyanuric acid and Hamilton wedge (HW) side chains can be assembled in an orthogonal manner.²³ We have recently introduced welldefined secondary structures in main-chain supramolecular

block copolymers⁴ and observed that the secondary structures remain intact and localized upon assembly both in solution and in the solid state. While these studies yield synthetic foldamers, multiple directional and orthogonal interactions must be integrated to fully probe and comprehend the folding behavior of more complex synthetic models.

Hierarchical designs analogous to protein structural classes (e.g., $\alpha+\beta$, and α/β proteins) require precisely sequencing multiple structural motifs in a proximal and well-defined manner.³⁸ Analogous hierarchical architectures are not likely to be realized in synthetic systems using solely pendant-chain interactions to drive assembly. Such structures, however, can be envisioned via *de novo* designs that feature secondary structure elements intrinsic to the backbone of each building block. Our strategy is to engineer a library of telechelic synthetic building blocks that emulate natural self-assembled materials. We hypothesize that such a library of well-defined synthetic polymers will lead to unique biomimetic tertiary structures through directed self-assembly. We disclose orthogonal supra-

molecular assemblies that feature three or more well-defined secondary structures that mirror proteinic α -helices, β -sheets, and random coils via delicate manipulation of both covalent and noncovalent bonds. The building blocks are obtained using a combination of ring-opening metathesis polymerization (ROMP), reversible addition—fragmentation chain-transfer (RAFT) polymerization, anionic polymerization, and/or atom-transfer radical polymerization (ATRP), affording helical, sheet-, and coil-based synthetic polymers.

A fundamental prerequisite for engineering tertiary structure mimics lies in sequencing the structural elements of proteins together with precision.³⁸ Our strategy uses main-chain supramolecular polymerization of secondary-structure-featuring polymer chains to engineer sequence-specific tertiary motifs. We achieve synthetic designs that feature α/β and $\alpha+\beta$ -like structures via *de novo* supramolecular synthesis of our telechelic building blocks (Scheme 1). Combinations of helical and sheet-like domains comprise prominent binding sites within enzyme folds; thus, investigation of synthetic α/β and $\alpha+\beta$ -like systems that not only can be achieved in a straightforward manner but, also feature unique intrinsic properties will provide for a comprehensive understanding of how to achieve complexity within synthetic designs while maintaining simple synthetic building blocks.

RESEARCH DESIGN

The selection criteria for our building blocks include three design requirements: (i) the propensity to form secondary structures; (ii) control over dispersity and molecular weights; and (iii) ease of functional end-group installment. We have reported telechelic helix, sheet, and coil-like building blocks using ROMP, RAFT, ATRP, and anionic polymerization, all of which had a single functional end-group either through the use of a functional initiator or terminating agent.⁴ Instrumental to the design of more complex main-chain supramolecular architectures featuring three or more unique and well-defined secondary structure building blocks is the capacity to facilitate multiple orthogonal assembly steps. While side-chain functionalization routinely leads to pendant interactions via monomer choice, only two well-defined dual-gated motifs have been achieved to date.³⁹ Judicious selection of monomers in concert with initiator and terminator design can afford scaffolds featuring both multiple functional building blocks and compartmentalized domains by design. Multiple living polymerization methods are reported that install molecular recognition units with high fidelity.^{4,8,23,40} We select ROMP for the preparation of the heterotelechelic building blocks, owing to the ability to utilize functional initiators and terminators in succession while avoiding post-polymerization functionalization routes.

Our design for the heterotelechelic building block is through the ROMP of a disubstituted paracyclophanediene (pCpd) in the presence of a functional initiator, and subsequent quenching with a functional chain terminator (CT). Essential to this design is the development of a new functional initiator based upon Grubbs II; we realize this through an iterative crossmetathesis—ring-opening metathesis polymerization (CM-ROMP) strategy that installs an α -chain end upon the PPV. We choose PPV scaffolds for multiple reasons: (i) conjugated polymer frameworks serve as hosts for a variety of applications, ranging from electronics to sensing;^{41–43} (ii) homopolymers and block copolymers featuring PPVs are well-studied in the context of optical properties and molecular structures;^{44–49} and (iii) spectroscopic methodologies that can be used to explicitly investigate conjugated polymer folding motifs have recently emerged.^{45,50,51}

We envision that the construction of a sheet-like building block featuring PPV π -strands would allow us to monitor folding modes through fluorescence spectroscopy, as PPVs that engage in persistent face-to-face $\pi - \pi$ stacking would be expected to exhibit fluorescence quenching relative to the unassembled parent polymers. We utilize orthogonal assembly approaches and ensuing cooperative effects to arrange heterotelechelic π -strands in both parallel and antiparallel sheet-like arrangements (Scheme 2). Parallel strands were realized via

Scheme 2. Noncovalent and Covalent Strategies toward (Left) Parallel and (Right) Antiparallel π -Stacked Sheets via Successive CM-ROMP and Self-Assembly



metallosupramolecular assembly of complementary heterotelechelic PPVs. Antiparallel strands are achieved using orthogonal supramolecular motifs. We rationalize that a covalent rod—coil—rod copolymer, wherein the coil includes a β -hairpin-like turn could promote $\pi - \pi$ stacking of antiparallel strands by design. The β -turn unit is engineered through supramolecular charge-transfer complexation of phenyl and perfluorophenyl units spatially separated within the coil block.

The ensuing folded block copolymers are then assembled with complementary polymers using recognition events that are orthogonal to the charge-transfer event. Complementary polymers were rationally chosen that feature a high density of pendant aromatic units that engage with the π -strands upon assembly. We hypothesize that successful assemblies, thus, would favor disruption of prominent PPV–PPV intrachain interactions while enforcing a compartmentalized structure that features either parallel or antiparallel π -sheets as a key component.

Our two helical blocks are based upon poly(N-1-(naphthalene-1-yl)ethyl)methacrylamide⁵² and <math>poly(aryl isocyanide) (PIC).^{53,54} We synthesize monotelechelic PMAc through RAFT polymerization in the presence of a functional chain-transfer agent (CTA), while telechelic PIC is prepared via anionic polymerization with an alkynyl-palladium-functionalized initiator.^{4,21} PMAc helices present a relatively more dynamic backbone, wherein polymer tacticity and sterics dictate helicity, as opposed to static PIC helices that demonstrate a

high inversion barrier and feature a rigid backbone.^{55,56} Helical PMAc can be influenced by its environment, while the overall structure is dependent on intrinsic hydrogen bonding⁵¹ akin to common biomolecular helices. Both static and dynamic helical domains are prominent in Nature;⁵⁷ thus, we envision that their combined incorporation into bio-inspired synthetic designs will engender investigations into the interplay of both helices, including how they assemble cooperatively. Additionally, interconversions between dynamic and static helices are well-documented, owing to the responsive nature of dynamic helices, and can be triggered by both soft confinement⁵⁸ and conformational constraints,⁵⁹ as well as solvent and staric effects.^{60,61}

For our random coil building block, we select poly(styrene) (PS). PS features the ability to install pendant side chains with relative ease, which can impact folding properties in more complex structures. Moreover, akin to sections of proteins lacking a well-defined structure that feature weak amino-based interactions between side chains, PS only organizes via weak intermolecular π - π interactions.

We have reported on monotelechelic helical polymer systems based upon PIC and PMAc,^{21,62,63} respectively that achieve high-fidelity directed assembly ($K_a \cong 10^3 - 10^4 \text{ M}^{-1}$) and retain their individual helicity during the assembly event. In addition, we have identified multiple homotelechelic coil-forming blocks including PS that can serve as a random coil mimic. Furthermore, we have demonstrated that PPVs can be functionalized to achieve main-chain supramolecular polymers with high-fidelity molecular recognition processes, affording supramolecular AA and AB diblock copolymers.

With these building blocks, we target synthetic tertiary architectures through supramolecularly directed sequencing of secondary structure elements. Bio-inspired sequences of helixsheet-coil and helix-sheet-helix are pursued. Helix-sheetcoil assemblies comprising both unimeric π -strand PPVs and antiparallel π -sheets are targeted owing to the prevalence of all three structural elements within biomacromolecules; we view these assemblies as models to study synergistic effects stemming from the integration of three synthetic conformations into a single compact structure. Helix-sheet-helix assemblies are more interesting structures. Sequences of α helices and β -sheets are dominant in key folding classes, such as $\alpha + \beta$ and α / β domains.⁶⁵ A mixture of solely α -helices and β sheets highlights the former class, while the latter is distinguished by parallel β -sheets that are surrounded with peripheral α -helices, with β - α - β motifs being prominent supersecondary structures.⁶⁶ Furthermore, α/β -barrel domains are common binding domains featured within enzyme folding pockets comprised of antiparallel sheet motifs.⁶⁷ We engineer helix-sheet-helix assemblies that, de facto, present both designed parallel and antiparallel β -sheet-like interior blocks.

RESULTS AND DISCUSSION

Synthesis of Monotelechelic Helical and Coil Building Blocks. Monotelechelic helical and coil building blocks are realized through controlled polymerization routes. Barbituratefunctionalized PMAc (**Ba-PMAc**) is synthesized via RAFT polymerization in the presence of a Ba-conjugated CTA, while pyridine-functionalized PIC (**Pyr-PIC**) is synthesized via anionic polymerization in the presence of a pyridine-functionalized palladium initiator. Both building blocks are evaluated through gel-permeation chromatography (GPC), wherein dispersity (*D*) values of 1.16 and 1.22 are observed for **Ba**- **PMAc** and **Pyr-PIC**, respectively (Figures S-15 and S-16). SCS-Pd^{II}-functionalized PS (**Pin-PS**) is available via ATRP in the presence of a 1,3-di(methylthiophenyl) phenyl ether moiety that undergoes post-polymerization palladation to install the SCS-Pd^{II} motif. **Pin-PS** is characterized through GPC, wherein a D of 1.21 is observed (Figure S-17).

Synthesis of HW-Functionalized GII and Subsequent Heterotelechelic Sheets via CM-ROMP. Taking advantage of ROMP to engineer heterotelechelic polymers with functional initiators and CTs, we synthesized α -HW-functionalized PPVs containing ω -Pin or Pyr moieties. The design necessitated the successful incorporation of the HW motif onto a GII initiator scaffold. Whereas the synthesis and isolation of functional Grubbs I-based initiators has been reported,⁶⁸ along with dyefunctionalized Hoveyda Grubbs derivatives,⁶⁹ GII-based functional initiators have not been realized to date for engineering telechelic polymers. Owing to the poor air stability of GII-based complexes in solution, we designed an iterative one-pot CM-ROMP strategy to achieve heterotelechelic PPVs. The CM of a HW-functionalized styrene in dichloroethane results in the formation of the desired HW-GII in one hour (Figure 1). The



Figure 1. Functionalized HW-GII and its ¹H NMR spectrum (CDCl₃, Av600).

GII carbene signal at δ = 19.15 decreases in intensity with the concomitant appearance of a new species at $\delta = 18.7$ ppm, consistent with the formation of the HW-GII carbene (1H NMR spectrum, Figure 1). The formation of HW-GII is also evidenced using both ¹³C NMR spectroscopy and MALDI-ToF (Figures S-8-S-10). The CM reaction proceeds in 98% conversion, and is used without purification to initiate the ROMP of pCpd. The polymerizations are monitored for completion via ¹H NMR spectroscopy, wherein the propagating carbene is always observed with an integration of 1H relative to the monomer feed ratio and/or polymer conversion. After the polymerization reaches completion, an excess of Pin- or Pyrsubstituted vinyl ether is added to afford the targeted heterotelechelic polymers. The ensuing polymers, HW-PPV-Pin and HW-PPV-Pyr are characterized by ¹H NMR spectroscopy, wherein resonances consistent with the successful orchestration of the CM-ROMP strategy are distinguished, as both end groups within the polymer backbone are observed. In particular, HW-amido protons are observed at 8.6 ppm as well as Pin-related resonances at 4.6 ppm. GPC was used to determine the D of HW-PPV-Pin and HW-PPV-Pyr (1.14 and 1.18, respectively, see Figures S-11 and S-12), while ¹H NMR spectroscopic analysis was used to yield more reliable molecular

weights through comparative integration of end group and backbone signals (Table 1).

| polymer | M_n (SEC) |) $M_{\rm w}$ (SEC) | Đ | $M_{\rm n} ({\rm NMR}^c)$ |
|-------------------------|-----------------------------|--------------------------|-------------------|---------------------------|
| HW-PPV- | Pin 33 000 | 39 000 | 1.18 ^a | 16 000 |
| HW-PPV- | Pyr 33 000 | 37 000 | 1.14 ^a | 18 400 |
| HW-1T-Pi | n 99 000 | 120 000 | 1.21 ^a | 23 700 |
| HW-1T-Py | vr 39 000 | 49 000 | 1.28 ^a | 17 800 |
| Pyr-PIC | 6 100 | 7 400 | 1.22 ^b | - |
| Ba-PMAc | 6 900 | 7 400 | 1.16 ^b | _ |
| Pin-PS | 14 000 | 17 000 | 1.21 ^b | 14 400 |
| ^a Recorded i | in CHCl ₃ , SEC. | ^b Recorded in | THF, SEC. | ^c Recorded in |
| CDCl ₃ , NM | R. | | | |

| Table 1 | 1. | Characterization | Data | for | Telechelic | Polymers |
|---------|----|------------------|------|-----|------------|----------|
| | | | | | | |

Dialing in Complexity: Synthesis of Heterotelechelic PPV Rod-Coil-Rod Block Copolymers Featuring Flexible Interior Segments via CM-ROMP. We sought to design a covalent block copolymer that aids in the organization of adjacent PPV blocks while featuring an antiparallel π -stacked sheet. There are reports detailing the use of flexible linkages to tether PPV backbones so as to attain collapsed order of chromophore interactions.⁷⁰ We envision a noncovalent analogue could enforce chromophore ordering via the collapse of a coil-like interior segment. Specifically, we hypothesize that the synthesis of a PPV-PNB-PPV scaffold, wherein the PNB features pendant phenyl groups adjacent to perfluorophenyl motifs⁷¹ that are able to undergo charge-transfer-assisted chain collapse within favorable solvent systems (e.g., chloroform),¹⁰ will lead to an interior flexible segment reminiscent of a β hairpin turn. The use of perfluoroarene/arene interactions has been exploited as a supramolecular synthon^{72,73} with the aptitude to preorganize both molecular and polymeric systems, affording molecular co-crystals,⁷⁴ as well as liquid crystals⁷⁵ and collapsed β -hairpin mimics.¹⁰

We utilize our CM-ROMP strategy to generate HWfunctionalized PPVs. Upon completion of the ROMP, an exonorbornene phenyl ester (Ph) is added to the polymerization solution and followed by a structurally analogous perfluorophenyl ester (PFP). We target incorporation of a PNB block such that the PNB:PPV ratio is less than 1.5.76 Smaller flexible units are demonstrated to induce PPV chromophore alignment.⁷⁷ The ensuing PPV-PNB_{Ph}-PNB_{PFP} block copolymer is then treated with a fresh equivalent of pCpd and polymerized to completion. Polymers are subsequently quenched with vinyl ethers containing either Pin or Pyr motifs, affording the desired HW-1T-Pin and HW-1T-Pyr (wherein 1T denotes the PPV-PNB_{Ph}-PNB_{PFP}-PPV backbone has one designed flexible turn) heterotelechelic block copolymers. The final polymers were characterized by ¹H NMR spectroscopy, wherein resonances consistent with the HW initiator end group, as well as both the PPV and PNB backbones were present. GPC was used to determine D of the Pin- and Pyr-terminated polymers (1.25 and 1.21, respectively, see Figures S-13 and S-14), while ¹H NMR spectroscopic analysis was required to estimate more reliable molecular weights (Table 1) and confirm block ratios. For instance, HW-1T-Pin features block ratios of 30:15:15:30. Following this iterative ROMP strategy, we are able to generate additional "turns" within the polymeric backbone, leading to essentially $A(BCA)_n$ covalent block copolymers of variable molecular weights.

Supramolecular ABC Triblock Copolymers via Orthogonal Metal Coordination and Hydrogen Bonding. Heterotelechelic HW-PPV-Pin and HW-PPV-Pyr can provide access to a variety of block copolymers via orthogonal assembly. The individual assembly behavior of HW-PPV-Pin and HW-PPV-Pyr were evaluated with two complementary secondary structure blocks. The assemblies were evaluated in a stepwise manner to allow for the characterization of the intermediate assembled products.

First, we investigated the formation of a helix– $(\pi$ -sheet)– coil ABC triblock copolymer using **HW-PPV-Pyr** as the internal heterotelechelic block. We targeted the metallosupramolecular assembly of **HW-PPV-Pyr** with **Pin-PS**,⁷⁹ followed by subsequent installation of helical **Ba-PMAc** via hydrogen bonding. The successful formation of **HW-PPV-Pin_Pyr-PS** was evidenced using ¹H NMR spectroscopy and GPC (Figure 2). The ¹H NMR spectrum displays an upfield shift of the



Figure 2. (Left) Partial ¹H NMR spectroscopic overlay of (top to bottom) HW-PPV-Pyr, HW-PPV-Pyr_Pin-PS, and Ba-PMAc_HW-PPV-Pyr_Pin-PS (CDCl₃). (Right) SEC traces (CHCl₃) of HW-PPV-Pyr (red) and HW-PPV-Pyr_Pin-PS (black) and schematic of supramolecular ABC triblock copolymer.

characteristic Pin-related resonance at 7.8 ppm to 7.7 ppm, on par with prior reports of Pin-Pyr coordination in PPV-based systems.⁴ Resonances related to the α -HW terminus are still present at 8.6 ppm, owing to their orthogonality to the metalcoordination event. Further evidence of successful assembly was confirmed via GPC, wherein a shift to a higher molecular weight species relative to **HW-PPV-Pyr** is observed, ($M_n = 32$ 800 to $M_n = 114$ 000) coupled with a low \mathcal{D} of 1.09. Subsequent assembly with helical **Ba-PMAc** was characterized by a downfield shift of the HW amide resonance at 8.6 ppm to 9.4 ppm, along with the appearance of the Ba hydrogenbonding signal at 12.2 ppm (Figure 2).

We investigate the capacity of **HW-PPV-Pin** to juxtapose two telechelic secondary structures, allowing for the fabrication of a helix–(π -sheet)–helix wherein both persistent dynamic and static helical blocks are incorporated. We first assemble **HW-PPV-Pin** with **Pyr-PIC** and evaluate the metallosupramolecular assembly using ¹H NMR spectroscopy. Upon coordination, we observe the disappearance of the α -Pyr resonance at 8.8 ppm. Addition of the **Ba-PMAc**, results in the shifting of the protons related to the HW amide from 8.6 to 8.9 ppm along with the concomitant appearance of a sharp

resonance related to the Ba hydrogen-bonding N–H protons at 12.7 ppm (Figure S-28).

Construction of a Parallel π -Stacked β -Sheet-like Supramolecular Block Copolymer. Having evaluated the assembly potential of HW-PPV-Pyr and HW-PPV-Pin, we looked to utilize their complementary end-groups to engineer a synthetic system that would conceptually mimic parallel β sheets. Given that the preliminary PPV-related assemblies are successful, we envisioned that the two polymers could additionally self-assemble into HW-PPV-Pin Pyr-PPV-HW, wherein the short saturated linkage between the blocks allows for the flexibility to manifest a hairpin-like turn. Prior studies using PPV systems have demonstrated that folded sheet-like structures can be engineered via interruption of the conjugated backbone with short saturated linkages⁷⁰ akin to those present leading up to the supramolecular junction. The self-assembly would, thus, allow for the further incorporation of complementary telechelic secondary structures, affording an ABB'A tetrablock copolymer via orthogonal assembly. Whereas oligoamide antiparallel β -sheet-like frameworks have been achieved via $\pi - \pi$ stacking,^{36,37} reports realizing parallel synthetic β -sheet-like architectures remain largely dormant. We view this as a platform to design symmetrical hierarchical structures, as the initiating end of the polymer species can be changed in a facile manner via CM reactions to engineer a versatile ABB'A building block.

The successful assembly of the PPV building blocks is characterized by ¹H NMR spectroscopy and GPC. Upon metal coordination, we observe that the HW-related downfield resonances are intact in the ¹H NMR spectrum, while signals related to the Pin and Pyr functionalities remain hidden within the backbone (Figure 3). A clean shift to higher molecular



Figure 3. (Left) Partial ¹H NMR spectroscopic overlay of (bottom to top) **HW-PPV-Pyr**, **HW-PPV-Pin**, **HW-PPV-Pin_Pyr-PPV-HW**, and **ABB'A** assembly (CDCl₃). (Right) SEC traces (CHCl₃) of **HW-PPV-Pin** (red), **HW-PPV-Pyr** (black), and **HW-PPV-Pin_Pyr-PPV-HW** (blue) and schematic of the supramolecular **ABB'A** tetrablock copolymer.

weight ($M_n = 96\ 000$ to $M_n = 107\ 000$) is observed by GPC proving the chain extension via self-assembly (Figure 3). Further assembly with the parallel-stacked π -sheet HW-PPV-Pin_Pyr-PPV-HW was conducted with complementary Ba-PMAc, whereupon the HW-related amide resonances at 8.6 ppm shift downfield to 9.3 ppm, along with concomitant appearance of the Ba N-H protons at 12.7 ppm. Diffusionordered spectroscopy (DOSY) is used to further evaluate **ABB'A** tetrablock copolymer formation, as the assembled structures should exhibit different diffusion coefficients in comparison to the parent **HW-PPV-Pin_Pyr-PPV-HW**. The metallosupramolecular PPV has a diffusion coefficient of 3.89×10^{-10} m² s⁻¹. Upon block copolymer formation with two equivalents of **Ba-PMAc**, the diffusion coefficient decreases to 2.36×10^{-10} m² s⁻¹.

Characterization of Tri- and Tetrablock Architectures. We characterized the supramolecular block copolymers by CD and fluorescence spectroscopies, along with wide-angle X-ray scattering (WAXS). CD spectroscopy is used to confirm the helical features of **Ba-PMAc** and **Pyr-PIC** upon assembly within the three different interior PPV blocks. Both helical domains retain the helical character in the ABC triblock copolymers, displaying wavelength-specific CD indicative of structures with helicity in enantiomeric excess (Figure 4).⁸⁰ For



Figure 4. CD spectra corresponding to ABC triblock copolymers: (left) red, Ba-PMAc; black, Ba-PMAc_HW-PPV-Pyr_Pin-PS; (right) purple, Ba-PMAc; red, Pyr-PIC; black, Ba-PMAc_HW-PPV-Pin_-Pyr-PIC). Spectra were obtained in dichloroethane.

the helix-sheet-coil assembly, only the helix block exhibits a CD trace. In contrast, the helix– $(\pi$ -sheet)–helix system displays two different helices, each varying in relative magnitude of their Cotton effects. In both supramolecular block copolymers, traces of a negative CD signal at 230 nm, along with positive CD at 236 and 283 nm are characteristic of contributions from Ba-PMAc, with the largest signal being the result of the naphthyl $\pi - \pi^*$ transitions. For the helix- $(\pi$ sheet)-helix assembly, the signature CD signals at 249 and 364 nm relate to the PIC backbone $n-\pi^*$ and $\pi-\pi^*$ transitions; in addition, those of Ba-PMAc are still maintained within the supramolecular block copolymer. The helicity of Ba-PMAc within the ABB'A block copolymer is also investigated, wherein upon assembly with the parallel π -sheet, a profile similar to that of the unassembled helical polymer is observed (Figure S-34). The CD profiles collectively depict that the helical structures of Ba-PMAc and Pyr-PIC are retained within the supramolecular multiblock copolymers.

We next evaluated the π -sheet PPV solid-state assemblies using WAXS. Both heterotelechelic polymers, being structurally similar to dioctyloxy PPV (DO-PPV), exhibit analogous signature peaks corresponding to the interbackbone separation of alkyloxy chains, interbackbone monomer repeat units, and interbackbone face-to-face $\pi-\pi$ stacking (d = 14.1-14.3 Å, 6.7 Å, and 4.5 Å, respectively)⁴⁸ that leads to 2D stacks sustained via $\pi-\pi$ stacking and alkyl–alkyl interdigitation between neighboring stacks in an orthogonal direction. To achieve compartmentalized π -sheet structures upon assembly, breaking up the PPV long-range order is essential. Unlike DO-PPV, the parent polymers display the more prominent alkyl–alkyl spacing peak at a shorter distance, owing to the heightened ability of the chains to tilt⁴⁸ with the lessened density of sidechains. DO-PPV scaffolds demonstrate a transverse span of 18.4 Å.⁴⁸ Whereas the majority of the homopolymer side-chains can remain tilted, both polymers feature a broadened shoulder between 19 and 22 Å, suggestive of some extended side chains being present (Figure 5).



Figure 5. WAXS diffractograms corresponding to ABC triblock copolymers obtained: (left) green, HW-PPV-Pyr; red, Ba-PMAc; blue, HW-PPV-Pyr_Pin-PS; black, Ba-PMAc_HW-PPV-Pyr-Pin-PS; (right) green, HW-PPV-Pin; red, Pyr-PIC; blue, HW-PPV-Pin_Pyr-PIC; black, Ba-PMAc HW-PPV-Pin-Pyr-PIC.

Following metal coordination with **Pin-PS** or **Pyr-PIC**, the $(\pi$ -sheet)-coil and $(\pi$ -sheet)-helix diblocks feature less intense signals in the low 2θ region, indicative of alkyl-alkyl interdigitation between stacks being lessened. Both diblock copolymers still feature a significant degree of π - π stacking, with **HW-PPV-Pin_Pyr-PIC** also featuring a broad signal centered at d = 21.5 Å that represents the hexagonal packing of PIC and correlates to the polymer stem, with overlap from the aforementioned shoulder of the parent PPV. Upon hydrogen bonding to **Ba-PMAc**, both ABC triblock copolymers feature signals related to π - π stacking (d = 4.2-4.8 Å). In both, the lessened intensity of the peaks related to the interbackbone alkyl-alkyl spacing signifies that the long-range order leading to 2D stacks is partially broken upon assembly; thus, the assembled polymers feature solely 1D π -stacked sheets.

In the **ABB'A** mutliblock copolymer, the metallosupramolecular assembly exhibits roughly identical signature peaks relative to the parent PPVs. The alkoxy side-chain separation remains the most prominent signal (d = 12.98 Å; Figure 6), with the concomitant broadening of the low 2θ shoulder corresponding to the presence of extended side chains (d =19.28 Å). Upon hydrogen bonding to **Ba-PMAc** to generate the



Figure 6. WAXS diffractograms corresponding to ABB'A multiblock copolymer: (left) metallosupramolecular assembly and (right) both assemblies (red, HW-PPV-Pin; black, HW-PPV-Pyr; blue, HW-PPV-Pin_Pyr-PPV-HW; and purple, ABB'A multiblock copolymer).

helix–(parallel π -sheet)–helix, we note that (i) the ABB'A assembly maintains a molecular structure featuring both alkyl– alkyl and face-to-face π – π interactions; (ii) upon assembly with the hydrogen-bonding helix, the degree of side-chain interactions is lessened; and (iii) the relative intensity of both signals, although broadened, suggests equal contributions of the two interactions in determining the long-range ordered structure. Prior to the integration of **Ba-PMAc**, the PPV backbones likely maximize both side-chain and backbone interactions to afford largely stacked 2D assemblies. The fully assembled **ABB'A** tetrablock copolymer appears to support equal contributions of interbackbone alkyl–alkyl and π – π stacking, suggestive of a parallel π -sheet being maintained in a compartmentalized manner, with the helical units suppressing further PPV–PPV interactions.

The homopolymers and assemblies are further evaluated using fluorescence spectroscopy. Although the complementary helices and coils do not exhibit fluorescence, the emission properties of PPV homopolymers⁸¹ and covalent block copolymers, as well as their aggregation-influenced properties are well documented.^{46,82,83} The heterotelechelic PPV homopolymers exhibit emission maxima at 520 nm with a broad shoulder at 560 nm (Figure S-33). Both ABC triblock copolymers exhibit mainly relative changes in intensity compared to their parent PPV polymers. Upon sequencing HW-PPV-Pyr_Pin-PS and Ba-PMAc_HW-PPV-Pyr_Pin-PS, we observe a decrease in intensity upon diblock formation. Triblock formation, however, partially restores some of the fluorescence behavior (Figure S-33). In contrast, with HW-PPV-Pin Pyr-PIC and Ba-PMAc HW-PPV-Pin Pyr-PIC, we observe that the fluorescence intensity maintains a steady decrease (ca. 50% overall) suggestive of achieving more face-toface π -stacks upon sequencing that would allow for quenching. Both systems exhibit a slight blue shift (2 nm) in the emission maximum upon hydrogen bonding assembly.

We then investigate the fluorescence of the assembled PPV diblock and **ABB'A** block copolymer (Figure 7). After metallosupramolecular self-assembly, we observe fluorescence that closely matches the parent polymers. Upon hydrogen bonding with **Ba-PMAc**, the **ABB'A** polymer exhibited sharply contrasting optical behavior, most notably a hypsochromic shift in emission, as well a sufficient decrease in fluorescence



Figure 7. Excitation (left) and emission (right) spectra related to the **ABB'A** parallel *π*-sheet supramolecular assembly (blue = **HW-PPV-Pyr**; red = **HW-PPV-Pin**; purple = **HW-PPV-Pin_Pyr-PPV-HW**; and black = **ABB'A**). Polymers are excited at 450 nm, and emission is fixed at 520 nm for each excitation scan in CHCl₃ (note: excitation spectra of **HW-PPV-Pin** and **HW-PPV-Pyr** are identical; we plot only one for clarity).

intensity (66% less intense), relative to the parent homopolymers and assembled diblock. Specifically, the emission maximum shifts to 510 nm, with a concomitant shift in the excitation maximum from 450 to 420 nm (Figure 7). The combined results suggest that the assembly with helical **Ba-PMAc** leads to compartmentalization and isolation of the PPV polymer chains (i.e., breaking of the 2D long-range order normally propagated by alkyl–alkyl interactions), with heightened face-to-face interactions leading to fluorescence quenching behavior akin to H-aggregates.⁸⁴ PPV systems are known to exhibit a blue-shifted emission as a result of strong interchain interactions and $\pi-\pi$ stacking within solution, and suppression of intrachain interactions.⁴⁶

Engineering of Supramolecular Block Copolymers Featuring Antiparallel π -Sheets. We pursued the construction of a helix–(antiparallel π -sheet)–coil ABC supramolecular triblock copolymer via orthogonal and stepwise assembly. HW-1T-Pyr is assembled with Pin-PS using metal coordination, with the assembled material characterized both by ¹H NMR spectroscopy and GPC (Figure 8). Upon



Figure 8. (Top) ¹H NMR spectra overlay (CDCl₃) of (bottom to top) HW-1T-Pyr, HW-1T-Pyr_Pin-PS, and Ba-PMAc_HW-1T-Pyr_Pin-PS. (Bottom) SEC traces (CHCl₃) highlighting a shift in molecular weight upon metal coordination (red, HW-1T-Pyr; black, HW-1T-Pyr_Pin-PS) and schematic depicting two orthogonal interactions and Ba-PMAc_HW-1T-Pyr_Pin-PS.

metallosupramolecular assembly, the HW amide proton resonance remains centered at approximately 8.5 ppm, while the Pin and Pyr resonances remain hidden within the aromatic backbone signals. GPC is used to confirm the assembly, wherein the trace obtained shows a distinct shift to a higher molecular weight ($M_n = 38\ 600$ to $M_n = 131\ 000$; D = 1.16) upon sequencing the antiparallel sheet and coil. After synthesizing the (antiparallel π -sheet)-coil metallosupramolecular block copolymer, we incorporate the helical block using hydrogen bonding between HW and Ba.

We evaluate the K_a using ¹H NMR spectroscopic titration, wherein the HW amido N-H protons are monitored upon addition of **Ba-PMAc** (Figure 9). Upon achieving a 1:1



Figure 9. Plot of (left) chemical shifts (in CDCl₃) related to hydrogen-bonding N–H amido protons upon addition of **Ba-PMAc** to **HW-1T-Pyr_Pin PS** and (right) specific viscosity (η_{sp}) versus concentration for related block copolymer assemblies in CHCl₃ (red, HW-2T-Pyr; black, HW-2T-Pyr_Pin-PS; and blue, Ba-PMAc_HW-2T-Pyr_Pin-PS).

assembly, the amido protons shift downfield from 8.5 to 9.2 ppm, along with concomitant appearance of the Ba imido protons at 12.5 ppm. The association constant of the supramolecular assembly was calculated to be $(3.41 \pm 0.6) \times$ 10⁴ M⁻¹, which correlates well with our previous assemblies,⁴ and others featuring HW-based hydrogen-bonding junctions.^{63,67,85} The overall helix–(antiparallel π -sheet)–coil sequence is further evaluated by measuring the specific viscosity (η_{sp}) upon supramolecular association relative to the parent heterotelechelic PPV-based polymer. The viscosity studies are conducted using an Ubbelohde viscometer at 25 °C in CHCl₃. Relative to the heterotelechelic PPV-based polymer, the η_{sp} increases upon addition of the Pin-PS block, and further increases with the installation of the hydrogen-bonding Ba-PMAc, which correlates with the increase in the estimated molecular weight of the assembled block copolymers (Figure 9).

The final supramolecular assembly target is a helix-(antiparallel π -sheet)-helix, wherein the terminal blocks comprise chemically distinct helical polymers. Pyr-PIC is coordinated to HW-1T-Pin, followed by the hydrogen bonding of the α -HW terminus to **Ba-PMAc**. The assembly is evaluated by ¹H NMR spectroscopy. HW amido protons exhibit a downfield shift from 8.5 ppm to 8.9 ppm, along with the emergence of Ba imido protons at 12.7 ppm upon assembly with both helical polymers (Figure S-32). Further NMR spectroscopic characterization of the supramolecular helix-(antiparallel π -sheet)-helix assembly was provided by DOSY experiments. Relative to HW-1T-Pin (diffusion coefficient = $8.43 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$), the diffusion coefficients of the metallosupramolecular diblock and ABC triblock are clearly decreasing with the increase in molecular weight $(7.19 \times 10^{-10} \text{ and } 4.84 \times 10^{-10} \text{ and } 8.84 \times 10^{-10} \text{ and } 8.84$ 10^{-10} m² s⁻¹, respectively). The successful helix–(antiparallel π -sheet)-helix main-chain sequencing is evidenced by viscometry measurements. Akin to the triblock copolymer obtained using HW-2T-Pyr, the $\eta_{\rm sp}$ relative to the parent 2T polymer increases upon addition of Pyr-PIC, with a further increase upon addition of the hydrogen-bonding Ba-PMAc (Figure 10).



Figure 10. (Left) Specific viscosity (η_{sp}) versus concentration for related helix–(antiparallel π -sheet)–helix block copolymer assemblies in CHCl₃ relative to **HW-2T-Pin**. (Right) CD spectral overlay of **Pyr-PIC** (red), **Ba-PMAc** (purple), and helix–(antiparallel π -sheet)–helix (black) measured in dichloroethane.

Characterization of ABC Triblock Copolymers Featuring Antiparallel π -Sheets. The effect of supramolecular assembly on Ba-PMAc was evaluated using CD. Within the helix-(antiparallel π -sheet)-coil assembly, the only contributions would stem from the helicity of Ba-PMAc. The supramolecular triblock copolymer exhibits a negative CD signal at 230 nm, along with positive CD at 236 and 283 nm (Figure S-36). The bisignate profile observed correlates well with the telechelic unassembled Ba-PMAc, suggestive of retaining helical structure. The helical features of Ba-PMAc and Pyr-PIC upon stepwise assembly with the antiparallel π sheet are also confirmed. We observe that the helix-(antiparallel π -sheet)-helix exhibits characteristic CD signals consistent with both helices. Specifically, traces of a negative CD signal at 230 nm, along with positive CD at 236 and 283 nm from the PMAc block naphthyl $\pi - \pi^*$ transitions, with additional signals at 249 and 364 nm related to the PIC backbone n- π^* and $\pi - \pi^*$ transitions are observed (Figure 10). At the corresponding wavelengths, signal intensities in the fully formed triblock copolymer result from the summation of absorbances contributed from each polymer species. The CD profiles collectively depict that the helix–(antiparallel π sheet)-helix triblock copolymers retain the helical structures of Ba-PMAc and Pyr-PIC.

Relative to DO-PPV, the WAXS of HW-1T-Pyr and HW-1T-Pin still feature strong Bragg diffraction peaks corresponding to the interbackbone alkyloxy chain separation, monomer repeat units, and face-to-face $\pi - \pi$ stacking. Additionally, the high 2θ peak is broadened owing to the perfluoroarene/arene interactions of the PNB interior block exhibiting Bragg diffraction at $2\theta = 17.5^{\circ}$ (Figures S-37 and S-38). Upon metallosupramolecular diblock formation, the most prominent feature corresponds to the face-to-face $\pi - \pi$ stacking of the PPV backbone as well as the perfluoroarene/arene interactions (d =4.56 Å). In HW-1T-Pyr Pin-PS, a broadened signal related to the loosely packed phenyl stacks within the coil-like Pin-PS backbone is still distinguishable. Upon hydrogen bonding with Ba-PMAc, the molecular structure remains mostly unaffected, although the intensity of the HW-1T-Pyr and HW-1T-Pin signature peaks are about equal (i.e., the relative influence of $\pi - \pi$ stacking is decreased), suggestive of the presence of unimers that do not interact with neighboring assemblies, unlike the parent polymer.

Fluorescence spectroscopy is used to gain insights into the assembly behavior of HW-1T-Pyr and HW-1T-Pin. We first compare the emission spectrum of HW-1T-Pyr to HW-PPV-Pyr. At the same concentration, HW-1T-Pyr displays a





Figure 11. Excitation (left) and emission (right) profiles related to HW-1T-Pyr supramolecular assembly (red, HW-1T-Pyr; black, HW-1T-Pyr_Pin-PS; blue, Ba-PMAc_HW-1T-Pyr_Pin-PS; and dashed purple, HW-PPV-Pyr). Polymers are excited at 450 nm, and emission is fixed at 520 nm for each excitation scan in CHCl₃.

backbone does not undergo a substantial hypsochromic shift, despite the presence of "defects" within the π -conjugated framework, as the interior PNB units break up electronic communication. The difference observed in intensity is attributed to the ability of **HW-1T-Pyr** to enforce $\pi - \pi$ stacking of the PPV backbones with a heightened degree of face-to-face stacking that suppresses fluorescence intensity.

Upon sequential block copolymer formation with **Pin-PS** and **Ba-PMAc**, we observe the relative emission intensity decreases (ca. 65% relative to parent **HW-1T-Pyr**), suggestive of more H-aggregate-like face-to-face stacking upon assembly. Additionally, both assemblies support a hypsochromic shift in excitation (450 to 440 nm), likely owing to the disruption of interactions that normally dominate the PPV aggregated state.^{46,48} For the helix–(antiparallel π -sheet)–helix upon both metal coordination and hydrogen bonding, we observe an overall decrease in fluorescence intensity (Figure S-39). These collective results suggest maintenance of the antiparallel π -sheets in the wake of assembly, while the complementary polymers successfully compete with the intrachain associations common in PPV-based scaffolds.

CONCLUSION

Herein, we report a versatile method to access architecturally well-defined Nature-inspired multiblock copolymers through designed supramolecular sequencing of telechelic helical, π sheet, and coil-forming polymers. Essential to our design is the one-pot iterative CM-ROMP strategy that first engineers a functional GII initiator, followed by heterotelechelic π -sheet PPVs. The heterotelechelic PPVs exploit orthogonal selfassembly or further living polymerization to achieve noncovalently driven parallel π -sheets or combined covalently and noncovalently driven antiparallel π -sheets, respectively. Both parallel and antiparallel π -sheets, which bear structural similarity, to proteinic β -sheets, are intentionally utilized as the interior assembly block to probe assembly. Complementary polymers were rationally chosen that feature a high density of aromatic units that engage with the π -strands upon assembly. Successful assemblies, thus, disrupt prominent intrachain PPV-PPV interactions while enforcing a compartmentalized

structure that can be facilely monitored using fluorescence spectroscopy.

Three unique structures are combined through hydrogen bonding and metal coordination, and retained within the final assemblies. We investigate PPV-based helix-sheet-coil and helix-sheet-helix assemblies as simple building systems that feature homology to α/β and $\alpha+\beta$ protein classes in wake of constituting a fully synthetic design. Supramolecular sequencing occurs in an orthogonal manner, while disrupting the intrachain PPV-PPV interactions and maintaining the helicity of both Ba-PMAc and Pyr-PIC. We demonstrate the realization of a parallel-stacked π -sheet based upon an ABB'A network, wherein the addition of helical termini aids in establishing a compartmentalized structure. The compartmentalized nature of the folded interior sheet was evidenced both in the solid state through WAXS and in solution via fluorescence spectroscopy, wherein hypsochromic shifts in excitation and emission, along with concomitant fluorescence quenching supported the lack of intrachain interactions and PPV aggregation, as well as enhanced degrees of face-to-face $\pi - \pi$ stacking.

We engineered a heterotelechelic PPV-based rod-coil-rod block copolymer featuring internal nonconjugated blocks that interact using perfluoroarene/arene stacking to aid in the establishment of an antiparallel π -sheet. We observe that HW-1T-Pin and HW-1T-Pyr feature heightened degrees of face-toface stacking as evidenced by both WAXS and fluorescence spectroscopy, likely owing to the ability of the PNB segments to be flexible enough to induce a folded structure, but rigid enough to prevent unwanted aggregation from occurring. Upon assembly with complementary helical and coil polymers, a decrease in the fluorescence intensity was observed, indicative of pronounced face-to-face $\pi - \pi$ stacking. All assemblies, despite the complex nature of the building blocks, maintain prominent secondary structures.

The introduced system provides a versatile platform to combine synthetic polymers in a well-defined and precise manner via a supramolecular sequencing strategy that supports the formation of tertiary structures. Our methodology presents an approach to utilize supramolecular interactions in concert to not only afford main-chain synthetic foldamers but also promote further assembly into more complex and compartmentalized systems. While much work is dedicated to the engineering of bio-inspired synthetic folding systems that feature individual helical and sheet-like segments, few nonamide systems dial in design complexity, while still maintaining simplistic routes to analyze assembled structures. We view this strategy as a rational platform to further develop directionally assembled polymer systems on demand while increasing the complexity of synthetic systems that feature structural homology to biomacromolecular architectures.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.7b06201.

Experimental details, including small-molecule and polymer synthesis and characterization: ¹H and ¹³C NMR spectroscopy, MALDI-ToF data, SEC traces, assembly studies, NMR spectroscopic titration and DOSY data, viscometry measurements, thermal characterization, fluorescence and CD spectral data, and WAXS measurements, including Figures S-1-S-39 (PDF)

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AUTHOR INFORMATION

Corresponding Author

*marcus.weck@nyu.edu

ORCID [®]

Elizabeth Elacqua: 0000-0002-1239-9560

Marcus Weck: 0000-0002-6486-4268

Notes

The authors declare no competing financial interest.

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