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Supramolecular Triblock Copolymer**

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Complete List of Authors:	Deng, Ru; New York University, Molecular Design Institute and Milton, Margarita; New York University, Molecular Design Institute and Pomarico, Scott; New York University, Molecular Design Institute and Weck, Marcus; New York University, Molecular Design Institute and

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ARTICLE

Synthesis of a Heterotelechelic Helical Poly(methacrylamide) and its Incorporation into a Supramolecular Triblock Copolymer†

Ru Deng,^a Margarita Milton,^a Scott K. Pomarico^a and Marcus Weck^{*a}Received 00th January 20xx,
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We report the first heterotelechelic helical poly(methacrylamide) (PMAc) bearing orthogonal supramolecular binding sites on its chain-ends synthesized through a combination of reversible addition-fragmentation chain-transfer (RAFT) polymerization and thiol-bromo “click” chemistry. The heterotelechelic PMAc was assembled with two monotelechelic polymers featuring different secondary structures, namely a coil-like poly(styrene) and a helical poly(isocyanide), resulting in the formation of a coil-helix-helix supramolecular triblock copolymer through orthogonal metal coordination and hydrogen bonding interactions. Triblock assembly was confirmed through ¹H NMR spectroscopy, isothermal titration calorimetry (ITC) and viscometry. The individual polymer blocks retained their secondary structures in the final triblock copolymer, as evidenced by circular dichroism (CD) spectroscopy. Our synthetic strategy expands the toolbox of triblock copolymers featuring structural motifs similar to the ones found in proteins and provides the potential for the development of other complex multifunctional polymeric ensembles.

Introduction

The design of well-defined, fully-synthetic hierarchical structures that act as analogs to naturally-occurring biomacromolecules remains an intriguing yet challenging area of research.^{1,2} Nature’s strategy for directed folding, despite its limited building blocks (i.e. amino acids), involves the assembly of poly(peptide)s into highly complex structures with exquisite function primarily through noncovalent interactions including metal-coordination, hydrogen bonding, electrostatic interactions, and van der Waals interactions.^{3,4} The fabrication of synthetic analogues of common domains found in proteins provides a potential pathway to elucidate structure-function relationships and allows for the synthesis of functional materials.⁵ Such protein mimics are not limited to the amino acid building blocks, and can still incorporate secondary structural elements such as coils, helices, and sheets into complex structures.^{6–8}

Chemists have developed various synthetic methodologies towards the synthesis of block copolymers featuring topologically diverse blocks. These methodologies include (i) pre-designed sequential polymerizations of different monomers and their collapse into complex structures such as coil-helix diblock copolymers,^{9,10} sheet-coil-helix triblock copolymers,¹¹ or helix containing single-chain polymeric nanoparticles;¹² and (ii) post-polymerization modifications that link two or more blocks through covalent or noncovalent interactions.^{13–16} In particular, the second strategy which

employs helix, coil and sheet-like polymers containing one or two functional handles, and their assemblies through complimentary supramolecular molecular recognition units has proven effective.^{17,18} We have reported a library of monotelechelic secondary structure-forming building blocks including helices, random coils, and sheets, and investigated their use in the formation of architecturally well-defined multiblock copolymers through precise, orthogonal supramolecular assemblies.^{19–23}

Controlled polymerizations such as reversible addition-fragmentation chain-transfer (RAFT) polymerization, atom-transfer radical polymerization (ATRP), ring-opening metathesis polymerization (ROMP), and anionic polymerization have been used in the preparation of well-defined supramolecular block copolymers.^{12,19,23} These methodologies allow for the fine-tuning of molecular weights and dispersities as well as quantitative functional group installation. While a handful of coil and sheet-like heterotelechelic polymer building blocks have been reported,^{20,23} a helical building block containing two distinct molecular recognition motifs along its chain-ends has not been realized to this date. This void in the literature can be

^a Department of Chemistry and Molecular Design Institute, New York University, New York, NY, USA. E-mail: marcus.weck@nyu.edu

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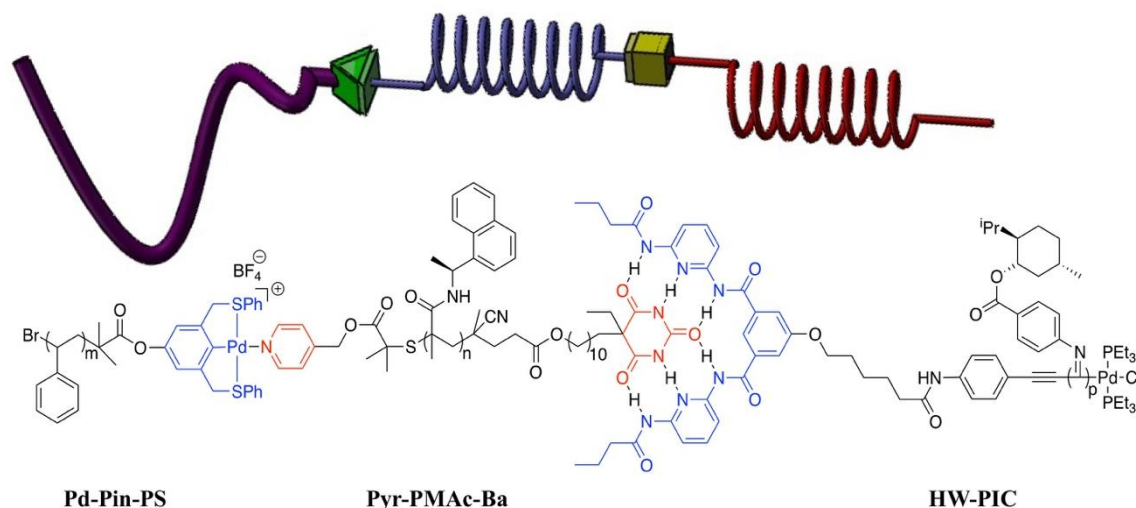
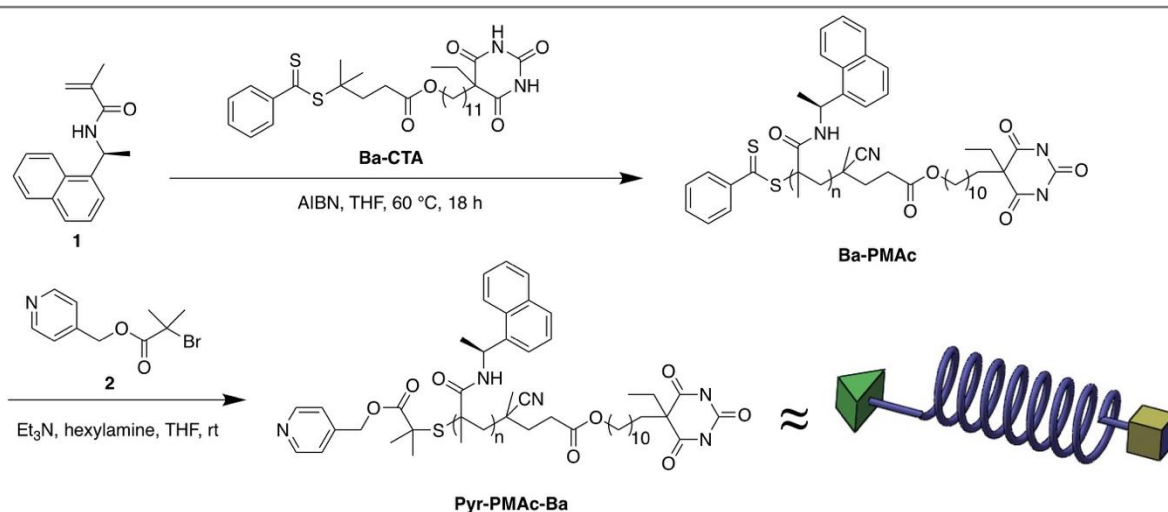


Figure 1. Schematic representation of the supramolecular assembly of poly(styrene) (coil), chiral poly(methacrylamide) (helix), and chiral poly(isocyanide) (helix) by orthogonal, noncovalent interactions.

attributed to the lack of synthetic toolkit needed to install two different end group functionalities onto a helical polymer's chain-ends; which only allows for the incorporation of the helical segment to either end of a multiblock material. This, in turn, limits the development of synthetic analogues to common natural protein motifs in which the helical segments are located in the middle, such as the triple helix or helix bundles, two of the most prevalent motifs found in nature.^{24–26}

Herein, we report the synthesis of a heterotelechelic helical poly(methacrylamide) (PMac) with orthogonal supramolecular recognition motifs at the chain-ends, and, as a proof of principle, the employment of the bifunctional helix in the assembly of a supramolecular coil-helix-helix block copolymer (Figure 1). Our strategy involves the combination of functional chain-transfer agent (CTA)-mediated RAFT polymerization and a post-polymerization thiol-bromo “click” reaction. Post-polymerization ligations following RAFT polymerizations increasingly employ metal-free, thiol-based reactions such as thiol-ene, thiol-yne, thiol-isocyanate and thiol-halogen reactions due to their robustness and high-yields.^{27–33} Our use of a barbiturate-functionalized CTA and the introduction of a

pyridine end-group via a thiol-bromo “click” reaction after the polymerization event, leads to the formation of a new class of heterotelechelic helical polymers containing a pyridine unit on the α -end and a barbiturate unit on the ω -end, and chiral naphthylethyl side-chains along the backbone. Subsequent supramolecular assemblies with complimentary SCS-pincer palladium and Hamilton Wedge (HW)-functionalized monotelechelic polymers results in a supramolecular triblock copolymer with multiple secondary structure elements.^{34–36} While the monotelechelic poly(styrene) (PS) block represents a flexible coil, the monotelechelic poly(isocyanide) (PIC) maintains a rigid helix driven by steric repulsion of its bulky side-chain units.³⁷ The PIC helix differs from the PMac-based helical system in which the helicity is maintained by intramolecular hydrogen bonding and steric repulsion resulting in a less static backbone.^{38–40} The molecular recognition events were characterized by ¹H NMR spectroscopy and isothermal titration calorimetry (ITC) while the block copolymer formation was confirmed by viscometry and circular dichroism (CD) spectroscopy.



Scheme 1. Synthetic route to the α -Pyr, ω -Ba functionalized heterotelechelic helical polymer Pyr-PMac-Ba.

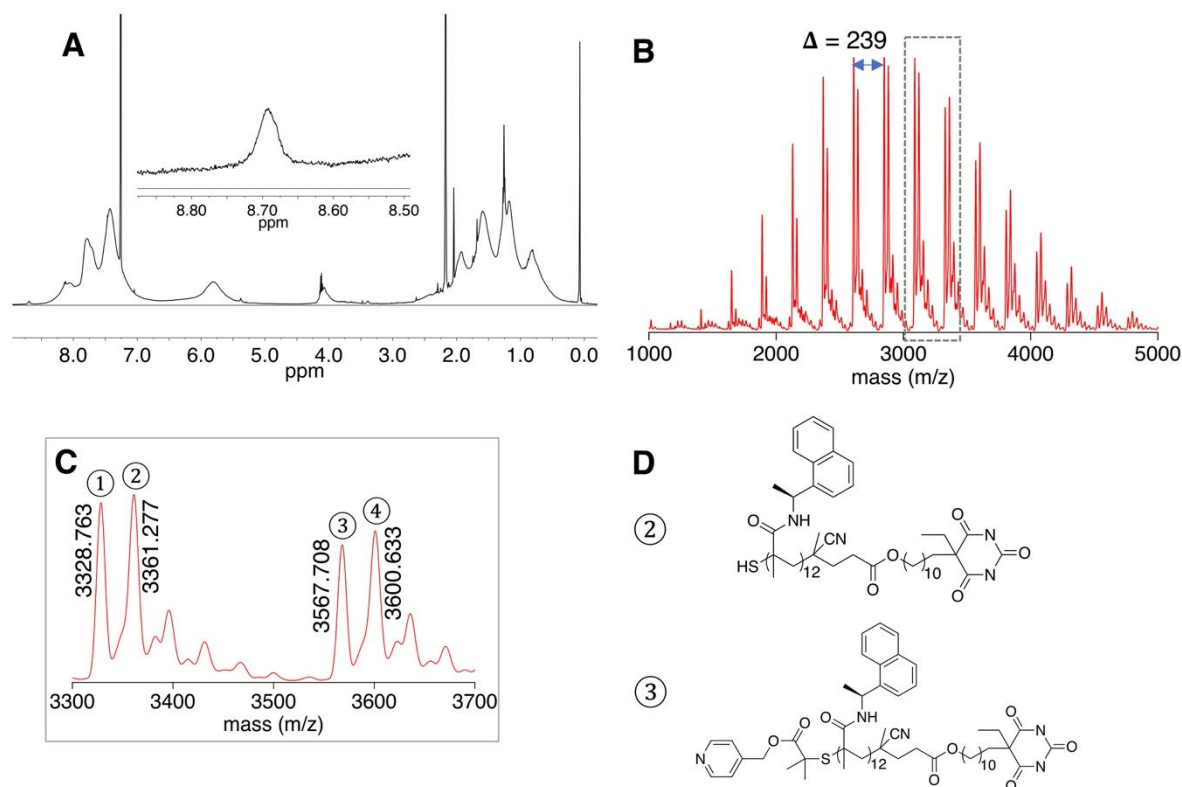


Figure 2. Spectroscopic characterizations of heterotelechelic **Pyr-PMAC-Ba**: (A) ^1H NMR spectrum and expansion of the pyridine region (CDCl_3 , 600MHz); (B) MALDI-ToF MS spectrum and (C) expansion of the two signals outlined in the full spectra denoting a series of two peaks. (D) In each set of peaks, the one on the left denotes the positively charged polymer (③) and the one on the right denotes molecular structures of dithioester cleaved species (②).

Results and Discussion

Scheme 1 depicts our synthetic strategy towards the synthesis of a heterotelechelic poly(methacrylamide) middle block (**Pyr-PMAC-Ba**). A barbiturate functionalized CTA (**Ba-CTA**) was used in the RAFT polymerization of (*S*)-*N*-(1-(naphthalen-2-yl)ethyl)methacrylamide (**1**) to afford the monotelechelic helical polymer (**Ba-PMAC**). The Ba-functionalized polymer was purified by dialysis against acetone. **Ba-PMAC** was characterized by gel-permeation chromatography (GPC) and a dispersity (\mathcal{D}) of 1.19 was obtained (Figure S7). The barbiturate imide protons are not visible in the ^1H NMR spectrum of the homoblock, but can be resolved upon association with its recognition partner, the Hamilton Wedge (*vide infra*).

The next step was to install the second functionality onto the polymer chain-end. The pyridine-containing α -bromoester (**2**) was prepared via an esterification reaction between 4-pyridinemethanol and α -bromoisobutyryl bromide. Successful conversion of the alcohol to the corresponding ester was confirmed through the visualization of ester signals at δ 5.2 ppm in the ^1H NMR spectrum, as well as δ 65.5 ppm and 171.3 ppm in the ^{13}C NMR spectrum (Figures S1 and S2). Subsequently, **Ba-PMAC** was functionalized at the chain-end with pyridine through a one-pot reaction in which the dithiobenzoate end-group on the RAFT agent was removed via aminolysis, followed

by a thiol-halogen “click” reaction between compound **2** and the free thiol group of **Ba-PMAC**. Hexylamine was used as the cleavage agent. The pink color of the intact RAFT agent disappeared after approximately 30 minutes, indicating that aminolysis had taken place. The mixture was subjected to prolonged reaction times (over six hours) to obtain quantitative yields. Upon purification by dialysis against acetone, the resulting **Pyr-PMAC-Ba** was analyzed by ^1H NMR spectroscopy. The appearance of the ortho proton of the pyridine (8.70 ppm, Figure 2A), along with the disappearance of the characteristic CTA phenyl proton signals (8.11, 7.69 and 7.52 ppm, Figure S3), provided evidence for cleavage of the CTA and installation of the pyridine at the polymer chain-end.

We also investigated the transformation of **Ba-PMAC** to **Pyr-PMAC-Ba** by MALDI-ToF MS spectrometry. The mass spectra were obtained in linear mode with dithranol and sodium iodide (NaI) as the matrix and the cationizing agent, respectively. As shown in Figure 2B, the spectrum of **Pyr-PMAC-Ba** displayed periodic fragmentation patterns separated by approximately 239 g/mol which is attributed to the mass of the monomer (239.32 g/mol). Each set of ions marked the presence of two peaks with similar intensities, along with other minor series. In each set of peaks, the ones with higher molecular weights (signals ② and ④ in Figure 2D) also appear in the **Ba-PMAC** spectrum (Figure S11). These peaks result from the cleavage of labile dithioester C-S bonds on the CTA end-groups. For example, the molecular weight of peak ② matches with an end-cleaved

Table 1. GPC characterizations of the telechelic polymers (obtained with THF as the eluent).

Polymer	M_n	M_w	\mathcal{D}
Pyr-PMAC-Ba	3000	3600	1.19
Pd-Pin-PS	10000	11000	1.11
HW-PIC	11600	14500	1.24

[SH-(MAC)₁₂-Ba + Na]⁺ species (observed m/z = 3361.277, calculated m/z = 3361.419, Figure 2D). Similar cleavage patterns were also reported for other RAFT polymers.^{30,33} The lower molecular weight signals (① and ③) are assigned to the positively charged polymers. Signal ③ at m/z = 3567.708, corresponds to a singly positively charged heterotelechelic polymer with 12 repeat units, i.e., [Pyr-(MAC)₁₂-Ba + Na]⁺ (calculated m/z = 3567.679). These results strongly suggest that the formation of **Pyr-PMAC-Ba** via the thiol-bromo “click” strategy was successful.

The monotelechelic blocks we chose as assembly partners for the new heterotelechelic helix were a pincer-functionalized poly(styrene) (**Pd-Pin-PS**) and a Hamilton Wedge-functionalized helical poly(isocyanide) (**HW-PIC**). The two blocks were prepared according to previously reported procedures.^{10,19,20} Specifically, **Pd-Pin-PS**, the coil-like block, was prepared by ATRP with a pincer-containing initiator, followed by metalation with Pd(PhCN)₂Cl₂. **HW-PIC** was obtained through transition metal-mediated isocyanide polymerization with a HW-functionalized palladium (II) initiator. All of the polymers were subject to GPC measurements prior to supramolecular assembly (Table 1).

We then targeted supramolecular assemblies of the three homoblocks. We decided to use metal coordination followed by hydrogen bonding because the pincer-pyridine metal coordination interaction is more robust than that of the HW/Ba.¹⁸ Assembly of the heterotelechelic helical polymer with **Pd-Pin-PS** was carried out in the presence of silver tetrafluoroborate (AgBF₄), which abstracts the chloride from the palladium and opens up a coordination site for the pyridine. In detail, a 1:1 molar ratio of **Pd-Pin-PS** and **Pyr-PMAC-Ba** was dissolved in freshly distilled, deuterated chloroform for NMR analysis. In the physical mixture, no changes were observed in the ¹H NMR spectrum with respect to the SPh protons of pincer (Figure 3A, middle). The metal coordination event was triggered by the addition of a five-fold excess of AgBF₄. After ten minutes of stirring at room temperature, the solution turned cloudy due to the formation of a white precipitate, namely AgCl. The mixture was then stirred for an additional 30 minutes to ensure complete coordination, followed by syringe filtration (0.45 μm) to remove precipitates. Comparison of the ¹H NMR spectra of the assembled diblock copolymer with the physical mixture of the two homoblocks showed a downfield shift of the SPh protons (Figure 3A, bottom) from 7.81 ppm to 8.06 ppm which is similar to the shift in the NMR spectra of other palladated pincer metal-coordination steps involving two polymer blocks reported in the literature,^{20,41,42} confirming the formation of a coil-helix diblock copolymer (**Pd-Pin-PS_Pyr-PMAC-Ba**).

With the supramolecular coil-helix diblock copolymer in hand, we then performed the hydrogen-bonding assembly

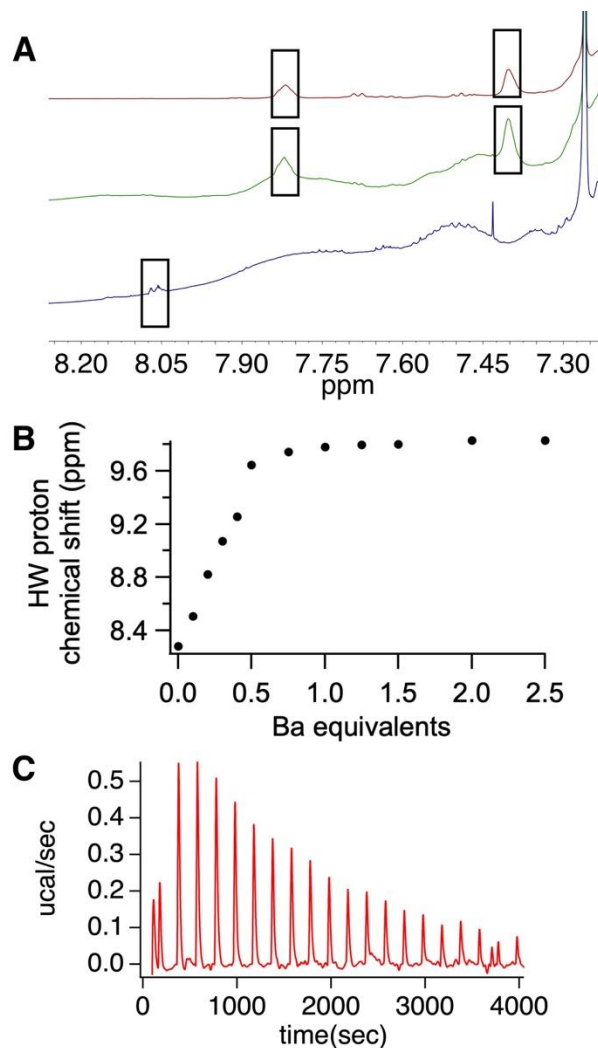


Figure 3. (A) Partial ¹H NMR (600 MHz) spectroscopic overlay of (top to bottom) **Pd-Pin-PS** (red), physical mixture of **Pd-Pin-PS** and **Pyr-PMAC-Ba** prior to the addition of AgBF₄ (green), and the assembled **Pd-Pin-PS_Pyr-PMAC-Ba** diblock copolymer (blue). Black boxes mark the shift of pincer SPh proton signals. (B) The change in the chemical shift of the HW imide protons of **HW-PIC** titrated with **Pd-Pin-PS_Pyr-PMAC-Ba** confirms triblock copolymer assembly by hydrogen bonding (CDCl₃, 600 MHz, 25.0 °C); (C) ITC binding isotherm between **Pd-Pin-PS_Pyr-PMAC-Ba** and **HW-PIC** recorded in dichloroethane at 25.00 °C.

between the barbiturate-containing diblock and **HW-PIC**. ¹H NMR spectroscopy titration study provides *in situ* information of the assembly process by tracking the characteristic chemical shifts of the imide protons on the barbiturate and the chemical shifts of the amide protons on the Hamilton Wedge. Previous studies demonstrated that the HW amide protons are easier to track than the barbiturate imide protons during the binding event as the barbiturate imide protons are not immediately visible in the ¹H NMR spectrum.^{19,23} Therefore, the Ba-containing diblock copolymer was titrated into the **HW-PIC** polymer. Titration studies were performed by adding **Pd-Pin-PS_Pyr-PMAC-Ba** into a 0.79 mmol **HW-PIC** solution (0.1 to 2.5 molar equivalents). The binding curve is shown in Figure 3B.

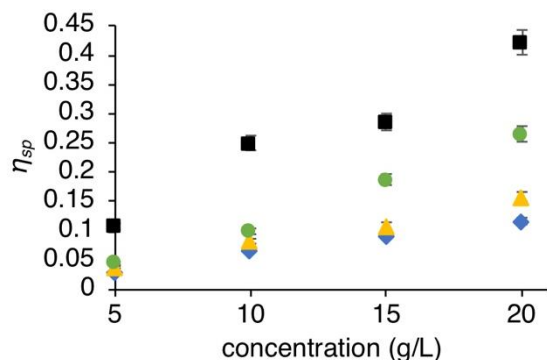


Figure 4. The increase in specific viscosity as a function of concentration for **Pyr-PMAC-Ba** (blue), **Pd-Pin-PS** (yellow) blocks, **Pd-Pin-PS_Pyr-PMAC-Ba** (green) diblock, and coil-helix-helix triblock copolymer (black) recorded in CHCl_3 at 25 °C.

Upon addition of one equivalent of **Pd-Pin-PS_Pyr-PMAC-Ba** to **HW-PIC**, the HW proton signal shifted from 8.28 ppm to 9.78 ppm. Further addition of **Pd-Pin-PS_Pyr-PMAC-Ba** shifted the proton signal to 9.83 ppm. A broad barbiturate amide proton signal was resolved at around 12.5 ppm which shifted upfield to 10.5 ppm as the assembly proceeded. From the binding curve, an association constant (K_a) of $3.04 \times 10^4 \text{ M}^{-1}$ was calculated, which is comparable to association constants of other reported Ba-HW polymeric systems.¹⁷ The strength of the hydrogen bonding interaction was further corroborated by ITC. The Ba-containing coil-helix diblock was dissolved in dichloroethane (DCE) and titrated into a **HW-PIC** DCE solution at 25 °C. The binding isotherm is shown in Figure 3C and the association constant was determined with the single-site binding model. The K_a was calculated to be $(3.40 \times 10^4) \pm 10\% \text{ M}^{-1}$, which is in close proximity to the association constant obtained from the NMR titration experiment.

After successful assembly and characterization of the SCS-pincer/pyridine and the HW/Ba molecular recognition unit pairs, we characterized the solution properties of the triblock copolymer. The main-chain self-assembled triblock copolymer possesses significantly higher molecular weight compared to the individual building blocks or the diblock copolymer **Pd-Pin-PS_Pyr-PMAC-Ba**. As a result, solutions of the assembled

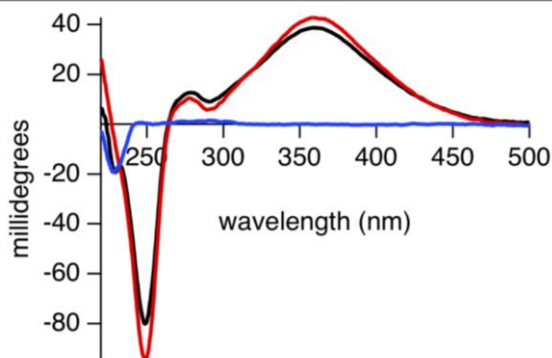


Figure 5. CD spectrum corresponding to helical **Pyr-PMAC-Ba** (blue), **HW-PIC** (red) blocks and the coil-helix-helix triblock copolymer (black) obtained in dichloro ethane at 25 °C.

copolymers should have higher viscosities. Viscometry tests were performed in chloroform at 25 °C with a Cannon-Ubbelohde semi-micro viscometer. Specific viscosities (η_{sp}) of heterotelechelic **Pyr-PMAC-Ba** and **Pd-Pin-PS** blocks were measured prior to assembly; the higher η_{sp} of the **Pd-Pin-PS** block correlates to its higher molecular weight. Upon metal coordination, the η_{sp} of the **Pd-Pin-PS_Pyr-PMAC-Ba** diblock copolymer solution is higher than any of the individual blocks at the same concentration, demonstrating diblock copolymer formation. A further η_{sp} increase upon addition of the hydrogen-bonding **HW-PIC** indicates that a higher molecular weight species had indeed formed: this further supports the formation of supramolecular triblock copolymers.

CD spectroscopy was performed to characterize structures of the two helical blocks and the extent to which the helical blocks maintained their optical activity after supramolecular assembly in solution. All CD spectra were obtained at 25 °C, in DCE at a constant concentration. The coil-like poly(styrene) backbone possesses no inherent chirality so it does not preferentially absorb right or left circularly polarized light, resulting in a flat CD trace (Figure S14). As shown in Figure 5, the CD trace of heterotelechelic **Pyr-PMAC-Ba** block is similar to the monotelechelic **Ba-PMAC** helical polymers, with a characteristic large negative Cotton effect at 225 nm and two Cotton effects at 245 and 290 nm.¹⁹ This indicates that the post-polymerization reaction does not affect the helicity of the polymer backbone. Additionally, the CD pattern of a 1:1:1 triblock copolymer was compared to the two helical homopolymers at the same concentration. **HW-PIC** displays characteristic CD signals at around 250 nm and 360 nm correlating to $n - \pi^*$ transitions of C=N in the polymer backbone and $\pi - \pi^*$ transitions of aromatic rings on the side chains, respectively.²³ The CD spectrum of the 1:1:1 triblock copolymer shows patterns of both the PIC and PMAC backbones. In particular, the peaks at 225 nm and 285 nm in the triblock copolymer are approximately the sum of contributions from both PIC and PMAC homopolymers. These results suggest that helical structures of **Pyr-PMAC-Ba** and **HW-PIC** building blocks are retained in the assembled triblock.

Conclusions

In summary, we report the synthesis of a heterotelechelic helical polymer capable of participating in orthogonal supramolecular assemblies, resulting in the formation of a main-chain triblock copolymer. With a monotelechelic, Ba-functionalized helical PMAC polymer in hand, we utilized a versatile thiol-bromo “click” reaction to introduce a pyridine functionality to the other end through post-polymerization treatment. This new heterotelechelic helical block and two polymers with complementary molecular recognition motifs were then chosen to fabricate a supramolecular coil-helix-helix triblock copolymer. Stepwise supramolecular assembly was achieved through metal coordination and hydrogen bonding and successful triblock copolymer formation was substantiated by ^1H NMR spectroscopy, ITC and viscometry. CD spectroscopy revealed that the two helical building blocks retained their distinctive helical structure after the assembly process. We view

this synthetic system as an expansion of our platform of multicomponent assemblies featuring well-defined unique 3D architectures, and a potential route for developing complicated multifunctional polymeric ensembles.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

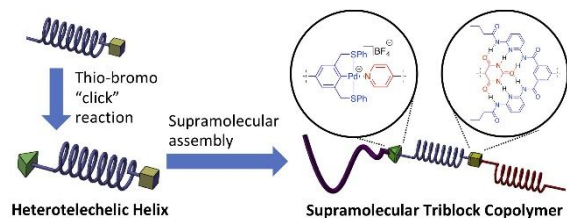
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Table of Contents Entry

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