

Supramolecular ABC Triblock Copolymers via One-Pot, Orthogonal Self-Assembly

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Abstract: A heterotelechelic poly(norbornene imide) containing two terminal and orthogonal hydrogen-bonding receptors, *N,N*-bis[6-(alkanoylamino)pyridin-2-yl] isophthalamide (often referred to as the Hamilton receptor or Wedge) and 2,7-diamido-1,8-naphthyridine (DAN), at the opposite ends of the polymer was synthesized via ring-opening metathesis polymerization (ROMP) through the employment of a Hamilton receptor-functionalized ruthenium initiator and a DAN-based chain-terminator. In parallel, two monotelechelic polymers containing either cyanuric acid (CA)- or ureidoguanosine (UG)-end groups that are complementary to the hydrogen-bonding receptors along the poly(norbornene imide) were synthesized either also via ROMP by terminating the polymerization of norbornene octyl ester with a CA-based chain-terminator or by the reaction of poly(ethylene oxide) with UG. Complete incorporations of the hydrogen-bonding receptors at the chain-ends of all polymers were confirmed by ¹H NMR spectroscopy. The telechelic polymers can be self-assembled into ABC triblock copolymers following either a stepwise or a one-pot, orthogonal self-assembly protocol. The self-assembly process was monitored by ¹H NMR spectroscopy, revealing full orthogonality of the two recognition pairs, Hamilton receptor–CA and DAN–UG. The resulting supramolecular ABC triblock copolymers were further characterized by a series of methods including 2-D NOESY, isothermal titration calorimetry, and viscometry, proving that the two orthogonal hydrogen-bonding interactions are strong enough to hold the three polymer chains together. We suggest that a self-assembly methodology solely based on the fully orthogonal hydrogen-bonding recognition motifs will allow for an easy and rapid synthesis of architecturally controlled supramolecular polymeric assemblies with a high degree of complexity.

Introduction

Block copolymers, as a result of their tunable phase separation behavior, are key building blocks for a variety of functional nanostructured materials with potential applications ranging from electronic devices to drug delivery.¹ In particular, triblock copolymers have been identified as important components for the fabrication of highly functionalized nanomaterials.² As compared to AB diblock copolymers, the presence of three different polymer blocks in an ABC triblock copolymer allows for the incorporation of additional functionalities as well as a greater variety of tunable morphologies in thin films and in

solution.^{2,3} For example, one of the blocks can be sacrificed to generate novel porous structures, while the other two can be used to introduce two distinct functionalities, affording bifunctional core-hollowed nanospheres for potential applications in tandem catalysis.⁴ Clearly, ABC triblock copolymers serve as useful building blocks for the creation of higher order vesicle or micelle-type structures.

The material properties of block copolymers can be tuned by introducing noncovalent interactions in place of covalent linkages between polymeric blocks resulting in the formation of supramolecular block copolymers. Such materials combine the phase separation behavior inherent to block copolymers with the responsiveness of supramolecular materials, thereby affording dynamic and reversible, that is, “smart” materials.^{5–7} This new class of block copolymers is prepared by the main-chain self-assembly of different, sometimes incompatible, polymers

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with complementary recognition units at their chain-ends. Despite the importance of ABC triblock copolymers, the vast majority of examples in the literature focuses on AB diblock and $(AB)_n$ multiblock copolymers assembled from corresponding monotelechelic and ditelechelic polymers.^{6,7} We reported recently the first example of a supramolecular ABC triblock copolymer.⁸ We suggest that the main reason for the lack of examples of supramolecular ABC triblock copolymers is the difficulty in preparing a well-defined heterotelechelic polymer that displays two different recognition moieties at its polymer ends thereby functioning as the middle B block. Heterotelechelic building blocks are typically prepared by postpolymerization functionalization, often resulting in nonquantitative conversions and requiring reaction conditions that may be incompatible with other functionalities on the polymer. Thus, the introduction of two different, orthogonal functionalities at the two ends of a polymer is nontrivial.^{7d}

In our initial report on supramolecular ABC triblock copolymers, we described the synthesis of a heterotelechelic polymer in a single step without any postpolymerization modification and demonstrated its stepwise self-assembly with complementary telechelic polymers to obtain a supramolecular ABC triblock copolymer. The noncovalent interactions employed were Hamilton receptor–cyanuric acid hydrogen bonding⁹ and palladated pincer–pyridine metal coordination.¹⁰ However, due to the incomplete orthogonality between the hydrogen bonding and metal coordination interactions used, the triblock copolymer could be self-assembled only by following a particular sequence beginning with the hydrogen bonding and ending with the metal coordination. In this contribution, we overcome this limitation by reporting the first supramolecular ABC triblock copolymer that has fully orthogonal recognition motifs, allowing for the realization of a one-pot methodology for triblock copolymers.

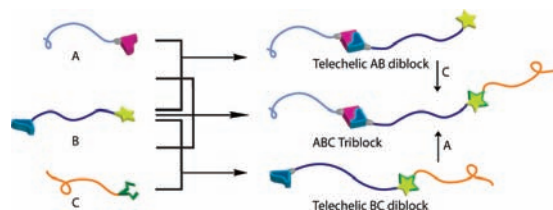


Figure 1. Schematic representation of a library of AB, BC, and ABC block copolymers from a pool of mono- and heterotelechelic polymers.

Our strategy also allows for the attachment of either telechelic polymer (A or C block) to the middle B block first followed by the other giving rise to a library of block copolymer materials with functional chain-ends (Figure 1). This unique combination of orthogonal noncovalent interactions within a single polymeric system represents an excellent tool for the synthesis of a new class of architecturally controlled supramolecular block copolymers.

Results and Discussion

For the realization of a modular synthesis of supramolecular ABC triblock copolymers, the selection of recognition motifs is crucial. All noncovalent recognition motifs must meet several criteria. First, the noncovalent interactions must have association constants that are high enough to hold the polymeric chains together; that is, they need to overcome the tendency of polymer mixtures to phase separate. Second, the noncovalent interactions must be highly specific; that is, they must be completely orthogonal to each other. Over the past decade, we and others started to investigate orthogonal recognition pairs in polymer chemistry.¹¹ While we reported a number of noncovalent interactions that can be used for orthogonal side-chain functionalization, we concentrate our focus in this contribution on the use of two hydrogen-bonding motifs. Hydrogen bonding has a number of advantages over other noncovalent interactions such as Coulombic charges and coordination chemistry including the easy tunability of hydrogen-bond strength in solution through the use of different solvents, the temperature dependence of hydrogen bonding allowing for temperature sensitive material, and the possibility of mix-and-match supramolecular chemistry, that is, no need for the addition of activators or counterions.¹² We selected two distinct hydrogen-bonding motifs that fulfill all of the requirements described above: (i) the Hamilton receptor–cyanuric acid (Wedge–CA) recognition pair and (ii) the diamidonaphthyridine–ureidoguanosine (DAN–UG)¹³ recognition pair (Figure 2). The synthetic as well as the supramolecular chemistries of these two recognition pairs have been well established.^{9,13} Both pairs display high association constants ($K_a \approx 10^5 \text{ M}^{-1}$ for Wedge–CA and $K_a \approx 10^7 \text{ M}^{-1}$ for DAN–UG) in halogenated solvents as well as very low self-association constants.^{9,13} Furthermore, both recognition pairs have been employed previously for the synthesis of supramolecular homotelechelic polymers.^{7b,e}

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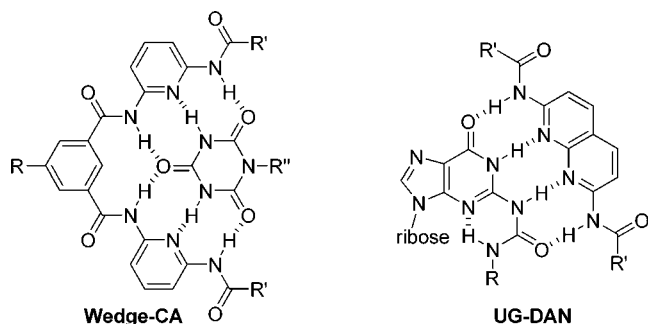


Figure 2. Complementary hydrogen-bonding pairs employed.

The orthogonality of these two recognition pairs, however, has not been demonstrated. We hypothesize that the two recognition events could be independent of each other. This is based on the fact that the patterns of the two hydrogen-bonding arrays are completely different from each other. The “wedge” displays a sextuple DAD–ADA pattern, whereas the DAN–UG interaction is based on a quadruple DAAD–ADDA hydrogen-bonding array. Thus, any undesirable interactions between the Wedge–CA and DAN–UG recognition pairs should be weak.

To investigate the orthogonality of the Wedge–CA and DAN–UG pairs, we synthesized their small molecule analogues: hexyloxy-substituted Hamilton receptor (sWedge),^{9f} dibutylbarbiturate (sCA),¹⁴ 2,7-bis(2-ethylhexanamido)-1,8-naphthyridine (sDAN),¹⁵ and acetyl-protected ureidoguanosine (sUG)^{13b} (see the Supporting Information) according to previously published procedures. We then carried out self-assembly studies with these compounds. We added to a mixture of the sDAN and sWedge in CD₂Cl₂ their respective complementary recognition units, sUG and sCA, and monitored the shifts of the NH protons of the two recognition pairs using ¹H NMR spectroscopy (Figure S5). First, upon the addition of 1 equiv of sUG to a mixture of 1 equiv each of sDAN and sWedge, the ¹H NMR spectrum (Figure S5C) of the sDAN–sUG complex revealed a strong shift of the amide protons (H_c) of the sDAN from 8.81 to 10.85–11.42 ppm as well as new proton signals of the complexed sUG at 9.06 (H_f), 11.54 (H_d), and 13.64 ppm (H_e). Subsequently, the addition of 1 equiv of sCA to a mixture of sWedge and the sDAN–sUG complex resulted in strong shifts of the amide protons (H_a and H_b) of the sWedge from 8.68 and 8.02 ppm to 9.78 and 9.47 ppm, respectively (Figure S5D). Furthermore, a new proton signal of the bound sCA at 12.38 ppm (H_g) was observed in the ¹H NMR spectrum. The signals of the sDAN–sUG complex at 9.06 (H_f), 10.85–11.42 (H_c), 11.54 (H_d), and 13.64 ppm (H_e) were unchanged, indicating that the sDAN–sUG complex is unaffected by the sWedge–sCA hydrogen-bonding event. These results demonstrate the orthogonality of both hydrogen-bonding interactions, that is, no interfering hydrogen-bonding interactions between the two individual recognition pairs. The orthogonal nature of the Wedge–CA and DAN–UG pairs was further supported by isothermal titration calorimetry (ITC) experiments on the noncomplementary sWedge–sUG, sWedge–sDAN, sCA–sUG, and sCA–sDAN pairs. Hydrogen-bonding interactions between these noncomplementary receptors were found to be negligible (Figure S6). Therefore, the Wedge–CA and DAN–UG recog-

nition pairs can be used for the self-assembly of telechelic polymers to form supramolecular ABC triblock copolymers.

After establishing the orthogonal character of the two recognition pairs, we designed a series of polymers that would allow for the formation of supramolecular ABC triblock copolymers. The most challenging part in the ABC triblock copolymer design is the middle block, the B block, because this block has to have two different hydrogen-bonding receptors at the chain-ends. We decided to use the Hamilton and DAN-receptors for the chain-ends of the B block and CA- and UG-terminated monotelechelic polymers as the A and C blocks.

Ring-opening metathesis polymerization (ROMP)¹⁶ is the preferred synthetic methodology for the preparation of the telechelic polymers. ROMP often polymerizes norbornene derivatives in a living fashion, and the living polymer can be terminated with functionalized chain-terminators (CTs) to install any desired functionality to the polymer chain-end.¹⁷ We have reported the synthesis of recognition motif-functionalized vinyl ethers as CTs and have demonstrated the fabrication of telechelic poly(norbornene)s in a single step.^{7i,8}

To incorporate a cyanuric acid motif at the chain-end of a polymer, cyanuric acid-containing CT **1** was synthesized by reacting 6-chloro-1-hexenyl methyl ether with cyanuric acid (Scheme 1). The second chain-terminator **5** is based on a DAN-functionalized symmetrical *cis*-olefin. In ROMP, internal *cis*-olefins have been used widely as chain-transfer agents (CTAs) to afford symmetrical telechelic polymers by secondary metathesis.¹⁸ When polymer repeat units are too bulky to undergo secondary metathesis, a *cis*-olefin can act instead as a chain-terminator to produce the monotelechelic polymer.¹⁹ DAN-based CT **5** was designed, and its synthetic pathway is outlined in Scheme 1.^{7f} The synthetic strategy starts with the reaction of dicarboxylic acid **3** with thionyl chloride to yield the corresponding diacyl chloride, which was subsequently converted to diamide **4** using concentrated ammonia. DAN-CT **5** was then obtained by Pd-catalyzed amidation of 7-amido-2-chloro-1,8-naphthyridine **2** with **4** in 1,4-dioxane.¹⁵

Preparation and Characterization of the Telechelic Polymers.

Unsymmetrically end-functionalized polymers can be prepared in a single step using ROMP when the polymerization is initiated with a recognition motif-functionalized ruthenium initiator followed by the termination of the polymerization with a recognition motif-functionalized CT. We have recently reported the Hamilton receptor-functionalized ruthenium initiator **9** that is not only active toward ROMP of norbornenes but affords living polymerizations of functionalized norbornenes as well, allowing for the preparation of the heterotelechelic poly(norbornene)s through the combination with a functionalized CT.⁸ Sterically bulky *tert*-butyl ester norbornene imide monomer (tBENI) **7** was chosen as the backbone of the middle block for the ABC triblock copolymer.¹⁹ With initiator **9** and CT **5** in hand, ROMP of **7** was carried out in CH₂Cl₂ with a M:I ratio of 20:1. After the polymerization was complete as evidenced by NMR spectroscopy, an excess of CT **5** was added to afford

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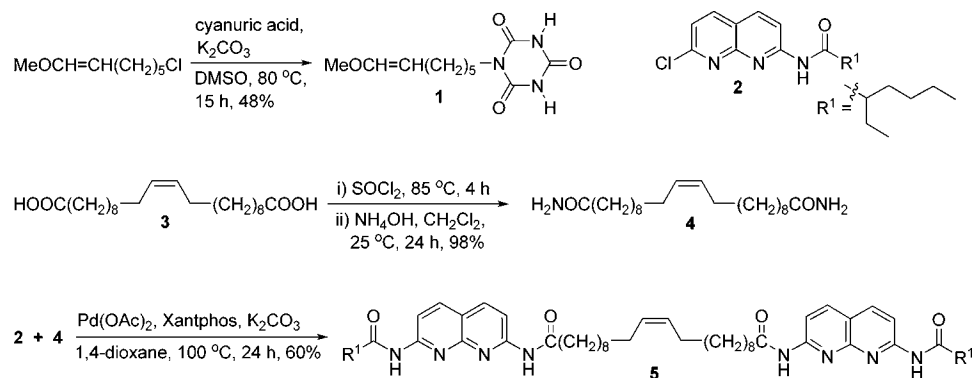
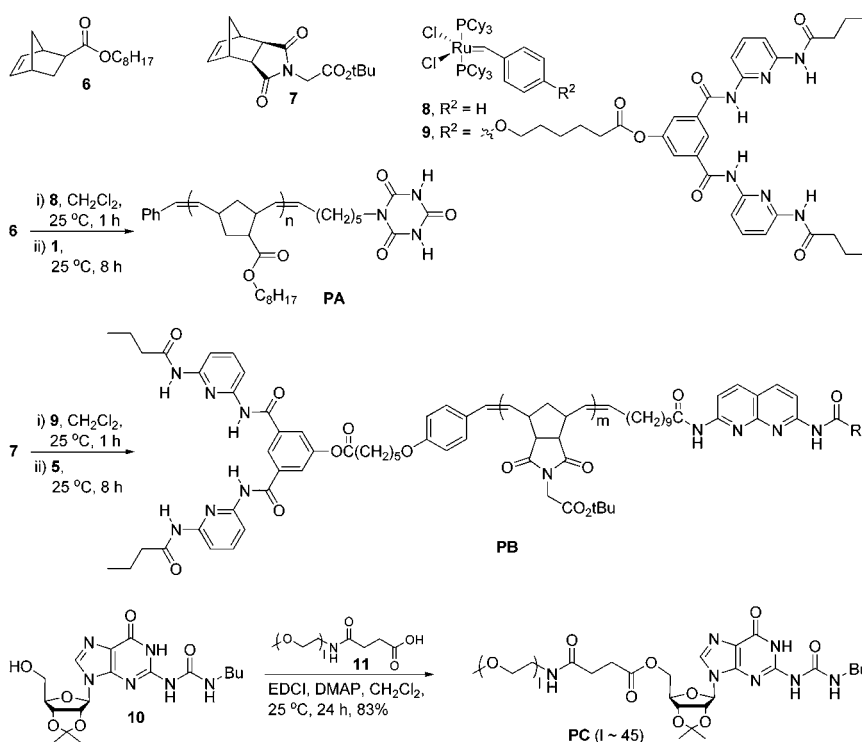
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Scheme 1. Synthesis of CTs **1** and **5**Scheme 2. Synthesis of Telechelic Polymers **PA**, **PB**, and **PC**

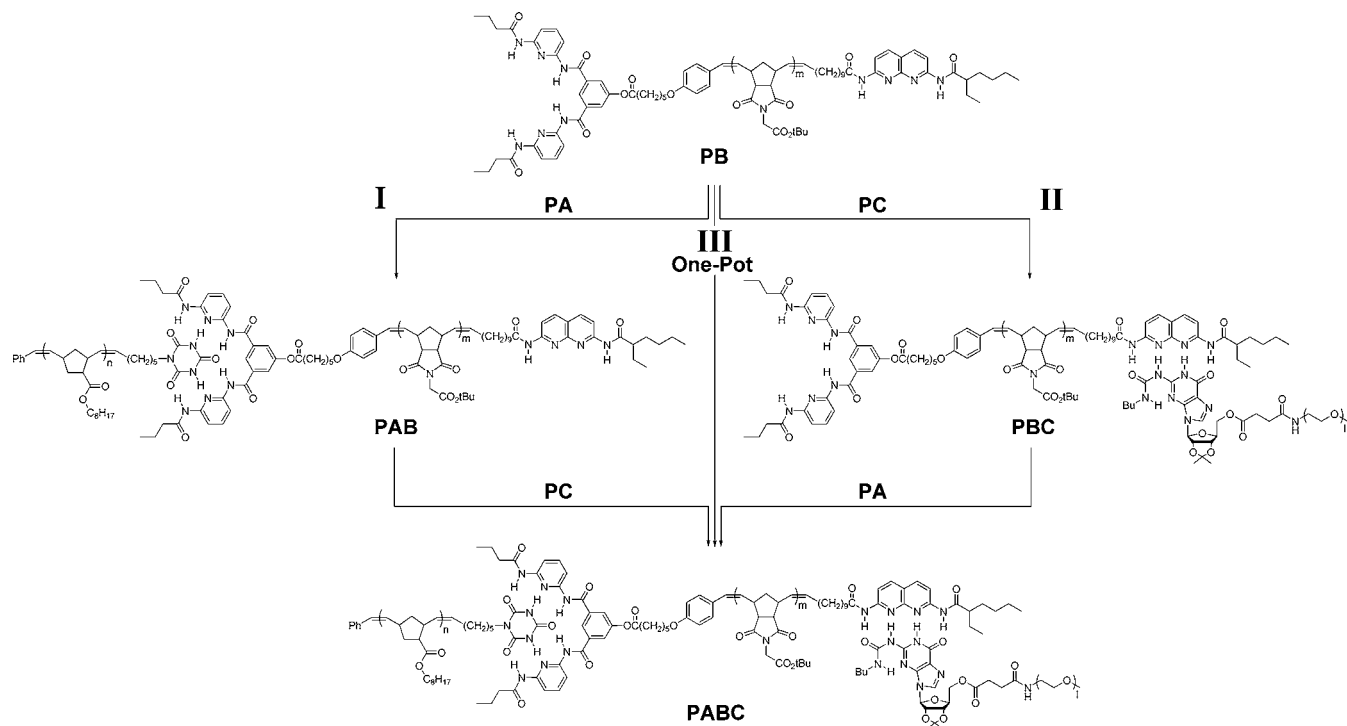
the targeted heterotelechelic polymer **PB** (Scheme 2). Complete initiation and termination were observed for the ROMP by ^1H NMR spectroscopy, demonstrating, within the error range of NMR spectroscopy, complete incorporation of both end group functionalities in the polymer. The ^1H NMR spectrum of **PB** showed all characteristic signals for the Hamilton receptor and DAN moieties consistent with those observed in both small molecule analogues, indicating no interference, that is, no hydrogen bonding, of the two recognition motifs with each other. The molecular weight and polydispersity index (PDI) of **PB** were determined by gel-permeation chromatography (GPC) (reported vs poly(styrene) standards). The number average molecular weight (M_n) of **PB** is 6500, while the PDI is 1.75.

After the successful synthesis of the central heterotelechelic poly(norbornene imide) **PB**, a homotelechelic CA-terminated poly(norbornene ester) **PA** and a homotelechelic UG-functionalized poly(ethylene oxide) (UG-PEO) **PC** were synthesized that are designed to serve as blocks A and C for our ABC triblock copolymer design. Thus, all three blocks for the target triblock copolymer consist of different polymer backbones. The monotelechelic polymer **PA** was synthesized by ROMP of

norbornene octyl ester **6** with 5 mol % of Grubbs' first-generation initiator **8** in CH_2Cl_2 , followed by termination with CT **1** (Scheme 2). Complete termination of the ROMP was observed by the disappearance of the polymeric carbene signal at 18.6 ppm in the ^1H NMR spectrum, allowing for quantitative end-functionalization based on NMR evidence. The number average molecular weight (M_n) and PDI of the polymer are 6500 and 1.30, respectively (reported vs poly(styrene) standards). UG-PEO **PC** was prepared by EDCI-mediated esterification of commercially available carboxylated PEO **11** ($l \approx 45$) with UG **10** in CH_2Cl_2 (Scheme 2).^{13b}

ABC Triblock Copolymer Formation via Self-Assembly. With all three polymeric building blocks in hand, we investigated the formation of block copolymers via hydrogen bonding. The self-assembly behavior of **PB** with **PA** and **PC** was examined following two distinct strategies: first, in a stepwise fashion, that is, the addition of two building blocks followed by the third one, and then a one-pot, orthogonal self-assembly approach. All three strategies are outlined in Scheme 3.

First, we explored the formation of the PABC triblock copolymer via the stepwise strategies. We followed two distinct

Scheme 3. ABC Triblock Copolymer Formation through Stepwise and One-Pot Self-Assembly

routes: one beginning with hydrogen bonding between the Hamilton receptor and CA followed by DAN–UG hydrogen bonding (Scheme 3I) and the other following the reverse order (Scheme 3II). Both of these routes can be followed by monitoring characteristic changes in the chemical shifts of the NH protons of the two recognition pairs using ^1H NMR spectroscopy. Figure 3 displays the ^1H NMR spectra of the stepwise self-assembly strategies.

Figure 3A–C shows the ^1H NMR spectra for the stepwise self-assembly of **PB** by route I. Upon the addition of 1 equiv of **PA** to **PB** (the ^1H NMR spectrum of the central **PB** block is shown in Figure 3C), the diblock copolymer **PAB** is formed. The ^1H NMR spectrum (Figure 3B) of **PAB** reveals strong shifts of the amide protons (H_a and H_b) of the Hamilton receptor from 8.82 and 8.07 ppm to 9.78 and 9.28 ppm, respectively. Furthermore, a new signal appears at 12.97 ppm (H_g) that corresponds to the bound cyanuric acid unit. Notably, no change in the signal at 8.19 ppm for the two amide protons of the DAN moiety (H_c) was observed, demonstrating that these amide protons do not take part in any hydrogen bonding. Subsequently, the addition of 1 equiv of **PC** to **PAB** (Figure 3A) resulted in a strong shift of the amide protons (H_c) of the DAN from 8.19 ppm to 11.58–12.32 ppm. Although the amide protons of DAN are not chemically equivalent, they appear as a single, slightly broad signal at 8.19 ppm. Upon complexation with UG protons, however, they appear as two separate broad signals between 11.58 and 12.32 ppm. These two signals can be assigned clearly to the two amide protons with the help of 2-D nuclear Overhauser effect spectroscopy (NOESY) experiments (see below). In addition, the signals of the Wedge–CA heterocomplex at 9.28 (H_b), 9.78 (H_a), and 12.97 ppm (H_g) are unchanged, while new proton signals of the complexed UG at 9.26 (H_f), 11.56 (H_d), and 13.67 ppm (H_e) are observed in the ^1H NMR spectrum. This demonstrates that the CA–Hamilton wedge complex is unaffected by the UG–DAN hydrogen-bonding event and suggests the formation of the target triblock copolymer

PABC. All characteristic signals observed for the Wedge–CA and UG–DAN hydrogen bonding are consistent with those reported above in our small molecule study and previously in the literature.^{9,13} These results demonstrate selective self-assembly of **PB** with **PA** and **PC** via the stepwise route I, resulting in the successful formation of the supramolecular ABC triblock copolymer **PABC**.

The formation of **PABC** through the stepwise route II was also investigated using ^1H NMR spectroscopy (Figure 3C–E) and compared to stepwise route I. Upon the addition of 1 equiv of **PC** to **PB** (Figure 3C), the same characteristic shifts (H_{c-f}) for the hydrogen bonding between the DAN–UG moieties were observed (Figure 3D) as those described above for stepwise functionalization route I. No change in the NMR signals of the amide protons (H_a and H_b) for the unbound Hamilton receptor was observed (Figure 3D), demonstrating the perfect orthogonality of the DAN–UG complex in the presence of the Hamilton receptor. Subsequently, the addition of 1 equiv of **PA** to **PBC** allowed for the formation of the ABC triblock copolymer **PABC**. The ^1H NMR spectrum of **PABC** formed via stepwise route II (Figure 3E) is identical to that in Figure 3A from stepwise route I. Thus, these ^1H NMR experiments demonstrate that the ABC triblock copolymer can be self-assembled starting from either chain-end of the B block and illustrate the versatility of our design.

Hydrogen-bonding complexes with high association constants are the key to the successful formation of hydrogen-bonding-based ABC triblock copolymers. Therefore, it is necessary to quantify the strengths of the hydrogen-bonding interactions. To elucidate the interaction strength, the formation of **PABC** via the stepwise self-assembly was investigated by ITC. Figure 4A,B and C,D shows the binding isotherms for the stepwise self-assembly via routes I and II, respectively. Association constants (K_a) for all stepwise self-assembly steps were determined by using a single-site binding model. The K_a for the CA–Wedge hydrogen bonding between **PA** and **PB** or **PBC** was found to

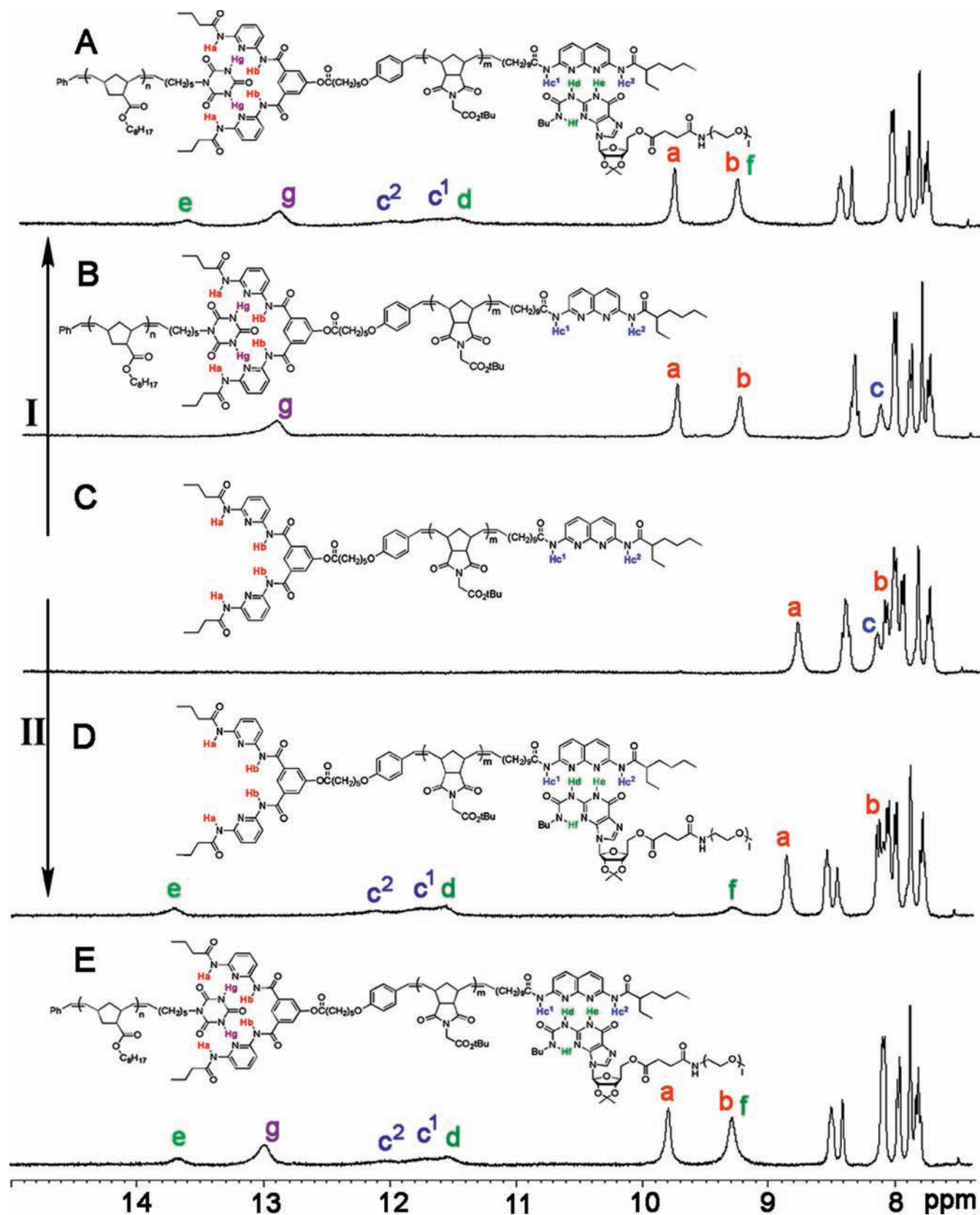


Figure 3. Partial ^1H NMR spectra representing the stepwise self-assembly of **PB** with **PA** and **PC** in CDCl_3 at 25°C (5 mM). ^1H NMR spectrum of (A) **PABC**, (B) **PAB**, (C) **PB**, (D) **PBC**, and (E) **PABC**.

be $(1.5 \times 10^4) \pm 5\%$ and $(1.4 \times 10^4) \pm 7\% \text{ M}^{-1}$, respectively, while the K_a for the UG–DAN hydrogen bonding between **PC** and **PB** or **PAB** was determined to be $(2.0 \times 10^4) \pm 5\%$ and $(1.7 \times 10^4) \pm 4\% \text{ M}^{-1}$, respectively. These K_a values for either

the UG–DAN or the CA–Hamilton receptor hydrogen-bonding events are similar irrespective of the self-assembly route followed, which is in perfect agreement with the ^1H NMR experiments. Furthermore, the K_a values for the CA–Wedge

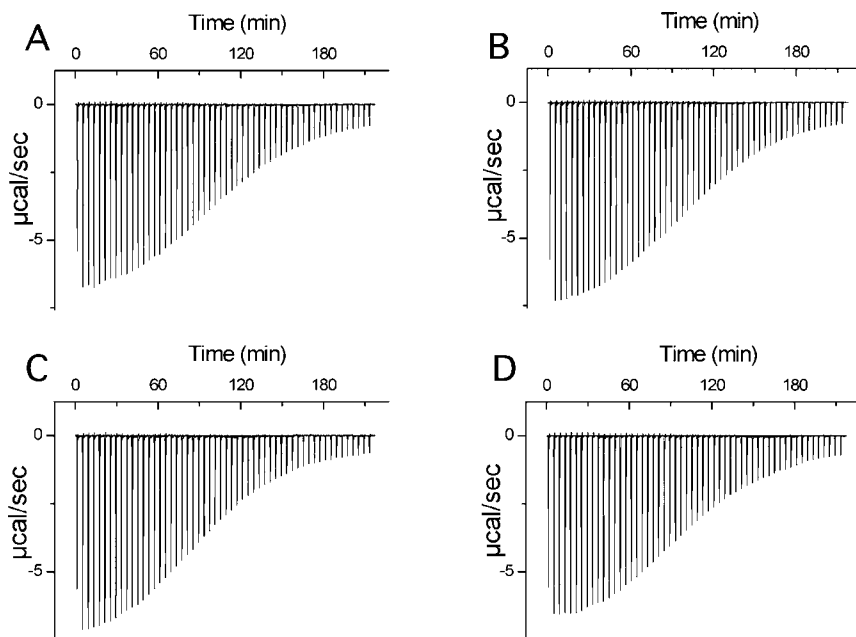


Figure 4. ITC binding isotherms for (A) PA–PB, (B) PC–PAB, (C) PC–PB, and (D) PA–PBC hydrogen bonding in CHCl_3 at 30 °C.

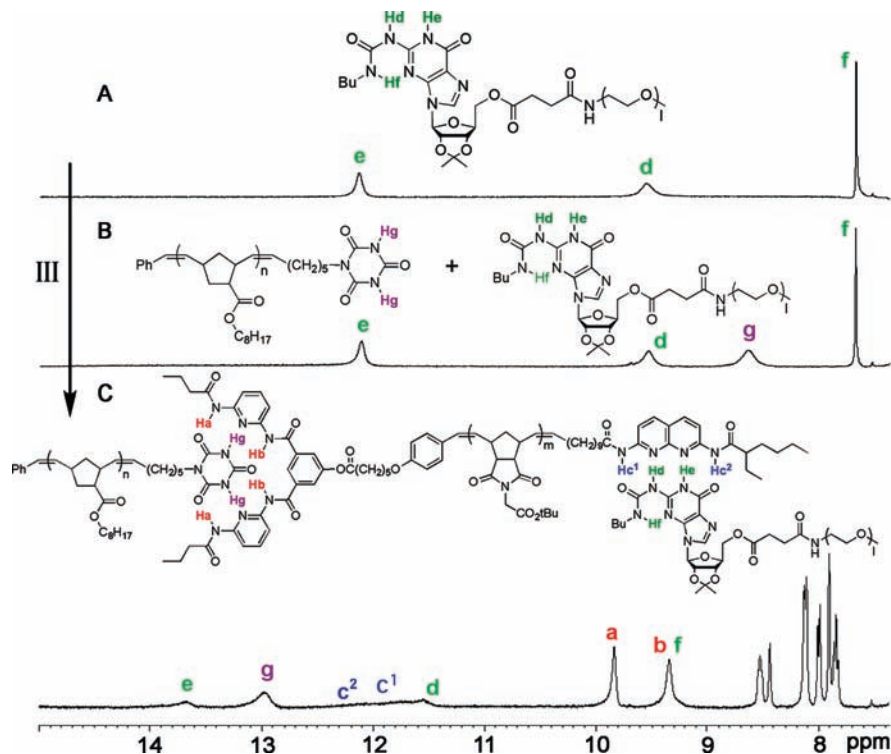


Figure 5. Partial ^1H NMR spectra representing the one-pot self-assembly of **PB** with **PA** and **PC** in CDCl_3 at 25 °C (5 mM). (A) **PC**, (B) a mixture of **PA** and **PC** at a 1:1 ratio, and (C) **PABC**.

recognition event are comparable to other polymeric CA–Wedge interactions reported in the literature.^{6f,7b,8} The shapes of all of the binding isotherms are also indicative of a strong interaction.

We next investigated our main goal, the preparation of the supramolecular ABC triblock copolymer via the one-pot self-assembly between two orthogonal hydrogen-bonding recognition pairs. We added 1 equiv of **PB** to a mixture of 1 equiv each of **PA** and **PC** in CDCl_3 at room temperature. The self-assembly was followed by ^1H NMR spectroscopy in close analogy to the above-described stepwise routes (Figure 5). Figure 5A shows

the ^1H NMR spectrum of **PC**, while Figure 5B shows the ^1H NMR spectrum of a 1:1 mixture of **PA** and **PC** (for clarity, the spectra are only shown from 7.3 to 15 ppm). Initially, no shifts in the ^1H NMR spectrum for either **PA** or **PC** are observed (for example, as can be seen in Figure 5, the signals corresponding to H_e and H_d did not change from Figure 5A to B), suggesting no interactions between the two hydrogen-bonding motifs, CA and UG. Upon the addition of 1 equiv of **PB** to the mixture, the supramolecular triblock copolymer **PABC** is generated in a single step. The ^1H NMR spectrum of **PABC** revealed all

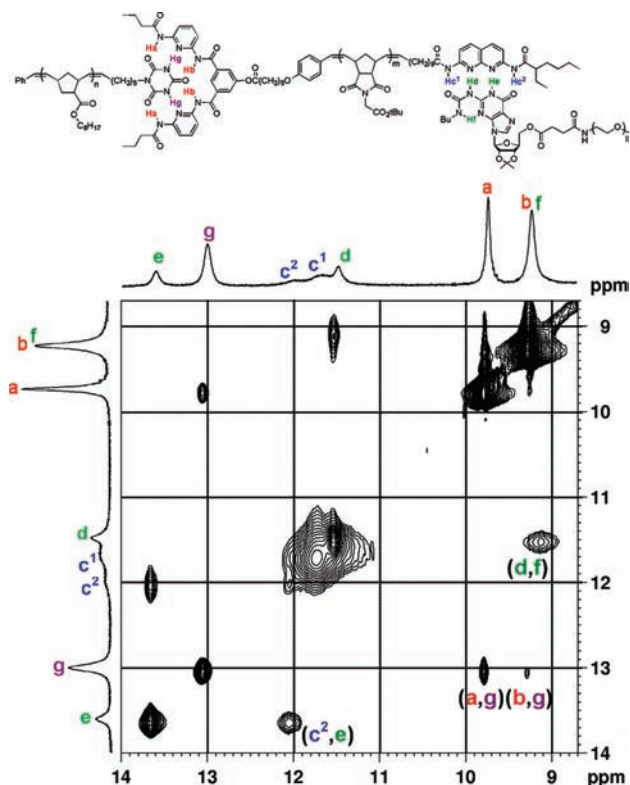


Figure 6. Partial 2-D NOESY spectrum (from 8.7 to 14 ppm) of **PABC** in CDCl_3 at 25 °C using 300 ms mixing time.

characteristic downfield shifts for the two recognition pairs: (1) CA (H_g , 8.63 ppm to 12.97 ppm) and the Hamilton receptor (H_a and H_b , 8.82 and 8.07 ppm to 9.81 and 9.31 ppm, respectively), and (2) DAN (H_c , 8.19 ppm to 11.58–12.32 ppm) and UG (H_e , H_d , and H_f , 12.11, 9.52, and 7.67 ppm to 13.67, 11.56, and 9.28 ppm, respectively) (Figure 5C).

The final ^1H NMR spectrum of **PABC** by this one-pot process (Scheme 3III) is identical to those obtained via the stepwise routes I and II, suggesting that the fully supramolecular polymeric materials are identical, independent of the chosen self-assembly route. Thus, ^1H NMR spectroscopy provides strong evidence for the formation of the supramolecular ABC triblock copolymer **PABC** via three different routes mediated by two strong and selective binding events between the complementary recognition units.

In addition to 1-D ^1H NMR spectroscopy, 2-D NOESY was used to study the two orthogonal hydrogen-bonding interactions involved in the formation of **PABC**. The NOESY spectrum of **PABC** generated by the one-pot process shows the signals for nuclear Overhauser effect interactions (NOEs) between the Hamilton receptor (H_a and H_b) and CA (H_g) protons, and between DAN (H_c) and UG (H_e) protons (Figure 6). The presence of NOE signals between “ H_d ” and “ H_f ” of UG and the absence of NOE signals between “ H_c ” and “ H_f ” show that UG is in a locked conformation (due to intramolecular hydrogen bonding) that allows the quadruple hydrogen-bonding recognition based on ADDA–DAAD pattern between UG and DAN. Furthermore, the two chemically unequivalent amide protons (H_{c1} and H_{c2}) of DAN can be clearly assigned with the help of NOESY spectrum. The NOE signals between “ H_{c2} ” and “ H_e ” of UG are clear enough for an unequivocal assignment that is consistent with the shown bonding pattern in DAN–UG complex. This result further indicates that the Hamilton receptor

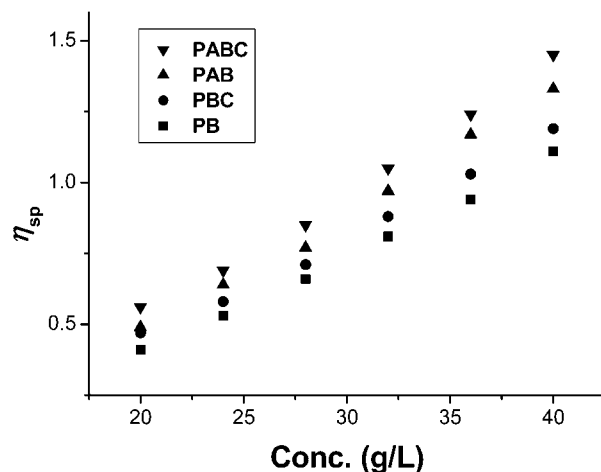


Figure 7. Plot of specific viscosity (η_{sp}) versus concentration for **PB** and block copolymers.

and DAN moieties of **PB** are indeed interacting through hydrogen-bonding recognition with CA unit of **PA** and UG unit of **PC**, respectively, resulting in the formation of **PABC**.

Upon the main-chain self-assembly through the complementary hydrogen-bonding motifs, the high molecular weight species of the resulting supramolecular block copolymers should possess higher solution viscosity as compared to that of their individual blocks. Thus, the self-assembled block copolymers in this study were characterized by measuring their solution viscosity. The viscosity studies were carried out using an Ubbelohde viscometer in CH_2Cl_2 at 25 °C, and the results are shown in Figure 7. The specific viscosity (η_{sp}) increases from **PB** to **PBC** to **PAB** to **PABC**, which correlates with an increase in the estimated molecular weights of the self-assembled block copolymers. For example, the molecular weight of **PBC** is lower than that of **PAB** because of the shorter PEO block, and hence its η_{sp} values are closer to those of **PB** than to those of **PAB**. As a control experiment, we carried out viscosity studies by employing **PB** and unfunctionalized analogues of **PA** and **PC** (**uPA** and **uPC**, respectively). The η_{sp} values of the mixture of **PB** with 1 equiv each of **uPA** and/or **uPC** were nearly the same as that of **PB** or even slightly lower (Supporting Information), suggesting that the increase in η_{sp} values is the direct result of the strong main-chain self-assembly between the constituent blocks. Therefore, in addition to ^1H NMR, 2-D NOESY, and ITC data, the solution viscosity results strongly suggest the formation of a supramolecular ABC triblock copolymer.

Conclusion

We have developed a one-pot methodology for the synthesis of supramolecular ABC triblock copolymers based on main-chain hydrogen bonding between telechelic polymers using two distinct and orthogonal hydrogen-bonding receptor pairs. The key step for this methodology is the successful preparation of a heterotelechelic polymer possessing two different hydrogen-bonding moieties at the chain-ends. This was accomplished in a single step using ROMP through the utilization of a functionalized ruthenium initiator and a functionalized chain-terminator. This strategy affords straightforward and near-quantitative incorporation of the two orthogonal recognition units into a single polymer chain. Self-assembly of the heterotelechelic polymer with monotelechelic polymers bearing complementary hydrogen-bonding motifs was achieved by both

stepwise and one-pot orthogonal self-assembly methodologies. The formation of the targeted supramolecular ABC triblock copolymer was substantiated by 1-D and 2-D ^1H NMR spectroscopy, ITC, and viscometry. The ^1H NMR spectra of the self-assembled polymers obtained in both the stepwise and the one-pot processes revealed that the final, fully self-assembled polymers are identical, independent of the chosen self-assembly routes, suggesting complete specificity and selectivity of each hydrogen-bonding interaction with its complementary recognition unit. It is noteworthy that the intermediate telechelic diblock copolymers are also useful building blocks for higher order supramolecular polymers with novel architectures.

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Supporting Information Available: Experimental procedures and characterization data for all new compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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