

Facile Preparation of Supramolecular H-Shaped (Ter)polymers via Multiple Hydrogen Bonding

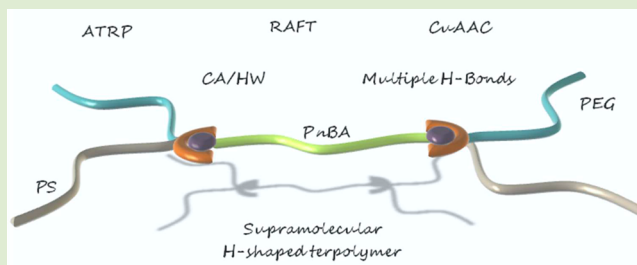
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Supporting Information

ABSTRACT: A well-defined Hamilton wedge (HW) mid-chain functionalized block copolymer, i.e., polyethylene glycol-*b*-polystyrene (PEG-HW-PS, $M_{n, GPC} = 5600$ Da, PDI = 1.03), was successfully synthesized via a combination of atom transfer radical polymerization (ATRP) and copper-catalyzed azide alkyne cycloaddition (CuAAC). An α, ω -cyanuric acid (CA) difunctional linear homopolymer poly(*n*-butylacrylate) (CA-PnBA-CA, $M_{n, GPC} = 8100$ Da, PDI = 1.09) was concomitantly prepared via reversible addition–fragmentation chain transfer (RAFT) polymerization. Supramolecular H-shaped macromolecules were—for the first time—prepared through supramolecular self-assembly between HW and CA recognition motifs to generate (PS-*b*-PEG)·PnBA·(PS-*b*-PEG) and (PS-*b*-PS)·PnBA·(PS-*b*-PS) in CH₂Cl₂ or dichloromethane-*d*₂ at ambient temperature. The self-assembly process (at a total concentration of the two species of close to 4.5 mM) was evidenced by proton nuclear magnetic resonance (¹H NMR) spectroscopy, diffusion-ordered NMR spectroscopy (DOSY), and dynamic light scattering (DLS) analyses. The results derived via DOSY NMR experiments and DLS combined with a Job plot analysis and in-depth NMR titration experiments indicate that the formation of supramolecular H-shaped macromolecules in 2:1 stoichiometry is efficiently occurring via the employed complementary recognition motifs with high binding constants (between 1.2 and 1.5 × 10⁵ L mol⁻¹ at ambient temperature).



Supramolecular polymers have received increasing attention in recent years due to their unique dynamic properties compared to conventional polymers, which ensure their potential application in a broad range of fields in chemistry, biology, and physics.¹ Supramolecular polymer chemistry employed in the realm of polymer science focuses on providing new complex polymeric materials through the incorporation of noncovalent interactions. These interactions offer a highly reversible, functional, and tunable strategy opposed to traditional polymers based on covalent bonds which are—in the majority of cases—often unidirectional and irreversible. Noncovalent interactions such as hydrogen bonding,² host–guest systems,³ metal–ligand coordination,⁴ and ionic interactions⁵ are extensively utilized to construct well-defined supramolecular architectures. Compared to alternative reversible noncovalent interactions characteristic for supramolecular chemistry, H-bonding has proven to be one of the most prominent supramolecular motifs, due to its ease of accessibility and strong binding constants.⁶ Moreover, hydrogen-bond-mediated self-assembly is a powerful strategy for complex macromolecular structure design that has been used to generate a variety of novel supramolecular materials through self-assembly of suitable polymeric building blocks such as block copolymers,⁷ graft polymers,⁸ star polymers,⁹ nanoparticles,¹⁰ and self-folding of single-chain synthetic polymeric systems.¹¹

Controlled/living radical polymerization (CLP) techniques have been extensively employed for the synthesis of well-defined polymers.¹² Especially atom transfer radical polymerization (ATRP) and reversible addition–fragmentation chain transfer (RAFT) polymerization are highly versatile and efficient controlled/living radical polymerization techniques, allowing for fine control over the macromolecular architecture, molecular weight and polydispersity of synthetic polymers.¹³ Combining these techniques with recent advances in modular and orthogonal polymer ligation protocols¹⁴ represents a powerful toolset which permits the synthesis of well-defined polymers with controlled functionality.

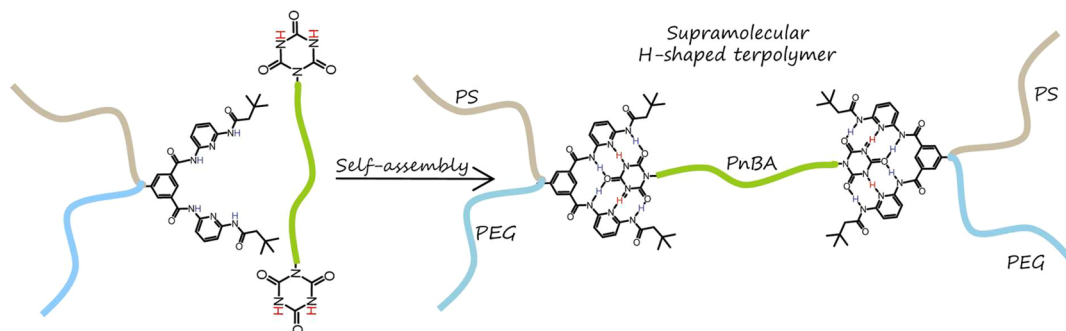
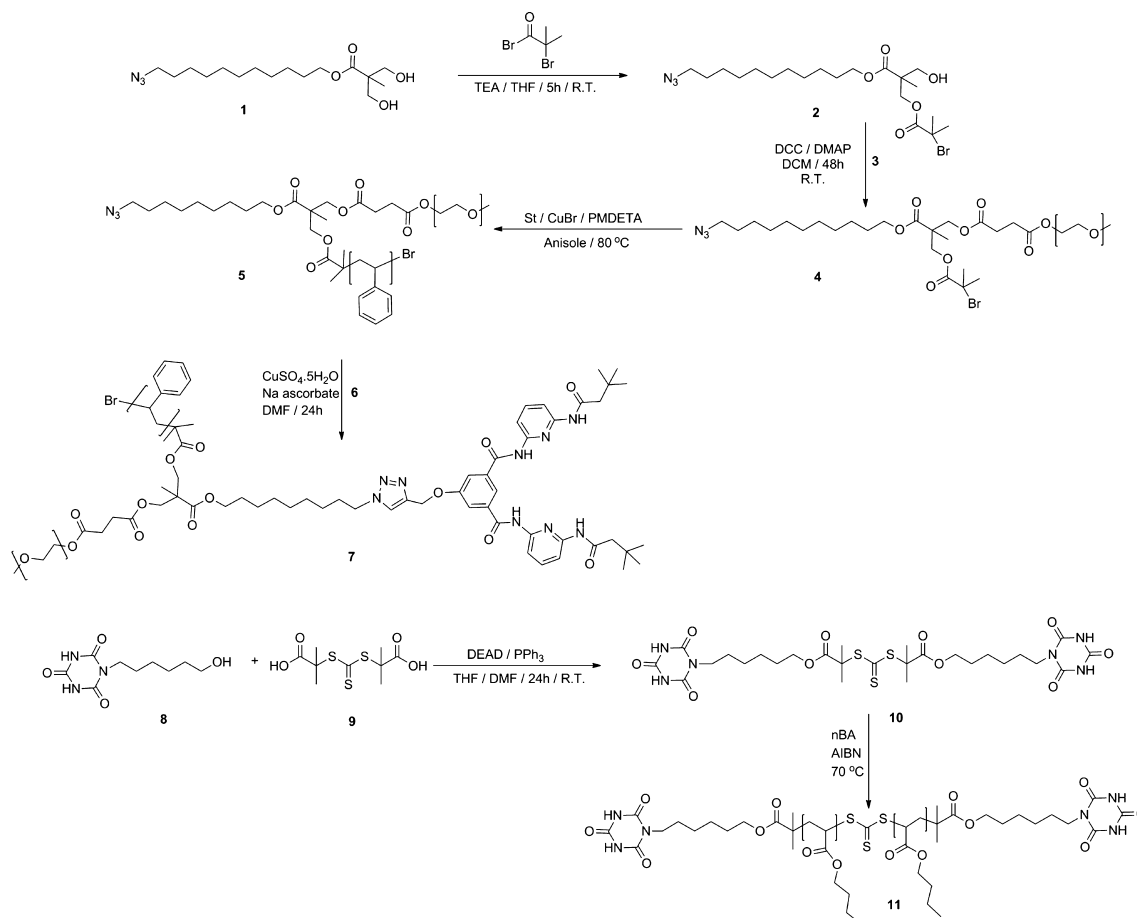
More recently, we reported examples of star and miktoarm star polymers using strong binding recognition motifs—specifically cyanuric acid (CA) and Hamilton wedge (HW)¹⁵ derivatives—through the combination of ATRP and Cu(I)-catalyzed azide alkyne cycloaddition (CuAAC) chemistry.^{9c} More recently, we have also demonstrated the construction of star-shaped macromolecules via nitroxide-mediated radical polymerization (NMP) and CuAAC coupled to supramolecular self-assembly.^{8c} In addition, we reported examples of the single-

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Scheme 1. General Strategy for the Preparation of Supramolecular H-Shaped (Ter)polymers

Scheme 2. Synthetic Strategy for the Preparation of Building Blocks with Complementary Recognition Motifs^a

^a(a) 2-Bromoisobutyrylbromide, TEA, and THF; (b) DCC, DMAP, DCM, MeO-PEG-COOH, 3; (c) styrene, CuBr, PMDETA, anisole, 80 °C; (d) CuSO₄·5H₂O, Na ascorbate, DMF, 6; (e) PPh₃, DEAD, THF, DMF; (f) AIBN, nBA, 70 °C.

chain self-folding of well-defined linear polymers carrying various orthogonal complementary recognition units at preselected positions within the polymer backbone, which emulate—on a simple level—the self-folding behavior of natural biomacromolecules.^{11a–c}

The preparation of H-shaped polymers via variable chemical design strategies is an interesting endeavor as this specialized architecture can be employed in the formation of micellar structures in solution—when amphiphilic designs are targeted—or nanophase separation in the solid state. Thus, efficient methodologies for their preparation, at best in a lego-like fashion, must be available. Consequently, significant research efforts have been made to achieve H-shaped copolymers with

various compositions, which are generated by combinations of CLP and modular ligation chemistries.¹⁶ However, to the best of our knowledge, there are no reports on supramolecular H-shaped terpolymers which have been prepared through noncovalent interactions. Herein—in a report that focuses on the chemical methodology—we describe a novel initiator molecule for ATRP carrying an azide and hydroxyl functionality as well as a novel chain transfer agent (CTA) bearing two cyanuric acid moieties for RAFT polymerization. HW mid-chain functionalized block copolymers and α,ω -CA functionalized linear polymers were prepared by ATRP/CuAAC and RAFT polymerization, respectively. Subsequently, we report—for the first time—the formation of supramolecular H-shaped

terpolymers using multiple hydrogen bonds in dichloromethane- d_2 which was successfully demonstrated by ^1H NMR spectroscopy (including NMR titration) as well as DOSY NMR experiments evidencing the stable and quantitative formation of H-shaped triblock copolymer structures (see Scheme 1). Furthermore, dynamic light scattering (DLS) was applied to evidence the self-assembly between the CA-bifunctional linear polymer and HW-functionalized block copolymer in CH_2Cl_2 at ambient temperature.

The current work focuses on the preparation of supramolecular H-shaped terpolymers through strong complementary multiple hydrogen bonds between Hamilton wedge (HW) mid-chain functionalized well-defined block copolymers and with α,ω -cyanuric acid (CA) functionalized well-defined linear polymer.

In this section, the preparation of Hamilton wedge functionalized block copolymer and cyanuric acid functional linear polymer are discussed. A HW mid-chain functionalized block copolymer (PEG-HW-PS), the HW mid-chain functionalized block homopolymer (PS-HW-PS, $M_{n,\text{GPC}} = 4600$ Da, PDI = 1.04, $M_{n,\text{NMR}} = 4200$ Da),^{9c} and an α,ω -CA end-functionalized block homopolymer PnBA (CA-PnBA-CA) were successfully prepared (see Scheme 2 and Scheme S1 in the Supporting Information (SI)) to serve as blocks for the H-shaped terpolymers. HW mid-chain functionalized well-defined block copolymers were prepared through a combination of atom transfer radical polymerization (ATRP) and Cu(I)-catalyzed azide alkyne cycloaddition (CuAAC). Initially, an azide and a hydroxyl functional ATRP initiator were synthesized via esterification of compound 1 with 2-bromoisobutyrylbromide in the presence of triethylamine (TEA) as a reagent and tetrahydrofuran (THF) as a solvent. The ^1H NMR spectrum of 2 indicates that the characteristic proton signals for the $\text{C}(\text{CH}_3)\text{CH}_2\text{OCO}$ and $\text{COC}(\text{CH}_3)_2\text{Br}$ are observed at 4.36 and 1.92 ppm, respectively (see Figure S1 and S2 in the SI). The ATRP macroinitiator 4 was obtained via esterification of 3 with PEG-COOH in the presence of DCC/DMAP.

The macroinitiator was purified via column chromatography, and its purity was determined by ^1H NMR and size exclusion chromatography (SEC). The ^1H NMR spectrum of 4 indicates that new signals associated with the PEG backbone and $\text{COCH}_2\text{CH}_2\text{CO}$ are observed at 3.58 and 2.55 ppm, respectively (see Figure S3 in the SI). Polymer 4 was employed as a macroinitiator for the ATRP of styrene in the presence of a CuBr/PMDETA complex system as a catalyst in anisole to yield polymer 5 ($M_n = 4400$ Da, PDI = 1.06) (see Figure S4 in the SI). Finally, utilizing CuAAC, PEG- N_3 -PS (5) and 6 were reacted to afford the corresponding PEG-HW-PS (7) in the presence of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and sodium ascorbate in DMF at ambient temperature. The ^1H NMR spectrum of 7 indicates that the resonances associated with CH_2N_3 of 5 have completely disappeared at 3.20 ppm, and new resonances associated with the CH_2 next to the triazole ring are observed at 4.31 ppm, indicating that the CuAAC reaction between 5 and 6 was quantitative (refer to Figure S5 in the SI). The number average molecular weight, M_n , of PEG-HW-PS was determined via SEC (molecular weight reported relative to PS standards) and—additionally—via ^1H NMR in CD_2Cl_2 via integration of the aromatic proton resonances of PS at 6.60–7.06 ppm, the proton resonances of PEG at 3.58 ppm, and the resonances next to the triazole ring (CH_2CH_2) at 4.31 ppm (refer to Figure S5 in the Supporting Information). The M_n of PEG-

HW-PS deduced via SEC and ^1H NMR reads 5600 and 5700 Da, respectively, indicating—within experimental error—a high end group fidelity. The number average molecular weights as well as the corresponding polydispersity values of all of the above compounds are collated in Figure 1.

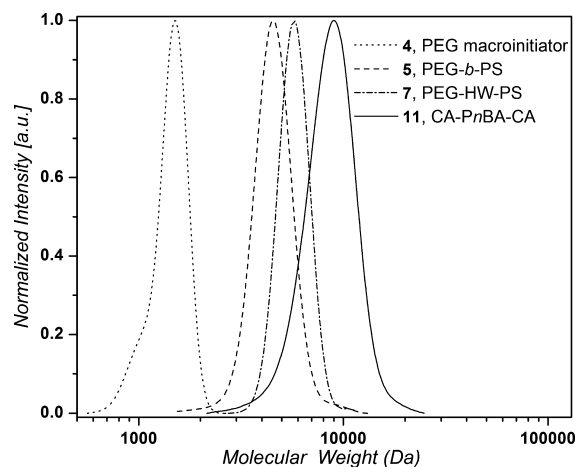


Figure 1. SEC traces of the precursor polymers: PEG macroinitiator (4, $M_{n,\text{GPC}} = 1400$ Da, PDI = 1.04), PEG-*b*-PS (5, $M_{n,\text{GPC}} = 4400$ Da, PDI = 1.06), PEG-HW-PS (7, $M_{n,\text{GPC}} = 5600$ Da, PDI = 1.03), CA-PnBA-CA (11, $M_{n,\text{GPC}} = 8100$ Da, PDI = 1.09, using Mark–Houwink parameters (MHKS) parameters for poly(*n*-butyl acrylate).

Well-defined linear polymers with α,ω -CA functionalities were prepared by RAFT polymerization. The esterification was successfully carried out between the diacid functionalized chain transfer agent (CTA) and hydroxyl functionalized CA via a Mitsunobu reaction to generate a di-CA-functionalized CTA which was purified via column chromatography. Its purity was determined by ^1H NMR and ^{13}C NMR (see Figure S6 and S7 in the SI). The performance of 10 in the RAFT polymerization of *n*-butyl acrylate was evaluated at 70 °C under bulk conditions affording a narrow monomodal molecular weight distribution (see Figure 1). The chemical structure of the obtained polymer was verified via ^1H NMR and SEC. The molecular weight of the final α,ω -cyanuric acid functional PnBA was finally determined by ^1H NMR in CD_2Cl_2 via integration of the protons of the polymer chains ($\text{COOCH}_2\text{CH}_2$) at 4.03 ppm and of the NH protons of the cyanuric acid end-group at 8.46 ppm ($M_{n,\text{NMR}} = 8400$ Da) (refer to Figure S8 in the SI). The NMR deduced number average molecular weight is in excellent agreement with the SEC based value of 8100 g mol^{-1} (based on a universal calibration procedure employing the MHKS parameters for poly(*n*-butyl acrylate)).

Now, the formation and characterization of supramolecular H-shaped polymers are discussed. The formation of supramolecular H-shaped macromolecules via multiple hydrogen bonding between the HW receptor and the CA located at the α,ω -position of the polymer backbone (as described in Scheme 2) was investigated. All self-assembly processes of the building blocks can be followed by monitoring the characteristic changes in the chemical shifts of the NH protons of the two recognition pairs using ^1H NMR spectroscopy.

It is paramount that the stoichiometry of the supramolecular self-assembly is quantitatively evaluated before undertaking the self-assembly between the building blocks carrying complementary recognition motifs. It is important to note that most host–guest equilibria are fast on the NMR spectroscopic time

scale, and the chemical shifts observed for a particular resonance represent a weighted average between the chemical shifts of the free and the bound species.¹⁷ The stoichiometry of the supramolecular self-assembly formed was assessed using the continuous variation technique (Job plot)¹⁸ based on the difference observed in the chemical shifts of the NH protons of CA-PnBA-CA in the presence of increasing amounts of the PEG-HW-PS (refer to Figure S10 in the SI). The total initial concentrations of the two species were maintained constant at 4.5 mM, and the ratio ($X_{\text{CA-PnBA-CA}}$) of the initial concentrations of CA-PnBA-CA was varied between 0.06 and 0.6 (refer to Table S1 in the Supporting Information). The 2:1 stoichiometry of the self-assembly for the (PEG-*b*-PS)·PnBA·(PEG-*b*-PS) was confirmed by a Job plot, evidencing a maximum at a 0.33 mol fraction of CA in dichloromethane (d_2) at ambient temperature (refer to Figure S11 in the SI). Furthermore, an NMR titration experiment was carried out to determine the association constant (K_a) of the (PEG-*b*-PS)·PnBA·(PEG-*b*-PS) complex via monitoring the downfield shift of the imide proton resonances of the CA moiety of **11** as a function of the addition of **7** (see Figure S12 and Figure S13 in the SI). The association constant for the supramolecular H-shaped terpolymer was calculated using the mathematical model provided in equation S1 in the SI. The association constants were found to be close to $1.2 \times 10^5 \text{ M}^{-1}$ for the (PEG-*b*-PS)·PnBA·(PEG-*b*-PS) system. After unambiguously establishing the stoichiometry between the precursor polymers, the formation of a supramolecular H-shaped terpolymer (PEG-*b*-PS)·PnBA·(PEG-*b*-PS) was investigated through the self-assembly between the PEG-HW-PS and the CA-PnBA-CA. After the addition of 2 equiv of the PEG-HW-PS to 1 equiv of the CA-PnBA-CA in CD_2Cl_2 , the ^1H NMR spectrum (refer to Figure 2) reveals

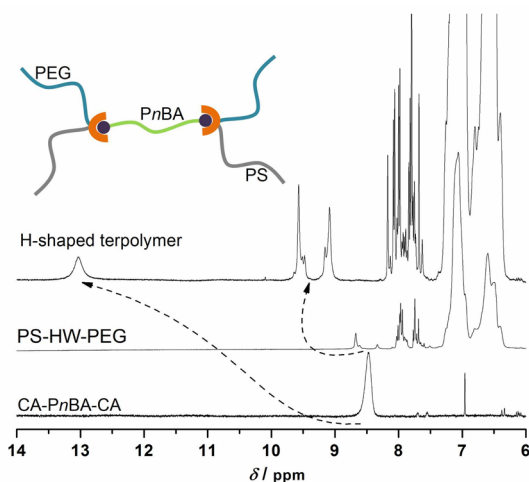


Figure 2. Expanded ^1H NMR spectrum of the building blocks and the (PEG-*b*-PS)·PnBA·(PEG-*b*-PS) supramolecular H-shaped terpolymer in dichloromethane (d_2) at ambient temperature.

shifts of the amide protons of the Hamilton receptor from 8.33 and 8.67 ppm (see Figure S9 in the SI) to 9.08 and 9.57 ppm (see Figure 2), respectively, thus evidencing that self-assembly—in this case the supramolecular H-shaped terpolymer (PEG-*b*-PS)·PnBA·(PEG-*b*-PS)—is formed. Furthermore, a new signal appears at 13.01 ppm that corresponds to the bound cyanuric acid unit during self-assembly (see Figure 2).

To further substantiate the formation of the supramolecular H-shaped complex macromolecular architectures, diffusion ordered spectroscopy (DOSY) NMR experiments were carried out, as the different sizes of the hydrogen-bonded self-assembled structures must exhibit different diffusion coefficients compared to the single host and guest polymers. The formation of the (PEG-*b*-PS)·PnBA·(PEG-*b*-PS) complex was consequently verified using diffusion ordered NMR spectroscopy (DOSY), in which the diffusion coefficient is measured by the signal decay within a defined gradient spin echo.¹⁹ In Figure 3a, the corresponding diffusion coefficients of the NMR signals associated with the single polymers, with diffusion coefficients of close to $D(\text{PS-HW-PEG}) = (3.37 \pm 0.08) \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ and $D(\text{CA-PnBA-CA}) = (3.05 \pm 0.06) \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$, are clearly higher than those associated with the complex, i.e., $D((\text{PEG-}b\text{-PS})\cdot\text{PnBA}\cdot(\text{PEG-}b\text{-PS})) = (1.7 \pm 0.1) \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$.

Following the above established calculation routine for the H-shaped terpolymer (PEG-*b*-PS)·PnBA·(PEG-*b*-PS), the stoichiometry for the association of the supramolecular H-shaped polymer (PS-*b*-PS)·PnBA·(PS-*b*-PS) was also determined via the continuous variation technique using the PS-HW-PS as a building block (refer to Figure S14 in the SI). The associated Job plot confirms that the complex formation has a maximum at 0.33 mol fraction indicating that the self-assembly (PS-*b*-PS)·PnBA·(PS-*b*-PS) possesses 2:1 stoichiometry (refer to Figure S15 in the SI). Moreover, an association constant (K_a) for H-shaped polymer (PS-*b*-PS)·PnBA·(PS-*b*-PS) was calculated via NMR titration experiments using eq 1 (refer to Figure S16 and Figure S17 in the SI). The association constant was found to be close to $1.2 \times 10^5 \text{ M}^{-1}$ for the (PS-*b*-PS)·PnBA·(PS-*b*-PS) complex. Such an association constant is in the range of those observed and successfully employed in typical H-bonding polymeric systems²⁰ and of comparable magnitude to the one of the (PEG-*b*-PS)·PnBA·(PEG-*b*-PS) system in the current study. In addition, the formation of a (PS-*b*-PS)·PnBA·(PS-*b*-PS) self-assembled structure between the PS-HW-PS and the CA-PnBA-CA in dichloromethane (d_2) at ambient temperature was studied. Upon the addition of 2 equiv of the PS-HW-PS to 1 equiv of the CA-PnBA-CA in dichloromethane (d_2), it is observed that the ^1H NMR spectrum reveals shifts of the amide protons of the Hamilton receptor from 7.80 and 8.52 ppm (see Figure S9 in the SI) to 8.77 and 9.30 ppm, respectively, thus evidencing that the H-shaped polymer (PS-*b*-PS)·PnBA·(PS-*b*-PS) is formed. A further new resonance appears at 13.01 ppm that corresponds to the bound cyanuric acid unit in the self-assembly motif (refer to Figure S18 in the SI). Again the data were verified via DOSY NMR experiments, which led to diffusion coefficients of $D(\text{PS-HW-PS}) = (7.5 \pm 0.13) \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ and $D(\text{CA-PnBA-CA}) = (3.05 \pm 0.06) \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ for the individual molecules and to $D((\text{PS-}b\text{-PS})\cdot\text{PnBA}\cdot(\text{PS-}b\text{-PS})) = (1.7 \pm 0.19) \times 1.7 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ for the corresponding complex as can be seen in Figure 3b. The result clearly evidences that the complexes and the precursor polymers have different diffusion constants, where the self-assembled polymers move more slowly than precursor polymers due to the fact that the hydrodynamic volume of the complexes is larger than that of the precursor polymers. In addition, it can be clearly seen that all arms of the H-shaped polymers diffuse jointly when the polymers are self-assembled. Dynamic light scattering (DLS) is a powerful and versatile tool for estimating the size distribution profile of small particles in suspension or polymers in solution, effective for particles in

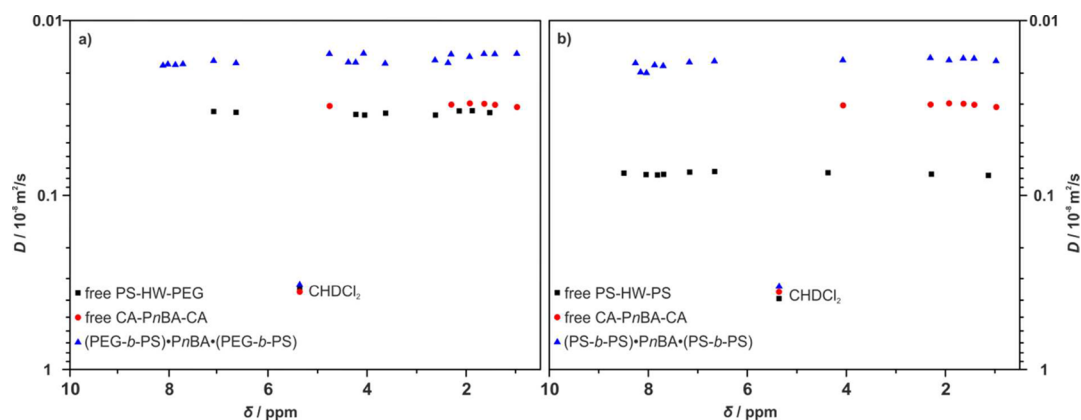


Figure 3. Diffusion coefficients D with respect to chemical shifts of the corresponding signals for the complex (PEG-*b*-PS)·PnBA·(PEG-*b*-PS) and the free building blocks CA-PnBA-CA and PS-HW-PEG (a) and, respectively, (PS-*b*-PS)·PnBA·(PS-*b*-PS), CA-PnBA-CA, and PS-HW-PS (b). The diffusion coefficients of the free building blocks are clearly in excess of those associated with the supramolecular complexes. Signals of residual CHDCl₂ solvent are annotated as well.

the size range of a few nanometers up to several micrometers. As a crucial assessment of the efficient formation of self-assembly of complex macromolecular architectures through multiple hydrogen bonding between host and guest (HW–CA) systems, comparative DLS analyses were performed in dichloromethane solutions.

While the ¹H NMR experiments indicated that self-assembly occurred between the HW-functional block copolymers and the CA-functional linear polymer, measurement of the hydrodynamic diameter (D_h) can provide evidence for the supramolecular H-shaped polymers. The linear polymer (CA-PnBA-CA) (11), the block copolymer (PEG-HW-PS) (7), or the block homopolymer (PS-HW-PS) (12) was exemplary subjected to DLS revealing a D_h of 3.8, 4.3, and 2.8 nm, respectively, in CH₂Cl₂. Furthermore, the supramolecular H-shaped polymers (PEG-*b*-PS)·PnBA·(PEG-*b*-PS) or (PS-*b*-PS)·PnBA·(PS-*b*-PS) in CH₂Cl₂ with an equimolar ratio of the (CA-PnBA-CA) and the (PEG-HW-PS) or the (PS-HW-PS) in terms of recognition units displayed a new population with a D_h equal to 6.7 or 6.5 nm, consistent with the formation of supramolecular H-shaped polymer from the association via the multiple hydrogen bonding motifs, indicating an increase in hydrodynamic volume due to formation of the H-shaped terpolymer. Moreover, no distribution in DLS corresponding to precursor polymers could be observed, thus supporting the formation of the supramolecular H-shaped polymers (see Figure 4 and Figure S19 in the SI). Thus, the DLS results carried out on the example of the supramolecular H-shaped polymer of (PEG-*b*-PS)·PnBA·(PEG-*b*-PS) or (PS-*b*-PS)·PnBA·(PS-*b*-PS) support the efficient formation of supramolecular H-shaped polymers driven by the complementary recognition units.

In summary, a novel trifunctional initiator bearing an azide and a hydroxyl group as well as a novel chain transfer agent (CTA) with two cyanuric acid functionalities were introduced for ATRP and RAFT polymerization, respectively. The initiator was employed for the preparation of a HW mid-chain functionalized linear block copolymer, and an α,ω -CA difunctional linear homopolymer was synthesized using the CTA. Supramolecular H-shaped polymers were—for the first time—prepared through multiple hydrogen bonds between complementary recognition motifs to generate (PEG-*b*-PS)·PnBA·(PEG-*b*-PS) and (PS-*b*-PS)·PnBA·(PS-*b*-PS) entities

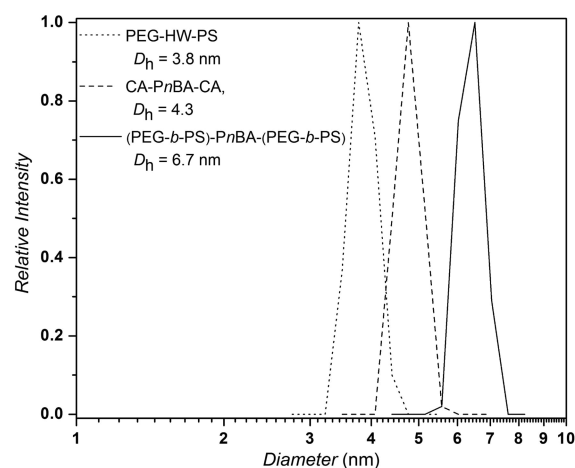


Figure 4. Mean hydrodynamic diameters of supramolecular grafted star-shaped macromolecules (PEG-*b*-PS)·PnBA·(PEG-*b*-PS) and polymeric building blocks determined at 90° in dichloromethane at ambient temperature.

in CH₂Cl₂ or CD₂Cl₂ at ambient temperature. The self-assembly process was successfully evidenced via proton nuclear magnetic resonance (¹H NMR) spectroscopy, NMR titration experiments, a Job plot analysis, diffusion ordered NMR spectroscopy (DOSY), as well as dynamic light scattering (DLS) analyses. The present results unambiguously prove that the formation of supramolecular H-shaped polymers on a very well-defined level is indeed possible employing high precision macromolecular design strategies.

■ ASSOCIATED CONTENT

Supporting Information

Further details regarding the employed materials, synthetic procedures, instrumentation, related structures, as well as additional detailed characterization and self-assembly data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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