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ARTICLE

Facile Preparation of Supramolecular (ABAC)_n Multiblock Copolymers from Hamilton Wedge and Barbiturate-Functionalized RAFT Agents

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

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Two original Hamilton wedge (HW)/barbiturate (Ba) functionalized symmetrical trithiocarbonates have been successfully synthesized and their capability to efficiently mediate the polymerization of styrene, *n*BuA and isoprene was investigated. Relying on supramolecular association of the recognition couple, telechelic macromolecular building blocks subsequently afford the formation of novel supramolecular (ABAC)_n multiblock copolymers, where A in a glassy state, B and C in a rubbery state. The successful generation of desired supramolecular structure was evidenced by ¹H NMR, ITC, viscometry, DLS as well as DSC.

Introduction

With the spread and expanding interest in supramolecular chemistry, there was growing realization of supramolecular multiblock copolymers over last decades.¹⁻¹⁰ So far, mainly two types of noncovalent interactions, i.e. hydrogen bonding,¹¹⁻¹⁵ and metal-ligand coordination,¹⁶⁻¹⁸ have been studied for creating well-defined supramolecular multiblock copolymers.

Owing to their high sensitivity to external stimuli such as temperature, shear or the polarity of the medium, H-bonding interactions have played a key role in the development of novel polymeric materials, and have been widely used to generate supramolecular block,¹⁹⁻³² graft,³³⁻³⁶ (miktoarm) star,³⁷⁻⁴² H-shaped⁴³ polymers, nanoparticles,⁴⁴⁻⁴⁶ and self-folding of single-chain synthetic polymeric systems.⁴⁷⁻⁵¹

On the basis of H-bonding interactions, supramolecular multiblock copolymers are essentially generated via two synthetic methods, i.e. the “*post*-polymerization modification” which introduces the molecular recognition units on polymer chain-ends, and the “*pre*-polymerization modification” which requires the initial synthesis of functionalized polymerization initiator bearing the desired binding motifs, and then grow the polymer chains in between these groups.

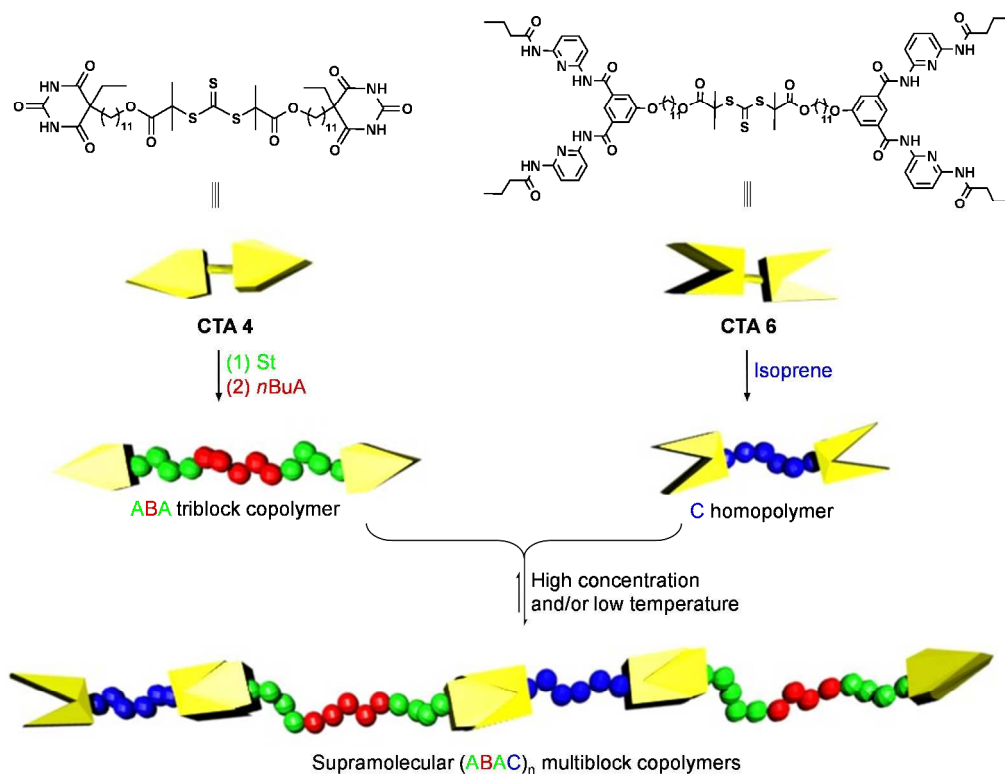
So far, most synthetic strategies towards supramolecular multiblock copolymers rely on “*post*-polymerization modification” steps.^{2, 6, 7} By taking advantage of strong interaction between ureidoguanosine (UG) and 2,7-diamino-1,8-naphthyridine (DAN), Zimmerman and co-workers recently developed a supramolecular multiblock copolymer in which the degree of polymerization depends on the concentration and ratio of the blocks in the mixture.¹⁴ In addition, we have

tailored different polymers by affixing thymine/triazine or Hamilton wedge/barbituric acid on their ends, resulting in new type of microphase-separated supramolecular (AB)_n multiblock copolymers.^{15, 25, 26, 28-31}

Although actively studied and rapidly developed over last few years, some “*post*-polymerization modification” suffer from the intrinsic difficulty of quantitatively functionalizing macromolecules termini.^{2, 12, 18, 22} In this context, another elegant strategy, “*pre*-polymerization modification”, was initially explored by Meijer¹² and Weck¹⁸, who prepared small molecules with the desired binding end groups and then grow the polymer chains in between these groups through the ring-opening metathesis polymerization (ROMP).

On the other hand, ATRP,²⁵ LCCP^{15, 29, 31} or ROP^{24, 27} combined with popular azide-alkyne click chemistry have been investigated in our group, successfully introducing various hydrogen bonding moieties (such as Hamilton wedge, barbituric acid, thymine or diamino-triazine-moieties) to different polymers. Additionally, the RAFT process also attracted our attention, as well-defined supramolecular *di*-, *tri*- or *tetra*-block copolymers were successfully generated by using either thymine/2,6-diaminopyridine²² or Hamilton wedge/barbiturate²³ complementary moieties functionalized RAFT agents.

Extending from our previous work and aiming at fabricating novel well-defined supramolecular *multiblock* copolymers, in this work we demonstrate the effectiveness of the present strategy in synthesizing symmetrical Hamilton wedge- and barbiturate-functionalized telechelic polystyrene-*b*-poly(*n*-butyl acrylate)-*b*-polystyrenes and polyisoprenes in a simple



Scheme 1: General strategy for preparing novel well-defined supramolecular (ABAC)_n multiblock copolymers.

manner from functional trithiocarbonates, and further investigate their subsequent self-assembly into novel well-defined (ABAC)_n supramolecular *multiblock* copolymers, where block A is in a glassy state, and blocks B and C are in a rubbery state. (see **Scheme 1**)

Experimental

Materials. All the chemicals were purchased from Sigma-Aldrich. All the monomers were filtered prior to passing through a column of basic aluminium oxide to remove inhibitors. Unless otherwise indicated the other chemicals were used without further purification.

Characterization methods. ¹H and ¹³C NMR spectra were recorded on a Bruker AVANCE400 (400 MHz) spectrometer using CDCl₃, CD₂Cl₂ or DMSO-*d*₆.

Bifunctionalized PS, PS-*b*-PnBuA-*b*-PS bearing barbiturate and PI bearing Hamilton wedge were analysed via Size Exclusion Chromatography (SEC) running in THF at 25°C (flow rate: 1 mL·min⁻¹) and equipped with a Viscotek VE 1121 automatic injector, three Waters HR5E columns and a differential refractive index detector (Viscotek VE3580). The average

molar masses of PS, PS-*b*-PnBuA-*b*-PS and PI were derived from a calibration curve based on PS standards.

Isothermal Titration Calorimetry (ITC) experiments were carried out with a NanoITC Low Volume (TA Instruments) in CHCl₃. The reference cell was filled with CHCl₃ and a solution containing CTA 4 (1.2mL, 0.5mM) or Ba-PS-*b*-PnBuA-*b*-PS-Ba (1.2mL, 0.3mM) was placed in the calorimeter cell. The titration syringe was loaded with a solution of CTA 6 or HW-PI-HW at a 10 times higher concentration than in the cell. Solutions were stirred at 250 rpm. Titrations were repeatedly carried out at 20 °C with 35 injections of 5 μL with time intervals of 600 seconds and ITC data were finally analysed with the NanoAnalyse software.

ESI-TOF MS measurements were performed on Bruker Daltonics microTOF time-of-flight ESI-MS system. Spectra were recorded in the positive mode with an accelerating voltage of 4.5kV, a transfer line with 180 °C, and a scan range of 50–15 000 m/z. The spectra were processed on a Bruker Daltonics ESI compass 1.3 for microTOF (Data Analysis 4.0). Samples were dissolved in methanol (5 mg/mL) and injected into ESI-ion source via a micro-syringe pump (injection speed of 300 μL/min).

MALDI-TOF MS measurements were performed on a Bruker Autoflex III system (Bruker Daltonics) operating in linear modes. Data evaluation was carried out on flexAnalysis software (3.4). Ions were formed by laser desorption (smart beam laser at 355, 532, 808, and 1064 ± 5 nm; up to 50 Hz repetition rate), accelerated by a voltage of 20 kV and detected as positive ions. The matrix solution was prepared by dissolving all-*trans*-retinoic acid (Vitamin A) in THF at a concentration of 20 mg/mL. Polymer samples were dissolved in THF at a concentration of 20 mg/mL. LiTFA were dissolved at a concentration of 10 mg/mL in THF. The solutions of the matrix, the polymer, and the salt were mixed in a volume ratio of 100:24:12, and 1 μ L of each mixture was spotted on the MALDI target. The instrument was externally calibrated with a poly(ethylene glycol) (PEG) standard ($M_p = 4500$ g mol⁻¹, Polymer Standard Services GmbH, PSS) applying an enhanced cubic algorithm calibration method with an error of 1–2 ppm.

Viscosity was measured in CHCl₃ using a Bohlin 88 Couette viscometer at 30 °C, combined with the use of a solvent trap cover, in order to avoid evaporation of CHCl₃ during measurements. Polymer solutions were filtered by PTFE membranes (0.45 μ m porosity) prior to measurements.

Dynamic Light Scattering (DLS) measurements were performed in toluene solutions on a Viscotek 802 using OmniSIZE software.

Differential Scanning Calorimetry (DSC) was conducted on Perkin Elmer Pyris Diamond instrument. The glass transition temperatures were determined by cooling the samples at -100 °C and then heating up to 200 °C, both at rate 10 °C min⁻¹ and repeating this process. The glass transition temperature is taken as a midpoint of a small heat capacity change upon heating from amorphous glass state to a liquid state.

SYNTHESIS OF CTA 4. Compound **2** was prepared as literature methods with slight modification.⁵² Sodium hydride (0.43 g of 60% dispersion in mineral oil, 10 mmol), was suspended in DMF (4 mL). Then diethyl 2-ethylmalonate (2.1 g, 11 mmol) was added dropwise at 0 °C, then the mixture was left stirring for 30 minutes until a clear, yellowish solution was obtained and no more gas release was observed. Cooling to 0 °C again, 11-bromo-1-undecanol (2.5 g, 10 mmol) in DMF (5 mL) was added dropwise and the mixture was heated to 60 °C for 20h, then it was cooled to room temperature and water (40 mL) was added. The organic phase was extracted with diethyl ether (2 \times 30 mL), washed with water (2 \times 30 mL), and evaporated to afford a yellow oil **1** which was used directly for next step without further purification.

Sodium hydride (1.2 g of a 60% w/w dispersion in mineral oil, 30 mmol) was added to DMF (5 mL), to the above solution was added dropwise a solution of urea (1.1 g, 18.5 mmol) in DMF (10 mL) at 0 °C. Subsequently, compound **1** (dissolved in 5 mL DMF) was added dropwise. The mixture was then left stirring at 100 °C during 24h. Then a saturated solution NaHCO₃ (200 mL) was added. The organic phase was extracted with ethyl acetate (3 \times 70 mL), washed with a 1M solution of hydrochloric acid (3 \times 30 mL), dried with MgSO₄. The solvent were evaporated and the resulting slightly yellow oil was

recrystallized from CH₂Cl₂ afford compound **2** (see **Figure S1&2**) as a white solid (2.5 g, 25% yield for two steps). ¹H NMR (DMSO-*d*₆) δ (ppm): 0.73 (t, 3H), 1.19–1.39 (br, 18H), 1.80 (m, 4H), 3.64 (t, 2H), 4.30 (br.s, 1H), 11.49 (br.s, 2H).

3^{22, 53} (0.13 g, 0.45 mmol), **2** (0.34 g, 1 mmol), and triphenylphosphine (PPh₃) (0.3 g, 1.14 mmol) were dissolved in freshly distilled THF in a three-neck round-bottom flask cooled with an ice bath under argon flow. Diisopropyl azodicarboxylate (DIAD) (0.23 g, 1.14 mmol) diluted in distilled THF was then added dropwise. The solution was allowed to reach room temperature and stirred overnight, then diluted with dichloromethane (150 mL) and washed with distilled water (2 \times 200 mL). The organic layer was collected and dried with MgSO₄. The solvent was removed under reduced pressure. The crude product, a yellow oil, was then purified by column chromatography (eluent: MeOH/CH₂Cl₂, 1/20, v/v). The solvent was removed under reduced pressure and the resulting yellow solid CTA **4** (0.74g, 82% yield), (see **Figure S3-5**). ESI-MS: calculated for (C₄₃H₇₀N₄O₁₀S₃+Na)⁺: 921.4146, Found: 921.4256. ¹H NMR (CDCl₃) δ (ppm): 0.82 (t, 6H), 1.16 (br, 32H), 1.58 (br, 16H), 1.96 (br, 8H), 3.99 (t, 4H), 8.76 (s, 2H), ¹³C NMR (CDCl₃) δ (ppm): 8.45, 24.18, 24.90, 27.34, 28.19, 28.23, 28.34, 28.42, 28.49, 28.51, 28.60, 31.46, 37.81, 55.10, 56.40, 65.23, 148.74, 172.08, 172.19, 217.19.

SYNTHESIS OF CTA 6. **3**^{22, 53} (0.064 g, 0.23 mmol), **5**²³ (0.34 g, 0.5 mmol), and triphenylphosphine (PPh₃) (0.15 g, 0.57 mmol) were dissolved in freshly distilled THF in a three-neck round-bottom flask cooled with an ice bath under argon flow. Diisopropyl azodicarboxylate (DIAD) (0.12 g, 0.57 mmol) diluted in distilled THF was then added dropwise. The solution was allowed to reach room temperature and stirred overnight, then diluted with dichloromethane (100 mL) and washed with distilled water (2 \times 150 mL). The organic layer was collected and dried with MgSO₄. The solvent was removed under reduced pressure. The crude product, a yellow oil, was then purified by column chromatography (eluent: MeOH/CH₂Cl₂, 1/25, v/v). The solvent was removed under reduced pressure and the resulting yellow solid CTA **6** (0.69 g, 86% yield) (see **Figure S6-8**). ESI-MS: calculated for (C₈₃H₁₁₀N₁₂O₁₄S₃+Na)⁺: 1617.7319, Found: 1617.7286. ¹H NMR (CDCl₃) δ (ppm): 0.95 (t, 12H), 1.23–1.55 (br, 36H), 1.69 (br, 8H), 2.33 (t, 8H), 3.89 (t, 4H), 4.00 (t, 8H), 7.50 (s, 4H), 7.64 (t, 4H), 7.79 (s, 2H), 7.89 (t, 8H), 8.03 (br.s, 4H), 8.45 (br.s, 4H) ¹³C NMR (CDCl₃) δ (ppm): 12.72, 17.77, 24.18, 24.94, 27.23, 27.45, 27.66, 27.87, 28.23, 28.48, 28.50, 28.54, 38.38, 55.13, 65.18, 67.73, 108.66, 109.25, 116.22, 116.23, 134.70, 139.63, 148.28, 148.94, 158.79, 163.64, 171.10, 171.79, 217.33.

SOLUTION POLYMERIZATION OF STYRENE. Solution polymerization of styrene was carried out using CTA **4** as RAFT agent, and AIBN as initiator. Typically, solution polymerization of styrene (1.37 mL, 1.2×10^{-2} mol) was carried out using AIBN (0.33 mg, 2.0×10^{-6} mol), **4** (18.0 mg, 2.0×10^{-5} mol), DMF (1.37 mL) and trioxane (127 mg, 1.4×10^{-3} mol) as an internal reference for the measurement of styrene consumption via ¹H NMR. A stock solution was transferred into Schlenk tubes which were thoroughly deoxygenated by

five consecutive freeze-pump-thaw cycles. The tubes were subsequently placed in an oil bath thermostated at 80°C. The reaction was stopped by plunging the tubes into liquid nitrogen. The polymer was subsequently precipitated twice into EtOH in order to eliminate residual monomer and trioxane. The polymer was dried under vacuum and characterized by ^1H NMR and SEC. The molar mass of pure α,ω -Ba functionalized polystyrene (Ba-PS-Ba) was finally evaluated by ^1H NMR (CD_2Cl_2) from relative integration of the aromatic protons of the PS backbone (5nH, $\delta = 6.05\text{--}7.47$ ppm, with n being the degree of polymerization) and of characteristic protons of the ester group ($-\text{[(O)=C-O-CH}_2\text{-CH}_2\text{]}_2-$, 4H, $\delta = 4.01$ ppm).

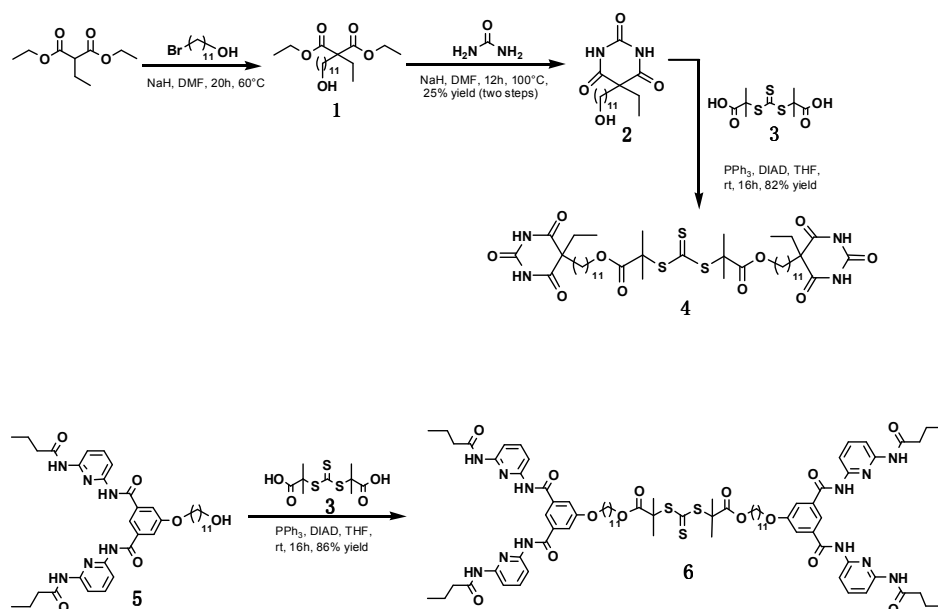
CHAIN EXTENSION OF BA-PS-BA WITH N-BUTYL ACRYLATE (nBuA). Solution polymerization of nBuA was carried out using Ba-PS-Ba4 as macroRAFT agent, and AIBN as initiator. Typically, solution polymerization of nBuA (0.63 mL, 4.5×10^{-3} mol) was carried out using AIBN (0.25 mg, 1.5×10^{-6} mol), Ba-PS-Ba4 (250 mg, 1.5×10^{-5} mol), toluene (1.3 mL) and trioxane (127 mg, 1.4×10^{-3} mol) as an internal reference for the measurement of nBuA consumption via ^1H NMR. A stock solution was transferred into Schlenk tubes which were thoroughly deoxygenated by five consecutive freeze-pump-thaw cycles. The tubes were subsequently placed in an oil bath thermostated at 65°C. The reaction was stopped by plunging the tubes into liquid nitrogen. The polymer was subsequently precipitated twice into methanol/ H_2O (2/1, v/v) in order to eliminate residual monomer and trioxane. The polymer was dried under vacuum and characterized by ^1H NMR and SEC. The molar mass of pure α,ω -Ba functionalized polystyrene-*b*-poly(nBuA)-*b*-polystyrene (Ba-PS-*b*-PnBuA-*b*-PS-Ba) was finally evaluated by ^1H NMR (CD_2Cl_2) from relative integration of the protons of the PnBuA backbone ($-\text{O-CH}_2\text{-CH}_2-$, 2mH, $\delta=3.94$ ppm, with m being the degree of

polymerization) and aromatic protons of the PS backbone (5nH, $\delta = 6.05\text{--}7.47$ ppm, with n = 75).

SOLUTION POLYMERIZATION OF ISOPRENE. Solution polymerization of isoprene was carried out using CTA 6 as RAFT agent, and dicumyl peroxide (DCP) as initiator. Typically, solution polymerization of isoprene (0.85 mL, 8.5×10^{-3} mol) was carried out using DCP (0.51 mg, 1.9×10^{-6} mol), CTA 6 (30.0 mg, 1.9×10^{-5} mol), DMF (1.2 mL) and trioxane (127 mg, 1.4×10^{-3} mol) as an internal reference for the measurement of styrene consumption via ^1H NMR. A stock solution was transferred into Schlenk tubes which were thoroughly deoxygenated by five consecutive freeze-pump-thaw cycles. The tubes were subsequently placed in an oil bath thermostated at 120°C. The reaction was stopped by plunging the tubes into liquid nitrogen. The polymer was subsequently precipitated twice into MeOH in order to eliminate residual monomer and trioxane. The polymer was dried under vacuum and characterized by ^1H NMR and SEC. The molar mass of pure α,ω -HW functionalized polyisoprene (HW-PI-HW) was finally evaluated by ^1H NMR (CDCl_3) from relative integration of the protons of the PI backbone (5.6-5.9 ppm for the $-\text{CH=CH}_2$ from the 1,2-addition polymerization, 5.0-5.5 ppm for $-\text{CH=C(CH}_3\text{)}-$ for the 1,4-addition polymerization, and 4.4-5.0 ppm for the mixture of $-\text{CH=CH}_2$ (1,2-addition) and $-\text{C(CH}_3\text{)=CH}_2$ (3,4-addition)) and of characteristic protons of Hamilton wedge end-groups ($-\text{CH}_2\text{-CH}_2\text{-CH}_3$), 4H, $\delta = 2.31$ ppm).

Results and discussion

SYNTHESIS OF H-BONDING CTAs. Aiming at preparing supramolecular multiblock copolymers through X-X and Y-Y bifunctional macromolecules, which are telechelic polymers bearing HW (X) and Ba (Y) end groups, two symmetrical trithiocarbonates (CTA 4 and 6) were targeted (see Scheme 2).



Scheme 2: Route to CTA 4 and 6.

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A hydroxyl substituted malonate **1** was first prepared from diethyl 2-ethylmalonate and 11-bromo-1-undecanol and subsequently reacted with urea to afford the hydroxyl functionalized barbiturate **2** on a multigram scale. α,ω -Ba functionalized CTA **4** was then obtained in good yield from the coupling between barbiturate **2** and compound **3**⁵³ under Mitsunobu conditions.^{22, 43} The successful synthesis of α,ω -Ba functionalized CTA **4** was clearly evidenced by ¹H NMR (**Figure S3**) and ¹³C NMR (**Figure S4**) as well as ESI-MS analysis (**Figure S5**), calculated for (C₄₃H₇₀N₄O₁₀S₃+Na)⁺: 921.4146, Found: 921.4256.

The high yield of CTA **4** relying on Mitsunobu reaction further encouraged us to design complementary H-bonding CTA **6** by utilizing the same strategy, the hydroxyl functionalized Hamilton wedge **5**²³ was reacted with **3** under Mitsunobu conditions to afford α,ω -HW functionalized CTA **6**, analogously, the reaction proceeded smoothly and the targeted CTA **6** was finally isolated in good yields (see **Scheme 2**). Again, the introduction of the H-bonding motif (HW) was confirmed by NMR with the appearance of a peak corresponding to the formation of an ester at 4.00 ppm and the presence of characteristic peaks of HW and of the

trithiocarbonate moieties (**Figure S6&7**), as well as ESI-MS analysis (**Figure S8**) calculated for (C₈₃H₁₁₀N₁₂O₁₄S₃+Na)⁺: 1617.7319, Found: 1617.7286.

Prior to undertaking any polymerization reaction, the capability of α,ω -Ba functionalized CTA **4** to associate through six hydrogen bonding interactions with α,ω -HW functionalized CTA **6** was examined by ¹H NMR analysis in CDCl₃ at 25 °C.

As shown in **Figure 1**, the signals appearing at 8.56 (**Figure 1A**, green cross) and 7.98/8.40 ppm (**Figure 1B**, red spot) were assigned to the NH protons of Ba and HW units, respectively. Addition of one equivalent of CTA **6** to **4** was accompanied by a significant downfield shift of the Ba NH protons from 8.56 to 12.55 ppm, and HW NH protons from 8.31/7.96 to 9.90/9.61 ppm, respectively (**Figure 1C**), which disclose the association of the heterocomplementary stickers and the formation of the expected supramolecular complex.

The strength of the heterocomplementary H-bonding association was subsequently investigated by ITC analysis (see **Figure 2**), a binding constant of about $5.1 \times 10^4 \text{ M}^{-1}$ was found in CHCl₃ at 20 °C.

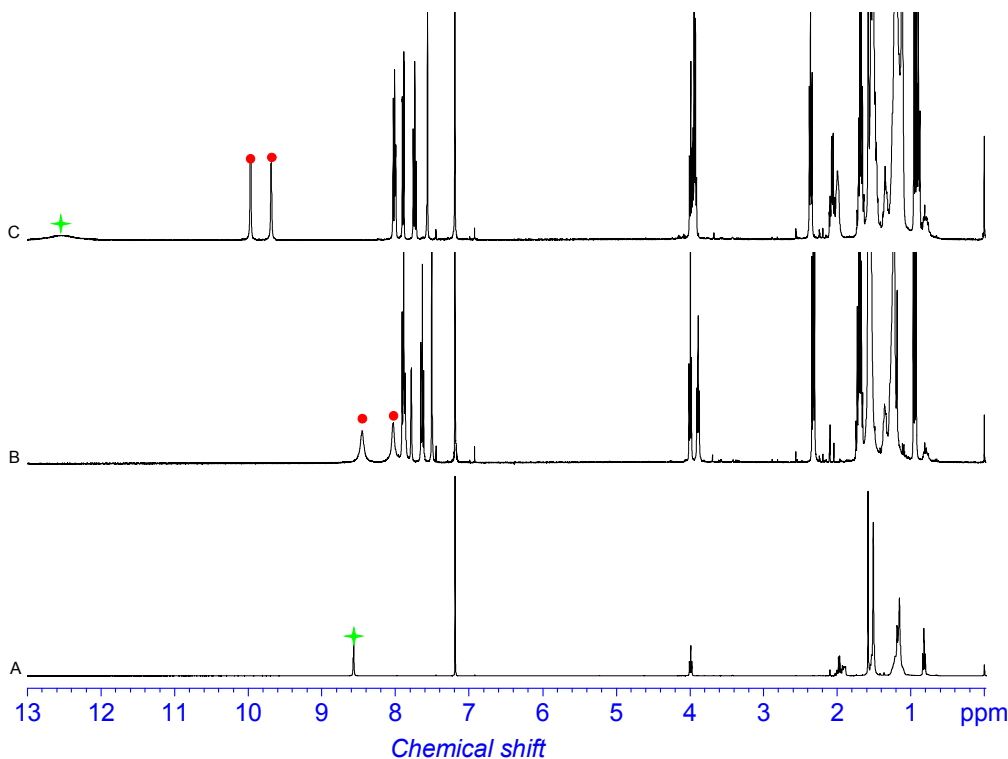


Figure 1: ¹H NMR spectra of CTA **4** (A), **6** (B) and a stoichiometric mixture of **4** and **6** (C), ([**4**] = [**6**] = 2.5 mM) at 25 °C in CDCl₃. Green cross: barbiturate NH protons, red spot: Hamilton wedge NH protons.

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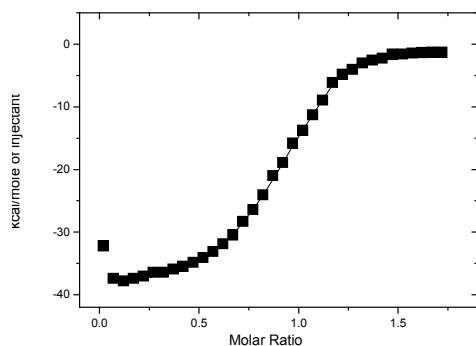


Figure 2: ITC titration of CTA **4** (0.5 mM) with the CTA **6** (5 mM) in CHCl_3 at 20 °C.

After demonstrating the affinity of CTA **4** and **6**, the capability of the sticker functionalized CTAs to efficiently mediate the solution polymerization of different monomers (styrene, *n*-butyl acrylate and isoprene) and to afford H-bonding polymers was then investigated. In all polymerization reactions, the CTA to initiator ratio was maintained as 10 in order to minimize the amount of chains bearing a thermal initiator adduct and generate polymers exhibiting quantitative sticker functionalization while maintaining reasonable polymerization kinetics. The number average molar masses and the

corresponding molar mass distribution of all the above polymers are given in **Table 1**.

As shown in **Table 1** and **Figure 3**, solution polymerizations of styrene and isoprene in the presence of CTA **4** and CTA **6** illustrate a controlled manner. In both cases, kinetic study highlighted a linear relationship between $\ln(1/(1-x))$ and time for both monomers (**Figure 3A, C**), moreover the telechelic polymers grew steadily with monomer conversion (**Figure 3B, D**), and the polydispersity indices remained below 1.40. The good correlation between the theoretical molecular weight and the experimental values obtained from SEC and NMR analysis (**Table 1**) also confirms the controlled/living character of the polymerization.

Intending to demonstrate the full utility of H-bonding polymer and build (ABAC)_n supramolecular multiblock copolymers, polystyrene (Ba-PS-Ba4, $M_{n, SEC} = 17000$ g/mol, $PDI = 1.26$) macroRAFT agent was further chain-extended with *n*-butyl acrylate. As expected, macroRAFT agent was proven to efficiently mediate the polymerization of *n*BuA (**Table 1** and **Figure 3E, F**), linear first order kinetic plots, and progressive shift of the SEC traces towards high molar mass, moreover the absence of a low molar mass shoulder confirmed the “livingness” of the polymerization and successful generation of fairly controlled triblock polymers PS-*b*-P*n*BuA-*b*-PS.

Table 1: Properties of the RAFT-made H-bonding polymers.

Sample	CTA	$[M]/[CTA]$	Conv ^a %	$M_{n, th}^b$ g/mol	$M_{n, NMR}^c$ g/mol	$M_{n, SEC}^d$ g/mol	PDI^d
Ba-PS-Ba1	4	600	9	6200	6700	7100	1.33
Ba-PS-Ba2	4	600	14	9700	12500	11200	1.29
Ba-PS-Ba3	4	600	20	13400	15400	14800	1.26
Ba-PS-Ba4	4	600	24	15900	18800	17000	1.26
Ba-PS- <i>b</i> -P <i>n</i> BuA- <i>b</i> -PS-Ba1	Ba-PS-Ba4	200	11	19800	21000	20700	1.38
Ba-PS- <i>b</i> -P <i>n</i> BuA- <i>b</i> -PS-Ba2	Ba-PS-Ba4	200	17	21300	22300	22800	1.37
Ba-PS- <i>b</i> -P <i>n</i> BuA- <i>b</i> -PS-Ba3	Ba-PS-Ba4	200	23	22900	23500	24700	1.35
Ba-PS- <i>b</i> -P <i>n</i> BuA- <i>b</i> -PS-Ba4	Ba-PS-Ba4	200	29	24400	26100	25200	1.33
HW-PI-HW1	6	450	10	4700	5500	5800	1.39
HW-PI-HW2	6	450	19	7400	9700	8600	1.37
HW-PI-HW3	6	450	27	9900	11900	11000	1.34
HW-PI-HW4	6	450	32	11400	13400	12500	1.31

^a: Conversion from ¹H NMR. ^b: Number-average molecular weight was evaluated from the following equation: $M_{n, th} = \text{Conv} \times ([M]/[CTA]) \times m_M + m_{CTA}$. ^c: Determined from relative integration of protons from ¹H NMR. ^d: From SEC in THF (PS calibration).

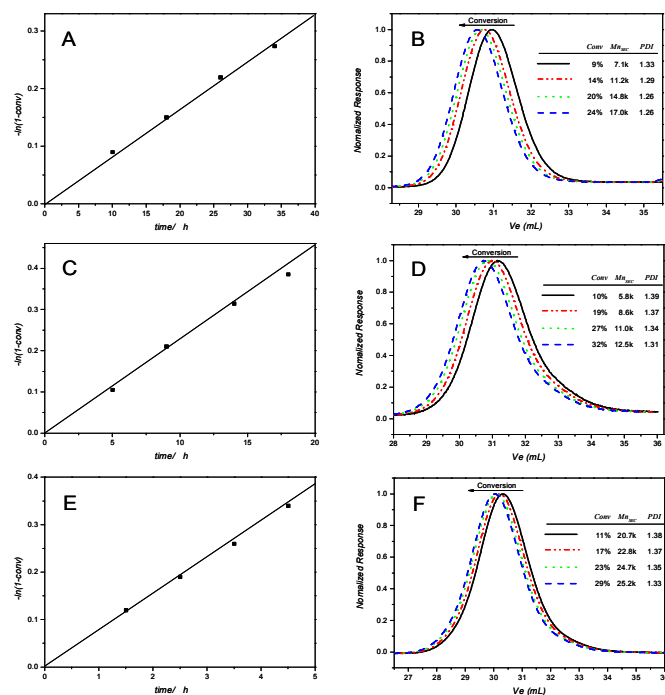


Figure 3. (A) First-order kinetic plots and (B) evolution of the SEC traces for the solution polymerization of styrene in DMF at 80°C mediated by CTA 4 using AIBN as initiator: $[M]/[CTA] = 600$, $[CTA]/[Initiator] = 10$. (C) First-order kinetic plots and (D) evolution of the SEC traces for the solution polymerization of isoprene in DMF at 120°C mediated by CTA 6 using DCP as initiator: $[M]/[CTA] = 450$, $[CTA]/[Initiator] = 10$. (E) First-order kinetic plots and (F) evolution of the SEC traces for the solution polymerization of *n*BuA at 65°C in toluene mediated by macroRAFT agent Ba-PS-Ba4 using AIBN as initiator: $[M]/[CTA] = 200$, $[CTA]/[Initiator] = 10$.

The effective incorporation of HW at both chain ends of homopolymer was assessed by ^1H NMR analysis for PI backbones, with the appearance of methylene group α to the amide at 2.34 ppm ($\text{CO}-\text{CH}_2-\text{CH}_2-\text{CH}_3$) and to NH amide protons at 8.43 ppm (Figure 4B). Similar conclusions were drawn in the case of the Ba-functionalized PS-*b*-P*n*BuA-*b*-PS chains with the presence of peaks at 8.04 ppm attributed to the NH amide protons (Figure 4A). ^{13}C NMR further supported the expected structure (Figure S9&10).

Chain functionalization of PI with HW was then investigated via MALDI-TOF mass spectrometry (Figure 5). The mass spectrum of HW-PI-HW4 observed in the linear mode, the best spectrum (Figure 5A) was obtained by ionization of chains assisted with all-trans-retinoic acid (Vitamin A) as matrix and LiTFA as the cationization agent. In a typical MALDI-TOF MS experiment, the matrix, the polymer solution and the salt were premixed in a ratio of 100:24:12 (dry-droplet method). The MALDI-TOF spectrum indicated the presence of singly charged main series (series ①) along with other three minor

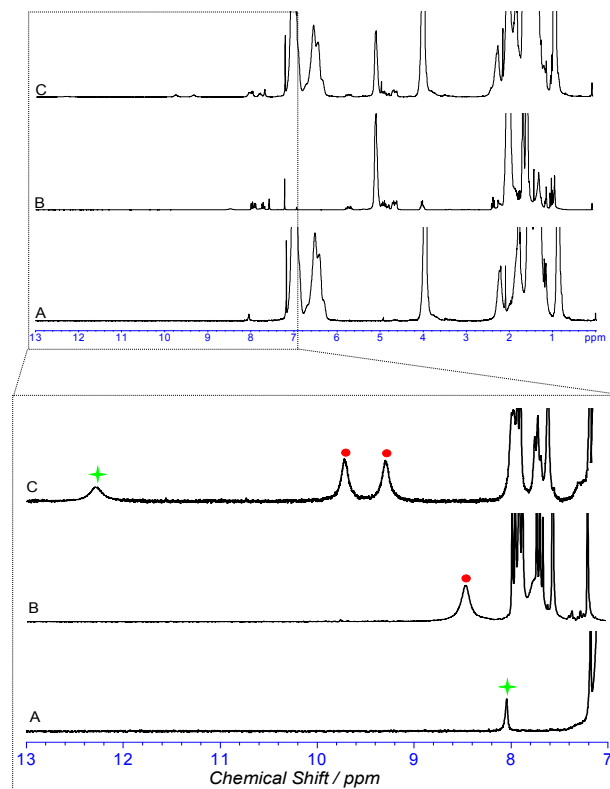


Figure 4. ^1H NMR spectra of Ba-PS-*b*-P*n*BuA-*b*-PS-Ba4 (A), HW-PI-HW4 (B) and of a stoichiometric mixture of Ba-PS-*b*-P*n*BuA-*b*-PS-Ba4 and HW-PI-HW4 (C) at 25°C in CDCl_3 ($[\text{Ba-PS-}b\text{-PnBuA-}b\text{-PS-Ba4}] = [\text{HW-PI-HW4}] = 1\text{mM}$). Green cross: barbiturate NH protons, red spot: Hamilton wedge NH protons (the second NH peak of HW is overlapping with the aromatic protons in spectrum B).

series (②-④) assigned in Figure 5B, where each set was separated by ~ 68 g/mol, the repeating unit of the isoprene monomer (calculated 68.12 g/mol). The trithiocarbonates elimination, known due to fragmentation of the labile C-S bond during MALDI-TOF MS analysis, lead to a drastic decrease in the average molecular mass ($M_n, \text{SEC} = 12500$ g/mol).⁵⁴ Nevertheless, the main isotopic pattern at $m/z_{\text{average}} = 3089.865$ g/mol, which corresponds to the assigned HW functionalized species $[\text{C}_{41}\text{H}_{53}\text{N}_6\text{O}_7(\text{C}_5\text{H}_8)_{33}\text{CS}_2+\text{Na}]^+$ agrees with the simulated pattern, $m/z_{\text{average}} = 3089.411$ g/mol (deviation approx. 147 ppm, Figure 5C). The presence of other ions in the spectra such as Na^+ and K^+ may be due to contamination of glassware or the use of synthetic grade solvents during the synthetic path. The observed isotopic patterns (m/z) of the three minor series (②-④), as illustrated in Figure 5C&D, matched well with the simulated structures.

Furthermore, the capability of the resulting bifunctional macromolecules to self-assemble into well-defined supramolecular (ABAC)_n multiblock copolymers relying on H-

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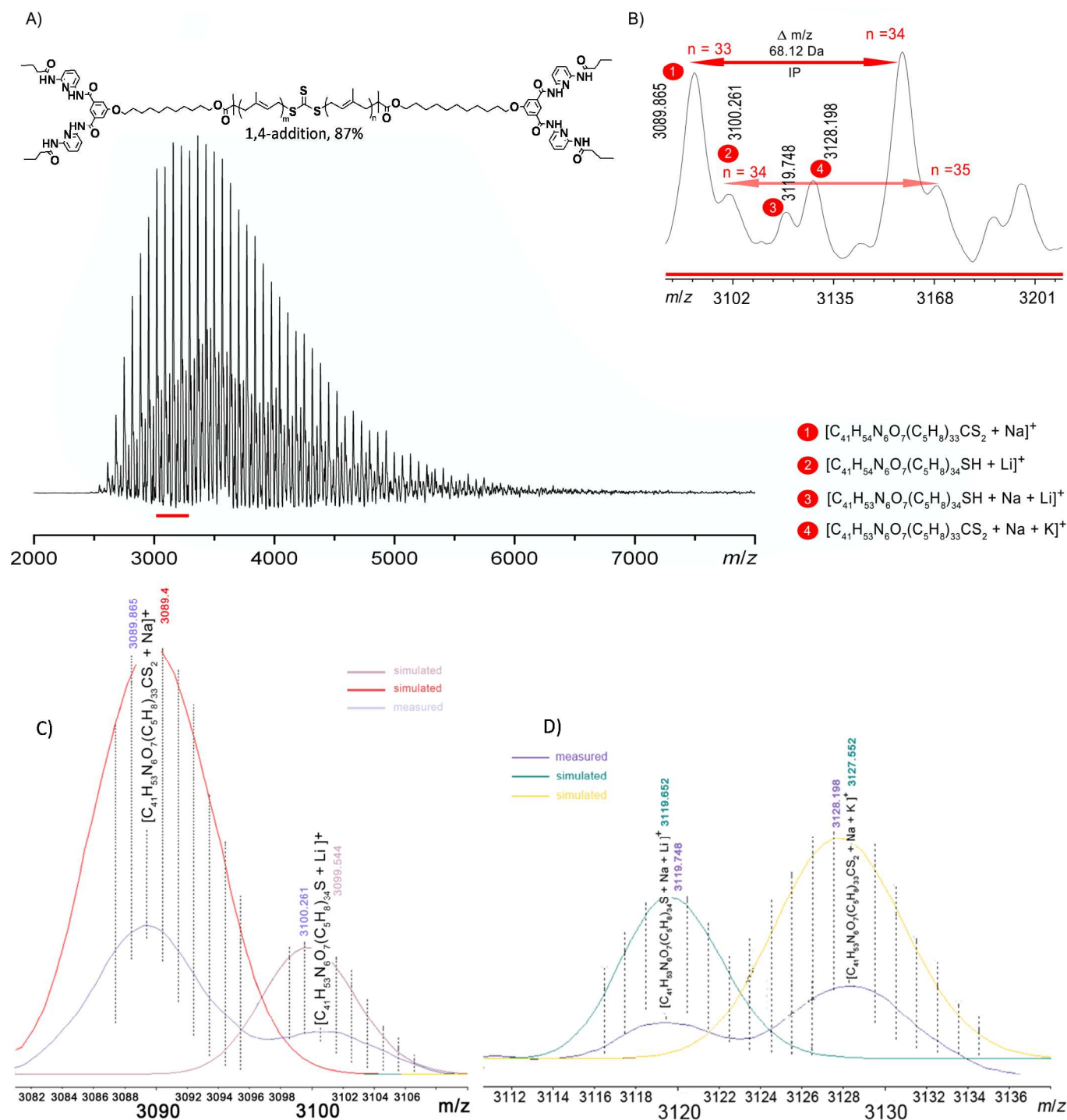


Figure 5: MALDI-TOF MS of HW-PI-HW4 (A) full spectrum, (B) expansion and (C&D) simulation of the isotope pattern.

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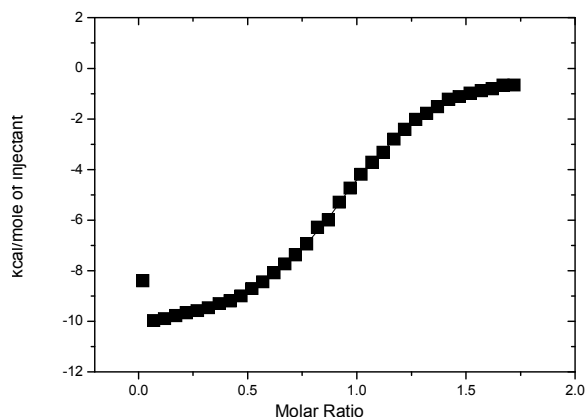


Figure 6: ITC titration of Ba-PS-*b*-PnBuA-*b*-PS-Ba4 with HW-PI-HW4 in CHCl₃ at 20°C.

bonding was subsequently evaluated by ¹H NMR, as can be seen in **Figure 4C**, the addition of 1 equiv of HW-PI-HW4 to Ba-PS-*b*-PnBuA-*b*-PS-Ba4 was accompanied by a significant downfield shift of the NH of barbiturate motifs from 8.03 to 12.22 ppm and the HW NH protons were observed at 9.25 and 9.61 ppm indicating the successful creation of six hydrogen bond arrays.

In analogy with a previous study for CTAs, the strength of the H-bonding polymeric building association was subsequently investigated by ITC in CHCl₃ at 20°C (**Figure 6**). K_a was found equal to $1.2 \times 10^4 \text{ M}^{-1}$ which is comparable with the value reported for the association of similar polymeric H-bonding interactions.^{19, 55}

Viscometry is a classic and convenient method to determine the propensity of macromolecules to self-assemble into

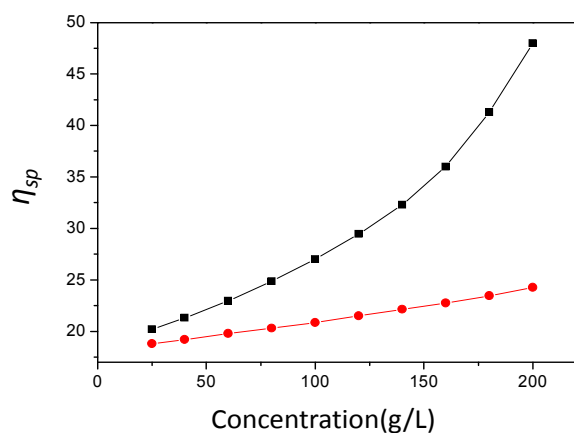


Figure 7: Specific viscosity (η_{sp}) of CHCl₃ solutions at 30 °C for 1/1 blend of Ba-PS-*b*-PnBuA-*b*-PS-Ba4/HW-PI-HW4 (black) and 1/1 blend of Ba-PS-*b*-PnBuA-*b*-PS-Ba4/PI_{unf} (red) versus concentration.

supramolecular polymer.⁵⁶ In analogy with previous studies,^{14, 19, 55} concentration-dependent comparative solution viscosities in CHCl₃ at 30 °C were subsequently investigated to further test the efficient formation of supramolecular structures. As can be seen in **Figure 7**, the viscosity of 1/1 blend of Ba-PS-*b*-PnBuA-*b*-PS-Ba4/HW-PI-HW4, where the formation of supramolecular multiblock copolymers is expected, exhibited a significantly larger increase with concentration than did a 1/1 blend of Ba-PS-*b*-PnBuA-*b*-PS-Ba4/PI_{unf} (PI_{unf} being an unfunctionalized PI with a molecular weight $Mn_{SEC} = 13400 \text{ g/mol}$, $PDI = 1.12$). These results undoubtedly indicate the effectiveness of the bifunctional macromolecules self-assembly through H-bonding, moreover, the properties of traditional covalent polymers could be dramatically modified by introducing H-bonding.

To gain insight into the self-assembly properties of a mixture between Ba-PS-*b*-PnBuA-*b*-PS-Ba4 and HW-PI-HW4 (1/1, molar ratio) in solution, DLS experiments were performed to determine the size of self-assembled supramolecular multiblock copolymers at different concentrations. As seen in **Figure 8**, the concentration was increased from 5 to 70 g/L at 25°C, showing two distributions in all cases. The appeared signals at higher sizes (53.1, 153.6 and 269.2 nm, respectively) evidenced the formation of supramolecular multiblock copolymer structures,¹⁴ as expected, at 70 g/L, both particle size and intensity increased strongly comparing to the lower concentrations, meanwhile, along with the presence of smaller particles (8.2, 6.5 and 5.9 nm, respectively), which could be estimated to the formation of dimer or oligomers by comparing these with the DLS results of precursor polymers (see **Figure S11**), moreover, a reduced R_h

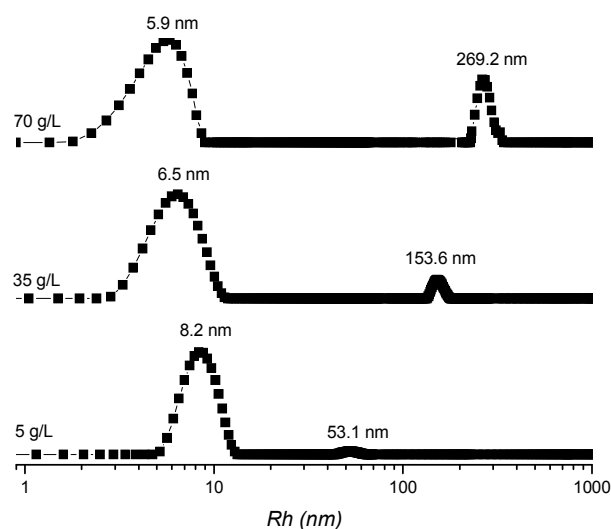


Figure 8: Hydrodynamic radius (R_h) for 1/1 blend of Ba-PS-*b*-PnBuA-*b*-PS-Ba4/HW-PI-HW4 measured by DLS at three concentrations in toluene at 25°C.

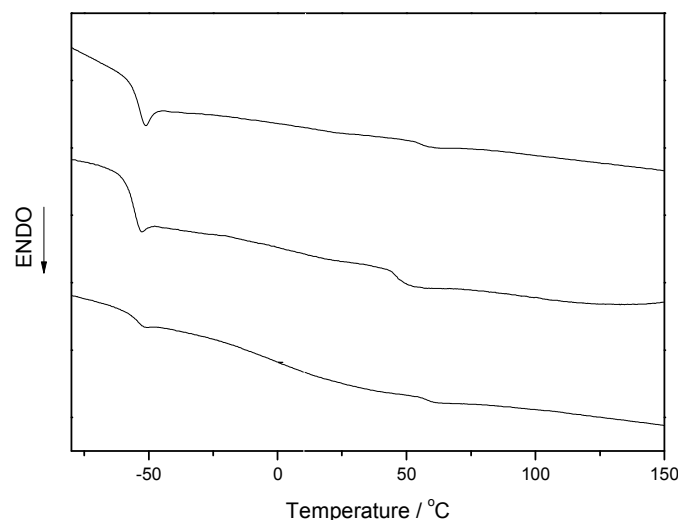


Figure 9: DSC curve of (A): Ba-PS-*b*-PnBuA-*b*-PS-Ba4, (B): HW-PI-HW4 and (C): 1/1 blend of Ba-PS-*b*-PnBuA-*b*-PS-Ba4/HW-PI-HW4, (2nd cycle).

(from 8.2 to 5.7 nm) for the smaller particles were observed, which might due to increased hydrodynamic repulsive forces between particles,¹⁴ or a progressive shift of dimers, oligomers to supramolecular structures. Thus, the DLS results further supported the efficient formation of novel supramolecular (ABAC)_n multiblock copolymers driven by the complementary recognition units.

In order to investigate our supramolecular (ABAC)_n multiblock copolymers indeed contain "glassy" and "rubbery" domains, the thermal properties have been subsequently investigated by DSC (**Figure 9**). As can be seen in **Figure 9A**, Ba-PS-*b*-PnBuA-*b*-PS-Ba4 displayed two distinct glass transition temperature (T_g): one corresponding to the PnBuA phase (-54 °C), and another corresponding to the PS phase (57 °C), which is ~40 °C lower than homopolymeric PS. This decreased T_g is in agreement with previous similar "hard-soft-hard" triblock copolymers containing PS.⁵⁷⁻⁵⁹ Surprisingly, HW-PI-HW4 also illustrated two distinct transition steps (**Figure 9B**). The T_g at -55 °C was assigned to PI phase, and another transition in the region between 44 to 52 °C, probably as a result of self-associated Hamilton wedges, which is supported by comparable DSC measurements between Hamilton wedge (compound **5**) and HW-PI-HW4 (see **Figure S12**). In the case of a 1/1 blend of Ba-PS-*b*-PnBuA-*b*-PS-Ba4/HW-PI-HW4 (**Figure 9C**), the formation of self-assembled structures between HW- and Ba-functionalized telechelic polymers was assessed by disappearance of the transition estimated by self-associated Hamilton wedges (in the region between 44 to 52 °C). Moreover, two T_g were indeed visible (-54 °C and 58 °C, respectively), proving that the supramolecular structure contains both phase segregated rubbery and glassy state. Nevertheless, additional experiments are required to clarify the thermal properties of H-bonding polymer, especially HW-PI-HW4.

Conclusions

We have first described the synthesis and characterization of two original symmetrical RAFT agents bearing Hamilton wedge and barbiturate motif, which are capable of controlled polymerizing styrene, *n*BuA and isoprene. Relying on the heterocomplementary motif couple, these resultant telechelic macromolecular building blocks subsequently afford the formation of novel supramolecular (ABAC)_n multiblock copolymers, where A in a glassy state, B and C in a rubbery state. The successful generation of desired supramolecular structure was evidenced by ¹H NMR, ITC, viscometry, DLS as well as DSC, the thermal properties of H-bonding polymer, especially HW-PI-HW4, a detailed investigation in this direction is undergoing and will be reported in due course.

Acknowledgements

The authors gratefully acknowledge Dr. Frédéric Lortie (IMP@INSA, Lyon, France) and Dr. Julien Bernard (IMP@INSA, Lyon, France) for their whole-hearted supports and insightful comments on the manuscript. We thank the German Science Foundation, DFG-project BI 1337/7-1 (WHB, SC, MS) for financial support.

Notes and references

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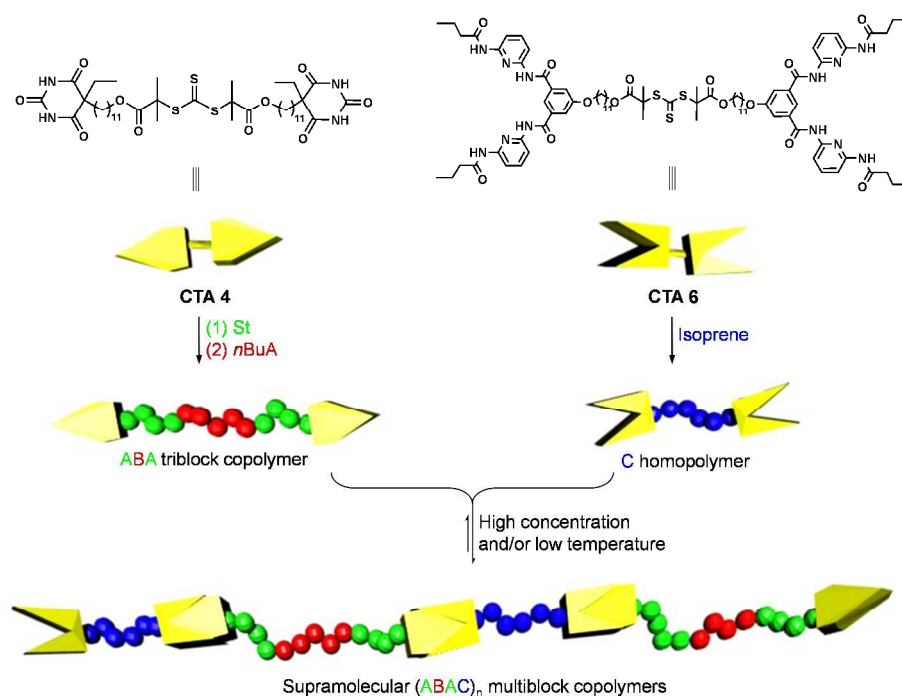
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Electronic Supplementary Information (ESI) available: [¹H and ¹³C NMR spectra of compound **2** and CTAs, ¹³C NMR spectra of Ba-PS-*b*-PnBuA-*b*-PS-Ba4 and HW-PI-HW4, ESI-TOF mass spectra of CTAs]. See DOI: 10.1039/b000000x/

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Graphical and textual abstract



The facile preparation of novel supramolecular (ABAC)_n *multiblock* copolymers from Hamilton wedge and barbiturate functionalized H-bonding RAFT agents is reported.