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Straightforward Preparation of Telechelic H-bonding Polymers From Difunctional Trithiocarbonates and Supramolecular Block Copolymers Thereof

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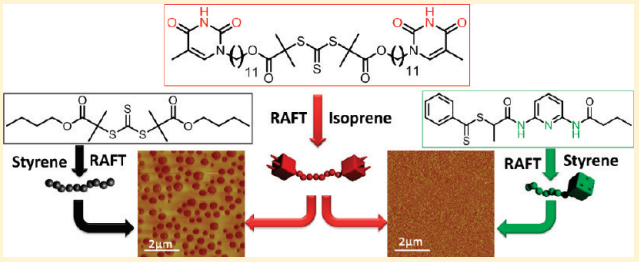
Supporting Information

ABSTRACT: We report an original strategy toward the straightforward preparation of precisely defined telechelic H-bonding polymers and the generation of supramolecular block copolymers thereof. Making use of an α,ω-functionalized symmetrical trithiocarbonate bearing thymine groups at both chain ends, a series of heterocomplementary H-bonding polymers were effortlessly generated by RAFT polymerization in a one step process. The resulting telechelic macromolecules selectively interacted with heterocomplementary α-DAP-functionalized chains to afford supramolecular block copolymers in solution and in bulk. These self-assemblies were evidenced by ^{1}H NMR and rheological measurements. As a consequence of these associations, whereas non functional homopolymer blends tended to microphase separate as observed by AFM analysis, H-bonding homopolymer blends exhibited homogeneous microstructures in accord with the formation of supramolecular block copolymers promoting the stabilization of the interface between the polymers.



INTRODUCTION

Over the last few decades, our scientific community has successfully extended the concept of self-assembling noncovalent interactions to the field of polymer materials.[1] In particular, the development of hydrogen bonding recognition units by Lehn together with others has paved the way to the design of supramolecular polymeric assemblies possessing a stimuli-responsive nature and self-healing abilities.[2] In analogy to covalent polymerizations, significant efforts have indeed gone into the development of homoditopic self-complementary or heterocomplementary monomers (A−A or A−A/B−B), heteroditopic heterocomplementary monomers (AB) or oligotopic monomers (AB_2, A_m, $m > 2$) respectively capable to self-organize to give birth to $(A-A)_n$, $(A-A-B-B)_n$, $(A-B)_n$ linear supramolecular polymers and supramolecular hyperbranched polymers and networks.[3]

In order to yield materials with valuable macroscopic properties, the preparation of tailor-made macromolecular counterparts (macromonomers), that is to say, linear polymer chains bearing, at their both extremities, H-bonding motifs promoting the reversible formation of original supramolecular edifices such as supramolecular homopolymers, block or multiblock copolymers and cross-linked architectures is also highly desirable.[4] However, a bottleneck to expanding the scope of this new class of materials is the difficulty of specifically and quantitatively introducing H-bonding moieties at both sides of a polymer chain. A generic approach toward α,ω-functionalized macromolecules relies on the postpolymerization functionalization of telechelic chains as previously reported by Binder, Meijer, Sijbesma, or Gong.[5] Unfortunately, this strategy usually suffers from incomplete yields and is therefore limited to low molecular weight polymer chains.

Alternatively, H-bonding stickers can be straightforwardly incorporated at the chain ends in the course of the polymerization process through the use of functionalized initiators, chain transfer agents or chain terminators.[6] Yet, the huge majority of the examples in the literature deal with the preparation of well-defined α or ω-functionalized macromolecules. A major step forward can be assigned to Weck and co-workers that recently reported the first one-pot synthesis of homotelechelic and heterotelechelic macromolecules from cyclooctene or norbornene derivatives via the combination of ring-opening metathesis polymerization (ROMP) with functional chain transfer agents (CTA) and the supramolecular block copolymers thereof.[7] One restriction of this elegant strategy lies though in the use of the

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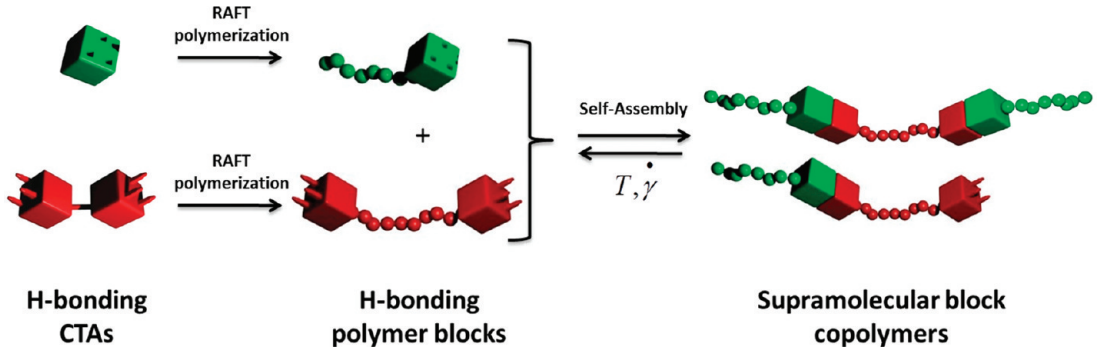
Scheme 1. General Strategy for the Synthesis of Supramolecular Block Copolymers



ROMP technique which is strictly limited to the polymerization of strained monomers and in the multistep synthesis of the CTAs and initiators.[7,8]

In this context, the RAFT process (reversible addition−fragmentation chain transfer), which is arguably the most versatile controlled/living free radical polymerization technique, with respect to monomer choice (vinyl esters, (meth)acrylates, (meth)acrylamides, styrenics, isoprene, ...) and experimental conditions is of particular interest. Indeed, the RAFT process has been extremely valuable to the preparation of end-functional polymers.[6i−k,9] In the specific case of α,ω-functional trithiocarbonates possessing a Z group having a C−S cleavable bond,[10] the RAFT process gives the quite unique opportunity to grow well-defined telechelic polymer chains in one step.

As part of our continuing studies on H-bonding RAFT-made polymers, we report in the present contribution a new and simple approach to the straightforward preparation of precisely defined telechelic H-bonding polymers by RAFT polymerization and the generation of supramolecular block copolymers thereof (see Scheme 1). Herein we demonstrate the effectiveness of the present strategy in synthesizing α,ω-thymine functionalized telechelic polystyrenes, poly(*n*-butyl acrylate)s and polyisoprenes in a very simple manner from functional trithiocarbonates and further investigate their subsequent self-assembly into supramolecular block copolymers with (RAFT-made) macromolecular blocks bearing complementary 2,6-diamidopyridine (DAP) hydrogen-bonding motifs.

EXPERIMENTAL SECTION

Materials. All reagents were purchased from Aldrich. All monomers were filtered prior to use by passing through a column of basic aluminum oxide to remove inhibitors. Unless otherwise stated, the other chemicals were used without further purification. *S*,*S*′-Bis(α,α′-dimethyl-α″-acetic acid)trithiocarbonate was synthesized according to a protocol found in the literature.[10] 1-(ω-hydroxyundecyl)thymine was prepared as previously reported from 11-bromo-1-undecanol and thymine.[6i] Dithiobenzoic acid was synthesized as previously reported.[11] Unless otherwise indicated the other chemicals were used without further purification.

Characterization Methods. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE250 (250 MHz) or AVANCE400 (400 MHz) spectrometer using $CDCl_3$ or CD_2Cl_2. ESI-MS spectra (m/z) of CTAs and initiator were measured on a Thermo-FinniganMat 95XL. α,ω-thymine-functionalized P*n*BuA, PS and PI and 2,6-diamidopyridine-functionalized PS, PVAc and P*n*BuA were analyzed with a SEC apparatus running in THF at 25 °C (flow rate: 1 mL.min^{-1}) or in DMF at 70 °C (flow rate: 0.7 mL.min^{-1}) and equipped with a Viscotek VE 1121 automatic injector, three columns (Waters HR2, HR1 and HR0.5), and a differential refractive index detector (Viscotek VE3580). The average molar masses of P*n*BuA, PS, PVAc, and PI were derived from a calibration curve based on a series of PS standards ranging from 500 to 50000 g·mol^{-1}.

All MALDI−TOF mass spectra were obtained with a Voyager-DE PRO (Applied Biosystems, Framingham, MA) equipped with a nitrogen laser emitting at 337 nm with a 3 ns pulse duration. The instrument was operated in linear or reflectron modes. The ions were accelerated under a potential of 20 kV. The positive ions were detected in all cases. The spectra were the sum of 300 shots and an external mass calibration of mass analyzer was used (a mixture of peptides, Sequazyme, Applied Biosystems, Framingham, MA). Samples were prepared by mixing 45 μL of 1,8,9-anthracenetriol (dithranol, purchased by Sigma-Aldrich) at 10 g·L^{-1} in THF with 5 μL of P*n*BuA solution (at 10 g·L^{-1} in THF). To enhance cationization of polymers, 5 μL of NaI (from Sigma-Aldrich, at 10 g·L^{-1} in acetone) were added to solutions. Finally, resulting mixtures (0.5 μL) were spotted on the MALDI sample plate and air-dried.

Dynamic rheological measurements were performed on a Physica MC301 (Anton Paar GmbH) stress controlled rheometer with 25 mm cone and plate geometry. The temperature was adjusted by a Peltier plate. Samples for the rheological measurements in solution were prepared by dissolving selected polymers in $CHCl_3$.

In order to perform atomic force microscopy measurements, silicon substrates (approximately 1 × 1 cm^2) were cleaned by ozonolysis treatment. Samples were prepared by spin-coating from toluene solutions (2800 rpm, 30 s), followed by drying during 72 h under vacuum. AFM images were acquired in air at room temperature using a Nanoscope IIIa Multimode (Digital Instruments/VEECO, CA). Intermittent contact imaging (i.e., tapping mode) was performed at a scan rate of 1 Hz. Uncoated silicon probes with a resonant frequency between 280 and 405 kHz, a spring constant 20 and 80 N/m, length of 115−135 μm, width of 30−40 μm and nominal tip radius of curvature less than 10 nm are used. Images were displayed and analyzed using the Nanoscope 6.14R1 software.

Synthesis of ***CTA1***. *S*,*S*′-Bis(α,α′-dimethyl-α″-acetic acid) trithiocarbonate (0.51 g, 1.81 mmol), 1-(ω-hydroxyundecyl)thymine (1.18 g, 3.98 mmol), and triphenylphosphine (PPh_3) (1.04 g, 3.97 mmol) were dissolved in distilled THF in a three-neck round-bottom flask cooled with an ice bath under argon. Diisopropyl azodicarboxylate (DIAD) (0.81 g, 4.01 mmol) diluted in distilled THF was then added dropwise. The solution was allowed to reach room temperature and stirred overnight. The solution was then heated at 40 °C during 3 h. The reaction mixture was subsequently cooled to room temperature, diluted with dichloromethane (150 mL) and washed with distilled water (2 × 200 mL). The organic layer was collected and dried with $MgSO_4$. The

solvent was removed under reduced pressure. The crude product, a yellow oil, was then purified by column chromatography, using dichloromethane:ethanol (30:1) as eluent. Pure fractions were combined and dried with $MgSO_4$. The solvent was removed under reduced pressure and the resulting yellow oil was placed in a fridge at 0 °C whereupon it slowly crystallized (0.46 g, 29%). ESI−MS: calculated for $(C_{41}H_{66}N_4O_8S_3+Na)^+$: 862.2. Found: 861.2. ^{1}H NMR ($CDCl_3$, δ, ppm): 1.27 (br, $-(CH_2)_9-$, 36H), 1.65 (s, $-S-C(CH_3)_2-CO$, 12H), 1.92 (s, $CH_3-C{=}C-$, 6H), 3.68 (t, $-N-CH_2-$, 4H), 4.06 (t, $-COO-CH_2-$, 4H), 6.98 (s, $CH_3-C{=}CH-$, 2H), 8.59 (s, *NH*, 2H). ^{13}C NMR ($CDCl_3$, δ, ppm): 12.30, 25.15, 25.89, 26.41, 28.32, 29.07, 29.16, 29.38, 29.41, 48.51, 56.07, 66.14, 110.47, 140.48, 151.11, 164.63, 172.73, 218.25.

Synthesis of ***CTA2***. **CTA2** was synthesized in three steps from 2,6-diaminopyridine (DAP). DAP (4.4 g, 40 mmol) and triethylamine (4.2 g, 40 mmol) were dissolved in dry THF (180 mL), and the solution was cooled to 0 °C in an ice bath. A solution of butyryl chloride (4.2 g, 38 mmol) in THF (20 mL) was added dropwise over a period of 1 h, and the reaction was allowed to proceed at 0 °C for another 3 h, before warming to room temperature. The reaction mixture was filtered, evaporated to dryness, and purified by column chromatography using ethyl acetate:cyclohexane (3:2) as eluent. **1** was obtained as a white powder (2.45 g, 51%).

To a solution of **1** (1 g, 5.2 mmol) and triethylamine (0.74 g, 7.3 mmol) in dichloromethane (100 mL) was slowly added 2-bromopropionylbromide (1.57 g, 7.3 mmol). The solution was stirred for 12 h, the solvent removed under reduced pressure and the resulting orange solid dissolved in ethyl acetate (100 mL) and successively extracted with brine (150 mL), saturated sodium bicarbonate (100 mL), and 0.1 M HCl (75 mL). The organic layer was collected and dried using $MgSO_4$, and the residue was purified by flash column chromatography on silica (1:1 cyclohexane:ethyl acetate). The resulting white solid (**2**) was vacuum-dried overnight (0.30 g, 18%).

Dithiobenzoic acid (15.60 g, 0.10 mol) was added to **2** (6.61 g, 0.02 mol) dissolved in THF (300 mL) and the reaction was stirred at 60 °C for 15 h. The reaction solution was cooled to room temperature, washed with brine, and then the organic layer was collected and dried using $MgSO_4$. The residue was purified by flash column chromatography on silica (3:1 cyclohexane:ethyl acetate) to remove unreacted dithiobenzoic acid and repurified by recrystallization (3:1 cyclohexane:ethyl acetate). **CTA2** was obtained as an orange solid (3.11 g, 40%). ESI−MS: calculated for $(C_{19}H_{21}N_3O_2S_2 + Na)^+$: 410.5. Found: 410.0. ^{1}H NMR ($CDCl_3$, δ, ppm): 0.99 (t, $-CH_2-CH_3$, 3H), 1.73 (d, $-S-CH-CH_3$, 3H), 1.75 (m, CH_3-CH_2-, 2H), 2.34 (t, $-(O{=}C)-CH_2-$, 2H), 4.92 (q, $-S-CH-CH_3-$, 1H), 7.2−7.7 (t, 3,4,5-Py*H*, 3H), 7.63 (t, 4-Py*H*, 1H), 7.85 (d, 2,6-Ph*H*, 2H), 7.90 (d, 3,5-PyH, 2H), 8.61 (s, N*H*, 2H). ^{13}C ($CDCl_3$ δ, ppm): 13.12, 19.04, 38.30, 47.72, 11.78, 128.24, 130.87, 141.42, 147.72, 169.35, 172.23, 222.52.

Synthesis of ***CTA3***. **2** (0.60 g, 1.91 mmol) and *O*-ethyl xanthic acid potassium salt (0.92 g, 5.73 mmol) were dissolved in dry acetone (100 mL) and the reaction was stirred overnight at room temperature. The white precipitate (KBr) was filtered off. The solution was concentrated under reduced pressure, and then precipitated twice in dichloromethane in order to remove the excess of *O*-ethyl xanthic acid potassium salt. Finally, the crude product was purified by column chromatography (9:1, dichloromethane:ethyl acetate). **CTA3** was obtained as a slightly yellow paste (0.20 g, 30%). ESI−MS: calculated for $(C_{15}H_{21}N_3O_3S_2 + Na)^+$: 378.5. Found: 378.0. ^{1}H NMR ($CDCl_3$, δ, ppm): 0.98 (t, $CH_3-CH_2-CH_2-C{=}O$, 3H), 1.40 (t, CH_3-CH_2-O-, 3H), 1.61 (d, $-S-CH-CH_3$, 3H), 1.73 (m, $CH_3-CH_2-CH_2-C{=}O$, 2H), 2.34 (t, $CH_3-CH_2-CH_2-C{=}O$, 2H), 4.47 (q, CH_3-CH_2-O-, 2H), 4.64 (q, $-S-CH-CH_3$, 1H), 7.62−7.95 (m, *PyH*, 3H), 7.77 (s, *NH*, 1H), 8.55 (s, *NH*, 1H). ^{13}C NMR ($CDCl_3$, δ, ppm): 13.79, 13.81, 16.26, 18.87, 39.73, 48.69, 71.26, 109.50, 109.85, 140.88, 149.23, 149.72, 169.42, 171.63, 213.35.

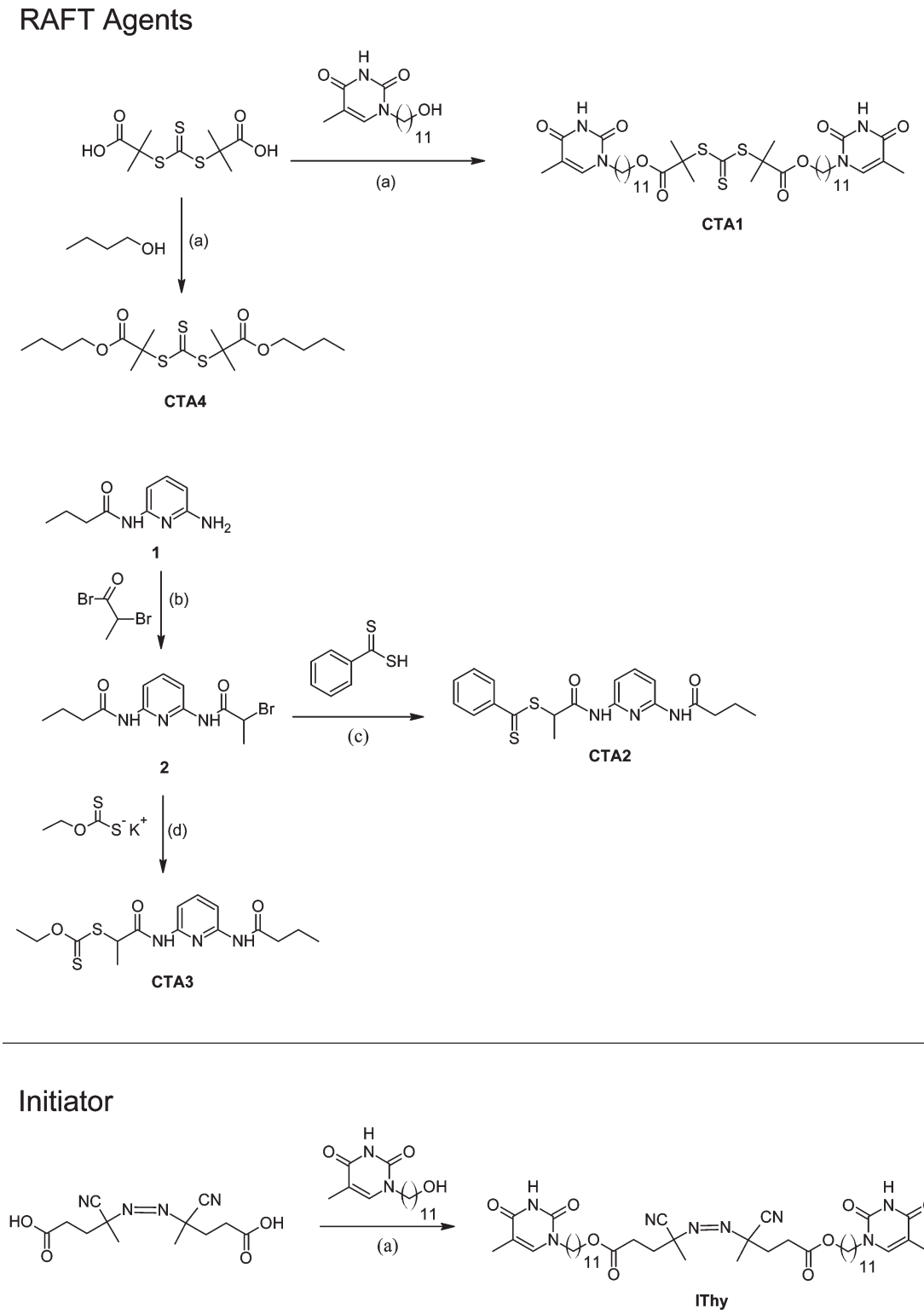
Synthesis of ***CTA4***. S,S′-Bis(α,α′-dimethyl-α″-acetic acid)trithiocarbonate (1 g, 3.54 mmol) and triphenylphosphine (PPh_3) (2.05 g, 7.81 mmol) were dissolved in anhydrous butanol (50 mL) in a three neck round-bottom flask cooled to 0 °C under argon. Diisopropyl azodicarboxylate (DIAD) (1.60 g, 7.91 mmol) diluted in anhydrous butanol (10 mL) was added dropwise. The solution was allowed to reach room temperature and stirred overnight. The solution was then heated at 40 °C during 3 h. The reaction mixture was cooled to room temperature, diluted with dichloromethane (150 mL) and washed with distilled water (2 × 250 mL). The organic layer was collected and dried with $MgSO_4$. The solvent was removed under reduced pressure. The crude product, a yellow oil, was then purified by column chromatography, using cyclohexane:ethanol (30:1) as eluent. Pure fractions were combined, dried under $MgSO_4$, and evaporated to dryness, giving **CTA4** as a yellow oil (850 mg, 57%). ESI−MS: calculated for $(C_{17}H_{30}O_4S_3 + Na)^+$: 417.6. Found: 417.0. ^{1}H NMR ($CDCl_3$, δ, ppm): 0.92 (t, CH_3-CH_2-, 6H), 1.66−1.32 (m, $CH_3-(CH_2)_2-CH_2-O-$, $-S-C(CH_3)_2-CO$, 20H), 4.08 (t, $-CH_2-O-C{=}O-$, 4H). ^{13}C NMR ($CDCl_3$, δ, ppm): 12.39, 18.19, 24.15, 29.42, 55.06, 64.86, 171.76, 217.27.

Synthesis of ***IThy***. 4,4′-Azobis(4-cyanopentanoic acid) (ACPA) (0.46 g, 1.64 mmol), triphenylphosphine (0.94 g, 3.58 mmol) and 1-(ω-hydroxyundecyl)thymine (1.06 g, 3.58 mmol), were dissolved in distilled THF, in a round-bottom flask cooled to 0 °C, under argon. DIAD (0.72 g, 3.58 mmol) diluted in distilled THF was then added dropwise. The solution was allowed to reach room temperature and stirred for 1 day. The solution was diluted with dichloromethane (150 mL) and washed with distilled water (2 × 200 mL). The organic layer was collected and dried with $MgSO_4$. The solvent was removed under reduced pressure. 2/3 of the crude product were then purified by column chromatography, using dichloromethane:ethanol (30:1) as eluent. Pure fractions were combined, dried with $MgSO_4$. **IThy** was obtained as a white solid (72.5 mg, 8%). ESI−MS: calculated for $(C_{44}H_{68}N_8O_8 + Na)^+$: 860.0. Found: 859.1. ^{1}H NMR ($CDCl_3$, δ, ppm): 1.27 (br, $-(CH_2)_9-$, 36H), 1.62 (t,$-CH_2-CH_2-COO-$, 4H), 1.72 (s, $CH_3-C-C{\equiv}N$, 6H), 1.92 (s, $CH_3-C{=}C-$, 6H), 2.47 (t, $-CH_2-COO-$, 4H), 3.67 (t, $-N-CH_2-$, 4H), 4.08 (t, $-COO-CH_2-$, 4H), 6.98 (s, $CH_3-C{=}CH-$, 2H), 9.29 (s, *NH*, 2H). ^{13}C NMR ($CDCl_3$, δ, ppm): 12.30, 25.15, 25.89, 26.41, 28.32, 29.07, 29.16, 29.38, 29.41, 48.51, 56.07, 66.14, 110.50, 117.50, 140.43, 150.97, 164.41, 171.38.

General Procedure for Bulk Polymerization of *n*-Butyl Acrylate (*n*BuA). Bulk polymerization of *n*BuA was carried out using **CTA1**, **CTA2**, or **CTA4** as RAFT agent, and **IThy** or AIBN as initiator. For instance, **CTA1** (90.9 mg, 1.1×10^{-4} mol), **IThy** (4.71 mg, 5.6×10^{-6} mol) and trioxane (78.5 mg, 8.7×10^{-4} mol, internal reference) were dissolved in *n*-butyl acrylate (1.5 mL, 1.1×10^{-2} mol) and transferred in a Schlenk tube, which was deoxygenated by five freeze−pump−thaw cycles. The Schlenk tube was immerged in an oil bath at 70 °C. The reaction was stopped by plunging the tube into liquid nitrogen. Conversion was estimated by analyzing an aliquot of the obtained mixture by ^{1}H NMR, weighting the integral of vinyl protons of the monomer (5.7−6.5 ppm) and the integral of trioxane (5.15 ppm). The polymer was precipitated twice in methanol:water (1:1), and dried under vacuum during 24 h. The molecular weight of the pure P*n*BuA was finally determined by ^{1}H NMR in $CDCl_3$, from integration of the protons of the polymer chains ($-COO-CH_2-$, 2*n*H, δ = 4.03 ppm, with *n* being the degree of polymerization) and of protons of the thymine end-group ($-C{=}CH-N$, 2H, δ = 6.97 ppm).

General Procedure for Bulk Polymerization of Styrene. Bulk polymerization of styrene was carried out using **CTA1**, **CTA2**, or **CTA4** as RAFT agent, and **IThy** or AIBN as initiator. For instance, **CTA1** (40 mg, 4.8×10^{-5} mol), **IThy** (1.03 mg, 1.2×10^{-6} mol), and trioxane (287 mg, 3.2×10^{-3} mol) were dissolved in styrene (2.2 mL, 1.9×10^{-2} mol), and then transferred in a Schlenk tube, which was

Scheme 2. Synthesis of Thymine and DAP-functionalized CTAs (CTA1-3), and non-functionalized CTA (CTA4), and Thymine-Functionalized Initiator (IThy)[a]



[a] Key: (a) PPh_3, DIAD, CH_2Cl_2; (b)NEt_3, CH_2Cl_2; (c) THF; (d) acetone.

deoxygenated by five freeze−pump−thaw cycles. The Schlenk tube was immersed in an oil bath at 80 °C. The reaction was stopped by plunging the tube into liquid nitrogen. Conversion was estimated by analyzing an aliquot of the obtained mixture by ^{1}H NMR, weighting the integral of vinyl protons of the monomer (5.7−6.5 ppm) and the integral of trioxane (5.15 ppm). The polymer was isolated by precipitation in methanol (2×) and dried under vacuum during 24 h. The molecular weight of the pure PS was finally determined by ^{1}H NMR in CD_2Cl_2,

Table 1. Characteristics of the Thy and DAP-Functionalized Polymers Generated by RAFT Polymerization of Styrene, *n*BuA, Isoprene, and VAc Mediated by CTA1, CTA2 or CTA3

sample	CTA	[M]/[CTA]	conv[a] %	$M_{n,th}$[a] (g/mol)	$M_{n,NMR}$[a] (g/mol)	$M_{n,SEC}$[b] (g/mol)	PDI
Thy-P*n*BuA-Thy1	1	100	48	7000	8000	8700	1.15
Thy-P*n*BuA-Thy2	1	100	70	9800	10 000	11 000	1.23
Thy-P*n*BuA-Thy3	1	250	6	2700	2800	3300	1.25
Thy-PI-Thy1	1	500	21	8000	9300	12 000	1.37
Thy-PI-Thy2	1	500	29	11 000	12 400	14 000	1.52
Thy-PS-Thy1	1	70	20	2300	2800	3400	1.07
Thy-PS-Thy2	1	200	35	8000	14 400	11 000	1.29
Thy-PS-Thy3	1	400	21	9600	15 600	10 500	1.28
Thy-PS-Thy4	1	400	24	10 800	14 600	10 500	1.22
P*n*BuA-DAP1	2	100	29	4100	4900	4800	1.32
P*n*BuA-DAP2	2	300	28	11 100	11 800	10 700	1.19
PS-DAP1	2	400	7	4000	3000	5200	1.25
PS-DAP2	2	400	10	4700	3200	4000	1.17
PS-DAP3	2	400	11	4900	4000	5100	1.26
PS-DAP4	2	400	20	9000	8300	9400	1.27
PVAc-DAP1	3	250	35	7800	7200	9200	1.38
PVAc-DAP2	3	250	66	14 600	15 900	16 000	1.45
PVAc-DAP3	3	250	80	17 500	17 100	20 000	1.43

[a] Calculated by ^{1}H NMR. [b] Evaluated by SEC in THF using polystyrene standards.

from integration of the aromatic protons of the polymer chains (Ar, 5*n*H, δ = 6.4−7.4 ppm, with *n* being the degree of polymerization) and of protons of the chain ends (−N−CH_2−, 4H, δ = 3.68 ppm).

General Procedure for Solution Polymerization of Isoprene. Solution polymerization of isoprene was carried out using **CTA1**, or **CTA2** as RAFT agent, and dicumyl peroxide (DCP) as initiator. For instance **CTA1** (34.5 mg, 4.1×10^{-5} mol), DCP (0.55 mg, 2.0×10^{-6} mol) and isoprene (2.1 mL, 2.1×10^{-2} mol) were dissolved in toluene (2.5 mL), and then transferred in a Schlenk tube, which was deoxygenated by five freeze−pump−thaw cycles. The Schlenk tube was immersed in an oil bath at 120 °C. The reaction was stopped by plunging the tube into liquid nitrogen. The mixture was then concentrated under reduced pressure. Conversion was estimated gravimetrically. The polymer was isolated by precipitation in methanol (2×) and dried under vacuum for 24 h. The molecular weight of the pure PI was finally evaluated by ^{1}H NMR ($CDCl_3$) from relative integration of the protons of the PI backbone (5.6−5.9 ppm for the −C*H*═CH_2 from the 1.2-addition polymerization, 5.0−5.5 ppm for −C*H*═C(CH_3)− for the 1,4-addition polymerization, and 4.4−5.0 ppm for the mixture of −CH═CH_2 (1.2-addition) and −C(CH_3)═CH_2 (3,4-addition)) and of characteristic protons of the thymine end group ((C═C*H*−N, 1H, δ = 6.97 ppm).

General Procedure for Bulk Polymerization of Vinyl Acetate (VAc). Bulk polymerization of styrene was carried out using **CTA3** as RAFT agent, and AIBN as initiator. For instance, **CTA3** (42 mg, 1.2×10^{-4} mol), AIBN (1.82 mg, 1.1×10^{-5} mol), and trioxane (160 mg, 1.8×10^{-3} mol) were dissolved in VAc (2.6 mL, 2.8×10^{-2} mol), and then transferred in a Schlenk tube, which was deoxygenated by five freeze−pump−thaw cycles. The Schlenk tube was immersed in an oil bath at 80 °C. The reaction was stopped by plunging the tube into liquid nitrogen. The polymer was precipitated twice into pentane to remove unreacted monomer. Conversion was estimated by analyzing an aliquot of the obtained mixture by ^{1}H NMR, weighting the integral of vinyl protons of the monomer (5.7−6.5 ppm) and the integral of trioxane (5.15 ppm). The molecular weight of the pure PVAc was finally evaluated by ^{1}H NMR ($CDCl_3$) from relative integration of the protons of the PVAc backbone (4.84 ppm, −CH_2−C*H*−O−C═O) and of protons of the chain end (7.5−8 ppm, PyH).

RESULTS AND DISCUSSION

Synthesis of H-Bonding CTAs. The versatility and the tolerance of the RAFT process in terms of functionality and polymerization conditions facilitate the preparation of polymers possessing H-bonding motif. To this end, three original H-bonding CTAs were designed (see Scheme 2).

A symmetrical trithiocarbonate bearing a thymine moiety at each extremity (**CTA1**) and thus capable to grow telechelic H-bonding polymers in a one step process was targeted. We first unsuccessfully attempted to adapt the procedure developed by Leung et al.[12] with disodium trithiocarbonate and a thymine functionalized secondary alkyl halide under phase transfer conditions. The introduction of the thymine moieties was then undertaken through esterification reactions between preformed trithiocarbonates and 1-(ω-hydroxyundecyl)thymine. Whereas the reaction involving the diacid chloride functionalized CTA and 1-(ω-hydroxyundecyl)thymine surprisingly failed at generating the expected compound, the coupling between 1-(ω-hydroxyundecyl)thymine and the diacid functionalized CTA proceeded smoothly under Mitsunobu conditions to generate **CTA1**. The pure product was finally isolated in moderate yield (30%) owing to difficult separation from thymine monofunctionalized CTA.

Aiming at investigating the association of α,ω-thymine functionalized polymers with blocks bearing heterocomplementary recognition unit, a dithiobenzoate (**CTA2**) and a xanthate (**CTA3**) bearing a DAP moiety were also prepared with moderate yields (30−40%) by coupling the alkylating agent **2** respectively with dithiobenzoic acid or *O*-ethyl xanthic acid potassium salt. The ^{1}H NMR spectra for the resulting sticker-functionalized CTAs are given in Supporting Information.

Prior to undertaking any polymerization reaction, the capability of **CTA1** and **CTA2** or **CTA3** to associate through hydrogen bonding interactions was examined by ^{1}H NMR analysis in $CDCl_3$ at 25 °C. The association of the heterocomplementary stickers was

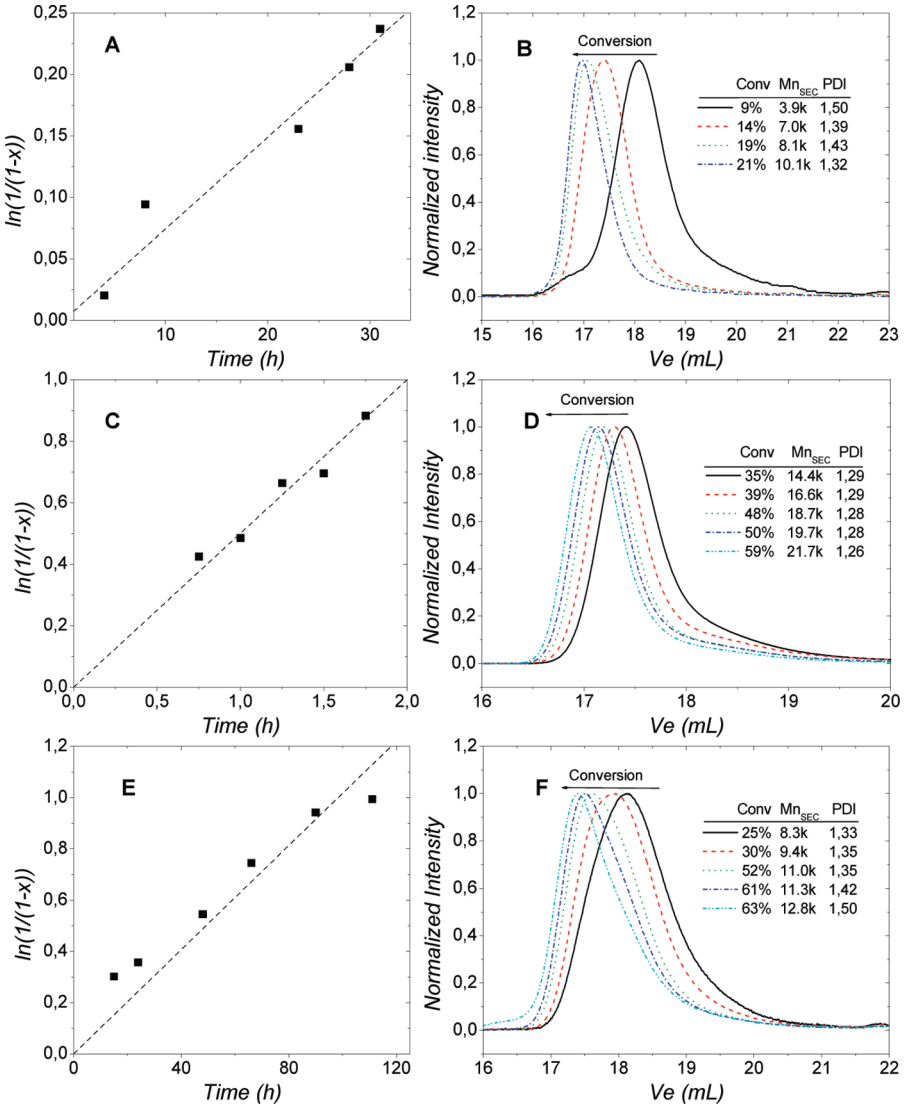


Figure 1. (A) First-order kinetic plots and (B) evolution of the SEC traces for the bulk polymerization of styrene at 80 °C mediated by **CTA1** using **IThy** as initiator: [M]/[CTA] = 400, [CTA][Initiator] = 80. (C) First-order kinetic plots and (D) evolution of the SEC traces for the bulk polymerization of *n*BuA at 70 °C mediated by **CTA1** using **IThy** as initiator: [M]/[CTA] = 250, [CTA][Initiator] = 20. (E) First-order kinetic plots and (F) evolution of the SEC traces for the polymerization of isoprene at 120 °C in toluene mediated by **CTA1** using DCP as initiator: [M]/[CTA] = 500, [CTA][Initiator] = 20.

undoubtedly evidenced by the downfield shift of the −NH− thymine proton of **CTA1** observed after addition of 1 equiv of heterocomplementary **CTA2**/**CTA3** ([Thy] = [DAP] = 2.5 × 10^{-2} mol) (from 8.74 to 10.71 ppm for **CTA2**, from 8.74 to 10.68 ppm for **CTA3**). Using titration experiments and a relevant mathematical model,[13] a binding constant consistent with reported values (110 M^{-1}) was determined (see Supporting Information).

Synthesis of Macromolecular Building Blocks. The RAFT polymerizations were carried out at adequate [CTA]/[initiator] ratio (typically 20/1, 40/1, or 80/1) to drastically limit the number of nonfunctionalized or monofunctionalized chains while maintaining reasonable polymerization rates. In addition, α,ω-thymine functionalized trithiocarbonate mediated RAFT polymerizations of *n*BuA and styrene were carried out in the presence of a functionalized initiator (**IThy**) specifically designed from ACPA initiator to exclusively release initiating radicals possessing thymine moieties.

As shown in Table 1 and Figure 1, bulk polymerizations of styrene and *n*-butyl acrylate in the presence of **CTA1** resulted in a good control. The telechelic polymers grew linearly with monomer conversion, and the polydispersity indices remained below 1.3. Experimental molecular weights were in very good agreement with those expected confirming that the number of chains is dictated by the CTA concentration. Moreover a linear relationship between $\ln(1/[1-x])$ vs time was observed indicating that the concentration of propagating species remains constant throughout the polymerization. Because of the poor solubility of α,ω-thymine functionalized trithiocarbonate in the monomer, the polymerization of isoprene was investigated in solution (toluene). The polymerizations were carried out at 120 °C in the presence of dicumyl peroxide. In contrast to styrene and *n*-butyl acrylate, **CTA1**-mediated polymerization of isoprene proceeded in a less controlled fashion (possibly due to chain−chain coupling) leading to polyisoprene possessing broader

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molecular weight distribution (PDI = 1.3−1.6). These results are consistent with those of Jitchum and Perrier,[14] who synthesized polyisoprenes of similar molar mass in the presence of trithiocarbonates. To demonstrate the full utility of this new H-bonding CTA, we further investigated the ability to generate triblock copolymers from the thymine functionalized homopolymers. As an illustration, we intended to prepare P*n*BuA-*b*-PS-*b*-P*n*BuA from a P*n*BuA macroRAFT agent. As can be seen in Figure 2, the chain extension of P*n*BuA macroRAFT agent ($\overline{M}_{n\,SEC}$ = 15600 g·mol^{-1}, PDI = 1.13, in DMF) with styrene resulted in a clear shift of the SEC peak toward higher molecular weight region ($\overline{M}_{n\,th}$ = 27800 g·mol^{-1}, $\overline{M}_{n\,RMN}$ = 34000 g·mol^{-1}, $\overline{M}_{n\,SEC}$ = 28200 g·mol^{-1}, PDI = 1.19 in DMF) consistent with the growth of the polystyrene blocks. Moreover, the absence of low molecular weight tailing ascertained that nearly all the P*n*BuA chains participate to the (co)polymerization process underlining the excellent efficiency of the thymine functionalized P*n*BuA macroRAFT agent.

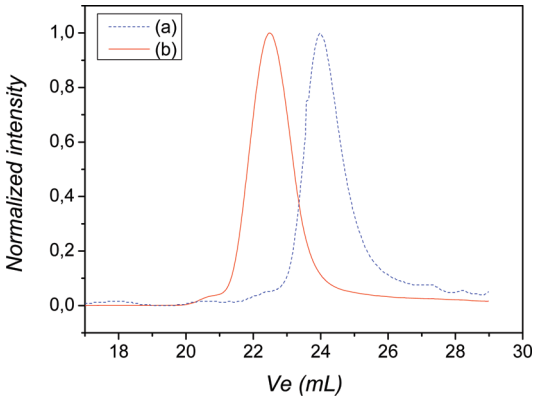

Figure 2. Overlaid SEC traces of (a) P*n*BuA macroRAFT agent and (b) PS-P*n*BuA-PS triblock copolymer (using DMF as eluent).

The effective incorporation of the thymine functionalities at both chain ends of the homopolymer was assessed by ^{1}H NMR analysis for the P*n*BuA and PI backbones, with the appearance of characteristic thymine peaks at 6.97 and 8.03 ppm (relative to −C═C*H*−N− and N*H*, respectively) and the excellent accord between the experimental molecular weights calculated by ^{1}H NMR (from relative integration of polymer backbone protons and the thymine protons) and theoretical values. At this point, it is important to note that the functionalization of the polystyrene chains could not be precisely determined in a similar manner due to peak overlapping with the aromatic protons of the PS backbone. However, the presence of thymine moieties was evidenced by ^{13}C NMR (thymine peaks at 12.9, 110.8, 139.7, 152.0, 164.2).

A structural investigation was also achieved by mass spectrometry to confirm the presence of thymine end-groups in the

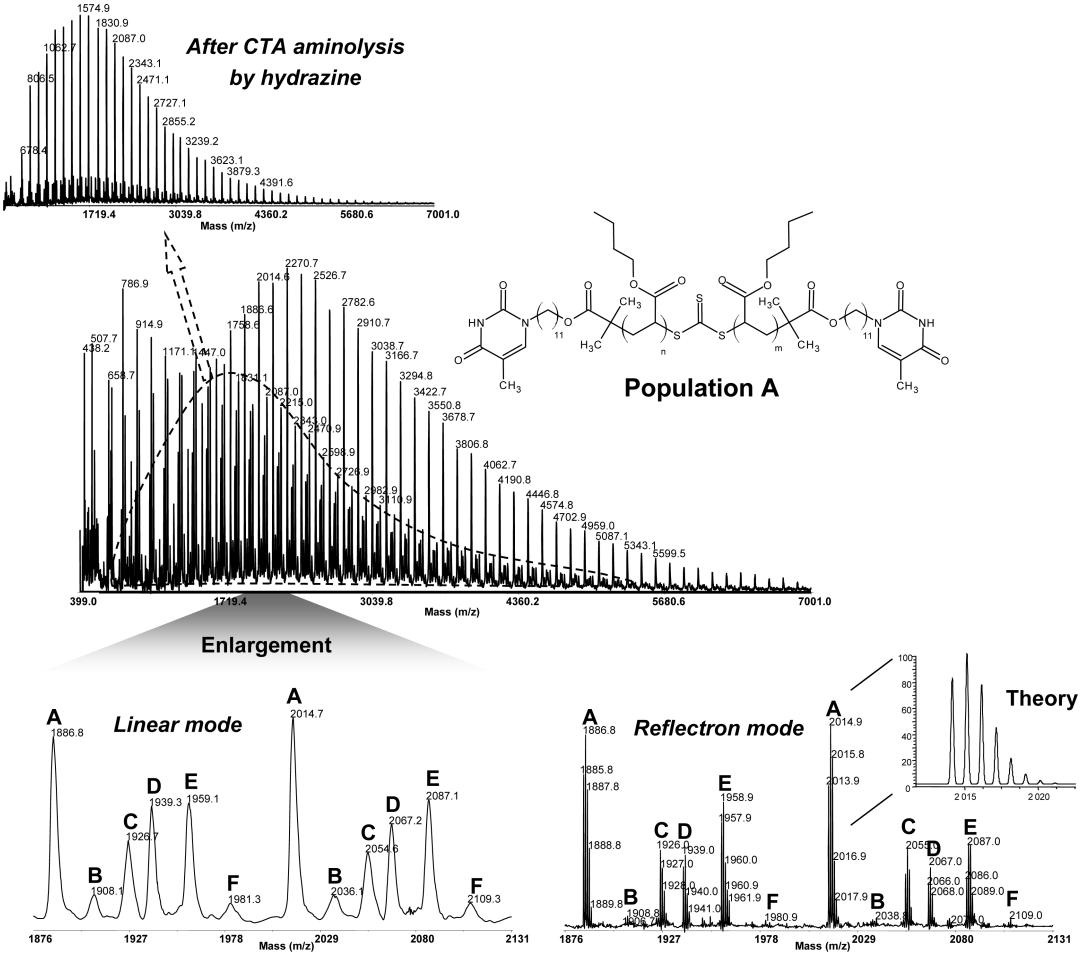

Figure 3. Positive ion MALDI−TOF mass spectrum of Thy-P*n*BuA-Thy3 (dithranol matrix, NaI salt, linear mode), and enlargements of mass spectra acquired in linear and reflectron modes (same *m*/*z* scale). Upper inset: MALDI−TOF mass spectrum of Thy-P*n*BuA-Thy3 after a chemical treatment by hydrazine ([hydrazine]/[P*n*BuA] = 20, 1 h, THF).

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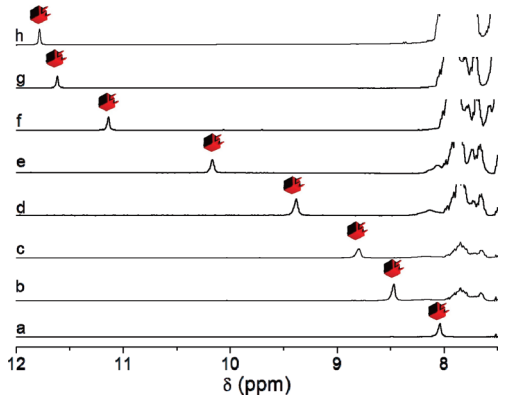

Figure 4. ^{1}H NMR spectra at 25 °C in $CDCl_3$ of a mixture of Thy-P*n*BuA-Thy1 and PS-DAP3, with [Thy-PnBuA-Thy] = 3×10^{-3} mol L^{-1} and various equivalents of PS-DAP3: (a) 0 equiv; (b) 1 equiv; (c); 2 equiv; (d) 4 equiv; (e) 8 equiv; (f) 16 equiv; (g) 24 equiv; (h) 32 equiv. Red symbol: thymine N*H* protons.

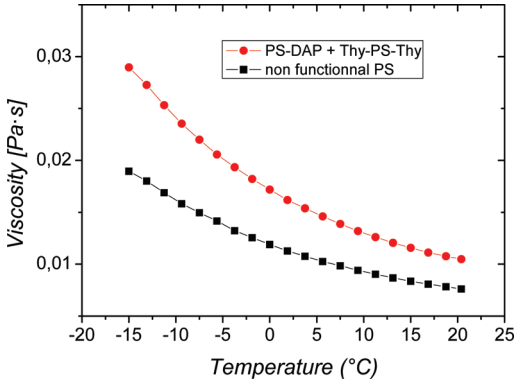

Figure 5. Viscosities of chloroform solutions (325 g·L^{-1}) containing both PS-DAP4 and Thy-PS-Thy2 ($\overline{M}_{n\,SEC}$ = 9400 g·mol^{-1} and $\overline{M}_{n\,SEC}$ = 11000 g·mol^{-1}, respectively) at a 1/1 DAP/Thy molar ratio or nonassociating PS ($\overline{M}_{n\,SEC}$ = 9000 g·mol^{-1}).

polymer chains (Figure 3 for Thy-P*n*BuA-Thy3, see Supporting Information for Thy-PS-Thy1). The MALDI mass spectrum of Thy-P*n*BuA-Thy3, acquired in linear mode, disclosed a main distribution of peaks separated by expected 128 mass units (i.e., a *n*BuA repeat unit), and centered at 2400 *m*/*z*. Besides this series, a second distribution at low *m*/*z* values was observed (dotted line, Figure 3). Thanks to an aminolysis reaction of the same Thy-P*n*BuA-Thy3 sample by hydrazine and a MALDI analysis of the resulting sample, this second distribution was assigned to a thiol-terminated P*n*BuA population (mass spectrum in upper inset). As a result of this chemical treatment, a drastic decrease in average molecular mass was also detected by SEC (before treatment: 3300 g·mol^{-1} and after 1870 g·mol^{-1}). The presence of this thiol-terminated population in Thy-P*n*BuA-Thy3 sample was thus attributed without a doubt to chain cleavage events (hydrolysis) during the purification process. Indeed, Thy-P*n*BuA-Thy3 exhibits very low molar mass (well-suited for a MALDI−TOF characterization) that enhances its susceptibility toward hydrolysis during the purification process (difficult precipitations in methanol:water 1:1). At this point it is also important to note that a quantitative analysis based on the proportions of the different populations identified by MALDI−TOF mass

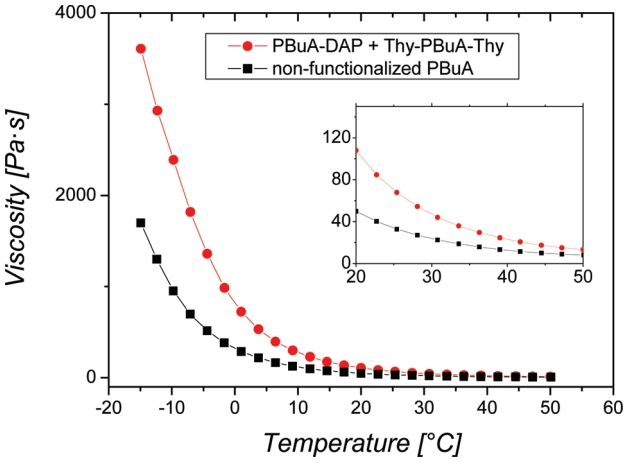

Figure 6. Bulk viscosities for a P*n*BuA-DAP2 ($\overline{M}_{n\,SEC}$ = 10700 g·mol^{-1}, PDI = 1.19) /Thy-P*n*BuA-Thy2 ($\overline{M}_{n\,SEC}$ = 11000 g·mol^{-1}, PDI = 1.23) blend at 1/1 DAP/Thy molar ratio and a nonfunctionalized P*n*BuA generated from **CTA4** ($\overline{M}_{n\,SEC}$ = 11700 g·mol^{-1}, PDI = 1.16).

spectroscopy is very delicate and that the presence of a second population resulting from hydrolysis has never been observed by SEC whatever the initial molar mass of P*n*BuA.

This thiol-terminated population corresponding to the population E in the enlargement of initial Thy-P*n*BuA-Thy3 mass spectrum was associated with 5 other distinct populations. The same enlargement in reflectron mode confirmed that the main population (peak A, Figure 3) matched the expected α,*ω*-thymine functionalized telechelic P*n*BuA chains (e.g., *m*/*z* monoisotopic masses: theo. 2014.1, found 2013.9). The simulated and experimental isotopic patterns of these dormant species were in good agreement (Figure 3). Concerning the population C, it was assigned to H-terminated species coming from a fragmentation process in the MALDI mass spectrometer (e.g., *m*/*z* monoisotopic masses: theo. 2054.3, found 2054.0), as previously discussed.[15] Minor populations (B and F peaks) located on each side of the thiol-terminated population (e.g., *m*/*z* monoisotopic masses: theo, 2086.3; found, 2086.0) probably correspond to Na-adducts. (peak B, $[A - H + Na + Na]^+$, *m*/*z* average masses: theo, 2037.7; found, 2036.1; peak F, $[E - H + Na + Na]^+$, *m*/*z* average masses: theo, 2109.8; found, 2109.3 in linear mode.) Finally, the identification of peak D peaks is unknown for this moment.

To evaluate the efficiency of these H-bonding telechelic polymers as building blocks for supramolecular architectures, polymers bearing a heterocomplementary DAP group were generated from bulk polymerization of *n*BuA and styrene mediated by **CTA2**, and from bulk polymerization of VAc mediated by **CTA3**. All polymerizations were well-controlled, as evidenced by the good accordance between molecular weights determined by SEC and NMR, and the theoretical values (see Table 1). Moreover, narrow polydispersity indexes (from 1.17 to 1.45) were measured (See Supporting Information).

Characterization of Polymer Self-Assembly by ^{1}H NMR. The self-assembly of α-*ω*-thymine functionalized polymers (Thy-P*n*BuA-Thy1, Thy-PS-Thy3, Thy-PS-Thy4 or Thy-PI-Thy1) with α-DAP functionalized polymers (respectively PS-DAP3, PS-DAP2, PVAc-DAP2, PS-DAP1) was subsequently investigated by ^{1}H NMR in $CDCl_3$. Similar to the association of corresponding H-bonding CTAs, increasing the concentration

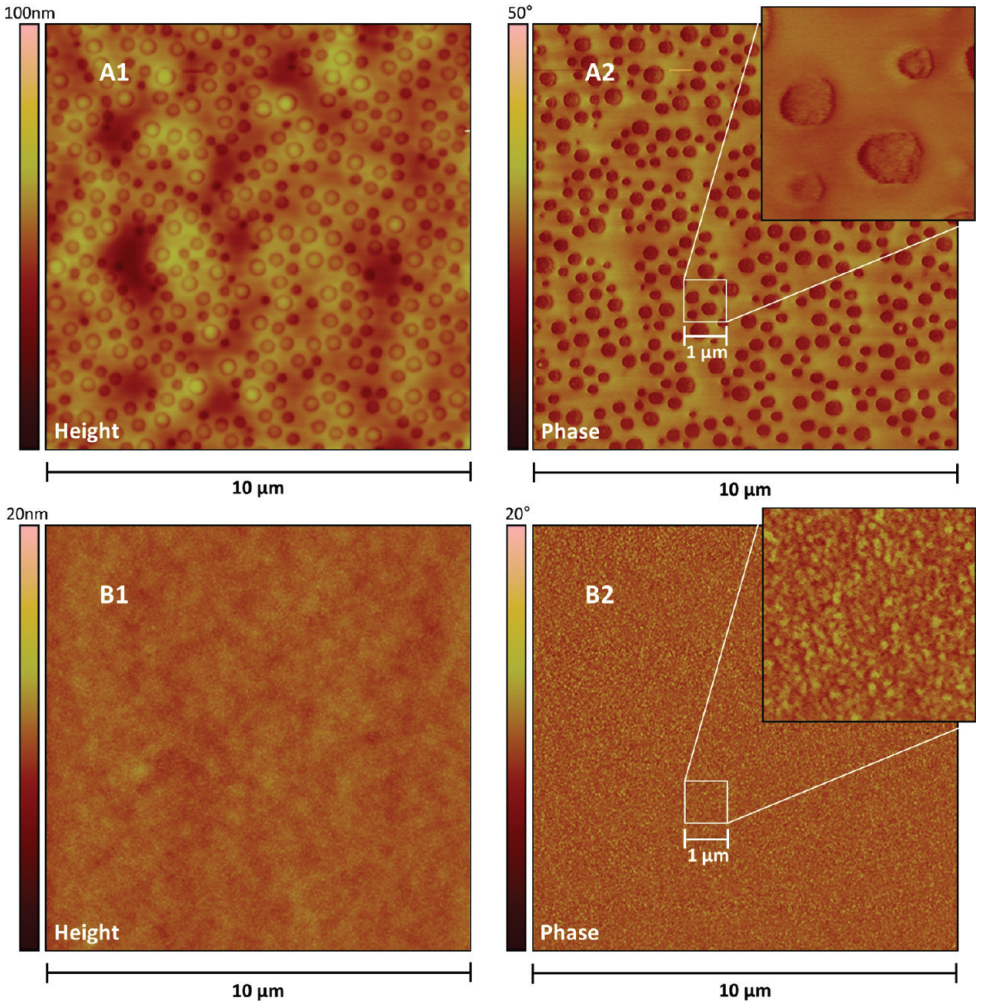

Figure 7. AFM images of mixture of (A): Thy-PI-Thy1 ($\overline{M}_{n\,SEC}$ = 12000 g·mol^{-1}) and nonfunctionalized PS ($\overline{M}_{n\,SEC}$ = 4000 g·mol^{-1}); (B): Thy-PI-Thy1 ($\overline{M}_{n\,SEC}$ = 12000 g·mol^{-1}) and PS-DAP1 ($\overline{M}_{n\,SEC}$ = 5200 g·mol^{-1}).

of PS-DAP or PVAc-DAP block in solution of heterocomplementary THY-P*n*BuA-Thy1, THY-PS-Thy3, Thy-PS-Thy4 and THY-PI-Thy1 blocks led to a significant downfield shift of the NH thymine proton (for instance with [DAP] = [Thy], from 8.04/8.05/7.98/7.95 to 8.80/8.67/8.73/8.52 ppm respectively) demonstrating the formation of supramolecular block copolymers (see Figure 4 for the association between Thy-P*n*BuA-Thy1 and PS-DAP3). Increasing the solution temperature up to 50 °C was also accompanied by a significant upfield shift of the NH thymine proton with respect to the thermoresponsiveness of the hydrogen bonds (see Supporting Information). In agreement with previous works on the self-assembly of THY/DAP functionalized polymers in $CDCl_3$, close values of association constants (ranging from 75 to 100 M^{-1}) were observed whatever the nature of the α,ω-thymine telechelic macromolecular block (See Supporting Information).[6j]

Characterization of Polymer Self-Assembly by Rheological Measurements. As a further test of the efficient formation of supramolecular structures through H-bonding, comparative rheological analyses were performed on chloroform solutions (325 g·L^{-1}) containing either Thy-PS-Thy2 ($\overline{M}_{n\,SEC}$ = 11000 g·mol^{-1}, PDI = 1.29) and PS-DAP4 ($\overline{M}_{n\,SEC}$ = 9400 g·mol^{-1}, PDI = 1,27) at a 1/1 DAP/Thy molar ratio or a nonassociating PS analogue generated from **CTA4** ($\overline{M}_{n\,SEC}$ = 9000 g·mol^{-1}, PDI = 1,14). Viscosities were collected over temperatures ranging from −15 °C to +20 °C using a shear rate of 100 s^{-1} (Figure 5). A maximum temperature of 20 °C was fixed, combined with the use of a solvent trap cover, in order to avoid evaporation of chloroform during measurements.

Supramolecular association was corroborated by significant viscosity enhancements observed for the mixture of PS-DAP4 and Thy-PS-Thy2. As expected, owing to the weakening of the hydrogen-bond association upon heating, the increase of temperature strongly impacted the rheological behavior of the solution, nicely complementing the ^{1}H NMR study on the thermo-reversibility of the system (See Supporting Information). Bulk rheological measurements were also performed over a large range of temperatures (from −15 to 50 °C using a shear rate of 10 s^{-1}) on associating and nonassociating P*n*BuA possessing equivalent molecular weights (see Figure 6). Again, a drastic increase of viscosity was detected for the blend of P*n*BuA-DAP2 and Thy-P*n*BuA-Thy2 confirming the effectiveness of the P*n*BuA blocks self-assembly in bulk through H-bonding. Above 50 °C, associating and non associating P*n*BuAs exhibited very similar viscosities suggesting that nearly all the three-points hydrogen bonded complex between DAP and thymine are disrupted.

Characterization of Polymer Self-Assembly by AFM. The phase behavior of thymine and DAP end-functionalized polymer blends was subsequently investigated. Thy-PI-Thy1/PS-DAP1 ([Thy] = [DAP]) blends as well as Thy-PI-Thy1/nonfunctionalized PS (generated from **CTA4**) blends (used as a reference, same ratio PS/PI w/w) were prepared by spin-coating on a silicon wafer from a solution in toluene (10% w/w). Morphologies of the polymer blends were then observed by Atomic Force Microscopy (AFM) in tapping mode. Height imaging results from the measurement of oscillation amplitude, giving information on the topology, while phase imaging results from measurement of the phase lag induced by variations in material properties, such as viscoelasticity or adhesion. As can be seen (Figure 7), whereas Thy-PI-Thy1/nonfunctionalized PS blends tend to microphase separate (Figure 7 A1/A2), functional Thy-PI-Thy1/PS-DAP1 blends exhibit a much finer structure consistent with the presence of supramolecular block copolymers that ensures the stabilization of the interface between the polymers (Figure 7 B1/B2).

■ CONCLUSIONS

In conclusion, we have described a simple and straightforward strategy toward the generation of precisely defined H-bonding telechelic polymer chains and supramolecular block copolymers thereof. Relying on the design of a novel α−ω-thymine functionalized symmetrical trithiocarbonate capable to grow well-defined telechelic polymer chains in one step, we produced an extensive range of α−ω end-functional polymers with predictable molar mass and narrow molar mass distribution from styrene, *n*-butyl acrylate and isoprene. In combination with RAFT-made polymers exhibiting complementary recognition units (DAP), these original telechelic macromolecular building blocks afford the formation of supramolecular block copolymers in solution as well as in bulk as clearly evidenced by ^{1}H NMR, rheological measurements and supramolecular blend phase behavior investigations. These novel H-bonding telechelic polymers constitute an attractive class of elementary blocks for elaborating innovative materials such as supramolecular networks. Studies in this direction are currently in progress.

■ ASSOCIATED CONTENT

Supporting Information. ^{1}H NMR spectra of the CTAs, ^{1}H NMR temperature dependence investigation of the polymer H-bonding association, THY-PS-THY1 ESI mass spectrum, evolution of molar masses and PDI with conversion for the polymerization of styrene, *n*BuA and isoprene mediated by CTA1, and determination of K_{assoc}. This material is available free of charge via the Internet at http://pubs.acs.org.

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