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Heterocomplementary H-Bonding RAFT Agents as Tools for the Preparation of Supramolecular Miktoarm Star Copolymers

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ABSTRACT: Supramolecular miktoarm stars (AB_2 type) composed of poly (methyl methacrylate)-polystyrene$_2$ (PMMA-PS$_2$), poly(isoprene)-polystyrene$_2$ (PI-PS$_2$), and poly(vinyl acetate)-polystyrene$_2$ (PVAc-PS$_2$) were successfully synthesized by assembling reversible addition−fragmentation chain transfer (RAFT)-polymerized chains bearing hydrogen-bonding heterocomplementary associating units. To this end, thymine and diaminopyridine-functionalized chain transfer agents were designed to efficiently mediate the polymerization of vinyl acetate, methyl methacrylate, isoprene, and styrene. The selective associations of the resulting hydrogen-bonding macromolecular building blocks PVAc/PS, PI/PS, and PMMA/PS were demonstrated by ^{1}H NMR in $CDCl_3$ solutions. Miktoarm stars formation in the bulk was also confirmed by transmission electronic microscopy.

Introduction

Despite the increasing attention paid to the construction of supramolecular edifices,[1] the development of well-defined supramolecular block copolymers or supramolecular stars from self-assembly of tailor-made (end-functional) hydrogen-bonding macromolecules remains in its infancy in comparison with covalent analogues.

Synthetic strategies affording the incorporation of hydrogen-bonding units at a specific region of a polymer backbone (chain ends, center of the chain) are indeed rather limited so far. Introduction of associating motifs can be achieved through postpolymerization functionalization as described by Meijer and Binder, together with others.[2] However, this approach potentially suffers from incomplete transformation of the macromolecules.

An elegant strategy to circumvent such synthetic issues consists in incorporating molecular recognition units during the polymerization process through the use of functionalized initiators, chain transfer agents or chain terminators. Hydroxyl-functionalized hydrogen-bonding modules based on 2,6-diamidopyridine (DAP),[3] 2-ureido-4[1*H*]-pyrimidone (Upy),[4] or bis-ureidodeazapterin (BisDeAP)[5] have, hence, been successfully used as initiators for the ring-opening polymerization of D,L-lactide and ε-caprolactone. A series of functionalized ruthenium ring-opening metathesis polymerization initiators,[6] chain terminators,[6] and chain transfer agents[7] have been recently developed to afford a panel of mono and bifunctional (homo and heterotelechelic) polymer chains. The ease and the versatility of radical polymerizations have also encouraged researchers to generate well-defined polymers bearing associating motifs through controlled radical polymerization (CRP).[8] Using uracil-functionalized alkoxyamine initiators, Mather et al. reported the synthesis of (chain-end-functionalized) H-bonding polystyrenes and poly(alkyl acrylate)s via nitroxide-mediated polymerization (NMP).[9] Atom transfer radical polymerization (ATRP) from H-bonding initiator (based on guanosine, DAP, UPy, 2,7-diamido-1,8-naphthyridine, or BisDeAP) associating units provided monofunctional and telechelic polymer chains,[10] macromolecules containing embedded binding sites,[3] and supramolecular stars,[5,11] as well as supramolecular block copolymers.[12]

Surprisingly, the preparation of supramolecular structures by a combination of the most versatile CRP technique, that is, reversible addition−fragmentation chain transfer polymerization/macromolecular design via interchange of xanthate process (RAFT/MADIX) and hydrogen bonding, has been scarcely explored so far.

We recently reported the first example of supramolecular hydrogen-bonding polymeric structures (poly(vinyl acetate) 3-arm stars) generated from chain transfer agents (CTA) bearing complementary associating units.[13]

Extrapolating from our previous work, the present paper aims at demonstrating that this strategy can afford a large range of polymeric structures paving the way to the design of not only synthetically challenging macromolecular architectures, but also temperature and shear responsive materials. We propose in this contribution an original approach to the versatile preparation of AB_2 type supramolecular miktoarm stars, a new class of hydrogen bonding polymeric structures, from the straightforward self-assembly of RAFT-made macromolecular blocks bearing complementary hydrogen-bonding motifs located either at one chain end (thymine) or in the middle of the chain (DAP; see Scheme 1). As a proof of concept, we describe herein the generation of typically synthetically challenging poly(isoprene)-polystyrene$_2$ (PI-PS$_2$), poly(methyl methacrylate)-polystyrene$_2$ (PMMA-PS$_2$), and poly(vinyl acetate)-polystyrene$_2$ (PVAc-PS$_2$)[14] supramolecular miktoarm stars from DAP- and thymine-functionalized heterocomplementary H-bonding RAFT agents.

Experimental Section

Materials. All the chemicals were purchased from Aldrich or Fluka. Vinyl acetate (VAc) was freshly distilled prior to polymerization. The other monomers were filtered prior to passing through a column of basic aluminum oxide to remove inhibitors. Unless otherwise indicated, the other chemicals were used without further purification. **CTA1** was synthesized as previously described.[13]

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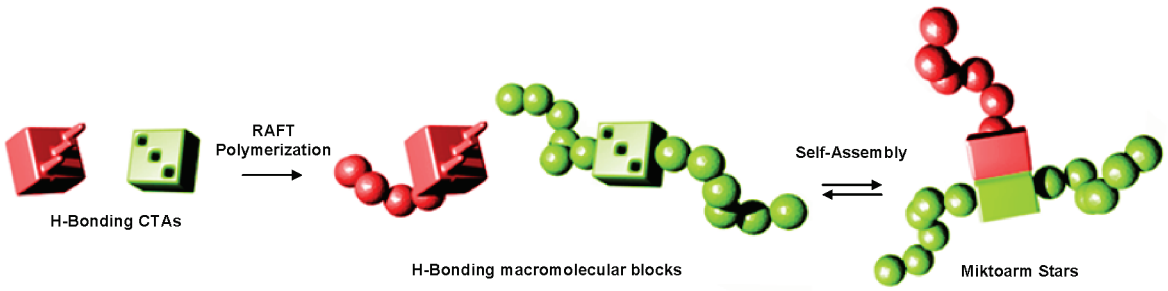
Scheme 1. General Strategy To Prepare AB_2 Supramolecular Miktoarm Stars



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) were measured on a Thermo-Finnigan Mat 95XL. Thymine-functionalized PVAc, PMMA, and PI and 2,6-diacyldiamino-pyridine-functionalized PS were analyzed with an apparatus 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 PVAc, PS, PI, and PMMA were derived from a calibration curve based on PS and PMMA standards respectively. In the case of PVAc samples, the obtained molar masses were subsequently corrected using the Mark−Houwink-Sakurada (MHS) relationship between PS and PVAc with MHS parameters at 25 °C: $K_{PS} = 14.1 \times 10^{-5}$ dL g^{-1}, $\alpha_{PS} = 0.70$; $K_{PVAc} = 16 \times 10^{-5}$ dL g^{-1}, and $\alpha_{PVAc} = 0.70$. 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 reflector mode. 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 or 20 μL of 1,8,9-anthracenetriol (dithranol, purchased by Sigma-Aldrich) at 10 g·L^{-1} in THF, with 5 or 20 μL of PVAc or PS solution (at 10 g·L^{-1} in THF), respectively. To enhance cationization of polymers, 5 μL of AgTFA or NaI (both from Sigma-Aldrich, at 10 g·L^{-1} in THF or acetone, respectively) were added to solutions. Finally, resulting mixtures (0.5 μL) were spotted on the MALDI sample plate and air-dried. TEM analyses were performed on a Philips CM120 Transmission electron microscope with an accelerating voltage of 80 kV, at the Centre Technologique des Microstructures of the University of Lyon. The samples were prepared from diluted polymer solutions (0.5 g·L^{-1} in THF) deposited onto carbon-coated Formvar copper grids. The solvent was evaporated at room temperature. The grids were subsequently exposed to RuO_4 vapors (2 wt % of Ruthenium III chloride in 50/50 water/sodium hypochlorite solution) for 20 min (to stain the PS domains).

Synthesis of CTA2. CTA2 was synthesized in three steps from thymine. 1-(ω-Hydroxyundecyl)thymine (**1**, 1.05 g, 89%) was first prepared as previously reported from 11-bromo-1-undecanol (1.0 g, 3.98 mmol) and thymine (10.0 g, 79.3 mmol).[13] To a solution of **1** (1 g, 3.36 mmol) and pyridine (1.7 g, 21.5 mmol) in anhydrous THF (150 mL), an excess of 2-chloro-2-phenylacetyl chloride (2.0 g, 10.5 mmol) was added dropwise. The solution was stirred for one day at 60 °C. After solvent removal, the resulting brown oil was dissolved in ethyl acetate and successively washed with brine, saturated sodium bicarbonate, and a 0.1 M HCl solution. The organic layer was subsequently dried over $MgSO_4$, and the product was purified by silica gel (Kiesigel-60) column chromatography (ethyl acetate/cyclohexane, 1/1, v/v) to give the benzyl halide **2** as a yellow solid (1.20 g, 80%). Compound **2** (1.2 g, 2.7 mmol) and freshly synthesized phenyldithiocarboxylic acid magnesium bromide (60 mmol) were dissolved in anhydrous THF and warmed for 24 h at 80 °C. Ice water was then added to the solution before extracting the organic products with diethyl ether three times. The combined organic extracts were rinsed with water and dried over $MgSO_4$. After solvent removal, column chromatography was undertaken (ethyl acetate/cyclohexane, 1/1, v/v) to afford **CTA2** as a red solid in moderate yield (0.91 g, 52%). ESI-MS Calcd for $(C_{31}H_{38}N_2O_4S_2+Na)^+$, 589.8; found, 589.3 m/z. ^{1}H NMR ($CDCl_3$; [**CTA2**] = 1.68×10^{-2} mol·L^{-1}; δ (ppm)): 1.26−1.65 (undecane CH_2 groups, 18H), 1.91 (3H, s), 3.66 (2H, t), 4.13 (2H, t), 5.74 (1H, s) 6.97 (1H, s), 7.30−7.41 (6H, m), 7.46−7.48 (2H, d), 7.77−7.83 (2H, d), 8.20 (1H, s). ^{13}C NMR ($CDCl_3$; δ (ppm)): 12.29, 25.72, 26.41, 26.93, 28.42, 29.16, 29.36, 29.64, 30.87, 40.78, 48.49, 58.97, 66.27, 110.38, 125.70, 125.79, 125.86, 125.90, 126.01, 128.41, 128.80, 129.01, 132.81, 133.46, 135.89, 140.51, 143.89, 151.23, 164.91, 168.83, 225.82.

Synthesis of CTA3. 2-Dodecylsulfanylthiocarbonylsulfanyl-2-methyl-propionic acid (1.0 g, 2.7 mmol, 1.0 equiv) was dissolved in dry freshly distilled dichloromethane (50 mL) in a round-bottom flask. The solution was cooled to 0 °C. Oxalyl chloride (1.03 g, 8.1 mmol, 3 equiv) was added slowly under a nitrogen atmosphere. The solution was allowed to reach room temperature and stirred for a total of 3 h. The resulting solution was concentrated under reduced pressure to yield the acid chloride **3** (1.0 g, 99% yield). Compound **1** (0.7 g, 2.36 mmol) was then dissolved in dry dichloromethane (40 mL) in a 100 mL round-bottom flask and the solution was cooled to 0 °C. A solution of triethylamine (0.73 mL) in dichloromethane (5 mL) was added dropwise over 10 min. A solution of **3** (1.0 g, 2.6 mmol) in dichloromethane (5 mL) was added dropwise, and the solution was allowed to reach room temperature while stirring for 3 h. The solution was diluted with dichloromethane (100 mL) and washed with saturated aqueous sodium bicarbonate solution (50 mL), brine (50 mL), and water (50 mL), successively. The organic layer was separated, dried over $MgSO_4$, and filtered. The supernatant was concentrated under reduced pressure. The thymine-functionalized trithiocarbonate **CTA3** was purified by chromatography on silica gel (the separation was started with methylene chloride/ethyl acetate 98/2, v/v and progressively ethyl acetate was incorporated to reach 7/3, v/v). A yellow paste was obtained (0.44 g, 29% yield). ESI-MS Calcd for $(C_{33}H_{58}N_2O_3S_3 + K)^+$, 666.1; found, 665.2 m/z. ^{1}H NMR ($CDCl_3$; [**CTA3**] = 1.68×10^{-2} mol·L^{-1}; δ (ppm)): 0.86 (t, 3H, CH_3-C_9H_{18}-CH_2-CH_2-S-C=S), 1.23−1.80 (m, 36H, CH3-C_9H_{18}-CH_2-CH_2S-C=S and N-CH_2-C_9H_{18}-CH_2-O), 1.71 (s, 6H, -S-C(CH_3)$_2$-CO, 1.90 (s, 3H, CH_3-C=CH), 3.22 (t, 2H, CH_3-C_9H_{18}-CH_2-CH_2-S-C=S), 3.64 (t, 2H, N-CH_2-C_9H_{18}-CH_2-O), 4.04 (t, 2H, N-CH_2-C_9H_{18}-CH_2-O), 6.97 (s, 1H, CH_3-C=CH-), 8.28 (s, 1H, NH). ^{13}C NMR ($CDCl_3$) δ (ppm): 12.63, 14.42, 22.97, 25.68, 26.18, 26.74, 27.20, 28.18, 28.64, 29.23, 29.40, 29.45, 29.49, 29.63, 29.71, 29.74, 29.85, 29.92, 32.20 37.15, 48.88, 56.32, 66.41, 110.81, 140.77, 151.21, 164.72, 173.32, 221.66.

Synthesis of CTA4. *N*,*N*′-2,6-Pyridinediylbis(2-bromopropanamide) **4** was prepared as previously reported.[3] Freshly synthesized dithiobenzoic acid (20.3 g, 130 mmol) and **4** (5 g, 13 mmol) were dissolved in THF (300 mL) and stirred at 60 °C for 15 h.

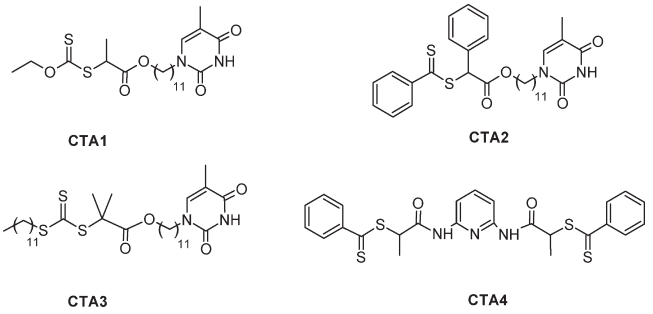
The reaction solution was then cooled to room temperature, washed with brine and water. The organic layer was collected and dried over $MgSO_4$. The product was purified by column chromatography (dichloromethane/cyclohexane, 2/1, v/v) to give **CTA4** as a red solid (3.1 g, 45%).ESI-MS Calcd for $(C_{25}H_{23}N_3O_2S_4 + Na)^+$, 548.7; found, 548.0 m/z. ^{1}H NMR ($CDCl_3$; [**CTA4**] = 3.36×10^{-2} mol·L^{-1}; δ (ppm)): 1.73 (6H, t), 4.85 (2H, q), 7.37 (4H, t), 7.55 (2H, t), 7.86 (2H, d), 7.98 (4H, t), 8.56 (NH, 2H). ^{13}C NMR ($CDCl_3$) δ (ppm): 15.99, 49.04, 110.01, 127.21, 127.22, 127.42, 127.45, 133.18, 140.75, 143.98, 149.22, 168.80, 226.81.

Polymerizations. *Polymerization of VAc*. Bulk polymerization of VAc was performed using 2,2′-azobisisobutyronitrile (AIBN) as initiator and **CTA1** as chain transfer agent. Typically, the polymerization of VAc (3 mL, 3.25×10^{-2} mol) was carried out using AIBN (2.2 mg, 1.34×10^{-5} mol), **CTA1** (62.4 mg, 1.32×10^{-4} mol), and trioxane (243 mg, 2.7×10^{-3} mol) as an internal reference for the measurement of VAc consumption via ^{1}H NMR. A stock solution was transferred into Schlenk tubes that were thoroughly deoxygenated by five consecutive freeze−pump−thaw cycles. The tubes were subsequently placed in an oil bath thermostatted at 60 °C. The reaction was stopped by plunging the tubes into liquid nitrogen. The polymer was subsequently precipitated twice into pentane to eliminate residual monomer and trioxane. The polymer was dried under vacuum and characterized by ^{1}H NMR and SEC. The molecular weights of the pure PVAc were finally evaluated by ^{1}H NMR ($CDCl_3$) from the relative integration of the protons of the PVAc backbone (CH_2-*CH*-, *n*H, δ = 4.85 ppm, with *n* being the degree of polymerization) and of characteristic protons of the thymine end group (C═C*H*-N, 1H, δ = 6.97 ppm).

Polymerization of Methyl Methacrylate. Solution polymerization of methyl methacrylate was performed using 2,2′-azobisisobutyronitrile (AIBN) as initiator and **CTA2** as chain transfer agent. Typically, the polymerization of MMA (3 mL, 2.8×10^{-2} mol) was carried out using AIBN (0.59 mg, 3.6×10^{-6} mol), **CTA2** (40 mg, 7.1×10^{-5} mol), toluene (6 mL, 5.7×10^{-2} mol), and trioxane (243 mg, 2.7×10^{-3} mol) as an internal reference for the measurement of MMA consumption via ^{1}H 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 thermostatted at 60 °C. The reaction was stopped by plunging the tubes into liquid nitrogen. The polymer was subsequently precipitated twice into cyclohexane to eliminate residual monomer and trioxane. The polymer was dried under vacuum and characterized by ^{1}H NMR and SEC. The molecular weights of the pure PMMA were finally evaluated by ^{1}H NMR ($CDCl_3$) from relative integration of the protons of the PMMA backbone (-O-C*H*$_3$, 3*n*H, δ = 3.58 ppm, with *n* being the degree of polymerization) and of characteristic proton of the thymine end group (C═C*H*-N, 1H, δ = 6.97 ppm).

Polymerization of Isoprene. Bulk polymerization of isoprene was performed using dicumyl peroxide (DCP) as initiator and **CTA3** as chain transfer agent. Typically, the polymerization of isoprene (4 mL, 4.0×10^{-2} mol) was carried out using DCP (1.08 mg, 4.0×10^{-6} mol) and **CTA3** (51.4 mg, 8.0×10^{-5} mol). A stock solution was transferred into Schlenk tubes that were thoroughly deoxygenated by five consecutive freeze−pump−thaw cycles. The tubes were subsequently placed in an oil bath thermostatted at 120 °C. The reaction was stopped by plunging the tubes into liquid nitrogen. The polymer was subsequently precipitated twice into methanol to eliminate residual monomer. The polymer was dried under vacuum and characterized by ^{1}H NMR and SEC. The molecular weights of the pure PI were 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, ^{1}H, δ = 6.97 ppm).

Scheme 2. Structure of Thymine and DAP-Functionalized H-Bonding CTAs



Polymerization of Styrene. Bulk polymerization of styrene was performed using 2,2′-azobisisobutyronitrile (AIBN) as initiator and **CTA4** as chain transfer agent. Typically, the polymerization of styrene (4 mL, 3.5×10^{-2} mol) was carried out using AIBN (0.36 mg, 2.2×10^{-6} mol), **CTA4** (22.8 mg, 4.4×10^{-5} mol), and trioxane (243 mg, 2.7×10^{-3} mol) as an internal reference for the measurement of styrene consumption via ^{1}H 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 thermostatted at 80 °C. The reaction was stopped by plunging the tubes into liquid nitrogen. The polymer was subsequently precipitated twice into ethanol to eliminate residual monomer and trioxane. The polymer was dried under vacuum and characterized by SEC and ^{1}H NMR.

Results and Discussion

Aiming at generating well-defined AB_2 type supramolecular miktoarm stars, four different CTAs (Z-CS_2-R) bearing either thymine or DAP heterocomplementary recognition units have been prepared: a thymine-functionalized xanthate (**CTA1**), a thymine-functionalized dithiobenzoate (**CTA2**), a thymine-functionalized trithiocarbonate (**CTA3**), and a DAP-functionalized dithiobenzoate (**CTA4**), respectively, expected to efficiently mediate the radical polymerization of VAc, MMA, isoprene, and styrene (see Scheme 2).

Because introducing the associating motifs through the *Z* "activating group" can be accompanied by an important loss of functionality due to hydrolysis, aminolysis, or termination reactions, thymine and DAP units were purposely incorporated as part of the "*R*" leaving/initiating group.

Using a well-established method based on ^{1}H NMR monitoring, supramolecular associations of **CTA1**, **CTA2**, and **CTA3**, with **CTA4** through selective three-points H-bonding complexation were evidenced in solution in deuterated chloroform by a significant downfield shift of the N*H* thymine proton (from 8.22 to 10.45 ppm for **CTA1**/**CTA4**, 8.19 to 10.38 ppm for **CTA2**/**CTA4**, and 8.28 to 10.36 ppm for **CTA3**/**CTA4**, see Figure 1) observed after addition of 1 equiv of heterocomplementary **CTA4**. Titration experiments and a relevant mathematical model were used to measure binding constants, which were found to be 120−140 M^{-1} for each couple of CTA (see Supporting Information).

Radical polymerizations were subsequently carried out in the presence of the appropriate H-bonding CTA and a minimum concentration of thermal initiator, that is, [CTA]/[initiator] = 10 for vinyl acetate and 20 for styrene, methyl methacrylate, and isoprene, to minimize the number of unfunctionalized (and, thus, nonassociating) chains.

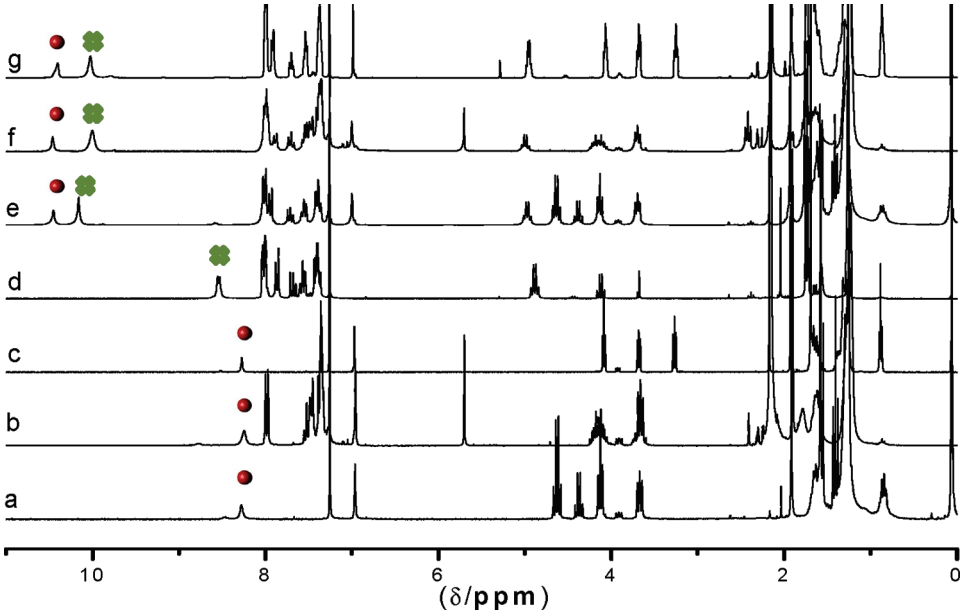


Figure 1. NMR spectra of thymine/DAP-functionalized CTAs (a, **CTA1**; b, **CTA2**; c, **CTA3**; d, **CTA4**) and their stoichiometric mixtures (e, **CTA1**/**CTA4**; f, **CTA2**/**CTA4**; g, **CTA3**/**CTA4**) at 20 °C in $CDCl_3$ ([THY] = [DAP] = 1.68×10^{-2} mol·L^{-1}). Red sphere: thymine N*H* protons; green cross: DAP N*H* protons.

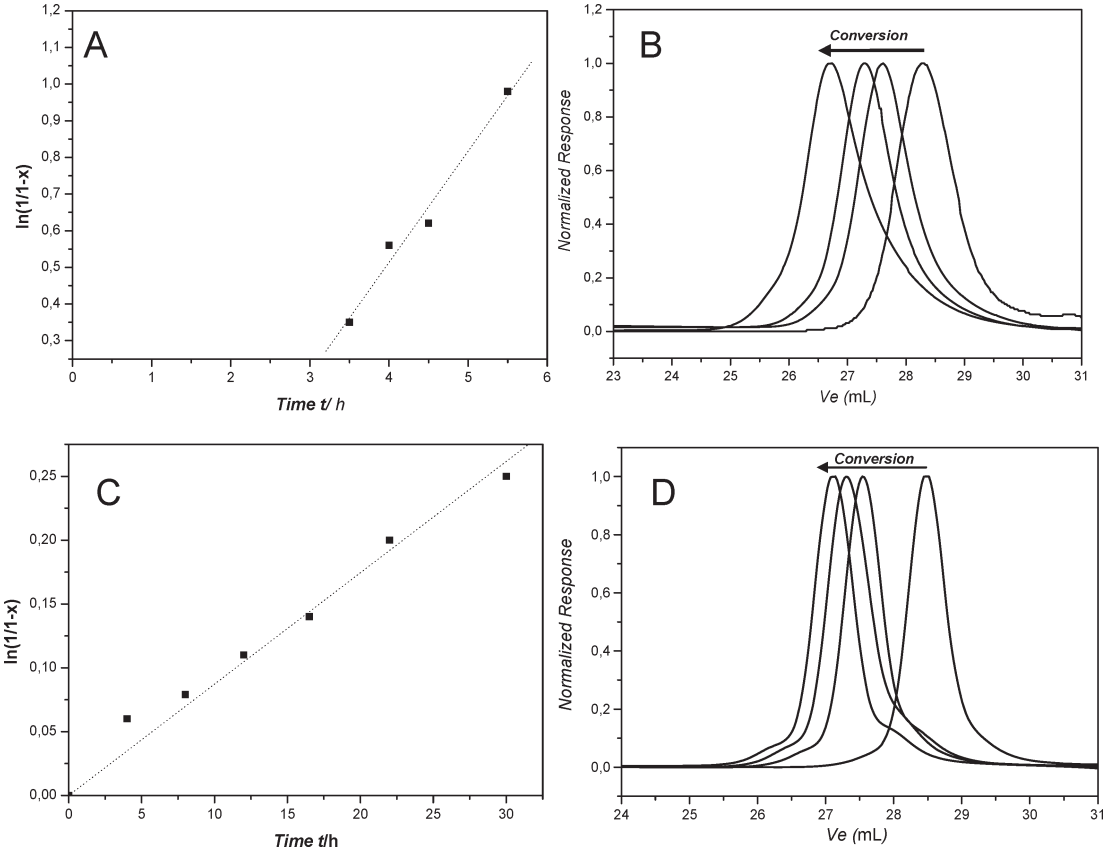


Figure 2. (A) First-order kinetic plot of the bulk polymerization of vinyl acetate at 60 °C in the presence of **CTA1**: [M]/[CTA] = 250, [CTA]/[AIBN] = 10. (B) Evolution of the normalized SEC traces in THF for the **CTA1**-mediated bulk polymerization of vinyl acetate at 60 °C ([VAc]/[**CTA1**] = 250; [**CTA1**]/[AIBN] = 10) at different conversions. From right to left, THY-PVAc2, THY-PVAc3, THY-PVAc4, and THY-PVAc5. (C) First-order kinetic plot of the bulk polymerization of styrene at 80 °C in the presence of **CTA4**: [M]/[CTA] = 800, [CTA]/[AIBN] = 20. (D) Evolution of the normalized SEC traces in THF for the **CTA4**-mediated bulk polymerization of styrene at 80 °C at different conversions: from right to left, PS-DAP-PS1, PS-DAP-PS2, PS-DAP-PS3*, and PS-DAP-PS4*. *The tail observed at low molecular weight reflects the presence of unfunctionalized chains generated from thermal decomposition of AIBN and thermal self-initiation of styrene.

All CTAs were proven to effect a good control of the polymerizations. As an example, conversion versus time plots for the polymerization of VAc and styrene, respectively, mediated with **CTA1** and **CTA4** are given in Figure 2A,C (details of MMA and

Table 1. Properties of the RAFT-Made H-Bonding Homopolymers

sample	CTA	[M]/ [CTA]	conv[a] %	$M_{n,th}$[b] (g/mol)	$M_{n,NMR}$[c] g/mol	$M_{n,SEC}$ g/mol	PDI
THY-PVAc1	**1**	250	4	1400	1400	1200[d]	1.40[d]
THY-PVAc2	**1**	250	30	6500	5000	5900[d]	1.29[d]
THY-PVAc3	**1**	250	43	9400	10800	11500[d]	1.28[d]
THY-PVAc4	**1**	250	46	10200	12600	13800[d]	1.34[d]
THY-PVAc5	**1**	250	62	13700	17500	18700[d]	1.44[d]
THY-PMMA1	**2**	400	17	7400	7900	9300[e]	1.34[e]
THY-PMMA2	**2**	400	26	10900	12100	13600[e]	1.37[e]
THY-PMMA3	**2**	400	37	15300	17500	18900[e]	1.33[e]
THY-PMMA4	**2**	400	45	18600	21900	21000[e]	1.35[e]
THY-PI1	**3**	500	23	6300	9800	9700[f]	1.30[f]
THY-PI2	**3**	500	28	10200	11700	12400[f]	1.31[f]
THY-PI3	**3**	500	38	13500	15000	14600[f]	1.26[f]
THY-PI4	**3**	500	50	17700	15900	16500[f]	1.35[f]
PS-DAP-PS1	**4**	800	6	5500	5100	6200[f]	1.19[f]
PS-DAP-PS2	**4**	800	11	9300	8700	10200[f]	1.18[f]
PS-DAP-PS3	**4**	800	18	14900	15800	16400[f]	1.17[f]
PS-DAP-PS4	**4**	800	22	18700	17900	19400[f]	1.18[f]
PS-DAP-PS5	**4**	70	15	1500	1800	1600[f]	1.33[f]

[a] Conversion from ^{1}H 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 ^{1}H NMR ($CDCl_3$) from relative integration of the thymine or aromatic chain end group peaks and polymer backbone peaks. [d] From SEC in THF (PS calibration). Molecular weight corrected with the following Mark−Houwink−Sakurada parameters at 25 °C: $K_{PS} = 14.1 \times 10^{-5}$ dL·g^{-1}, $\alpha_{PS} = 0.70$; $K_{PVAc} = 16 \times 10^{-5}$ dL·g^{-1}, $\alpha_{PVAc} = 0.70$. [e] From SEC in THF (PMMA calibration). [f] From SEC in THF (PS calibration).

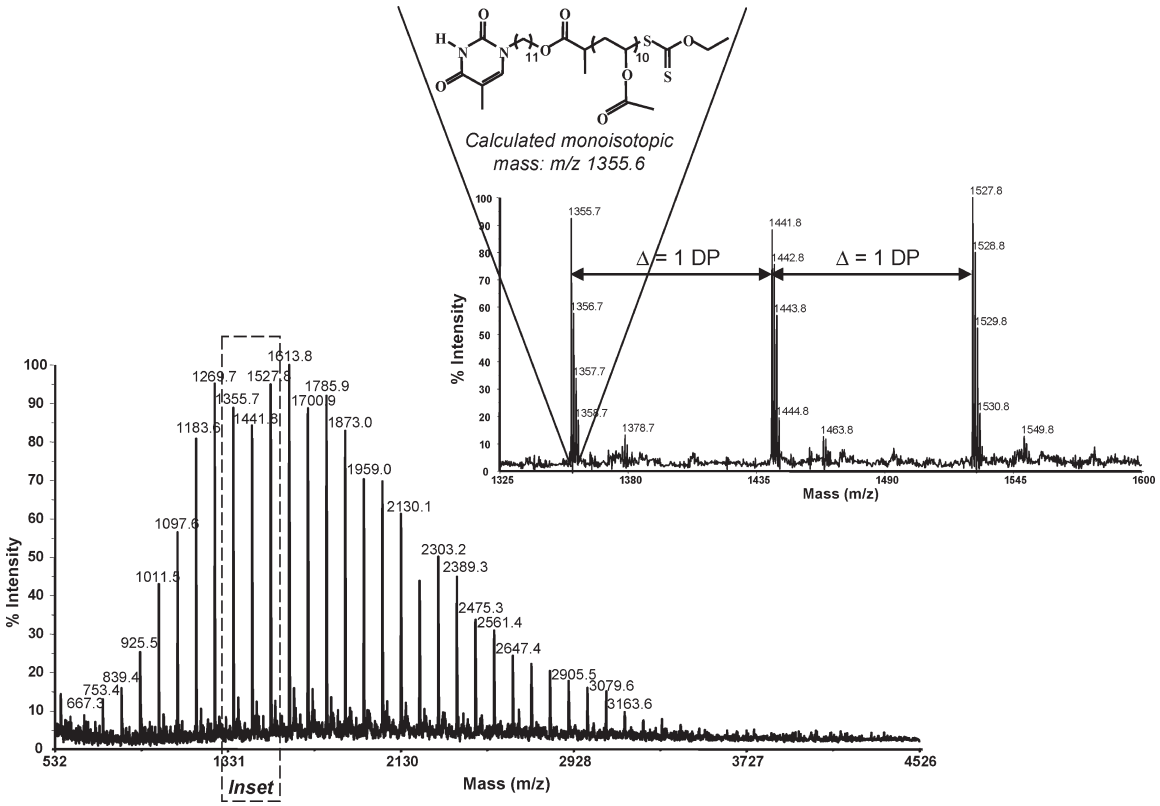


Figure 3. Positive MALDI-TOF mass spectrum of THY-PVAc1 (with NaI salt and dithranol matrix) in the reflector mode. The inset shows an enlarged region of this mass spectrum and illustrates the agreement between experimental and calculated monoisotopic mass (example given for DP = 10, $C_{62}H_{96}N_2O_{25}S_2Na$). The assignment of minor population at ca. +22 m/z vs main population is unknown for the moment.

isoprene polymerization are given in Supporting Information). Polymerizations proceeded with pseudo-first-order kinetics, indicative of a constant number of propagating centers. As expected for a controlled process, molar masses increased linearly with conversion, and SEC traces exhibited monodisperse peaks. Molar masses determined by SEC were close to theoretical values (Table 1).

A further evidence of the growth of the polymers in a controlled fashion was given by the polydispersity index, which typically is comprised of values between 1.17 and 1.44, with molar masses ranging from 1.2 to 21×10^3 g/mol (Table 1).

The ^{1}H NMR analyses clearly demonstrated the incorporation of the thymine functionality in α-position of the PMMA, PI and PVAc backbones with the presence of characteristic peaks at 6.97 and 8.13 ppm (respectively -C═C*H*-N- and N*H*) and the molar masses evaluated from relative integration of the protons of the polymer backbones and of the protons of the associating chain end were in very good agreement with theoretical values.

Further evidence of the chain functionalization were given by MALDI-TOF mass spectroscopy analyses. For instance, the MALDI-TOF mass spectrum of THY-PVAc1 observed in the reflector mode (Figure 3) highlighted the presence of dominant

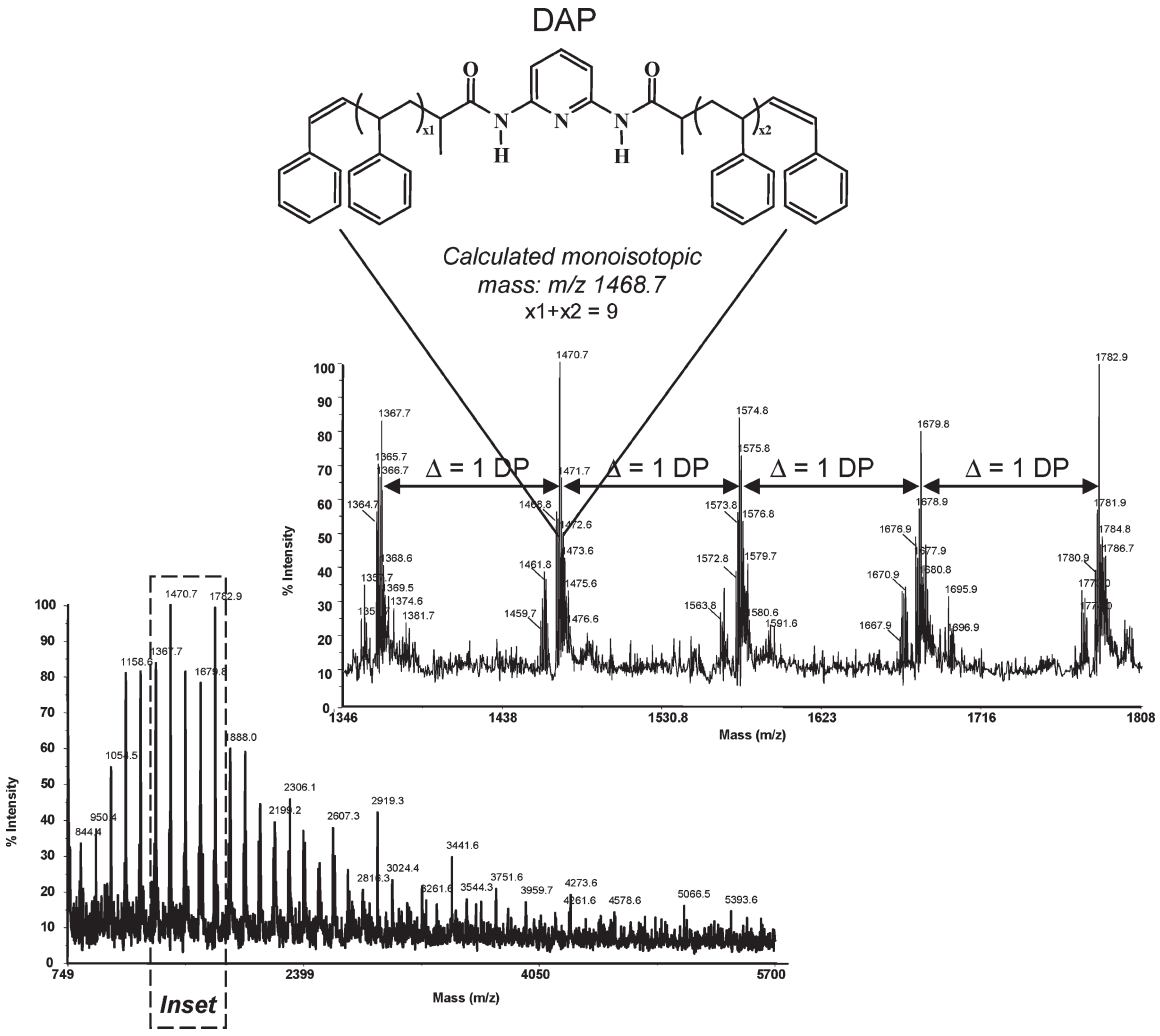


Figure 4. Positive MALDI-TOF mass spectrum of PS-DAP-PS5 (with AgTFA salt and dithranol matrix) in the reflector mode. The inset shows an enlarged region of this mass spectrum and illustrates the agreement between experimental and calculated monoisotopic mass for DP = 9 ($C_{99}H_{99}N_3O_2Ag$, experimental = 1468.8 *m*/*z*, theoretical = 1468.7 *m*/*z*). The assignment of minor population at −9 *m*/*z* vs main population is unknown for the moment.

species undoubtedly corresponding to PVAc chains bearing a thymine α-extremity and a xanthate *ω*-extremity as confirmed by the very satisfactory agreement between (i) the experimental and calculated monoisotopic mass (illustration on the degree of polymerization, DP of 10 in the inset of Figure 3) and (ii) the experimental and simulated isotopic peak pattern (see Supporting Information).

Concerning PS-DAP-PS5, MALDI-TOF mass spectrometry technique also confirmed the functionalization of PS chains by the DAP moiety (Figure 4). Unfortunately, the labile dithioester end groups (particularly in the PS chains) were difficult to detect by this technique. The dithioester elimination in the mass spectrometer, due to the weakness of the C−S bond between PS and CTA, leads to a stable conjugated double bond.[15,16] As a result, the main population detected in the PS-DAP-PS5 mass spectrum was (Ph)CH═CH-PS_{x1}-DAP-PS_{x2}-CH═CH(Ph). Nevertheless, the control of molecular weights with conversion (Table 1) and ^{1}H NMR analyses clearly corroborated the presence of dithiobenzoate moieties in the polymer chains.

As previously shown by Binder, Weck, and others,[2d,6,7a] ^{1}H NMR monitoring constitutes one of the most suitable techniques to study the H-bonding association of macromolecular blocks and determine the association constant of the system. Consequently, the formation of the miktoarm stars by self-assembly through hydrogen bonding of PVAc (THY-PVAc2), PI (THY-PI1), or PMMA ((THY-PMMA1)/PS (PS-DAP-PS1)) heterocomplementary polymeric building blocks was investigated by ^{1}H NMR in deuterated chloroform. As expected for the formation of the selective three-point hydrogen-bonded THY-DAP complex, the addition of 1 equiv of PS-DAP-PS1 to THY-PI1, THY-PMMA1, and THY-PVAc2 was accompanied by a significant downfield shift of the N*H* thymine proton from 8.0/8.05/8.08 to 8.74/8.72/8.75 ppm, respectively, that clearly demonstrated the generation of PI-PS_2, PMMA-PS_2, and PVAc-PS_2 supramolecular miktoarm stars (see Figure 5; the association between THY-PI1 and PS-DAP-PS1 is given in Supporting Information). The strength of the heterocomplementary hydrogen-bonding polymeric building association was subsequently investigated by plotting the thymine N*H* chemical shift as a function of PS-DAP-PS1 to THY-PVAc2, THY-PI1, or THY-PMMA1 concentrations (see Supporting Information). The K_{ass} for the THY-DAP association between PS and PVAc, PI or PMMA H-bonding chains were comparable (80−90 ± 5 M^{-1}), suggesting that the chemical nature of the polymer backbones does not interfere with the H-bonding recognition process in $CDCl_3$ solutions. The association constants are quite lower than K_{ass} (120−140 M^{-1}) of the H-bonding CTAs, indicating that the presence of the polymeric chains slightly affects the association ability of thymine and DAP moieties possibly due to the altered accessibility of the DAP group at the center of the PS chain.

Finally, 1:1 bulk mixtures of THY-PVAc2/PS-DAP-PS1 and $PVAc_{unf}$/ PS-DAP-PS1 as reference ($PVAc_{unf}$ being an unfunctionalized PVAc with molecular weight -$M_{n,SEC}$ = 5600 g·mol^{-1}

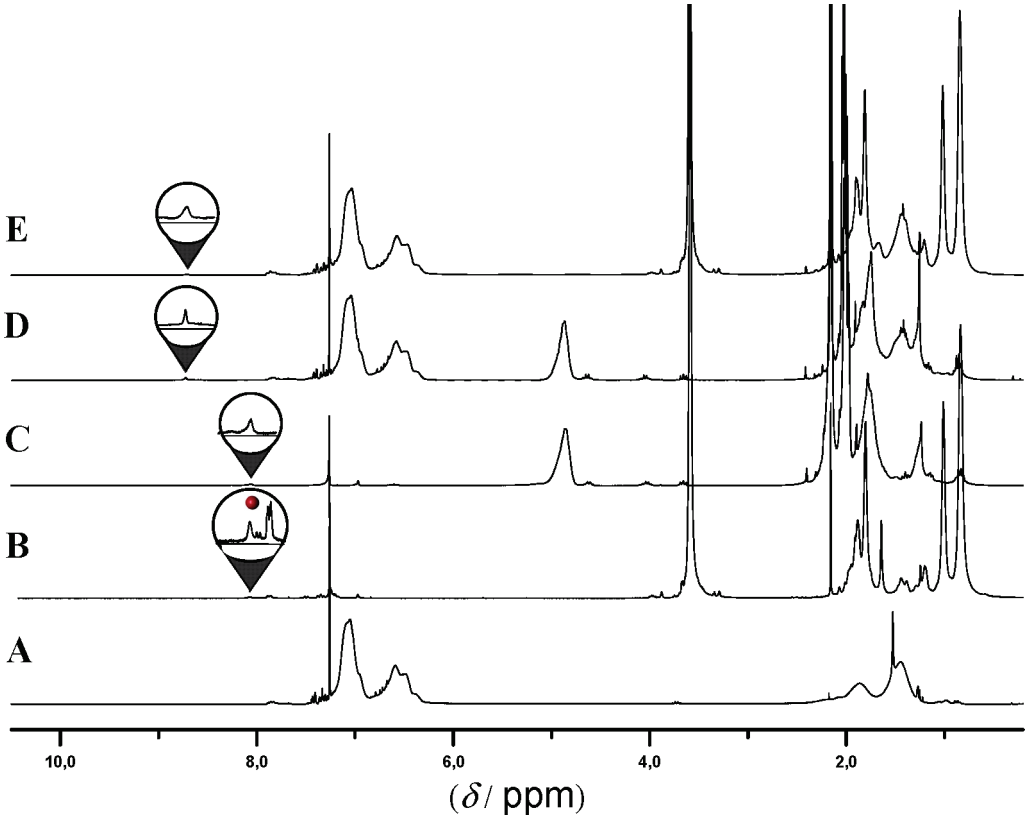


Figure 5. NMR spectra of PS-DAP-PS1 (A), THY-PMMA1 (B), THY-PVAc2 (C), THY-PVAc2/PS-DAP-PS1 stoichiometric mixture (D), and THY-PMMA1/PS-DAP-PS1 stoichiometric mixture (E) at 20 °C in $CDCl_3$ ([THY] = [DAP] = 3×10^{-3} mol·L^{-1}).

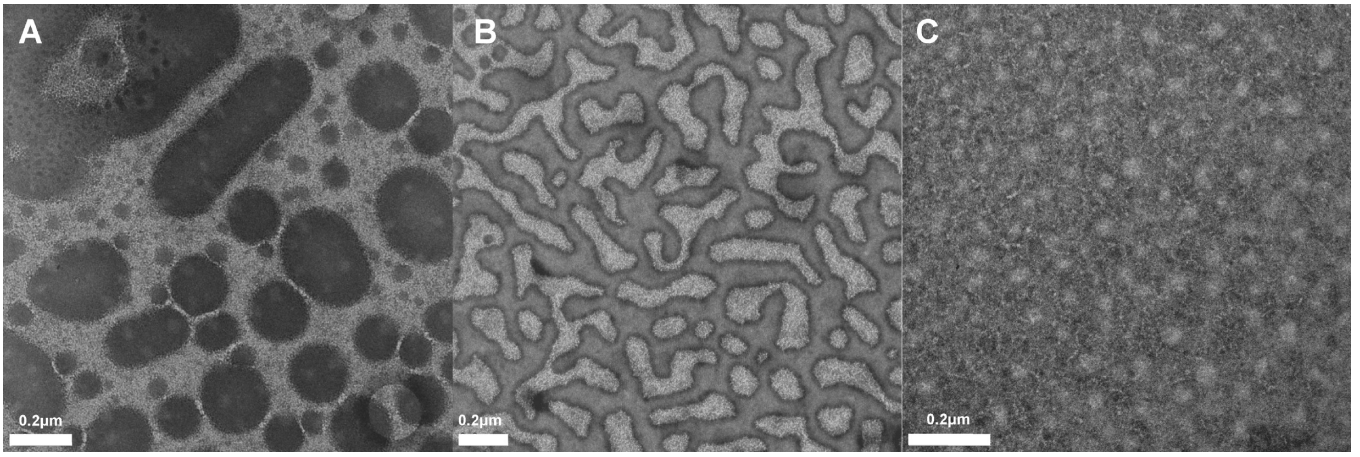


Figure 6. TEM pictures of 1/1 blend of $PVAc_{unf}$/PS-DAP-PS1 (A), 0.5/0.5/1 blend $PVAc_{unf}$/THY-PVAc2/PS-DAP-PS1 (B), and 1/1 blend of THY-PVAc2/PS-DAP-PS1 (C).

and PDI = 1.36, in close agreement with THY-PVAc2) were generated by simply mixing polymer chains in an appropriate solvent for block solubilization followed by slow evaporation of the solvent. The resulting morphologies were subsequently observed by transmission electron microscopy (Figure 6), whereas unfunctionalized PVAc and PS-DAP-PS1 polymer blends clearly exhibited poorly dispersed domains, macrophase separation was prevented for H-bonding PVAc and PS macromolecular blocks blends, in agreement with the formation of supramolecular miktoarm stars (Figure 6C).

In summary, we have designed a series of original heterocomplementary H-bonding chain transfer agents allowing the generation of a panel of well-defined macromolecular building blocks with associating motifs located either at one chain end or in the middle of the chain. The self-assembly of these heterocomplementary H-bonding polymer chains afforded the straightforward generation of synthetically challenging supramolecular miktoarm stars. We envisage that this new category of RAFT agents would constitute a versatile platform for the design of a large array of tailored supramolecular polymers. In addition, the reversible nature of the association between the building blocks paves the way to new properties as compared to the covalent counterparts.

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Supporting Information Available: Kinetic studies, determination of K_{ass}, and comparisons between experimental and simulated isotopic peak patterns of THY-PVAC1 obtained by MALDI-TOF mass spectroscopy. This material is available free of charge via the Internet at http://pubs.acs.org.

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