

Well-Defined Phosphonate-Functional Copolymers Through RAFT Copolymerization of Dimethyl-*p*-vinylbenzylphosphonate

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ABSTRACT: Dibenzyltrithiocarbonate-mediated RAFT polymerization of dimethyl-*p*-vinylbenzylphosphonate and its copolymerization with styrene are studied in order to access well-defined statistical and block copolymers containing controlled amounts of dimethylphosphonate groups. NMR and SEC analysis of the (co)polymers confirm the controlled character of the polymerizations. ABA triblock copolymers are treated with TMSiBr/MeOH in order to transform the dimethylphosphonate groups into phosphonic acids while keeping the midchain tri-

thiocarbonate group and triblock nature unaffected. Alternatively, the combination of trithiocarbonate aminolysis with TMSiBr/MeOH treatment of the same triblock copolymers leads to phosphonic acid-functional diblock copolymer counterparts. © 2014 Wiley Periodicals, Inc. *J. Polym. Sci., Part A: Polym. Chem.* **2014**, *00*, 000–000

KEYWORDS: amphiphiles; block copolymers; phosphonic acid; reversible addition fragmentation chain transfer (RAFT)

INTRODUCTION Phosphorus-containing polymers have gained increasing attention due to their specific properties and great potential for a broad range of applications like biomedicine,¹ fuel cell membranes,² scale inhibition,³ or metal ligation.⁴ Among them, polymers bearing phosphonate groups, and more particularly phosphonic acids, are an important subclass of phosphorus-based materials.⁵ Their use in dental cementing,⁶ adhesion to metal,⁷ corrosion inhibition,⁸ and flame retardancy⁹ is well documented.

In comparison with most other functional monomers reactive in free-radical polymerization, phosphonate-containing monomers have been far less studied mainly because of their limited commercial availability and high associated cost. As a consequence, the access to phosphonate-functional complex polymer architectures remains a relatively poorly explored field even after 20 years of intensive research in reversible deactivation radical polymerization.¹⁰ Phosphonated styrenic derivatives were the first reported monomers to be efficiently polymerized according to RDRP approaches. Indeed, diisopropyl^{11,12} and diethyl^{13–15} *p*-vinylbenzylphosphonate were polymerized by atom transfer radical polymerization. Aminoxyl-mediated polymerization of diethyl¹⁶ and dimethyl¹⁷ *p*-vinylbenzylphosphonate were also carried out in a controlled manner in the presence of nitroxyl stable radicals.

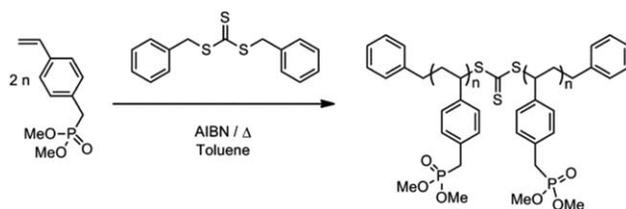
More recently, RAFT polymerization has appeared to be the most straightforward strategy to produce controlled

poly(phosphonates) and most importantly unprotected poly(phosphonic acids). For instance, our group recently reported the aqueous RAFT/MADIX polymerization of vinylphosphonic acid.¹⁸ Camicioni et al.¹⁹ successfully studied RAFT polymerization of dimethyl(methacryloyloxy)methyl phosphonate and its phosphonic acid derivative. Graillot et al.²⁰ described the trithiocarbonate-mediated RAFT polymerization of a phosphorus-based acrylamide monomer, namely diethyl-2-(acrylamido)ethylphosphonate and its incorporation into thermoresponsive block copolymers with *N*-isopropylacrylamide. Unexpectedly, only two articles report the use of a *p*-vinylbenzyl phosphonic acid dialkyl ester monomer in RAFT polymerization. Lacroix-Desmazes and coworkers^{21,22} synthesized gradient copolymers from diethyl-*p*-vinylbenzylphosphonate and 1,1,2,2-tetrahydro perfluorodecyl acrylate²¹ and a low molar mass statistical copolymer with styrene (St).²² After transformation of the phosphonate into a phosphonic acid group, the resulting polymers could act as metal complexing surfactants for supercritical carbon dioxide processes²¹ and dispersants for cerium oxide nanoparticles before the synthesis of hybrid latexes,²² respectively.

Therefore, it appeared to us that the scope and limitations of the RAFT polymerizability of dialkyl-*p*-vinylbenzylphosphonate monomers were still to be investigated. To do so, dimethyl-*p*-vinylbenzylphosphonate (DMVBP) was selected because of its ease of access²³ and commercial availability.²⁴ In the following study, DMVBP is

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SCHEME 1 General scheme for RAFT polymerization of DMVBP in presence of DBTTC.

homopolymerized in the presence of the dibenzyltrithiocarbonate RAFT agent and copolymerized with St. Different strategies for the synthesis of statistical, diblock, and triblock copolymers are presented. Finally, the dimethyl phosphonate functionality was transformed into phosphonic acid in order to yield PO_3H_2 -functional copolymers with well-defined composition and location of the phosphonic acid functionality along the chain.

EXPERIMENTAL

Materials

St (99%, Aldrich) was purified by passing through a column filled with neutral alumina. Azobisisobutyronitrile (AIBN) (99%, Aldrich) was recrystallized from methanol. DMVBP (97%, **Specific Polymers**), S,S'-dibenzyl trithiocarbonate (DBTTC) (97%, Arkema), bromotrimethylsilane (TMSiBr) (97%, Fluka), *n*-hexylamine (99%, Acros), methyl methanethiosulfonate (MTS) (97%, Aldrich), dithiothreitol (DTT) (98%, Aldrich), zinc powder (99%, Aldrich), and solvents were used as received.

Characterizations

Average molar masses and dispersity (M_n , M_w and \bar{D} , respectively) were determined by size exclusion chromatography (SEC). Tetrahydrofuran (THF) was used as eluent with a flow rate of 1.0 mL min^{-1} . SEC was equipped with a Waters 2414 refractive index (RI) detector, a multiangle light scattering detector (MALS) mini DAWN TREOS (Wyatt Technology) and a set of two columns (Shodex KF-802.5 and KF-804) thermostated at 35°C . The RI increment (dn/dc) of samples was determined at 35°C with a DnDc-2010, WGE Dr BURES. In some cases, M_n determined by SEC-MALS was compared to values obtained by single RI detection with a

calibration curve obtained from polystyrene standards ($1200\text{--}295,800 \text{ g mol}^{-1}$). UV-vis spectroscopy was performed on a UV-vis spectrometer Agilent 8453.

^1H NMR and ^{31}P NMR analyses were recorded on a 300-MHz Bruker spectrometer using CDCl_3 as solvent at room temperature and chemical shifts were reported in ppm. Monomer conversions were determined by ^1H NMR, ^{31}P NMR spectroscopy and by gravimetric analysis.

General Procedure for the RAFT Homopolymerization of DMVBP with Various Concentrations of DBTTC

In a typical polymerization procedure, DMVBP (1 g , $4.42 \times 10^{-3} \text{ mol}$), AIBN (6.9 mg , $4.2 \times 10^{-5} \text{ mol}$), DBTTC (30 mg , 10^{-4} mol), and toluene (0.9 mL) were placed in a 5-mL Schlenk flask. The solution was degassed by purging with argon for 15 min and heated to 60°C for 72 h. Samples were taken periodically from the mixture and analyzed by SEC and NMR. The polymer was recovered through precipitation in pentane, dried under vacuum at 90°C and then analyzed. 93.3 % of DMVBP was converted into polymer at the end of the reaction as determined by ^{31}P NMR. $M_{n,\text{th}}=9330 \text{ g mol}^{-1}$, $M_{n,\text{PS}}=6240 \text{ g mol}^{-1}$ ($\bar{D}=1.22$), $M_{n,\text{MALS}}=11,900 \text{ g mol}^{-1}$ ($\bar{D}=1.09$).

General Procedure for the RAFT Copolymerization of DMVBP with St $[\text{P}(\text{St}_x\text{-stat-DMVBP}_y)]_2\text{CS}_3$

In a typical polymerization procedure, DMVBP (1.09 g , $4.8 \times 10^{-3} \text{ mol}$), St (0.5 g , $4.8 \times 10^{-3} \text{ mol}$), AIBN (15 mg , $9.1 \times 10^{-5} \text{ mol}$), DBTTC (98 mg , $3.4 \times 10^{-4} \text{ mol}$), and toluene (1.45 mL) were placed in a 5-mL Schlenk flask. The solution was degassed by purging with argon for 15 min and heated to 70°C for 48 h. The resulting statistical copolymer was precipitated in pentane, dried under vacuum at 90°C , and then analyzed. The total conversion of monomers was 98.9% as determined by ^1H NMR and ^{31}P NMR. $M_{n,\text{th}}=4950 \text{ g mol}^{-1}$, $M_{n,\text{MALS}}=4950 \text{ g mol}^{-1}$ ($\bar{D}=1.10$).

General Procedure for the RAFT Block Copolymerization of DMVBP with St $[\text{P}(\text{St}_x\text{-stat-DMVBP}_y)\text{-}b\text{-PSt}_z]_2\text{CS}_3$ and $[\text{PDMVBP}_x\text{-}b\text{-PSt}_y]_2\text{CS}_3$

In a typical polymerization procedure, the first $[\text{P}(\text{St}_7\text{-stat-DMVBP}_7)]_2\text{CS}_3$ block (204.09 mg , $6.02 \times 10^{-5} \text{ mol}$), St (1 g , $9.6 \times 10^{-3} \text{ mol}$), AIBN (15 mg , $9.1 \times 10^{-5} \text{ mol}$), and

TABLE 1 Homopolymerization of DMVBP with Various Concentrations of DBTTC RAFT Agent^a

Entry	[DBTTC] ₀ (mmol L ⁻¹)	Conv ^b (%)	$M_{n,\text{th}}^c$ (g mol ⁻¹)	M_n (PS) ^d (g mol ⁻¹)	\bar{D} (PS)	$M_{n,\text{MALS}}^e$ (g mol ⁻¹)	\bar{D} (MALS)	dn/dc (mL g ⁻¹)
1	775.9	85.2	850	1,115	1.26	2,090	1.10	0.111
2	116.8	91.4	4,570	3,290	1.34	6,523	1.16	0.146
3	56.6	93.3	9,330	6,240	1.22	11,900	1.09	0.151
4	27.9	93.8	18,760	7,900	1.34	21,470	1.05	0.158
5	0	93.6		111,300	1.58	136,600	1.53	0.160

^a $[\text{DMVBP}]_0 = 2.43 \text{ mol L}^{-1}$, $[\text{AIBN}]_0 = 14.6 \text{ mmol L}^{-1}$, $T = 60^\circ\text{C}$.

^b Determined by ^{31}P NMR.

^c $M_{n,\text{th}} = M_{\text{DBTTC}} + [M_{\text{DMVBP}} \times (\text{conversion of DMVBP}) \times ([\text{DMVBP}]_0 / [\text{DBTTC}]_0)]$.

^d Measured by SEC-RI in THF with PS standards.

^e Measured by SEC-MALS in THF.

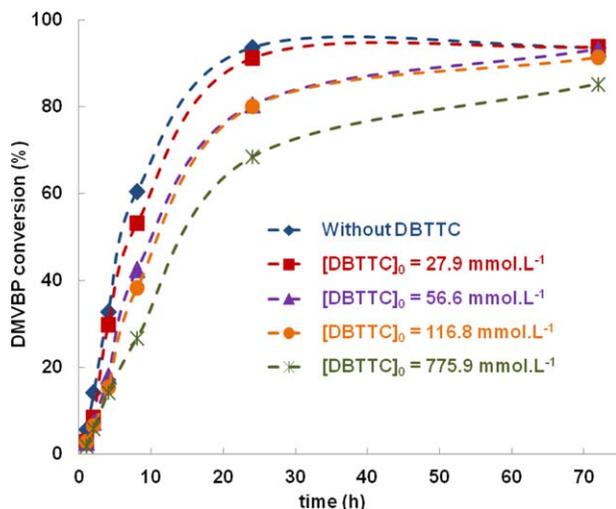


FIGURE 1 Time-conversion curves during the RAFT polymerization of DMVBP at different initial DBTTC concentrations. $[DMVBP]_0 = 2.43 \text{ mol L}^{-1}$, $[AIBN]_0 = 14.6 \text{ mmol L}^{-1}$, $T = 60 \text{ }^\circ\text{C}$.

toluene (0.9 mL) were placed in a 5-mL Schlenk flask. The solution was degassed by purging with argon for 15 min and heated to $70 \text{ }^\circ\text{C}$ for 48 h. The resulting diblock copolymer was precipitated in pentane, dried under vacuum at $90 \text{ }^\circ\text{C}$, and then analyzed. The conversion of monomer was 56.9% (determined by gravimetric analysis).

$M_{n,th} = 13,330 \text{ g mol}^{-1}$, $M_{n,MALS} = 11,910 \text{ g mol}^{-1}$ ($D = 1.21$). A similar procedure was followed when a PDMVBP homopolymer was used as first block.

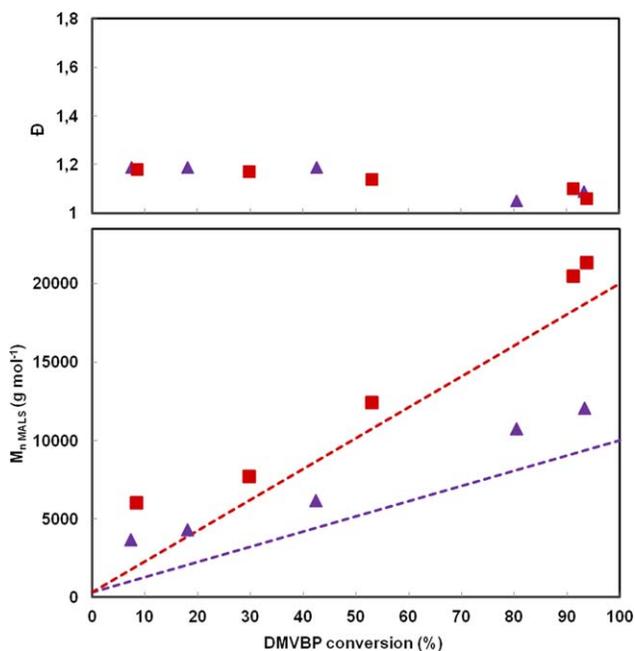


FIGURE 2 Evolution of $M_{n,MALS}$ with time for PDMVBP of $10,000 \text{ g mol}^{-1}$ (triangles) and $20,000 \text{ g mol}^{-1}$ (squares). Dotted lines represent theoretical values.

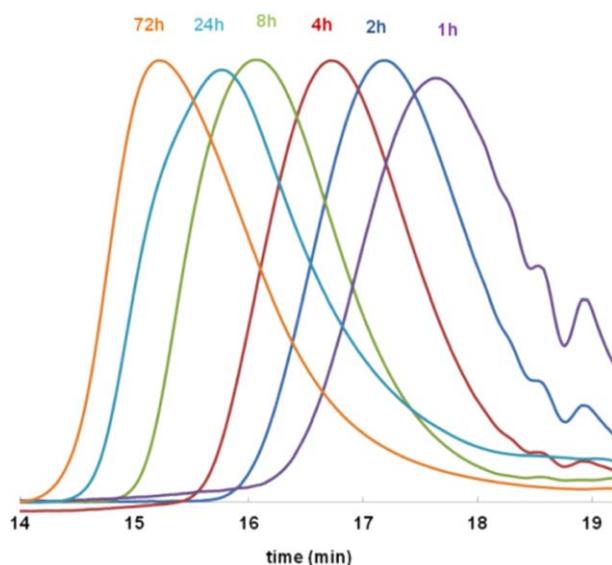
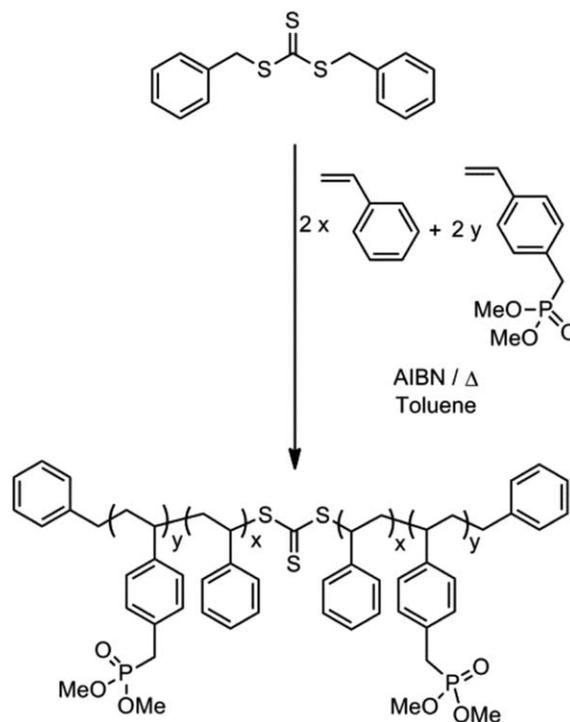


FIGURE 3 Overlay of SEC chromatograms during RAFT polymerization of DMVBP mediated with DBTTC. $M_{n,th} = 10,000 \text{ g mol}^{-1}$.

General Procedure for the Cleavage of the Trithiocarbonate Junction in DBTTC-Based St/DMVBP Copolymers with *n*-Hexylamine

$[PDMVBP_4\text{-}b\text{-}PSt_{67}]_2CS_3$, $M_{n,MALS} = 13,300 \text{ g mol}^{-1}$ ($D = 1.32$), (200 mg , $1.5 \times 10^{-5} \text{ mol}$) was solubilized in 20 mL of THF into a Schlenk flask in the dark under an argon atmosphere. *n*-Hexylamine ($17.8 \text{ } \mu\text{L}$, $12.5 \times 10^{-5} \text{ mol}$) was



SCHEME 2 Synthesis of St/DMVBP statistical copolymers with DBTTC RAFT agent.

TABLE 2 RAFT Statistical Copolymerization of Styrene with DMVBP^a

Entry	Molar Ratio St/DMVBP	Polymers	Conv ^b (%)	$M_{n,th}^c$ (g mol ⁻¹)	$M_{n,MALS}^d$ (g mol ⁻¹)	\bar{D}	Molar Composition ^e	dn/dc (mL g ⁻¹)
1	50/50	[P(St ₇ -stat-DMVBP ₇)] ₂ CS ₃	98.9	4,950	4,090	1.10	53.8/46.2	0.192
2	90/10	[P(St ₁₃ -stat-DMVBP ₂)] ₂ CS ₃	99.2	4,950	3,980	1.11	91.3/8.7	0.207

^a [DMVBP]₀ = 1.66 mol L⁻¹, [St]₀ = 1.66 mol L⁻¹ (Entry 1), [DMVBP]₀ = 0.43 mol L⁻¹, [St]₀ = 4.33 mol L⁻¹ (Entry 2), [AIBN]₀ = 31.7 mmol L⁻¹, [DBTTC]₀ = 117 mmol L⁻¹, *T* = 70 °C.

^b Determined by ¹H NMR.

^c $M_{n,th} = ([DMVBP]_0 \times \text{Conversion of DMVBP}) * M_{DMVBP} / [DBTTC]_0 + ([PS]_0 \times \text{Conversion of PS}) * M_{PS} / [DBTTC]_0 + M_{DBTTC}$.

^d Measured by SEC-MALS.

^e Determined by ³¹P NMR and by ¹H NMR.

added to this solution. The resulting solution was stirred at room temperature for 24 h. Subsequently, the resulting polymer was precipitated in pentane, dried under vacuum at 90 °C and then analyzed. $M_{n,MALS} = 11,500$ g mol⁻¹ ($\bar{D} = 1.32$).

Cleavage of the Trithiocarbonate Junction in DBTTC-Based St/DMVBP Copolymers with *n*-Hexylamine/MTS

[PDMVBP₄-*b*-PSt₆₇]₂CS₃, $M_{n,MALS} = 13,300$ g mol⁻¹ ($\bar{D} = 1.32$), (200 mg, 1.5×10^{-5} mol) was solubilized in 20 mL of THF into a Schlenk flask in dark under an argon atmosphere. To this solution, (37.7 μL, 40×10^{-5} mol) of MTS were added and then (17.8 μL, 12.50×10^{-5} mol) *n*-hexylamine were added. The resulting solution was stirred at room temperature for 24 h. Subsequently, the resulting polymer was precipitated in pentane, dried under vacuum at 90 °C and then analyzed. $M_{n,MALS} = 11,600$ g mol⁻¹ ($\bar{D} = 1.33$).

General Procedure for the Reduction of Disulfide Bond with Zn/Acetic acid

The copolymer resulting from the aminolysis of [PDMVBP₄-*b*-PSt₆₇]₂CS₃, $M_{n,MALS} = 11,500$ g mol⁻¹ ($\bar{D} = 1.32$), (200 mg, 1.5×10^{-5} mol) was solubilized in 10 mL of THF into a Schlenk flask under an argon atmosphere and treated with acetic acid (4 mL) and zinc powder (8.4 mg) for 4 h. After the removal of solid components by filtration, the resulting polymer was precipitated in pentane, dried under vacuum at 90 °C, and then analyzed. $M_{n,MALS} = 11,300$ g mol⁻¹ ($\bar{D} = 1.30$).

General Procedure for the Reduction of Disulfide Bond with DTT

The copolymer resulting from the aminolysis of [PDMVBP₄-*b*-PSt₆₇]₂CS₃, $M_{n,MALS} = 11,500$ g mol⁻¹ ($\bar{D} = 1.32$), (200 mg, 1.5×10^{-5} mol) was dissolved in 6 mL of THF into a Schlenk flask under an argon atmosphere. DTT (0.128 g, 8.3×10^{-4} mol) was added to the mixture and stirred at 60 °C for 24 h. The polymer was then precipitated in pentane, dried under vacuum at 90 °C and analyzed by SEC. $M_{n,MALS} = 11,500$ g mol⁻¹ ($\bar{D} = 1.31$).

General Procedure for the Production of Phosphonic Diacid-Functional Copolymers from Phosphonate Ester Precursors

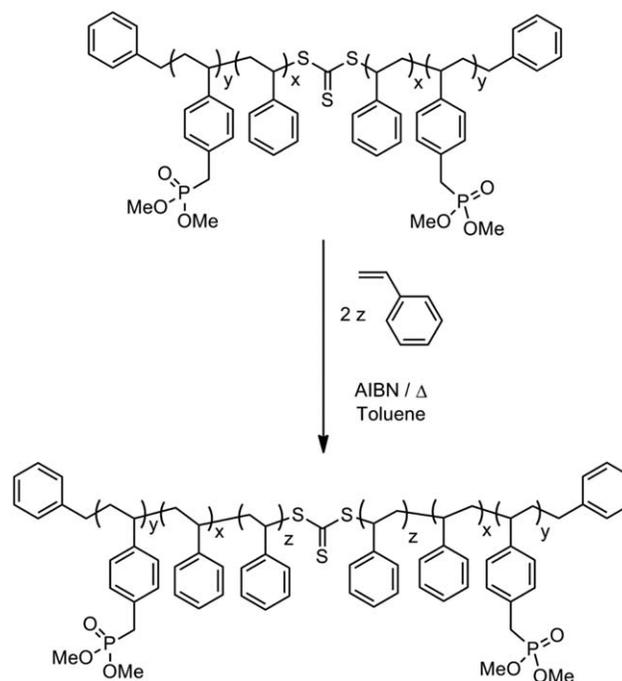
A general procedure is described as follows: [PDMVBP₄-*b*-PSt₆₇]₂CS₃, $M_{n,MALS} = 13,300$ g mol⁻¹ ($\bar{D} = 1.32$), (200 mg,

1.5×10^{-5} mol) was dissolved in 2 mL of dichloromethane in a round-bottom flask equipped with a condenser under an argon atmosphere. (9.5 mg, 6.25×10^{-5} mol) of BrSiMe₃ was added dropwise for 30 min. The reaction mixture was stirred at room temperature for 6 h. After the reaction, the solvent was evaporated and 5 mL of methanol were added. The mixture was stirred for 2 h, then the solvent was evaporated and the residue was dried under vacuum at 90 °C. The yield was 99.9% (³¹P NMR).

RESULTS AND DISCUSSIONS

RAFT Homopolymerization of DMVBP

Conventional polymerization of DMVBP was first carried out in toluene in the presence of AIBN as initiator. Best experimental conditions were found at 60 °C with DMVBP and AIBN concentrations of 2.43 and 14.6×10^{-3} mol L⁻¹, respectively. Under these conditions, M_n was slightly greater than 10^5 g mol⁻¹ ($M_{n,PS} = 111,300$ g mol⁻¹ and $M_{n,MALS} =$



SCHEME 3 General scheme for the synthesis of [P(St_x-stat-DMVBP_y)-*b*-PSt_z]₂CS₃ block copolymers.

TABLE 3 Block Copolymerization of St with Various Macro-RAFT Agents Based on DMVBP^a

Entry	Polymers	Conv. ^b (%)	$M_{n,th}$ ^c (g mol ⁻¹)	$M_{n,MALS}$ ^d (g mol ⁻¹)	\mathcal{D}
1	[P(St ₇ -stat-DMVBP ₇)-b-PSt ₄₀] ₂ CS ₃	56.9	13,330	11,910	1.21
2	[P(St ₁₃ -stat-DMVBP ₂)-b-PSt ₄₀] ₂ CS ₃	57.4	13,100	11,210	1.25
3	[PDMVBP ₄ -b-PSt ₆₇] ₂ CS ₃	58.2	12,460	13,300	1.32
4	(PSt ₄₃) ₂ CS ₃	58	9,280	8,140	1.15

^a [St]₀ = 4.8 mol L⁻¹, [AIBN]₀ = 31.7 mmol L⁻¹, [macro-RAFT agents]₀ = 30.1 mmol L⁻¹, T = 70 °C.

^b Determined by gravimetric analysis.

^c $M_{n,th} = M_{(macro-RAFT\ agent)} + (M_{St} \times (St\ conversion) \times ([St]_0/[macro-RAFT\ agent]_0))$.

^d Measured by SEC- MALS.

136,600 g mol⁻¹ (Entry 5 in Table 1), with a conversion reaching 93.6% after 72 h.

This result led us to consider the RDRP of DMVBP in the range 1000–20,000 g mol⁻¹ by using DBTTC as a reversible transfer agent (Scheme 1). DBTTC was selected because it was reported to be an efficient RAFT agent for St,²⁵ a structurally similar monomer to DMVBP. Table 1 contains experimental results for the polymerization of DMVBP with four initial DBTTC concentrations.

For all the polymerizations, PDMVBP is obtained with high monomer conversion (between 91 and 94%). Average molar masses were determined by SEC using both PS standards and MALS detector. As expected for a well-controlled RAFT polymerization, SEC-MALS analysis gave M_n values that were inversely proportional to the initial DBTTC concentration. M_n were slightly greater than targeted (Entries 1–4 of Table 1). In order to obtain accurate $M_{n,MALS}$ measurements, the incremental RI (dn/dc) was measured for each sample. In contrast to SEC-MALS data, $M_{n,PS}$ determined by SEC-RI were much lower than targeted, especially for the highest theoretical M_n . Differences in hydrodynamic volumes between PS and PDMVBP and/or specific interactions of PDMVBP with the SEC columns may be responsible for this deviation. Dispersities (\mathcal{D}) obtained from SEC-MALS were found to be low (1.05–1.16) as expected for an efficient RAFT polymerization. In contrast, dispersities obtained with PS standards were higher with a dispersity of 1.58 for a classical radical polymerization and \mathcal{D} values dropping to 1.22–1.34 when using DBTTC. Nevertheless, based on these different observations, it can be concluded that DBTTC plays its role by regulating average molar masses of polymers and reducing the dispersity values. Thus, for the rest of the study, we used SEC-MALS to determine molar masses and to measure the dispersity.

The evolution of DMVBP conversion with time was followed for different DBTTC concentrations in order to study its impact on the rate of polymerization. Under our conditions, we observed a small retardation effect on the kinetics of polymerization, with DMVBP conversions decreasing as the concentration of DBTTC increased. This phenomenon has previously been observed by Chernikova et al. in St polymerization.²⁵ However, after 70 h, all polymerizations reach a similar DMVBP conversion of around 80% (Fig. 1). Samples obtained at regular intervals during

DMVBP polymerization using DBTTC concentrations of 27.9 and 56.6 mmol L⁻¹ (corresponding to targeted PDMVBP of 10,000 and 20,000 g mol⁻¹, respectively) were analyzed by SEC-MALS. $M_{n,MALS}$ were found to be only slightly above the theoretical values (Fig. 2), and as expected, DBTTC acts like an efficient RAFT agent, with $M_{n,MALS}$ increasing nearly linearly with conversion for both polymerizations and with dispersities remaining below 1.2 throughout the polymerization.

Superposition of SEC traces also illustrates the controlled nature of the polymerization, with SEC traces gradually shifting towards higher molar masses (Fig. 3).

We next investigated the copolymerization of DMVBP with St in the presence of DBTTC in order to access various copolymers of controlled molar masses and composition.

RAFT Copolymerization of Dimethyl-*p*-vinylbenzylphosphonate with Styrene P(St_x-stat-DMVBP_y)CS₃

Two statistical DMVBP/St copolymers were synthesized with a targeted composition of P(St₇-stat-DMVBP₇) and P(St₁₃-stat-DMVBP₂) and M_n of 4950 g mol⁻¹ (Scheme 2).

Copolymerizations of St with DMVBP were carried out in toluene at 70 °C in the presence of AIBN as initiator and DBTTC to control the polymerization. Both polymerizations occurred with very high monomer conversion (>98.9%), and expected compositions as determined by ¹H NMR spectroscopy (See Supporting Information ESI1). SEC-MALS analysis of copolymers gave very similar molar masses for both copolymers as expected for a controlled polymerization, as well as similar dispersities of \mathcal{D} =1.10 (Table 2). In the case of [P(St₇-stat-DMVBP₇)]₂CS₃ with a 1/1 molar ratio in both monomers, we followed the conversion of each monomer with time by ³¹P NMR to access the DMVBP conversion and used ¹H NMR for St conversion and calculated the resulting composition (See Supporting Information ESI2). It appeared that in the early stages of the copolymerization, St is consumed slightly faster than DMVBP, but without strong compositional drift along the polymer chain. These two copolymers demonstrate that we can efficiently incorporate DMVBP in polystyrene using RAFT technology and control both composition and molar masses.

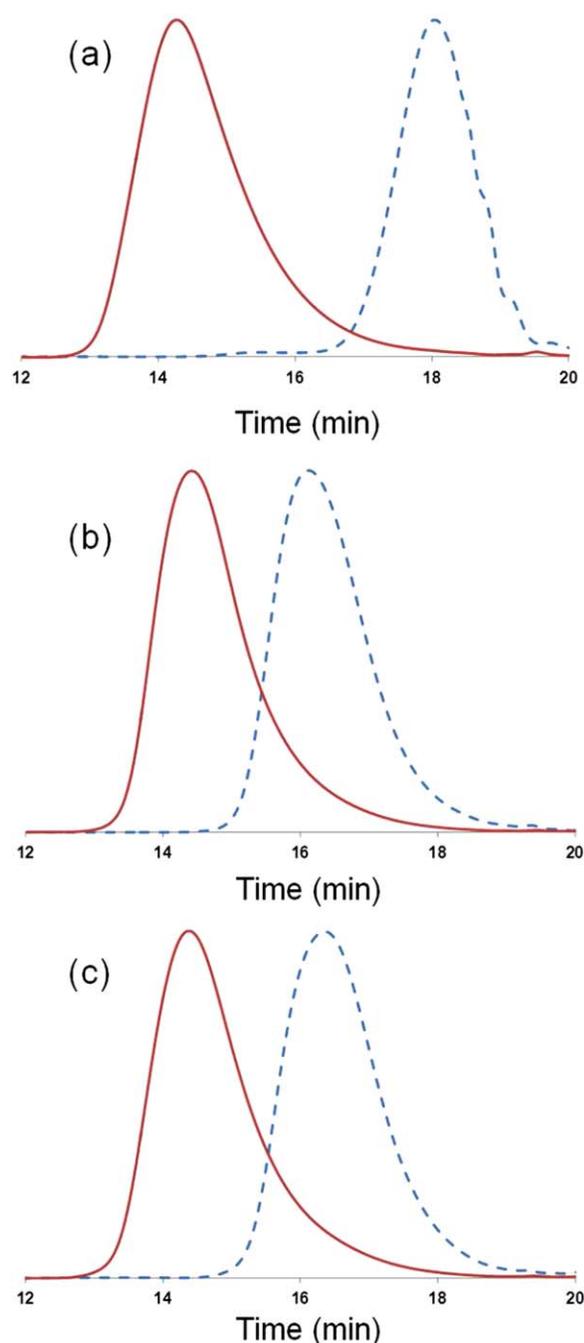


FIGURE 4 Evolution of SEC traces after styrene polymerization from different macro-RAFT agents (dotted lines) to block copolymers (plain lines). (a) $[PDMVBP_4\text{-}b\text{-}PSt_{67}]_2CS_3$ (Table 3, Entry 3), (b) $[P(St_{13}\text{-}stat\text{-}DMVBP_2)\text{-}b\text{-}PSt_{40}]_2CS_3$ (Table 3, Entry 2), (c) $[P(St_7\text{-}stat\text{-}DMVBP_7)\text{-}b\text{-}PSt_{40}]_2CS_3$ (Table 3, Entry 1).

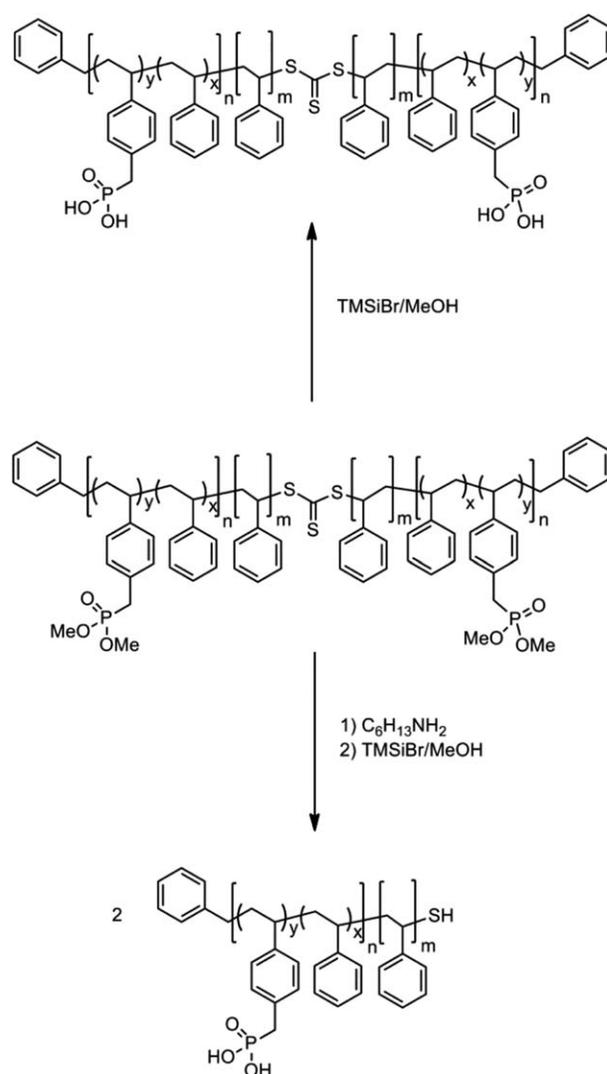
RAFT Block Copolymerization of Dimethyl-*p*-vinylbenzylphosphonate with Styrene

Following the polymerization of DMVBP and its statistical copolymerization with St, we took advantage of the chain-end control of the RAFT polymerization and used our previously synthesized (co)polymers as macro-RAFT agents in block copolymerization with St. The purpose was to obtain

styrenic ABA triblock copolymers of controlled architecture and with controlled phosphonate concentration in PDMVBP or $P(St_x\text{-}stat\text{-}DMVBP_y)$ outer A blocks (Scheme 3).

We synthesized three different block copolymers by polymerizing St in the presence of $[P(St_7\text{-}stat\text{-}DMVBP_7)]_2CS_3$, $[P(St_{13}\text{-}stat\text{-}DMVBP_2)]_2CS_3$, and $[P(DMVBP_4)]_2CS_3$ as macro-RAFT agents.

All polymerizations occurred with St conversion reaching 60% after 48 h polymerization, which is similar to the conversion obtained for St polymerization in the presence of DBTTC under the same experimental conditions (Table 3, Entry 4). SEC-MALS analysis of block copolymers gave $M_{n,MALS}$ values in good agreement with theory and dispersities slightly higher than the initial macro-RAFT agent with $D = 1.2\text{--}1.3$. Superposition of SEC traces between the initial macro-RAFT agent and the final block copolymer clearly



SCHEME 4 Synthesis of phosphonic acid containing diblock or triblock copolymers starting from $[P(St\text{-}stat\text{-}DMVBP)\text{-}b\text{-}PSt]_2CS_3$.

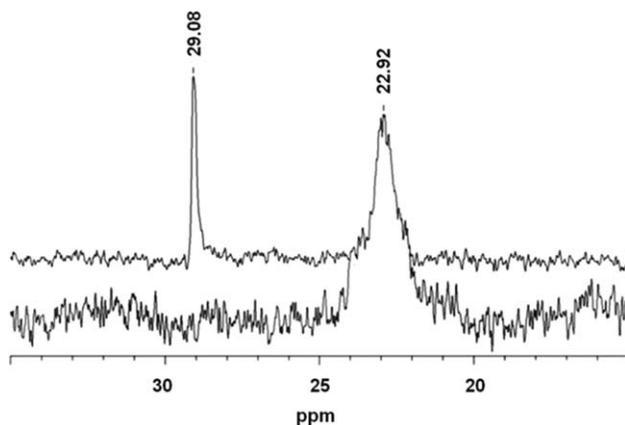


FIGURE 5 ^{31}P NMR spectrum of a $[\text{PDMVBP}_4\text{-}b\text{-PSt}_{67}]_2\text{CS}_3$ block copolymer before TMSiBr/MeOH treatment (upper NMR spectrum) and after treatment (lower NMR spectrum).

shows the controlled character of the block copolymerization, with the initial macro-RAFT agent being completely consumed, leading to the formation of copolymers of higher molar masses, but with a slightly less symmetrical shape along with higher dispersities compared to that of the RAFT polymer precursor (Fig. 4).

Deprotection of the Dimethylphosphonate Groups

The use of DBTTC as a transfer agent results in (co)polymer chains bearing a central trithiocarbonate fragment. As a result, a triblock copolymer with a $[\text{P}(\text{St}\text{-}stat\text{-DMVBP})\text{-}b\text{-PSt}]_2\text{CS}_3$ structure can be regarded as a synthetic platform, potentially leading to two different copolymer structures depending on the type of post-treatment it will be involved in. A cleavage reaction of the trithiocarbonate function will lead to the formation of a $\text{P}(\text{St}\text{-}stat\text{-DMVBP})\text{-}b\text{-PSt}\text{-SH}$ diblock copolymer where the dimethylphosphonate functions could be further deprotected in order to release the phosphonic acid moieties. Alternatively, if the triblock copolymer $[\text{P}(\text{St}\text{-}stat\text{-DMVBP})\text{-}b\text{-PSt}]_2\text{CS}_3$ was directly involved in a deprotection reaction of the dimethylphosphonate groups without any impact on the midchain trithiocarbonate fragment, this should lead to a triblock structure bearing free phosphonic acid functions (Scheme 4).

To our knowledge, the best “soft” procedure allowing the transformation of a dimethylphosphonate group into a phosphonic acid one is a reaction involving the TMSiBr/MeOH couple.^{20,26} Therefore, we decided to apply this deprotection methodology and use $[\text{PDMVBP}_4\text{-}b\text{-PSt}_{67}]_2\text{CS}_3$ as a model substrate, as its low phosphonic acid content would still allow the deprotected copolymer to be dissolved and thoroughly characterized.

By direct treatment of $[\text{PDMVBP}_4\text{-}b\text{-PSt}_{67}]_2\text{CS}_3$ with TMSiBr/MeOH, we quantitatively obtained the corresponding copolymer with all phosphonic ester functions converted into phosphonic acids (Fig. 5). ^{31}P NMR analysis clearly shows a shift from 29.08 ppm, characteristic of the dimethylphosphonate ester, to 22.92 ppm corresponding to the phosphonic acid

function. We ensured that this relatively soft procedure left the trithiocarbonate function intact in the copolymer chain, by quantitatively measuring the UV absorption of the trithiocarbonate function after reaction (See Supporting Information ESI3). The integrity of the triblock copolymer backbone remains unchanged after treatment, the latter allowing the complete transformation of phosphonate ester groups into phosphonic acids.

Following a different strategy, when $[\text{PDMVBP}_4\text{-}b\text{-PSt}_{67}]_2\text{CS}_3$ was reacted with *n*-hexylamine in the dark before TMSiBr/MeOH treatment, we observed a total extinction of the trithiocarbonate absorbance by SEC-UV (See Supporting Information ESI4), thus proving that we quantitatively cleaved the trithiocarbonate group. Concomitantly, a shift of the SEC trace toward lower molar masses indicated the formation of the $\text{PDMVBP}_4\text{-}b\text{-PSt}_{67}\text{-SH}$ diblock copolymer (Fig. 6). Unexpectedly, the M_n of $\text{PDMVBP}_4\text{-}b\text{-PSt}_{67}$ ($M_{n,\text{MALS}} = 11,500 \text{ g mol}^{-1}$) was found to be close to that of the starting triblock copolymer $[\text{PDMVBP}_4\text{-}b\text{-PSt}_{67}]_2\text{CS}_3$ ($M_{n,\text{MALS}} = 13,300 \text{ g mol}^{-1}$) (Table 4, Entry 1–2). After this result, further studies were necessary in order to satisfactorily conclude on the transformation of the triblock copolymer into its diblock counterpart. As in the $[\text{PDMVBP}_4\text{-}b\text{-PSt}_{67}]_2\text{CS}_3$ copolymer, the trithiocarbonyl moiety is directly linked to two polystyrene blocks, the same aminolysis was directly conducted on a $(\text{PSt}_{43})_2\text{CS}_3$. Following the same experimental conditions, $(\text{PSt}_{43})_2\text{CS}_3$ ($M_{n,\text{MALS}} = 8140 \text{ g mol}^{-1}$) led unambiguously to the expected $\text{PSt}_{43}\text{-SH}$ with a M_n roughly divided by two ($M_{n,\text{MALS}} = 4860 \text{ g mol}^{-1}$) (Table 4, Entries 3–4). At this stage, it remains unclear why in the case of a styrenic block copolymer containing phosphonate ester groups located far away from the trithiocarbonyl function, the M_n of the copolymer resulting from the aminolysis is relatively far from expected.

In order to rule out a possible oxidation of the terminal thiol into disulfide that could be responsible for the deviation of M_n , we conducted the same aminolysis of $[\text{PDMVBP}_4\text{-}b\text{-PSt}_{67}]_2\text{CS}_3$

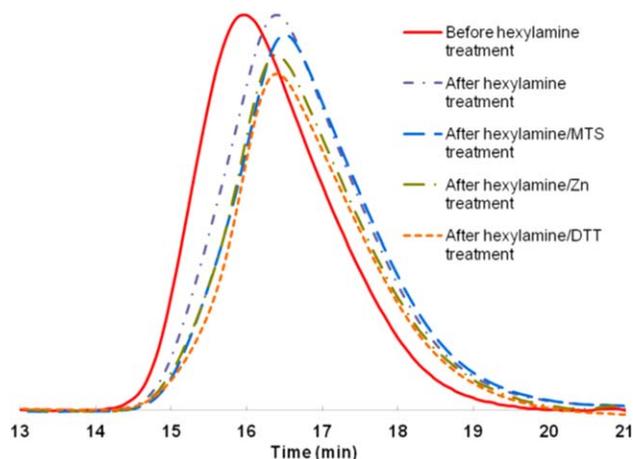


FIGURE 6 Superposition of SEC traces for $[\text{PDMVBP}_4\text{-}b\text{-PSt}_{67}]_2\text{CS}_3$ before and after aminolysis. SEC traces after treatment are scaled for clarity.

TABLE 4 Aminolysis of [PDMVBP₄-*b*-PSt₆₇]₂CS₃ with Different Conditions

Entry	Aminolysis Conditions	Copolymers	$M_{n,MALS}^a$ (g mol ⁻¹)	\bar{D}
1	–	[PDMVBP ₄ - <i>b</i> -PSt ₆₇] ₂ CS ₃	13,300	1.32
2	<i>n</i> -Hexylamine	PDMVBP ₄ - <i>b</i> -PSt ₆₇	11,500	1.32
3	–	(PSt ₄₃) ₂ CS ₃	8,140	1.15
4	<i>n</i> -Hexylamine	PSt ₄₃ SH	4,860	1.16
5	<i>n</i> -Hexylamine/MTS	PDMVBP ₄ - <i>b</i> -PSt ₆₇	11,600	1.33
6	<i>n</i> -Hexylamine, then Zn/CH ₃ CO ₂ H	PDMVBP ₄ - <i>b</i> -PSt ₆₇	11,300	1.30
7	<i>n</i> -Hexylamine, then DTT	PDMVBP ₄ - <i>b</i> -PSt ₆₇	11,500	1.31

^a Measured by SEC-MALS.

in the presence of MTS (Table 4, Entry 5) which is known to react with macromolecular thiols to form polymers of general structure P_{*n*}-S-S-CH₃ with unreactive terminal disulfide groups.²⁷ In addition, we treated the copolymer resulting from the aminolysis of [PDMVBP₄-*b*-PSt₆₇]₂CS₃ with DTT (Table 4, Entry 7) as well as with Zn/acetic acid (Table 4, Entry 6)²⁸ in order to reduce *in situ* possibly created disulfide bonds into thiol.²⁹ It appeared to us that whatever the strategy used, all final copolymers PDMVBP₄-*b*-PSt₆₇-SH were found to have the same average molar mass (Table 4), with an almost perfect superposition of all SEC traces (Fig. 6). All these results tend to prove that the cleavage of the trithiocarbonyl group is effective with no oxidation of the resulting thiol.

As expected, the final treatment of PDMVBP₄-*b*-PSt₆₇-SH with TMSiBr/MeOH, quantitatively led to the phosphonic acid-based copolymer based on ³¹P NMR, with the characteristic signal of the phosphonic acid at 23 ppm and no trace of the original phosphonate ester at 29 ppm. The same procedure applied to the other block copolymers with a higher content in DMVBP led to a virtually insoluble material after TMSiBr/MeOH treatment and thus could not be characterized in a satisfactory manner.

CONCLUSIONS

DMVBP was successfully homopolymerized and copolymerized with St in the presence of the DBTTC RAFT agent. DBTTC was found to control the molar mass of (co)polymers by a reversible chain transfer process with limited impact on the overall kinetics of polymerization. Evidence of a high degree of retention of trithiocarbonate functionality was obtained through the successful synthesis of triblock (co)polymers by polymerizing St from (PDMVBP)₂CS₃ and [P(St-*stat*-DMVBP)]₂CS₃ precursors. The post-treatment of [PDMVBP₄-*b*-PSt₆₇]₂CS₃, taken as one example for dimethyl phosphonate containing (co)polymers, with TMSiBr/MeOH allowed the complete transformation of phosphonate ester groups into phosphonic acid while keeping the triblock structure unchanged. In contrast, the use of a primary amine before TMSiBr/MeOH treatment led to quantitative cleavage of the trithiocarbonyl midchain group, leading to structurally new diblock copolymers bearing free phosphonic acid moieties. These findings open up interesting possibilities such as the study of the self-assembling properties of the block

copolymers in water with targeted applications due to the specificity of the phosphonic acid function.

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