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ARTICLE TYPE

Synthesis and characterization of Quaternary phosphonium-containing, trithiocarbonate RAFT agents

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In this article the syntheses of quaternary phosphonium-containing trithiocarbonate RAFT agents (RAFT-PR_3, R= Bu and Ph) and their use in the bulk, thermally initiated polymerization of styrene were examined. It was found that the thermal stabilities of RAFT-PR_3 were enhanced compared to comparable quaternary ammonium-containing RAFT agents, which significantly improved the retention of the cationic end-functionality of the polystyrene obtained by high temperature bulk polymerization. The crude polystyrene was further purified via column chromatography to yield high purity hemi-telechelic polystyrene cationomers.

Introduction

Hemi-telechelic cationomers, polymers bearing a cationic group at one end, are an interesting class of end-functional polymers. In a previous publication the authors demonstrated the synthesis of quaternary ammonium-containing RAFT agents useful for the synthesis of hemi-telechelic cationomers. [1] While telechelic cationomers with quaternary ammonium cations have been popular in a number of applications due to their affordability and accessibility, [2 - 8] quaternary phosphonium cations have been attracting attention for their higher thermal stability,[9,10] improved antimicrobial activity, [11] and improved gene delivery, [12 - 15] compared to quaternary ammonium salts.

(Hemi)telechleic quaternary phosphonium cationomers have been synthesized with various methods, such as anionic polymerization, [16] cationic polymerization, [17 - 20] polycondensation,[21] group transfer polymerization,[22] free radical polymerization with a functional chain transfer agent,[23] and atom transfer radical polymerization.[24] However, to our knowledge, the synthesis of hemi-telechelic, quaternary phosphonium cationomers via reversible addition fragmentation chain transfer (RAFT) polymerization have not been reported. RAFT polymerization is a reversible deactivation radical polymerization (RDRP) technique compatible with a wide range of monomer functionalities and reaction conditions. [25] In addition, the functional groups present in the initial RAFT agent (CTAs) are retained in the final polymer. This allows the synthesis of telechelic polymers with a wide range of α- or ω-end groups via the design of RAFT agents.[25,26,27]

For telechelic or hemi-telechelic ionomers, the thermal stability of the ionic groups controls the upper temperature limit for processing or use. For example, Charlier and co-workers studied the thermal stability of telechelic polystyrene ionomers terminated with quaternary ammonium iodide groups or ammonium sulfonate groups and found both types of ionic groups thermally degraded below 200 ^{o}C.[28] When used with oppositely charged telechelics to generate supramolecular block copolymers, macrophase separation and loss of the supramolecular structure was lost at ca. 200 ^{o}C due the decomposition of the ionic groups. [29 - 31] Our previous investigation of the quaternary ammonium-containing trithiocarbonate RAFT agents demonstrated that significant degradation of the quaternary ammonium groups occurred during bulk self-initiated polymerization of polystyrene at 120°C reducing the end-functionality of the obtained polymers.1 High purity hemi-telechelic cationomers can be obtained by using low polymerization temperature and subsequent purification via column chromatography, but the moderate thermal stability of the quaternary ammonium end-groups presented in these telechelic cationomers would limit the melt processing such as under shear[32] or thermal annealing[33] and upper use temperature. In this article, the syntheses of quaternary phosphonium-containing, trithiocarbonate RAFT agents (RAFT-PR_3) (Fig. 1) and the bulk thermally initiated polymerization (i.e. thermal polymerization) of styrene using RAFT-PR_3 are presented. The thermal polymerization is a direct demonstration of the higher thermal stability of the quaternary phosphonium-containing RAFT agents compared to quaternary ammonium-containing RAFT agents. This is further investigated by thermo-gravimetric analysis. In addition, the applicability of the RAFT agents is shown by the synthesis hemi-telechelic poly(butyl acrylate) and poly(styrene-*b*-butyl acrylate).

Experimental Section

Materials

α,α'-Azobisisobutyronitrile (98%, Sigma-Aldrich) was recrystallized from methanol and dried under vacuum prior to use. Styrene (99%, stabilized, Acros Organics) and butyl acrylate

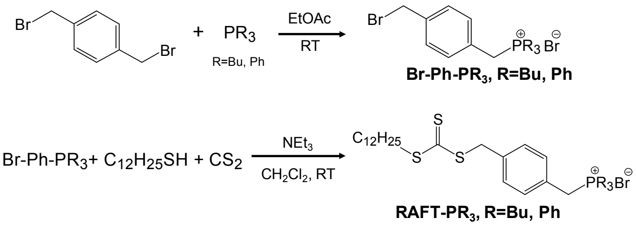

Fig. 1 Synthesis of quaternary phosphonium containing trithiocarbonate RAFT agents, RAFT-PR_3 (R=n-butyl and phenyl).

(Alfa Aesar, 98%) was purified by passing over a column of basic alumina. Silica gel (Dynamic Adsorbents 60Å, 32–63 µM, flash grade) was used for column chromatography. Thin layer chromatography plates (250 µm, with fluorescent indicator activated at 2540 Å) were supplied from J. T. Baker. Benzyl dodecyl trithiocarbonate was synthesized according to previous report.1 All other chemicals used in this article were obtained commercially with high purity and used as received.

Instrumentation

^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra were collected using either a Varian Gemini 300 MHz or a Varian 500 MHz spectrometer. Thermogravimetric analysis (TGA) was performed on a TA Instruments TGA Q50 from room temperature to 700 ^{o}C at a heating rate of 20 ^{o}C /min in nitrogen atmosphere. All mass spectrometry experiments were acquired on an HCT Ultra II quadrupole ion trap mass spectrometer (Bruker Daltonics, Billerica, MA) equipped with an electrospray (ESI) source. The molecular weight and molecular weight distribution of the polymer products was characterized by size exclusion chromatography (SEC) with a Waters Breeze system equipped with a column set at 35 ^{o}C and a refractive index detector (Waters 2414). The column set consists of a Styragel® HR 4 THF column (4.6 × 300 mm) with an effective molecular weight range 5 k to 600 k Da, a Styragel® HR 3 THF column (4.6 × 300 mm) with an effective molecular weight range 0.5 k to 30 kDa, and a Styragel® HR 4E THF column (4.6 × 300 mm) with an effective molecular weight range 0.05 k to 100 kDa. The SEC was calibrated using PS standards of narrow molar mass dispersity (Đ) with the molecular weight of 1300 Da to 400 kDa (Alfa Aesar).

Synthesis of 4-(bromomethyl)benzyltri-*n*-butylphosphonium bromide (Br-Ph-PBu_3)

Tri-*n*-butylphosphine (1.008 g, 4.9 mmol) was added to a stirred solution of α,α'-dibromo-*p*-xylene (2.643 g, 10.0 mmol) in 20 mL ethyl acetate. The reaction mixture was allowed to stir for 48 hours. The product, Br-Ph-PBu_3, gradually precipitated as a fine white powder. Br-Ph-PBu_3 was recovered by filtration, washed with 40 mL ethyl ether and dried in a vacuum oven (2.222 g, 96% yield). Due to the lipophicity of the mono-substituted product, the obtained product contained ca. 1 mol% (calculated by ^{1}H NMR) di-substituted compound, i.e. 1,4-bis(tri-*n*-butylphosphoniummethyl)benzene dibromide. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.49 (dd, J = 8.1 Hz, 2.2 Hz, 2H, $(CH_{ar})_2CCH_2P^+(CH_2CH_2CH_2CH_3)_3$), 7.36 (d, J =8.1 Hz, 2H, $BrCH_2C(CH_{ar})_2(CH_{ar})_2C$), 4.45 (s, 2H, $BrCH_2C(CH_{ar})_2$), 4.38 (d, J = 15.4 Hz, 2H, $(CH_{ar})_2CCH_2P^+(CH_2CH_2CH_2CH_3)_3$), 2.41 (m, 6H, $(CH_{ar})_2CCH_2P^+(CH_2CH_2CH_2CH_3)_3$), 1.45 (m, 12H, $(CH_{ar})_2CCH_2P^+(CH_2CH_2CH_2CH_3)_3$), 0.91 (t, J=6.8 Hz, 9H, $(CH_{ar})_2CCH_2P^+(CH_2CH_2CH_2CH_3)_3$). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 137.9 (d, J_{CP} = 3.7 Hz), 130.5 (d, J_{CP} = 5.1 Hz), 129.7, 129.0 (d, J_{CP} = 8.8 Hz), 32.6, 26.7 (d, J_{CP} = 45.1 Hz), 23.8 (d, J_{CP} = 14.0 Hz), 23.5 (d, J_{CP} = 4.7 Hz), 18.8 (d, J_{CP} = 46.5 Hz), 13.3. ^{31}P NMR (121.5 MHz, $CDCl_3$) δ (ppm): 31.4. MS (ESI-MS) calcd for $C_{20}H_{35}BrP$ (m/z), 385.1; found, 385.3 [M-Br^-].

Synthesis of 4-(bromomethyl)benzyltriphenylphosphonium bromide (Br-Ph-PPh_3)

Triphenylphosphine (1.357 g, 5.2 mmol) was added to a stirred solution of α,α'-dibromo-*p*-xylene (1.317 g, 5.0 mmol) in 20 mL ethyl acetate. The reaction mixture was stirred for 48 hours, during which Br-Ph-PPh_3 gradually precipitated as a white powder. Br-Ph-PPh_3 was recovered by filtration, washed with 40 mL ethyl ether and dried in a vacuum oven (2.357 g, 90% yield). The obtained product was free of di-substituted compound. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.75 - 7.51 (m, 15H, $(CH_{ar})_2CCH_2P^+Ph_3$), 7.06 (m, 4H, $BrCH_2C(CH_{ar})_2(CH_{ar})_2C$), 5.46 (d, J = 14.7 Hz, 2H, $(CH_{ar})_2CCH_2P^+Ph_3$), 4.32 (s, J = 1.2 Hz, 2H, $BrCH_2C(CH_{ar})_2$). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 138.1 (d, J_{CP} = 4.2 Hz), 134.9 (d, J_{CP} = 3.3 Hz), 134.4 (d, J_{CP} = 9.8 Hz), 132.0 (d, J_{CP} = 5.6 Hz), 130.1 (d, J_{CP} = 12.6 Hz), 129.3 (d, J_{CP} = 3.3 Hz), 127.7 (d, J_{CP} = 8.8 Hz),118.1 (d, J_{CP} = 85.6 Hz), 32.8, 30.6 (d, J_{CP} = 47.0 Hz). ^{31}P NMR (121.5 MHz, $CDCl_3$) δ (ppm): 23.5. MS (ESI-MS) calcd for $C_{26}H_{23}BrP$ (m/z), 445.1; found, 444.9 [M-Br^-].

Synthesis of S-1-dodecyl-S'-(methylbenzyltributylphosphonium bromide) trithiocarbonate RAFT agents (RAFT-PBu_3)

Triethylamine (0.525 g, 5.2 mmol) was added dropwise to a stirred solution of 1-dodecanethiol (0.8642 g, 4.3 mmol) and CS_2 (1.6087 g, 21.1 mmol) in CH_2Cl_2 (5 mL) at room temperature. After stirring for 3 hours, Br-Ph-PBu_3 (2.0691 g, 4.4 mmol) was directly added into the reaction mixture. The reaction mixture was stirred for another 30 hours, diluted with an additional amount of CH_2Cl_2 (20 mL) and washed with deionized water in a separatory funnel for four times. A small amount of concentrated sodium bromide aqueous solution was added to the separatory funnel to facilitate the phase separation. The organic phase was collected, dried over $MgSO_4$, and rotary evaporated to produce a viscous yellow liquid. The product was further dried in a vacuum oven at 50 ^{o}C (2.760 g, 97% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.47 (m, 2H, $(CH_{ar})_2CCH_2P^+(CH_2CH_2CH_2CH_3)_3$), 7.35 (m, 2H, $S{=}CSCH_2C(CH_{ar})_2(CH_{ar})_2C$), 4.61 (s, 2H, $S{=}CSCH_2C(CH_{ar})_2$), 4.34 (d, J = 14.9 Hz, 2H, $(CH_{ar})_2CCH_2P^+(CH_2CH_2CH_2CH_3)_3$), 3.41 (t, J = 7.0 Hz, 2H, $CH_3C_9H_{18}CH_2CH_2CS{=}S$), 2.43 (m, $(CH_{ar})_2CCH_2P^+(CH_2CH_2CH_2CH_3)_3$), 1.72 (m, 2H, $CH_3C_9H_{18}CH_2CH_2CS{=}S$), 1.21-1.55 (br m, 30H, $(CH_{ar})_2CCH_2P^+(CH_2CH_2CH_2CH_3)_3$ and $CH_3C_9H_{18}CH_2CH_2CS{=}S$), 0.92 (m, 12H, $(CH_{ar})_2CCH_2P^+(CH_2CH_2CH_2CH_3)_3$ and $CH_3C_9H_{18}CH_2CH_2CS{=}S$). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm):

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223.2, 136.0 (d, J_{CP} = 3.7 Hz), 130.5 (d, J_{CP} = 4.7 Hz), 130.2 (d, J_{CP} = 3.3 Hz), 128.0 (d, J_{CP} = 8.4 Hz), 40.5, 37.2, 31.9 (m), 29.6-22.6, 26.9 (d, J_{CP} = 45.1 Hz), 24.0 (d, J_{CP} = 15.4 Hz), 23.7 (d, J_{CP} = 5.1 Hz), 19.0 (d, J_{CP} = 46.5 Hz), 14.1, 13.4. ^{31}P NMR (121.5 MHz, $CDCl_3$) δ (ppm): 31.6. MS (ESI-MS) calcd for $C_{33}H_{60}PS_3$ (m/z), 583.4; found, 583.5 [M-Br$^-$].

Synthesis of S-1-dodecyl-S'-(methylbenzyltriphenylphosphonium bromide) trithiocarbonate RAFT agents (RAFT-PPh$_3$)

RAFT-PPh$_3$ was synthesized following an analogous procedure as described above and was obtained as a yellow solid upon drying (2.966g, 96% yield.) ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.79 - 7.52 (m, 15H, $(CH_{ar})_2CCH_2P^+Ph_3$), 7.07 (m, 4H, $S{=}CSCH_2C(CH_{ar})_2(CH_{ar})_2C$), 5.46 (d, J = 14.4 Hz, $(CH_{ar})_2CCH_2P^+Ph_3$), 4.49 (d, J = 1.5 Hz, $S{=}CSCH_2C(CH_{ar})_2(CH_{ar})_2C$), 3.35 (t, J = 7.3 Hz, 2H, $CH_3C_9H_{18}CH_2CH_2CS{=}S$), 1.68 (m, 2H, $CH_3C_9H_{18}CH_2CH_2CS{=}S$), 1.44-1.18 (br m, 18H, $CH_3C_9H_{18}CH_2CH_2CS{=}S$), 0.87 (t, J = 6.8 Hz, 3H, $CH_3C_9H_{18}CH_2CH_2CS{=}S$). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 223.1, 135.5 (d, J_{CP} = 4.2 Hz), 134.9 (d, J_{CP} = 2.8 Hz), 134.3 (d, J_{CP} = 9.8 Hz), 131.7 (d, J_{CP} = 3.7 Hz), 130.1 (d, J_{CP} = 12.6 Hz), 129.4, 126.8 (d, J_{CP} = 8.4 Hz), 117.9 (d, J_{CP} = 86.1 Hz), 40.6, 37.1, 31.8 (m), 30.4 (d, J_{CP} = 46.5 Hz), 29.6-22.6, 14.1. ^{31}P NMR (121.5 MHz, $CDCl_3$) δ (ppm): 23.3. MS (ESI-MS) calcd for $C_{39}H_{48}PS_3$ (m/z), 643.3; found, 643.4 [M-Br$^-$].

RAFT bulk polymerization of styrene at 120 °C

Bulk styrene polymerizations with either RAFT-PBu$_3$ or RAFT-PPh$_3$ were carried out at 120°C. For all the polymerizations conducted for polymerization kinetics study, the theoretical molecular weight targeted was 25,000 g/mol. The following procedure is typical: A master batch was prepared by dissolving RAFT-PBu$_3$ (0.8370 g, 1.26 mmol) in styrene (30.68 g, 294.6 mmol). 4 mL aliquots of the master batch were charged to separate flasks each equipped with a magnetic stir bar and sealed with a rubber septum. The flasks were sparged with dry nitrogen for 20 min, placed into a preheated oil bath at 120 °C and finally quenched by placing the flasks in ice water at selected time points to terminate the polymerizations. A drop of the reaction mixture was taken out to determine the monomer conversion by ^{1}H NMR using the following equation,

$$conversion = \frac{(A_{6.3-7.8} - 6A_{5.25})/5}{A_{5.25} + (A_{6.3-7.8} - 6A_{5.25})/5}$$

where $A_{5.25}$ denotes the integral area of peak at 5.25 ppm due to the styrene vinyl peak (one proton, Ph-CH=CHH_{cis}), $(A_{6.3-7.8} - 6A_{5.25})$ as a whole denotes the integral area due to polystyrene between 6.3 to 7.8 ppm (5 protons, ArH). The polymer was isolated by precipitation twice into methanol and dried in a vacuum oven at 50 °C.

To further demonstrate the capability of both RAFT agents to control the polymerization, polymerization targeting either 15,000 g/mol or 40,000 g/mol were also performed with 6 h polymerization for RAFT-PBu$_3$ and 8 h polymerization for RAFT-PPh$_3$.

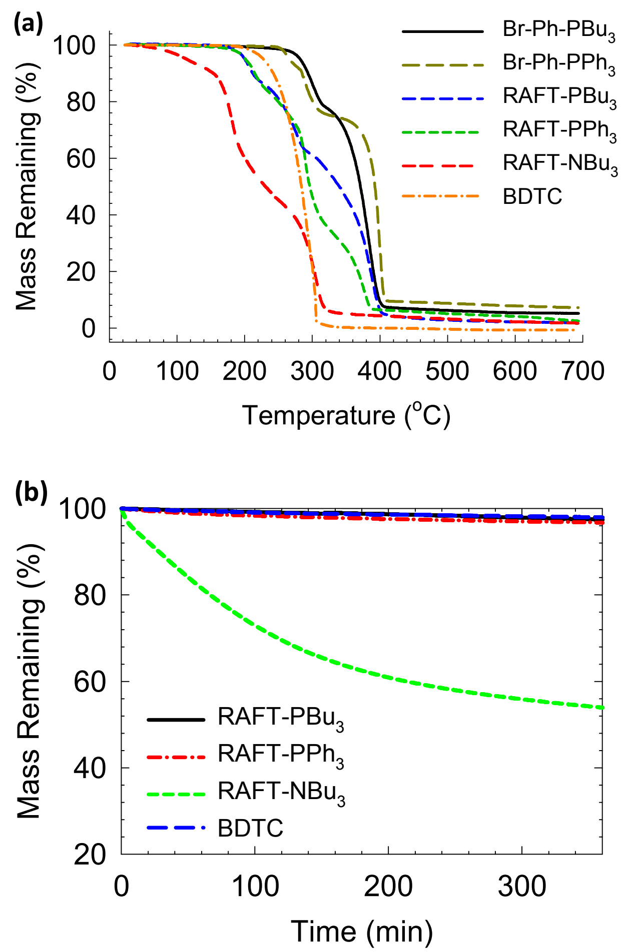

Fig. 2 (a) Temperature-ramp TGA traces (20 °C/min) for Br-Ph-PBu$_3$ (black), Br-Ph-PPh$_3$ (olive), RAFT-PBu$_3$ (blue), RAFT-PPh$_3$ (green), RAFT-NBu$_3$ (red), and BDTC (orange). Data of RAFT-NBu$_3$ and BDTC were adapted from Ref.1 with permission from The Royal Society of Chemistry. (b) Isothermal TGA traces (120 °C) for RAFT-PBu$_3$, (black), RAFT-PPh$_3$ (red) RAFT-NBu$_3$ (green) and BDTC (blue). Both TGA tests were performed in nitrogen atmosphere.

RAFT polymerization of butyl acrylate

Butyl acrylate (BA) monomer was polymerized using either RAFT-PBu$_3$ or RAFT-PPh$_3$. Reactant ratios of [M]/[RAFT]/[AIBN]=100:1:0.1 were applied. Chlorobenzene was used as the solvent and was added with the same volume as that of the BA monomer to make a 50% v/v mixture. For the polymerization of BA using RAFT-PBu$_3$, the typical procedure was conducted as follows. Butyl acrylate (3.2159 g, 25.1 mmol), RAFT-PBu$_3$ (0.1660 g, 0.025 mmol), AIBN (0.0041 g, 0.0025 mmol), and 3.58 mL chlorobenzene were mixed in a 15 mL round-bottom flask with a magnetic stir bar and sealed with a rubber septum. The mixture was sparged with dry nitrogen from 20 min before the flask was placed in a preheated oil bath at 70 °C. After 3 h, the polymerization was terminated by quenching the flask in ice water. The polymerization mixture was precipitated into methanol/water (1/1 v/v) to isolate poly(butyl acrylate). PBA was dissolved in acetone, dried over $MgSO_4$, and the acetone was evaporated by rotary evaporation. The polymer was further dried in vacuum oven at 70 °C. Conversion = 94%, M_n SEC = 17600 Da, Đ = 1.19, M_n NMR = 15200 Da.

The polymerization of BA using RAFT-PPh_3 was performed in an analogous procedure. Conversion= 83%, M_n SEC = 16700 Da, Đ = 1.23, M_n NMR = 13300 Da.

Synthesis of PS-b-PBA via sequential RAFT polymerization

Polystyrenes obtained from bulk styrene polymerization using either RAFT-PBu_3 or RAFT-PPh_3 were used as macro-RAFT agents for chain extension with BA to prepare PS-b-PBA block copolymers (PS-PBA-PR_3, R=Bu or Ph). Reactant ratios of [M]/[RAFT]/[AIBN]=250:1:0.1 were applied. Chlorobenzene was used as the solvent to make monomer concentration 50% v/v.

A macro-RAFT agent, PS-PBu_3 (M_n = 10000 Da, Đ = 1.24), was obtained from bulk styrene polymerization using RAFT-PBu_3 at 120 °C for 6 h, with a target molecular weight of 25,000 Da. To synthesize PS-PBA-PBu_3, BA (0.9636 g, 7.52 mmol), PS-PBu_3 (0.2988 g, 0.03 mmol), AIBN (0.000493g, 0.003 mmol), and chlorobenzene (1.05 mL) were mixed in a 15 mL round-bottom flask equipped with a magnetic stir bar and sealed with a rubber septum. The flask was sparged with dry nitrogen for 20 min and then immersed in an oil bath at 70 °C. After 3 h, the polymerization was terminated by quenching the flask to ice water. Then the polymer was isolated by precipitating the reaction mixture to methanol and dried in a vacuum oven at 70 °C.For PS-PBA-PBu_3, M_n SEC = 59700 Da, Đ = 1.35, M_n NMR = 39300 Da.

To prepare PS-PBA-PPh_3, a macro-RAFT agent, PS-PPh_3 (6000 Da, Đ = 1.33), was obtained from bulk styrene polymerization using RAFT-PPh_3 at 120 °C for 6 h, with a target molecular weight of 25,000 Da. All the other polymerization conditions were the same as PS-PBA-PBu3. For the obtained PS-PBA-PPh_3, M_n SEC = 54500 Da, Đ = 1.33, M_n NMR = 31600 Da.

Results and discussion

Syntheses of the RAFT agents

Two RAFT-PR_3 compounds were synthesized in two steps, as shown in Fig. 1. First, selective quaternization of α, α'-dibromo-*p*-xylene with PBu_3 or PPh_3 was carried out by driving the precipitation of the mono-substituted compounds (Br-Ph-PR_3 in Fig. 1) in ethyl acetate under mild conditions. Compared to their quaternary ammonium analogues,[1] mono-substituted compounds containing phosphonium salts exhibited less lipophicity and precipitated from the reaction solution more readily. It should be noted that following previously reported procedures produced precipitates containing either di-substituted compounds in the case of tributylphosphine or by-products in the case of triphenylphosphine.[34] In the second step, the corresponding trithiocarbonate RAFT agents were prepared in high yield via the reaction of the alkyl trithiocarbonate anion and the benzyl bromide functionality present in the mono-substituted compounds. The ^{1}H NMR and ^{31}P NMR spectra of all the mono-substituted compounds and the corresponding RAFT agents are shown in the supporting information (Fig. S1-Fig. S8).

Table 1 Degradation temperature when weight loss=5%

Sample	$T_{d,5\%}$/°C
Br-Ph-PBu_3	282
Br-Ph-PPh_3	267
RAFT-PBu_3	200
RAFT-PPh_3	201
RAFT-NBu_3	114
BDTC	228

Thermal stability of the synthesized RAFT agents

Following the successful syntheses of the RAFT-PR_3, their thermal stabilities were evaluated via temperature-ramped TGA (Fig. 2a) and isothermal TGA (Fig. 2b). $T_{d,5\%}$, the temperature where weight loss of the sample is 5%, of all the tested samples are summarized in Table 1. The two mono-substituted precursor compounds, i.e. Br-Ph-PBu_3 and Br-Ph-PPh_3, showed relatively high thermal stability. $T_{d,5\%}$ of both were higher than 260 °C. However, their corresponding RAFT agents showed lower thermal stabilities and $T_{d,5\%}$ of both were approximately 200 °C. A nonionic RAFT agent, benzyl dodecyl trithiocarbonate (BDTC), which has the same structure as the other RAFT agents except the cationic end group, was synthesized as a control sample to study the thermal stabilities. BDTC showed a single-step degradation starting from 200 °C and $T_{d,5\%}$ of BDTC is 228 °C, higher than both RAFT-PR_3. Compared to their quaternary ammonium analog (RAFT-NBu_3),[1] RAFT-PBu_3 exhibited enhanced thermal stabilities with a $T_{d,5\%}$ of the RAFT-PBu_3 86 °C higher than that of the RAFT-NBu_3. Therefore, by replacing the quaternary ammonium group with quaternary phosphonium groups significantly improves the thermal stability of the cationic functionality. Both the Br-Ph-PR_3 and RAFT-PR_3 show more complex decay profiles than the BDTC. In addition, the Br-Ph-PR_3 has a higher thermal stability than the RAFT-PR_3. Therefore, the initial decay in the RAFT-PR_3 is likely due to the incorporation of the trithiocarbonate group. However, the decomposition pathway is complex and would need further analysis, such as TGA coupled with GC-MS, to understand fully.

Due to its dynamic nature, temperature-ramp TGA is known to overestimate the thermal stability of the analyzed samples.[35] Therefore, isothermal TGA was employed to better assess the thermal stability of the RAFT agents at a desired temperature. Isothermal TGA of four RAFT agents was performed at 120 °C, as shown in Fig. 2(b). BDTC and both RAFT-PR_3 exhibited less than 5% weight loss while RAFT-NBu_3 showed ~50% weight loss after 6 hours. This result was consistent with the result of temperature-ramp TGA. Since TGA only reflects the change in mass but not in chemical structure, each sample was collected after the isothermal TGA tests and characterized with ^{1}H NMR (Fig. S9 to Fig. S12). The results showed the chemical structures of BDTC and RAFT-PBu_3 were well retained while RAFT-PPh_3 slightly degraded. In contrast, the ^{1}H NMR showed RAFT-NBu_3 severely degraded.

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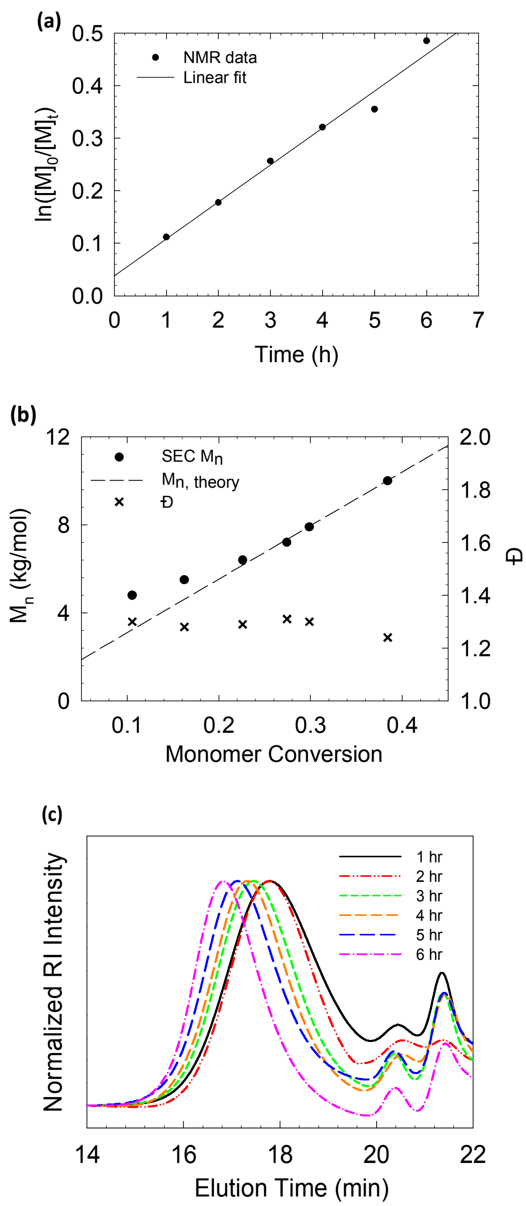

Fig. 3 (a) Pseudo first-order kinetic plot for the bulk styrene polymerization using RAFT-PBu$_3$ at 120 °C. The solid line is a linear fit of the data. (b) Plot of M_n and PDI versus monomer conversion. (c) SEC traces of different polymerization time.

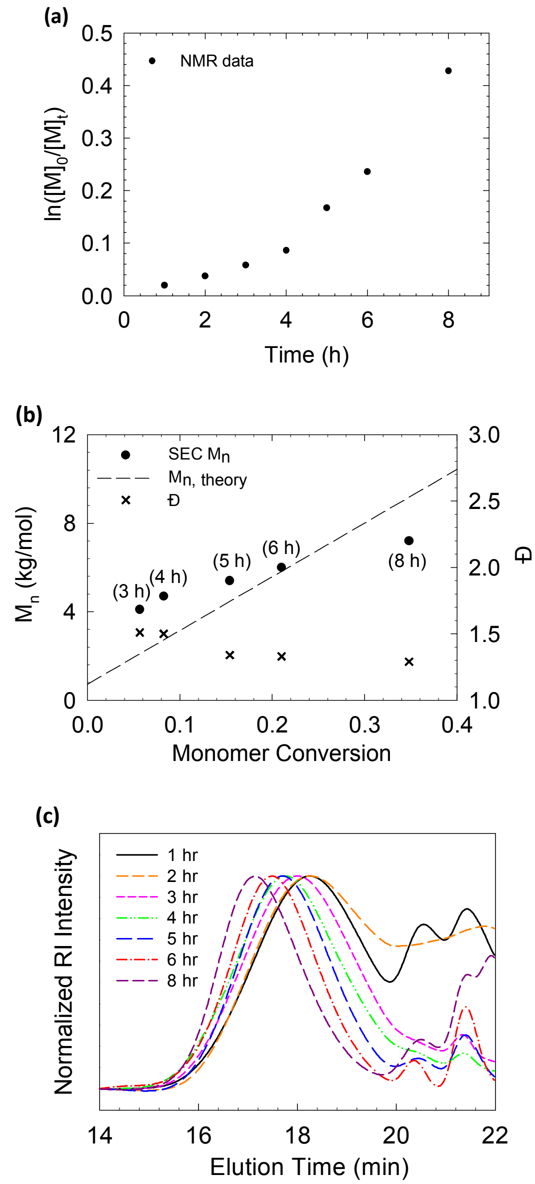

Fig. 4 (a) Pseudo first-order kinetic plot for the bulk styrene polymerization using RAFT-PPh$_3$ at 120 °C. (b) Plot of M_n and PDI versus monomer conversion. The SEC M_n shown in this plot starts from 3 h. (c) SEC traces of different polymerization time.

Bulk styrene polymerizations using RAFT-PR$_3$

Quaternary ammonium groups thermally degraded when quaternary ammonium-containing trithiocarbonate RAFT agents were applied to bulk polymerization of styrene at 120 °C. This thermal stability issue was overcome by performing styrene polymerization at 65 °C, a much lower temperature than 120 °C, with free radical initiator, such as AIBN. However, the bulk polymerization of styrene at higher temperature has advantages compared to solution polymerization including faster polymerization rates; additional solvent, which must be removed after the polymerization, is not required; and additional free radical initiator is not required due to the thermal initiation of styrene at elevated temperature.[1,36,37] In addition, the thermal polymerization at elevated temperature is a good test of the improved thermal stability of both RAFT-PR$_3$ to control the bulk styrene polymerization. Therefore, based on the excellent thermal stability of both RAFT-PR$_3$, their capability to control the bulk styrene polymerization at 120 °C was examined. The plots of pseudo first-order kinetics, evolution of number average molecular weight (M_n) and molar mass dispersity (Đ) with monomer conversion, and SEC traces for the polymerizations using RAFT-PBu$_3$ are shown in Fig. 3 while those for the case using RAFT-PPh$_3$ are shown in Fig. 4. The pseudo first-order kinetic plot in Fig. 3(a) is linear, which is consistent with a constant radical concentration during the polymerization. In Fig. 3(b), M_n increases with increasing monomer conversion. At higher conversion region, M_n is in good agreement with the

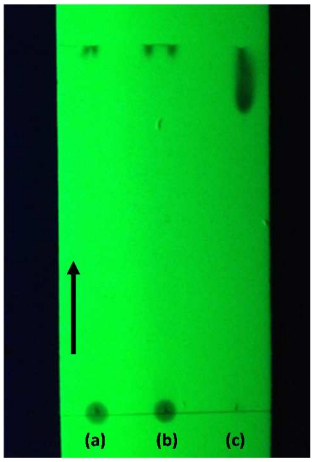

Fig. 5 TLC test of polystyrene obtained from bulk polymerization using (a) RAFT-PBu_3, (b) RAFT-PPh_3, and (c) BDTC at 120 ºC.

theoretical predication while in the lower conversion region, i.e. shorter polymerization time, M_n is slightly higher than theoretical value. This indicates RAFT-PBu_3 has a low chain transfer coefficient and the RAFT agents were not completely consumed when the monomer conversion was low.[27] Since the theoretical curve is calculated based on the full consumption of the RAFT agents, the observed M_n will be higher than the theoretical values if the RAFT agents were not completely consumed. As expected for a reversible deactivation radical polymerization, relatively narrow Đ (Đ<1.3) is observed for all polymerizations. These SEC results were obtained using an older column set that had previously been treated many times with a 2 wt% solution of tri-*n*-octylamine in THF.[38] Using a new set of Styragel columns no elution of the phosphonium terminated polymers was observed. Therefore, the older column set has been conditioned for ionic polymers. An SEC of a 3350 MW polystyrene standard showed a Đ of 1.07 and 1.13 for the new and old columns respectively, so there is a slight broadening of the older columns. In Fig. 3(c), all the SEC curves show single, symmetric peaks and these peaks systematically shift to the lower retention time as the polymerizations proceed. All these observations in Fig. 3 are expected for a reversible deactivation radical polymerization.

For the bulk styrene polymerization mediated by RAFT-PPh_3, however, the polymerization showed inhibition and retardation at the beginning of the polymerization and an increased rate after 4 hours, as shown in Fig. 4(a). It has been discussed that the retardation phenomena in RAFT polymerizations could be due to slow reinitiation by the fragmentation radicals, slow fragmentation of adduct intermediate radicals, the reversible/irreversible cross-terminations, impurities or functional groups that cause retardation or inhibition, and improper degassing.[25, 39 - 45] Considering that RAFT-PBu_3 and previously studied quaternary ammonium RAFT agents[1] have the same structure as RAFT-PPh_3 except the R-group, the retardation in the present case could be plausibly attributed to either unidentified inhibiting impurities generated in the synthesis procedure of the RAFT-PPh_3 or the poor re-initiation of RAFT-PPh_3 R-group in the pre-equilibrium stage. If impurities were not present slow re-initiation by the R-group is consistent with the molecular weight being higher than the theoretical molecular weight in the beginning of the polymerization and the increase in the polymerization rate with conversion. The radical stability can be influenced by both electronic and steric effects.[39,42] In this case steric effects may be more likely due to the distance of the PPh_3 group from the benzyl radical. However, more detailed studies would be required to determine the exact source of the inhibition and retardation for the RAFT-PPh_3 polymerization. In Fig. 4(b), despite the departure from the theoretical prediction, the molecular weights of the polystyrene grow linearly as the monomer conversion increases, which implies the RAFT polymerization is still somewhat controlled. The Đ keeps decreasing as the monomer conversion increases and is lowered to 1.29 when the monomer conversion is 35%. The SEC curves in Fig. 4(c) show single peaks for all the polymerization times. Although the SEC curves of the low molecular weight samples overlap with the solvent peaks after 20 min, the systematic shift of the polymer peak to the lower retention time indicates the build-up of the molecular weights as the polymerization proceeds.

The ability of both RAFT agents to control the bulk styrene polymerizations were further demonstrated by performing polymerization with two other target molecular weights, i.e. 15,000 g/mol or 40,000 g/mol, as summarized in Table S1. Both polymerizations using RAFT-PBu_3 show good control ability to bulk styrene polymerization, affording polystyrene with M_n close to theoretical value and narrow molar mass dispersity. When RAFT-PPh_3 was used, polymerization targeting 40,000 g/mol provides a polystyrene with closer molecular weight to the theoretical value, compared to polymerization targeting 15,000

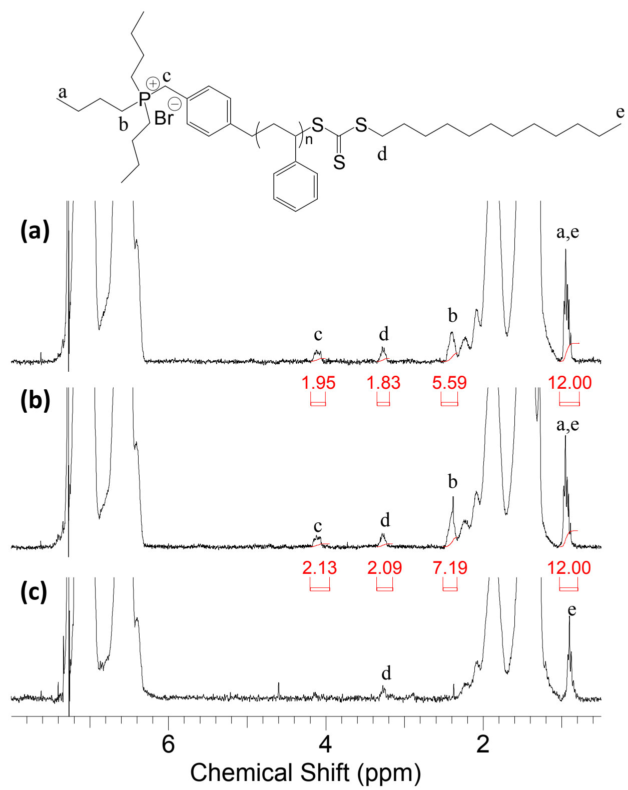

Fig. 6 ¹H NMR spectra of a) crude polystyrene from styrene bulk polymerization using RAFT-PBu_3 at 120 ºC, b) the purified polystyrene ($CHCl_3$/acetone/methanol fraction), c) toluene fraction.

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g/mol or 25,000 g/mol. This implies polymerization is better controlled with less amount of RAFT-PPh_3, which is likely due to the reasons discussed above.

Polystyrene obtained using both RAFT agents, were first characterized via thin layer chromatography (TLC) to qualitatively examine the end-group fidelity. When a nonpolar solvent, e.g. toluene, was used, the ion-containing polymers exhibited much lower R_f value compared to nonionic polymers. As shown in Fig. 5, both polystyrene samples exhibit very high end-functionality, since the fraction of R_f=0 is much larger than that of R_f=1. Here BDTC polymerized PS was used as a control, non-polar polymer. The variation in retention of the unquaternized polymer in the RAFT-PR_3 and BDTC polymers is attributed to the different non-ionic end groups in these systems. This is in contrast to the TLC result of the polystyrene based on quaternary ammonium-containing RAFT agents, for which a large fraction of cationic groups were degraded during the polymerization at 120 °C.1

Both crude polystyrenes prepared with the two phosphonium-containing RAFT agents were further purified via column chromatography by eluting toluene and then $CHCl_3$/acetone/methanol (1:1:0.1). The ^{1}H NMR spectra of the crude polystyrene, purified polystyrene and the toluene fraction from the polymerization using RAFT-PBu_3 are shown in Fig. 6. Compared to the crude polystyrene from styrene bulk polymeirzation using RAFT-PBu_3 (PS-PBu_3), the $CHCl_3$/acetone/methanol fraction shows >99% end-functionality while the toluene fraction lacks the peaks from the benzyl phosphonium groups. The ^{1}H NMR spectra of the polystyrene based on RAFT-PPh_3 is shown in Fig. 7. The crude polystyrene from styrene bulk polymerization using RAFT-PPh_3 (PS-PPh_3)

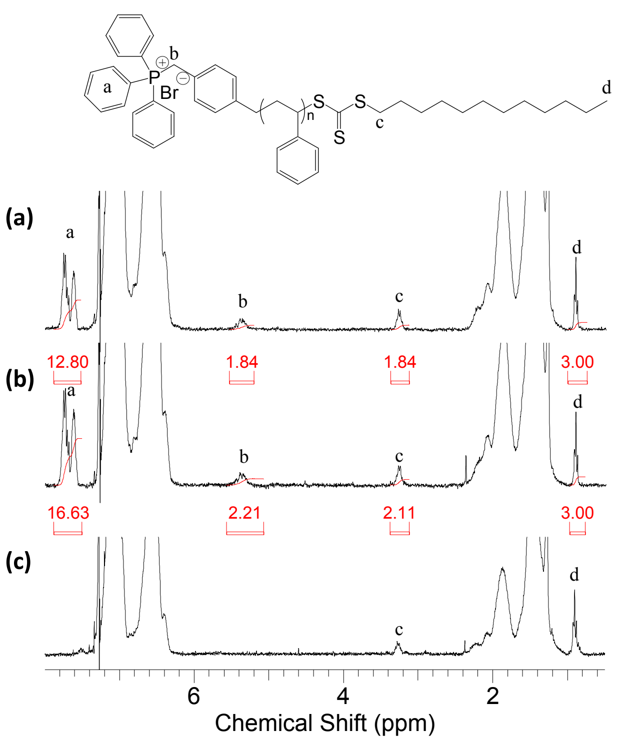

Fig. 7 ^{1}H NMR spectra of a) crude polystyrene from styrene bulk polymerization using RAFT-PPh_3 at 120 °C, b) the purified polystyrene ($CHCl_3$/acetone/methanol fraction), c) toluene fraction.

exhibited high end functionality while column purification further enhanced the end functionality. It should be noted that the chemical shift and the integral area of the methylene of the benzyl group in the crude PS-PPh_3 are both expected for the benzyl phosphonium groups "inherited" from RAFT-PPh_3. This is consistent with the benzyltriphenylphosphonium functional group being retained during the polymerization. Therefore, though the styrene polymerization via RAFT-PPh_3 exhibited retardation, nevertheless, polymers with PDI<1.3 with high end functionality was obtained at higher monomer conversion.

Polystyrenes obtained using both RAFT agents were used as macro-RAFT agents for chain extension with butyl acrylate to synthesize PS-b-PBA block copolymers (PS-PBA-PR_3,R=Bu or Ph). Compared to the macro-RAFT agents, both PS-PBA-PR_3 block copolymers show a clear shift to high molecular weight on the SEC traces, as shown in Fig. S13 and Fig. S14. The molar mass dispersity of both PS-PBA-PR_3 block copolymers is less than 1.35, though PS-PBA-PPh_3 shows a small high-molecular-weight shoulder, which is due to the termination by coupling of the propagating radicals.[39] No low-molecular-weight tail is noticeable for both SEC curves. The efficient chain extension of the macro-RAFT agents to PS-PBA-PR_3 block copolymers demonstrated the high retention of the trithiocarbonate groups in macro-RAFT agents, which can be readily available for block copolymerization.

Butyl acrylate was also polymerized using both RAFT-PR_3 with reactant ratios of [BA]/[RAFT]/[AIBN]=100:1:0.1 at 70 °C for 3 h. Monomer conversion of both polymerization was much higher (94% for RAFT-PBu_3 and 83% for RAFT-PPh_3) compared to the bulk styrene polymerization, which is due to the higher propagation rate of butyl acrylate compared to styrene.[46] The end-functionality of the obtained PBA-PBu_3 and PBA-PPh_3 were estimated by ^{1}H NMR (Fig. S15 and Fig. S16) as 95% and 88%, respectively.

An ion-exchange experiment was performed to visualize the presence of the cationic end groups in both PS-PBu_3 and PS-PPh_3. D&C Green 5 was used as the dye since it contains sulfonate groups that can ion exchange with the bromide groups presented in the obtained end-functional polystyrene. The ion-exchange process is depicted in Fig. 8 and the results of ion-exchange experiments are shown in Fig. 9. Before mixing, the contents of each vial were as follows: Vial #1 with toluene at the top layer and with water and D&C Green 5 at the bottom layer; Vial #2 with toluene and PS-PBu_3 at the top layer and with water at the bottom layer; Vial #3 with toluene and PS-PBu_3 at the top layer and with water and D&C Green 5 at the bottom layer; Vial #4 with toluene and PS-PPh_3 at the top layer and with water at the bottom layer; Vial #5 with toluene and PS-PPh_3 at the top layer and with water and D&C Green 5 at the bottom layer. The vials were vigorously vortexed to facilitate the ion exchange process and then placed in the hood for one day. As shown in Fig. 9, vial #1 shows that D&C Green 5 partitions to aqueous phase while vial #2 and #4 show that both PS-PBu_3 and PS-PPh_3 partitions to toluene phase. However, when the dye was mixed with the polymer solution, ion exchange occurred and the dye was extracted into the toluene phase, as implied by the color change of the toluene layer from yellow, which is a characteristic color of polymers obtained from RAFT polymerization, to blue-green,

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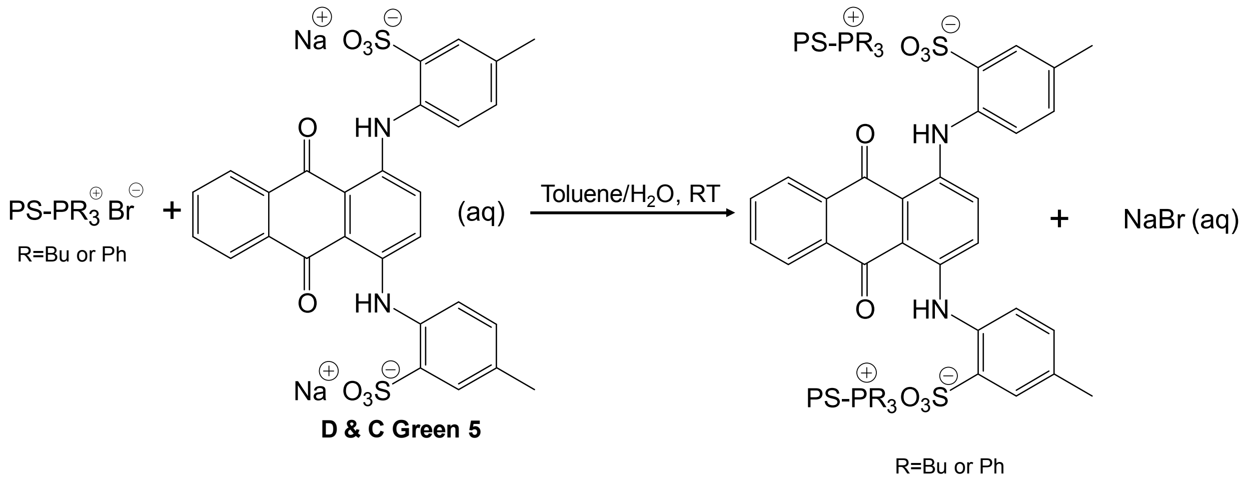

Fig. 8 Schematic representation of the ion exchange process between PS-PR$_3$ and D & C Green 5 to form the phosphonium sulfonate and sodium bromide.

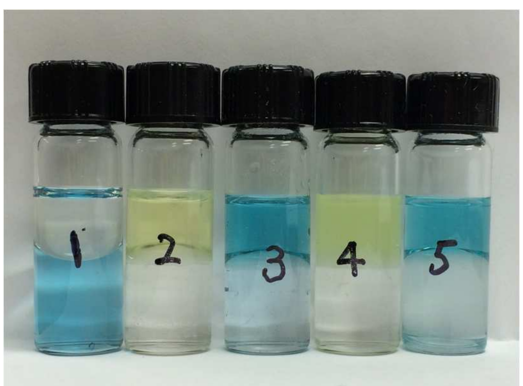

Fig. 9 The ion exchange test that visualizes the cationic functionality. The vials were vortexed to facilitate ion exchange and then placed in the hood for one day. The contents of each vial before mixing were as follows: Vial #1: toluene (top layer) & water+D&C Green 5 (bottom layer); Vial #2: toluene+PS-PBu$_3$ (top layer) & water (bottom layer); Vial #3: toluene+PS-PBu$_3$ (top layer) & water+ D&C Green 5 (bottom layer); Vial #4: toluene+PS-PPh$_3$ (top layer) & water (bottom layer); Vial #5: toluene+PS-PPh$_3$ (top layer) & water+ D&C Green 5 (bottom layer)

which is a characteristic color of the dye. In addition, the color of the aqueous phase of via #3 and #5 was colorless, which also indicated the dye disappeared from the aqueous phase.

Conclusions

Two quaternary phosphonium-containing RAFT agents were synthesized and examined in terms of thermal stability. Their capability to control polymerization, including bulk styrene polymerization, polymerization of butyl acrylate, and block polymerization of styrene and butyl acrylate, was also investigated. It was found that the thermal stability of cationic groups was significantly improved when quaternary phosphonium was employed compared to the ammonium analogues. This allows the use of these cationic RAFT agents at higher temperatures, such as the thermal RAFT polymerization of PS as shown.

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† Electronic Supplementary Information (ESI) available: [This supporting information contains a) ^{1}H NMR, ^{31}P NMR spectra of compounds (Br-Ph-PBu$_3$, Br-Ph-PPh$_3$, RAFT-PBu$_3$, RAFT-PPh$_3$). b) ^{1}H NMR spectra of four RAFT agents (RAFT-PBu$_3$, RAFT-PPh$_3$, RAFT-NBu$_3$, BDTC) before and after isothermal TGA tests.] See DOI: 10.1039/b000000x/

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Quaternary phosphonium-containing RAFT agents were synthesized and used to prepare hemi-telelchelic polystyrene ionomers with high end-group functionality by bulk, thermally-initiated polymerization.