Synthesis of Well-Defined Polystyrene with Primary Amine End Groups through the Use of Phthalimido-Functional RAFT Agents

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ABSTRACT: Phthalimidomethyl trithiocarbonates are used as reversible addition fragmentation chain transfer (RAFT) agents to provide low polydispersity α-(phthalimidomethyl)polystyrene with number-average molecular weight in the range 1000−100000 g mol^{-1}. The activity of the phthalimidomethyl trithiocarbonates in RAFT polymerization of styrene, which appears to be similar to that of analogous benzyl trithiocarbonates, is attributed to the electrophilic character of the phthalimidomethyl group. The trithiocarbonate functionality in the products was quantitatively transformed to inert chain ends either by radical-induced reduction with tributylstannane or by thermal elimination, allowing the phthalimido end groups to be cleanly converted to primary amine end groups by hydrazinolysis. Thermolysis experiments, in which the polymers are cleaved at the trithiocarbonate linkage, also provide information on the mechanism of RAFT polymerization. In the case of the symmetrical bis(phthalimidomethyl) trithiocarbonate the two chains grow stepwise indicating that this RAFT agent has a higher transfer constant than the phthalimidomethyl polystyrene trithiocarbonate and that polystyrene propagating radical is a better homolytic leaving group than the phthalimidomethyl radical.

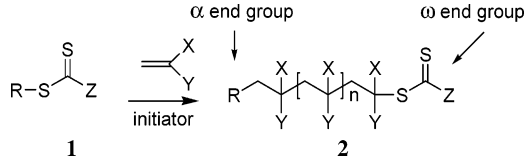
Introduction

The synthesis of polymers with amine chain ends has recently attracted much attention due to their potential uses in such fields as surface science, compatibilization of polymer blends, adhesion, and various biomedical applications.[1] Our interest in these polymers relates to their potential use in the synthesis of block and graft copolymers with well-defined segment lengths by interchain polymer reactions. Polymers with amine chain-ends have greater utility than those with other reactive functionalities (carboxyl, hydroxy, thio), because of their higher reactivity.[2]

Several strategies for synthesizing polymers with amine end groups may be envisaged. Most processes require that the primary amine group is incorporated in some latent form to be converted to the desired functionality in a post-polymerization deprotection step. The amine end group (or its precursor) can be incorporated into chain initiating or chain terminating species through the use of an appropriately designed initiator, transfer agent or chain terminator. Thus, primary amine end-functional polymers have previously been synthesized by conventional radical polymerization (with use of functional initiators,[3,4] transfer agents,[5,6] or dithiuram disulfide iniferters[7]), by atom transfer radical polymerization (ATRP)[8−14] or by anionic polymerization.[15−21]

We[22−25] and others[25] have shown that end-functional polymers can be efficiently synthesized by reversible addition fragmentation chain transfer (RAFT) polymerization. The overall RAFT process is shown in Scheme 1. In using RAFT polymerization to synthesize end-functional polymers, a variety of factors need to be considered. Introducing functionality through the "Z" activating group of the RAFT agent (ω-functionalization) is usually not appropriate as the functionality would be lost with cleavage of the thiocarbonylthio group. The alternative of introducing the functionality as part of the "R" leaving/reinitiating group (α-functionalization) was therefore employed.

Scheme 1. Overall Process for RAFT Polymerization



The RAFT process is compatible with a wide range of functional groups including acid, amide, and tertiary amine groups.[23−25] However, the RAFT process is generally not compatible with unprotected primary or secondary amine groups since the thiocarbonylthio group reacts rapidly by aminolysis to form, in the first instance, a thiol and a dithiocarbamate.[22] It is, therefore, necessary to protect amine end groups during RAFT polymerization and to remove the thiocarbonylthio groups before the deprotection step.

For the present work, a variant on the Gabriel/Ing−Manske procedure[26−28] was adopted. This involved introducing a latent primary amine group as a phthalimidomethyl residue. Related strategies have previously been used to introduce amine functionality during "conventional" radical polymerization. Clouet and Juhl[7] made use of a phthalimido-functional iniferter in the synthesis of an α,ω-primary amino-functional polyisoprene. Meijs et al.[6] prepared phthalimido-functional polystyrene, poly(butyl acrylate), and poly(methyl methacrylate), making use of functional allyl sulfide chain transfer agents. In a recent paper,[29] we reported the synthesis of polystyrene with primary amine end groups using a Gabriel/Ing−Manske strategy that

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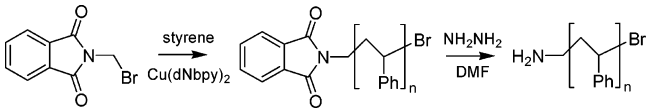
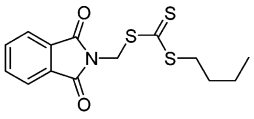
Scheme 2. Amine Functional Polystyrene Synthesis by ATRP



made use of *N*-(bromomethyl)phthalimide as a novel initiator for atom transfer radical polymerization (ATRP) (Scheme 2).

There are reports of RAFT agents with phthalimido functionality as part of the "R" or "Z" groups in the patent literature,[30,31] though not of the RAFT agents described here and not as precursors of amino-functional polymers.

This paper reports the use of phthalimidomethyl trithiocarbonate[32] RAFT agents (**3**−**5**) in the synthesis of primary amino-functional polystyrene.[24] An accompanying paper[33] reports the use of the trithiocarbonate **3** or the analogous phthalimidomethyl xanthate (**6**) in RAFT polymerization of butyl acrylate, *N*-isopropylacrylamide, *N*-vinylpyrrolidone and vinyl acetate.



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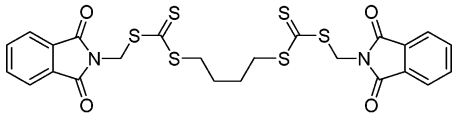

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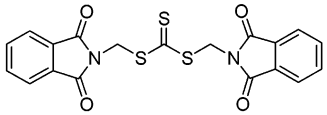

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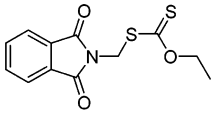

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Experimental Section

General Data. Solvents were of AR grade and were distilled before use. Reagent chemicals [butanethiol (99%), triethylamine (99.5%), carbon disulfide (99.5%), 1,4-butanedithiol (97%), (1-bromoethyl)benzene (97%), tributylstannane (97%), and tris-(trimethylsilyl)silane (97%)] were purchased from Aldrich. *N*-(Bromomethyl)phthalimide (98%) was obtained from Epsilon Chemie. Azobis(isobutyronitrile) (AIBN) was obtained from DuPont and purified by crystallization from chloroform/methanol. Styrene (99%, Aldrich) was purified by filtration through neutral alumina (70−230 mesh), to remove inhibitors, immediately prior to use.

NMR spectra were obtained with a Bruker Advance Bruker AC200 spectrometer (200 MHz for ^{1}H) or, where indicated, a Av400 spectrometer (400 MHz for ^{1}H) on samples dissolved in deuteriochloroform. Chemical shifts are reported in ppm from external tetramethylsilane. Monomer conversions were determined by integrating the signals attributable to the styrene olefinic hydrogens (δ 5.25 and 5.75) in the ^{1}H NMR spectrum of the polymerization mixtures. The number-average molecular weight ($\bar{M}_n^{NMR}$) was evaluated from the ^{1}H NMR spectrum of the isolated polymer by integration of signals attributable to the phthalimido end group (δ 7.6−8.0) relative to those for the polystyrene aromatics (δ 6.3−7.4). High-resolution electron impact (HREI) and high-resolution fast atom bombardment (HRFAB) mass spectra (MS) were obtained with a ThermoQuest MAT95XL mass spectrometer. Electrospray (ESI) spectra were obtained with a Waters (Milford, MA) QTOF2 mass spectrometer equipped with Quadrupole and time-of-flight (TOF) analyzers. The sample solution was introduced by a Harvard syringe pump coupled to an infusion electrospray source. The block and desolvation temperatures were set to 80 and 120 °C respectively; the cone voltage was 35 V; nitrogen was used as the nebulizing and desolvation gas.

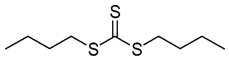
Gel permeation chromatography (GPC) was performed on a Waters 515 HPLC pump and Waters 717 Plus Autosampler equipped with Waters 2414 refractive index detector and 3×Mixed C (7.5 mm×300 mm, 5 μm particle size, linear molecular weight range 200−2000000) and 1 mixed E PLgel column (7.5 mm×300 mm, 3 μm particle size, linear molecular weight range up to 30000) from Polymer Laboratories. Tetrahydrofuran (THF) with a flow rate of 1.0 mL min^{-1} was used as eluent at 22±2 °C. The columns were calibrated with narrow polydispersity polystyrene standards (Polymer Laboratories) ranging from 600 to 7.5 × 10^6 g mol^{-1}. Number ($\bar{M}_n$) and weight-average ($\bar{M}_w$) molecular weights were evaluated using Waters Millennium software. A third-order polynomial was used to fit the log M vs time calibration curve, which appeared to be linear across the molecular weight range 2 × 10^2 to 2 × 10^6. Thin-layer chromatography (TLC) was run on MERCK aluminum sheet, silica gel 60 F_{254} plates with CH_2Cl_2 as the eluent. Small scale thermolysis experiments were carried out with a Mettler Toledo TGA/SDTA521 thermogravimetric balance equipped with a TSO 801RO sample robot. Thermolyses were carried out under a flow (50 mL min^{-1}) of high purity nitrogen.

RAFT Agent Synthesis. Butyl Phthalimidomethyl Trithiocarbonate (3). The compound was synthesized using the general procedure described elsewhere.[34] Butanethiol (3.0 g, 0.033 mol), carbon disulfide (5.06 g, 0.066 mol) and chloroform (20 mL) were placed in a dry three necked round-bottomed flask. Triethylamine (6.9 g, 0.068 mol) was added dropwise with stirring. The solution became yellow/orange as the addition proceeded with formation of the intermediate triethylammonium butyl trithiocarbonate. The solution was stirred at room temperature for a further 3 h. TLC R_f = 0.1. *N*-(Bromomethyl)phthalimide (7.99 g, 0.033 mol) was then added slowly, causing the mixture to thicken with formation of the bromide salt. The reaction mixture was stirred for 16 h and the extent of reaction was confirmed by TLC (R_f = 0.60). The reaction mixture was diluted with an additional chloroform (20 mL) prior to washing sequentially with 2 × 50 mL of each: deionized water, 2 M H_2SO_4(aq), deionized water, and saturated brine. The solution was dried over $MgSO_4$ and filtered, and the solvent was removed by rotary evaporation to give a yellow solid. Yield = 10.39 g (95.9%); mp = 89−91 °C. ^{1}H NMR δ: 0.92 (tr, J = 7.2 Hz, 3H, C**H**$_3$−), 1.41 (m, J = 7.3 Hz 2H, CH_3C**H**$_2CH_2CH_2$−), 1.67 (m, J = 7.4 Hz, 2H, CH_3CH_2C**H**$_2CH_2$−), 3.36 (tr, J = 7.4, 2H, (−C**H**$_2$−S), 5.64 (s, 2H, N−C**H**$_2$−S), 7.74 (m, 2H, Ar**H**), 7.87 (m, 2H, Ar**H**). ^{13}C NMR δ: 13.5 (**C**H$_3$−), 22.0 (CH_3**C**H$_2CH_2CH_2$−), 29.8 (CH_3CH_2**C**H$_2CH_2$−), 36.9 (−**C**H$_2$−S), 41.9 (N−**C**H$_2$−S), 123.7 (2 × *o*-Ph, **C**H), 131.8 (2 × Ph, **C**), 134.4 (2 × *p*-Ph, **C**H), 166.6 (**C**═O), 220.8 (**C**S$_3$). MS (HREI, +VE, +LMR) *m*/*z* 325.0260 (M$^+$) ($C_{14}H_{15}NO_2S_3$ requires 325.0265).

1,4-Bis((phthalimidomethylsulfanylthiocarbonyl)sulfanyl)-butane (4). A similar procedure to that described above was used. 1,4-Butanedithiol (2.45 g, 0.02 mol), carbon disulfide (6.09 g, 0.080 mol) and chloroform (20 mL) were placed in a dry three necked round-bottomed flask. Triethylamine (8.10 g, 0.080 mol) was added dropwise with stirring, the solution became yellow/orange as the addition proceeded with formation of the intermediate triethylammonium salt. An ice bath was used to control the temperature. The mixture was stirred for 1 h. The suspended salt turned to an immiscible oil on warming to room temperature that dissolved on addition of dichloromethane (20 mL). To this solution was then added *N*-(bromomethyl)phthalimide (5.039 g, 0.021 mol) slowly, with the mixture thickening on the formation of the bromide salt. The reaction was complete after 16 h (TLC, R_f = 0.37). Work up as described above for **3** gave 1,4-bis((phthalimidomethylsulfanyl-

thiocarbonyl)sulfanyl)butane (**4**) as a yellow solid (NMR yield 96%) which was recrystallized from ethanol to give 1.94 g (31.2%) of pure **4**; mp = 179−181 °C. Further fractions isolated from the mother liquor were found to contain significant amounts of decomposition products, **7** and **8** (see below). ^{1}H NMR δ: 1.81 (br tr, 4H, −C**H**$_2$−), 3.38 (br tr, 4H, S−C**H**$_2$−), 5.63 (s, 4H, N−C**H**$_2$−S), 7.74 (m, 4H, Ar**H**), 7.86 (m, 4H, Ar**H**). ^{13}C NMR δ: 27.2 (2 × −**C**H$_2$−), 36.3 (2 × S−**C**H$_2$−), 42.0 (2 × N−**C**H$_2$−S), 123.7 (4 × *o*-Ph, **C**H), 131.8 (4 × Ph, **C**), 134.4 (4 × *p*-Ph, **C**H), 166.6 (4 × **C**═O), 220.4 (2 × **C**S$_3$). MS (AP−) *m*/*z* 592.0 (M$^+$); (EI, +VE, +LMR) *m*/*z* 592.0 (M$^+$) (C$_{24}$H$_{20}$N$_2$O$_4$S$_6$ requires 591.9747); (HRFAB, +VE, +LMR) *m*/*z* 593.1 (M + 1), 724.8786 (M + Cs) (C$_{24}$H$_{20}$N$_2$O$_4$S$_6$·Cs requires 724.8802).

Bis(phthalimidylmethyl) Trithiocarbonate (5). The title compound was prepared by applying to the general procedure described by Leung et al.[35] Potassium hydroxide (2.06 g, 0.037 mol), carbon disulfide (6.32 g, 0.083 mol), and water (20 mL) were placed in a dry three necked round-bottomed flask. The phase transfer catalyst, tetrabutylammonium hydrogensulfate (0.17 g, 5.00 × 10^{-4} mol), was added with stirring. A dark red color, attributed to potassium trithiocarbonate, formed at the interface. The reaction mixture was stirred at room temperature for 2 h when *N*-(bromomethyl)-phthalimide (1.20 g, 0.005 mol) was added slowly. The resultant orange solution, was then stirred for 24 h during which time a yellow solid formed. This solid was dissolved in chloroform (30 mL) prior to washing with 3×100 mL of the following: brine, 2 M H_2SO_4(aq), deionized water, and brine. The solution was dried over $MgSO_4$ and filtered, and the solvent was removed by rotary evaporation. The crude product (1.18 g) was dissolved in hot ethanol (20 mL), a white crystalline solid filtered off, and solvent removed to leave a yellow oil that slowly crystallized on standing. TLC R_f = 0.27; yield = 0.461 g (43.0%); mp = 219−220 °C. ^{1}H NMR, δ: 5.65 (s, 4H, N−C**H**$_2$−S), 7.75 (m, 4H, Ar**H**), 7.88 (m, 4H, Ar**H**). ^{13}C NMR δ 42.2 (2 × N−**C**H$_2$−S), 123.8 (4 × *o*-Ph, **C**H), 131.8 (4 × Ph, **C**), 134.5 (4 × *p*-Ph, **C**H), 166.6 (4 × **C**═O), 217.1 (**C**S$_3$). MS (HREI) *m*/*z* 427.9947 (M$^+$) (C$_{19}$H$_{12}$N$_2$O$_4$S$_3$ requires 427.9959).



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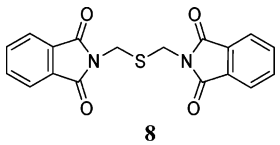
Dibutyl Trithiocarbonate (7). Dibutyl trithiocarbonate (**7**) was isolated as a byproduct from the large scale synthesis of **3** when a partially hydrolyzed (pH 4) sample of *N*-(bromomethyl)phthalimide was used. The mother liquor from the recrystallization of (**3**), was subjected to flash chromatography on silica and the eluent evaporated in vacuo to leave a yellow oil (**7**). TLC R_f = 0.80. ^{1}H NMR δ: 0.93 (tr, J = 7.4 Hz, 2 × 3H, C**H**$_3$−), 1.43 (m, J = 7.5 Hz 2 × 2H, CH$_3$C**H**$_2$CH$_2$CH$_2$−), 1.68 (m, J = 7.5 Hz, 2 × 2H, CH$_3$CH$_2$C**H**$_2$CH$_2$−), 3.36 (tr, J = 7.5, 2 × 2H, −C**H**$_2$−S). ^{13}C NMR δ: 13.6 (2 × **C**H$_3$−), 22.1 (2 × CH$_3$**C**H$_2$CH$_2$CH$_2$−), 30.1 (2 × CH$_3$CH$_2$**C**H$_2$CH$_2$−), 36.5 (2 × −**C**H$_2$−S), 224.8 (**C**S$_3$). MS (HREI, +VE, +LMR) *m*/*z* 222.0565 (M$^+$) (C$_9$H$_{18}$S$_3$ requires 222.0571).



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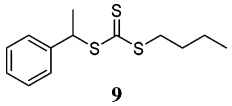
Bis(phthalimidomethyl)sulfane (8). An additional byproduct from the large scale synthesis of **3**, bis(phthalimidomethyl)sulfane (**8**), crystallized from the recrystallization mother liquors on further standing as a white, fluffy crystalline solid. TLC R_f = 0.17, mp 236−237 °C. ^{1}H NMR δ: 5.14 (s, 2H, N−C**H**$_2$−S), 7.75 (m, 2H, Ar**H**), 7.88 (m, 2H, Ar**H**). ^{13}C NMR δ: 40.4 (2 × N−**C**H$_2$−S), 123.6 (4 × *o*-Ph, **C**H), 132.1 (2 × Ph, **C**), 134.2 (2 × *p*-Ph, **C**H), 167.4 (**C**═O). MS (EI, +VE, +LMR) *m*/*z* 352.0512 (M$^+$) (C$_{18}$H$_{12}$N$_2$O$_4$S requires 352.0518).



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Butyl 1-Phenylethyl Trithiocarbonate (9). Triethylamine (67.3 g, 0.665 mol) was added dropwise to a solution of 1-butanethiol (30.0 g, 0.333 mol) and carbon disulfide (50.7 g, 0.666 mol) in 200 mL of chloroform with stirring at room temperature. The solution became orange as addition processed. After addition, the mixture was stirred at room temperature for a further 3 h when TLC showed only one yellow spot (R_f = 0.14). (1-Bromoethyl)-benzene (60.4 g, 0.326 mol) was added dropwise to the solution and the mixture was stirred overnight at room temperature (TLC showed only one yellow spot, R_f = 0.65). Workup as described for **3** gave butyl 1-phenylethyl trithiocarbonate (**9**) as a yellow oil (88.1 g, ∼100%). ^{1}H NMR δ: 1.00 (t, 3H, C**H**$_3$CH$_2$CH$_2$CH$_2$−), 1.50 (m, 2H, CH$_3$C**H**$_2$CH$_2$CH$_2$−), 1.73 (m, 2H, C**H**$_2$−S), 1.81 (d, 3H, C**H**$_3$(CH−)−), 3.41 (t, 2H, −S−C**H**$_2$), 5.41 (q, C**H**), 7.42 (m, 5H, Ar**H**). ^{13}C NMR δ: 13.7 (**C**H$_3$CH$_2$CH$_2$CH$_2$−), 21.4 (**C**H$_3$CH), 22.1 (CH$_3$**C**H$_2$CH$_2$CH$_2$−), 30.1 (CH$_3$CH$_2$**C**H$_2$CH$_2$−), 36.5 (−**C**H$_2$−S), 50.1 (**C**H), 127.7 (*p*-Ph, **C**H), 127.8 (*m*-Ph, **C**H), 128.7 (*o*-Ph, **C**H) 141.2 (Ph, **C**), 223.1 (**C**S$_3$). MS (HREI) *m*/*z* 270.0562 (M$^+$) (C$_{13}$H$_{18}$S$_3$ requires 270.0565).

RAFT Polymerization. Small Scale RAFT Polymerization. The following procedure is typical. RAFT agent **3** (0.0943 g, 2.90×10^{-4} mol) and styrene (9.13 g, 8.76×10^{-2} mol) were combined to form a stock solution of which 6 equal aliquots of ∼1.6 mL were transferred to ampules, degassed with 4 freeze−evacuate−thaw cycles and sealed under vacuum. The ampules were heated at 110 °C for 1, 2, 4, 8, or 16 h when the polymerizations were quenched by placing the ampules in liquid nitrogen. Samples of the monomer/polymer mixture were diluted with THF or $CDCl_3$ for GPC or NMR analysis, respectively. Results of the analysis are provided in Table 1.

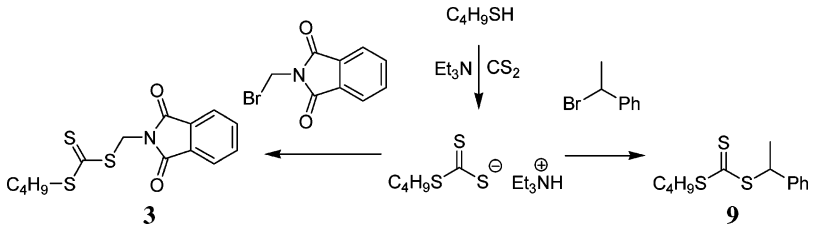
Large Scale RAFT Polymerization. The following procedure is typical. RAFT agent **3** (9.07 g, 2.79 × 10^{-2} mol) and styrene (200 g, 1.92 mol) were transferred to a 500 mL flask, purged with argon for 3 h, degassed with three evacuate-argon admission cycles, and sealed under a slight positive pressure of argon. The mixture was then heated at 110 °C for 24 h when polymerization was quenched by cooling to ambient temperature. The mixture was diluted with THF (∼300 mL) and the polymer was precipitated into methanol (2.5 L), collected by filtration and dried in a vacuum oven at 40 °C for 16 h. Samples of the polymerization mixture and of the precipitate were diluted with THF or $CDCl_3$ for GPC or NMR analysis, respectively. Results of the analyses are provided in Table 4.

End Group Removal. Reduction with Tributylstannane. Polystyrene **20** (51 mg, $\bar{M}_n$ 51100 g mol^{-1}, $\bar{M}_w/\bar{M}_n$ 1.17), tributylstannane (11.7 mg, 4.02×10^{-5} mol) and AIBN (0.3 mg, 1.83×10^{-6} mol), and benzene (1 mL) were placed in an argon flushed ampule. The contents were degassed by three freeze−evacuate−thaw cycles, sealed, and heated in a constant-temperature bath at 70 °C for 3 h. Solution was observed to change from yellow to colorless. The product had $\bar{M}_n$ 30000 g mol^{-1}, $\bar{M}_w/\bar{M}_n$ 1.11 (**21**). The GPC of the product (**21**) and the precursor polystyrene (**20**) are shown in Figure 3a.

Reduction with Tris(trimethylsilyl)silane. Reduction with tris-(trimethylsilyl)silane was performed under conditions similar to those used for reduction with tributylstannane but with polystyrene **20** (51 mg, $\bar{M}_n$ 51100 g mol^{-1}, $\bar{M}_w/\bar{M}_n$ 1.17), tris(trimethylsilyl)-silane (13.3 mg, 5.35×10^{-5} mol), AIBN (1.1 mg, 6.70×10^{-6} mol) and benzene (1 mL). The GPC of the product suggested incomplete trithiocarbonate group removal (Figure 3b).

Reaction with AIBN. A solution of polystyrene **10** (112 mg, $\bar{M}_n$ 1370 g mol^{-1}, $\bar{M}_w/\bar{M}_n$ 1.18), AIBN (1.1 mg, 6.70 × 10^{-6} mol) in toluene (2 mL) was placed in an ampule and degassed through three freeze−thaw evacuated cycles then sealed. The ampule was heated at 80 °C for 2.5 h then cooled to room temperature, opened and the solvent removed by evaporation under

Scheme 3. Procedure for Nonsymmetrical Trithiocarbonate Synthesis



nitrogen. The residue had $\bar{M}_n$ 1556 g mol^{-1}, $\bar{M}_w/\bar{M}_n$ 1.16. The residue was purified by precipitation from chloroform into methanol for ^{1}H NMR analysis (~50% recovery, $\bar{M}_n$ 1828 g mol^{-1}, $\bar{M}_w/\bar{M}_n$ 1.18). The size of the ^{1}H NMR resonance at δ 4.7 (−C**H**(Ph)S-(C═S)SCH$_2$C$_3$H$_7$) was consistent with 5% of chains retaining trithiocarbonate ends.

Isothermal Thermolysis. The following procedure is typical. Pale yellow polystyrene **20** (19.1 mg, $\bar{M}_n$ 51100 g mol^{-1}, $\bar{M}_w/\bar{M}_n$ 1.17) was weighed into an alumina crucible and placed in the sample furnace of the thermogravimetric balance. The sample was heated isothermally under nitrogen at 210 °C for 3 h then cooled to ambient temperature. The colorless residue (polystyrene **24**) was dissolved in chloroform and analyzed directly by ^{1}H NMR spectroscopy and GPC ($\bar{M}_n$ 27100 g mol^{-1}, $\bar{M}_w/\bar{M}_n$ 1.17). The molecular weight distribution for this sample is shown in Figure 5.

Following the same procedure, polystyrene **10** (22.3 mg, $\bar{M}_n$ 1850 g mol^{-1}, $\bar{M}_w/\bar{M}_n$ 1.20) was thermolyzed to produce polystyrene **24** ($\bar{M}_n$ 1740 g/mol, $\bar{M}_w/\bar{M}_n$ 1.18). The ^{1}H NMR spectrum and ESI mass spectrum for this sample are shown in Figure 6 and Figure 7, respectively.

Thermolysis in the Presence of Copper Powder. Polystyrene **10** (10 mg, $\bar{M}_n$ 1850 g mol^{-1}, $\bar{M}_w/\bar{M}_n$ 1.20) and copper powder (9.88 mg, 1.55 × 10^{-4} mol) were intimately mixed and placed in an alumina crucible and inserted in the sample furnace of the thermogravimetric balance. The sample was heated isothermally under nitrogen at 165 °C for 3 h and then cooled to ambient temperature to provide a residue (a mixture containing polystyrenes **24** and **30**) that was dissolved in chloroform and analyzed directly by ^{1}H NMR spectroscopy and GPC ($\bar{M}_n$ 2339 g mol^{-1}, $\bar{M}_w/\bar{M}_n$ 1.36). The ^{1}H NMR spectrum for this sample is shown in Figure 6.

Dynamic Thermolysis. Polystyrene **10** (~5 mg, $\bar{M}_n$ 1850 g mol^{-1}, $\bar{M}_w/\bar{M}_n$ 1.20) was heated from 50 to 600 °C at a rate of 10 °C min^{-1} under nitrogen, and the mass loss observed between 200 and 270 °C corresponded to 7.5% of total mass (9.0% expected for loss of $C_5H_{10}S_3$). The thermogram for this sample has been shown in a preliminary communication.[36]

Large Scale Thermolysis. The following procedure was typical. Polystyrene **10** (130 g, $\bar{M}_n$ 1370 g mol^{-1}, $\bar{M}_w/\bar{M}_n$ 1.18) was placed in the 1 L flask of a Kugelrohr (Aldrich) and heated at 220 °C under vacuum for 3.5 h. The residue (115 g) was dissolved in chloroform (150 mL), precipitated into methanol (1.5 L) collected by filtration and dried. Volatile sulfur compounds (butanethiol, carbon disulfide) are produced during the thermolysis and appropriate precautions should be taken to contain these. The crude product prior to precipitation also possessed a strong odor attributed to contamination with butanethiol (stench). GPC showed $\bar{M}_n$ 1320 g mol^{-1}. Each of the samples listed in Table 4 was thermolyzed to provide the samples listed in Table 5.

Hydrazinolysis. The following procedures are typical.

***N,N*-Dimethylformamide Solvent.** Hydrazine hydrate (1.5 mL) was added to a solution of polystyrene **21** (0.4 g) in *N,N*-dimethylformamide (DMF) (3 mL) and the resultant mixture stirred at room-temperature overnight. Chloroform (20 mL) was added and the solution washed with water (3 × 20 mL) and brine (20 mL) and dried over anhydrous $MgSO_4$. The polystyrene (**22**) was isolated by precipitation into methanol and dried in a vacuum oven for 16 h to give a pale pink polymer with a slight odor. The NMR spectra for this sample are shown in Figure 4.

Tetrahydrofuran/Ethanol Solvent. Ethanol (ca. 1 mL) was added to a two phase mixture comprising a solution of the end-functional polystyrene **24** (0.8 g) in THF (10 mL) and hydrazine monohydrate (0.5 mL) in sufficient quantity to give a homogeneous solution which was then heated under reflux for 16 h. The solution was observed to turn yellow after ca. 2 h due to formation of phthalyl hydrazide. The polystyrene was isolated by precipitation into methanol and dried in a vacuum oven for 16 h to give a colorless polymer **25**. The end group purity was determined by derivatization with trichloroacetyl isocyanate. The results of analysis of a series of polystyrenes are presented in Table 5.

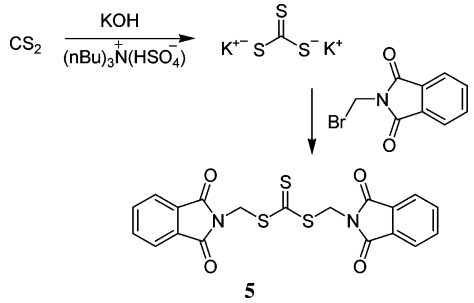
Derivatization with Trichloroacetyl Isocyanate. Details of the analysis procedure have been published elsewhere.[37,38] The following procedure is typical. A sample of polystyrene **25** (~40 mg) was dissolved in $CDCl_3$ (0.5 mL) and the solution transferred to a 5 mm NMR tube. An excess of trichloroacetyl isocyanate (10 μL, 6.3 mg, 33.4 μmol) was then added and the ^{1}H NMR spectrum obtained. Derivatization was complete within the time taken to place the tube in the spectrometer (<10 min). The α-methylene and the amidic and imidic hydrogens of the end group of polystyrene **31** appear in a clear regions of the spectrum as broad "doublets" at δ 3.2, 7.5, and 8.2, respectively.[38] The results of analysis of a series of samples are shown in Table 5.

Results and Discussion

RAFT Agent Synthesis. Previous work showed that trithiocarbonate RAFT agents are readily synthesized in high purity and high yield from a thiol, carbon disulfide, and an alkylating agent in a one-pot synthetic procedure (Scheme 3).[34,39] Yields are generally high (>70%) for substitution of primary and secondary alkyl halides, but can be low for tertiary halides (5−40%) and these are best synthesized by other methods.[24] The trithiocarbonates RAFT agents **3** (>95% yield) and **4** (>95% yield) were synthesized with 1-butanethiol and 1,4-butanedithiol respectively as the thiol and with *N*-(bromomethyl)phthalimide as alkylating agent. The synthesis of **9** (>95% yield) made use of the same procedure with (1-bromoethyl)benzene as the alkylating agent. The phthalimide derivatives were recrystallized from warm ethanol to provide purities of >98%. A large scale synthesis of **3** that made use of unpurified *N*-(bromomethyl)-phthalimide gave a lower yield (~37%) and two main byproducts **7** and **8** were obtained in isolated yield of ~25−30%. The lower yield of **3** is attributed to the commercial *N*-(bromomethyl)phthalimide as received being slightly acidic (pH ~4) due to partial hydrolysis. It is important to purify *N*-(bromomethyl)phthalimide before use in this synthesis both to obtain high yield and because product purification is difficult. Small amounts of both **7** and **8** were also observed to form during the recrystallization of **3** from hot ethanol after a prolonged time in solution.

The synthesis of **3** was also attempted using *N*-(chloromethyl)phthalimide as the alkylating agent. However, more forcing reaction conditions (16 h reflux vs 3 h at room temperature) were required to provide a substantially lower conversion (8.9%) than obtained with *N*-(bromomethyl)phthalimide.

Scheme 4. Procedure for Symmetrical Trithiocarbonate Synthesis



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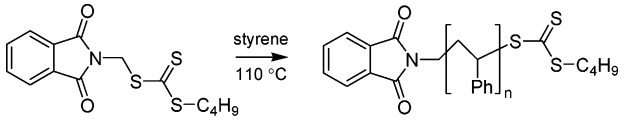
Scheme 5. Overall Process for RAFT Polymerization of Styrene



3 **10**

The symmetrical RAFT agent **5** was obtained by adapting a procedure developed by Leung et al.[35] for the synthesis of dibenzyl trithiocarbonate under phase transfer conditions (Scheme 4). The isolated yield (43%) was low, which is attributed to the hydrolytic sensitivity of *N*-(bromomethyl)phthalimide in the presence of base which is enhanced by the extended reaction time. The low solubility of the alkylating agent and reaction intermediates in the medium may also be an issue.

Primary Phthalimido End-Functional Polystyrene. The overall process for synthesis of α-(phthalimidomethyl)polystyrene using RAFT agent **3** is shown in Scheme 5. Molecular weights, polydispersities and conversions obtained in small scale styrene polymerizations with RAFT agents **3**−**5** are summarized in Tables 1 and 2. Plots showing the evolution of the molecular weight and polydispersity with conversion are provided in Figure 1a−c. Most polymerizations were conducted at 110 °C with thermal initiation. Styrene polymerization with RAFT agent **3** was also successfully conducted at 60 °C with AIBN initiation (Table 2).

RAFT polymerization of styrene in the presence of agents **3** and **4** resulted in good control. Molecular weights were close to those expected and polydispersities were low ($\bar{M}_w/\bar{M}_n < 1.2$ at high conversion, Figure 1a,b). The presence of the initial RAFT agent **3** can be detected by NMR spectroscopy for conversions <20%, the polydispersity reaches a minimum of 1.12 between 60 and 80% conversion. The RAFT agent **5** also gave good control (Figure 1c). However, its use was complicated by its very low solubility in styrene at room temperature. Each of the RAFT agents **3**−**5** was soluble in styrene at the polymerization temperature of 110 °C. Data for butyl 1-phenylethyl trithiocarbonate (**9**) obtained under similar experimental conditions (thermal initiation, 110 °C) is provided for comparison in Figure 1d. Data for dibenzyl trithiocarbonate (**12**) under similar conditions has been published.[40]

The compounds **7** and **8** were present as impurity in some samples of the RAFT agent **3**. Dibutyl trithiocarbonate **7** is not an effective RAFT agent. Polystyrene formed in the presence of **7** was of only slightly lower molecular weight than that of the control and no narrowing of the molecular weight distribution was evident (Table 1). This observation is rationalized in terms of the butyl radical being a poor homolytic leaving group. Thus, if or when radicals add to **7**, the intermediate formed undergoes no reactions other than rapid reversion to starting materials. Sulfides generally show very low transfer constants (e.g., C_{tr} for dibutylsulfide is 0.0022);[41] thus, **8** should also be effectively inert during polymerization. Slightly impure RAFT agent (contaminated with ∼5 mol % **7** and **8**) was successfully used in large scale polymer synthesis without adverse effect (Table 4). Pure (>99% **3**) was used for the experiments described in Table 1.

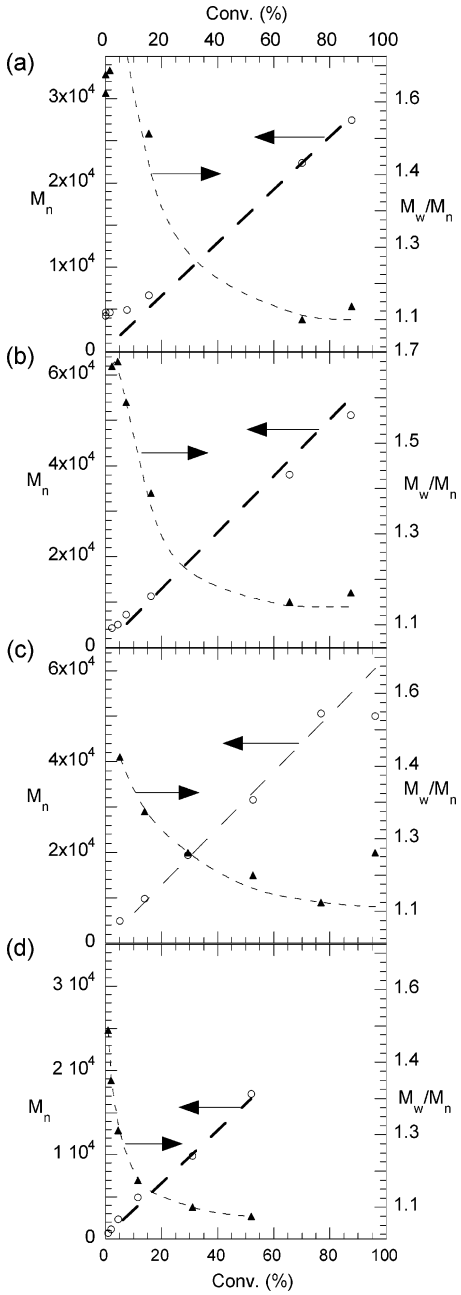


Figure 1. Evolution of number-average molecular weight ($\bar{M}_n$) (○) and polydispersity ($\bar{M}_w/\bar{M}_n$) (▲, - - -) with conversion for bulk thermal styrene polymerization at 110 °C in the presence of (a) trithiocarbonate **3** with $[\text{styrene}]_0/[\mathbf{3}]_0 = 3.03 \times 10^{-2}$, (b) trithiocarbonate **4** with $[\text{styrene}]_0/[\mathbf{4}]_0 = 5.94 \times 10^{-2}$, (c) trithiocarbonate **5** with $[\text{styrene}]_0/[\mathbf{5}]_0 = 5.96 \times 10^{-2}$, and (d) trithiocarbonate **9** with $[\text{styrene}]_0/[\mathbf{9}]_0 = 3.03 \times 10^{-2}$. Dashed line (− −) is calculated molecular weight.

RAFT Agent Activity in Styrene Polymerization. The transfer constants for the initial RAFT agents (**1**) in the polymerization of monomer (M) can be calculated using eq 1 (refer to Scheme 6).

$$\frac{d[\mathbf{9}]}{d[M]} \approx C_{tr}\frac{[\mathbf{1}]}{[M] + C_{tr}[\mathbf{1}] + C_{-tr}[\mathbf{11}]} \quad (1)$$

Table 1. Molecular Weights and Polydispersities of Polystyrene Samples Obtained from Bulk Thermal Polymerization of Styrene in the Presence of Various Concentrations of Reversible Addition−Fragmentation Chain Transfer (RAFT) Agents (3−5, 7 or 9) at 110 °C

RAFT agent	time (h)	$[RAFT]_0$[a] (M)	$[styrene]_0/[RAFT]_0 \times 10^{-2}$	$\bar{M}_n^{Calc}$ [b] (g mol^{-1})	$\bar{M}_n$ [c] (g mol^{-1})	$\bar{M}_w/\bar{M}_n$[c]	convn[d] (%)
control	16	0			279 000	1.92	58
control	24	0			287 000	1.95	77
3	2	0.0290	3.01	2710	4920	1.74	7.7
3	24	0.436	0.200	1670	1460	1.21	65
3	24	0.0873	1.00	7220	6840	1.16	68
3	24[d]	0.0288	3.03	20 700	22 400	1.12	70
3	24	0.0146	6.04	36 900	43 200	1.16	67
4	2	0.0147	5.95	5100	7220	1.59	7.5
4	24	0.436	0.200	1770	1470	1.25	57
4	24	0.0873	1.00	6590	6650	1.14	59
4	24	0.0291	3.00	18 900	19 800	1.12	60
4	24[d]	0.0146	5.94	36 100	38 100	1.15	66
5	16[d]	0.0146	5.96	29 300	31 600	1.20	52
5	32[d]	0.0147	5.92	49 100	50 600	1.14	77
7	24	0.150	0.581	4740	174 000	1.96	76
7	24	0.0150	5.79	45 200	265 000	1.90	89[e]
9	16[d]	0.0288	3.03	15 700	17 200	1.10	52

[a] Concentration at 22 °C based on [styrene] = 8.728 M. [b] The number-average molecular weight ($\bar{M}_n^{Calc}$) was evaluated using eq 9 with $\bar{X}_n^{Calc}$ from eq 8. [c] Number-average molecular weight ($\bar{M}_n$) and polydispersity ($\bar{M}_w/\bar{M}_n$) determined by gel permeation chromatography. [d] Conversion from ^{1}H NMR. Data for other times/conversions are shown in Figure 1. [e] Gravimetric conversion.

Table 2. Molecular Weights and Polydispersities for Polystyrene Samples Obtained from Bulk Polymerization of Styrene in the Presence of Reversible Addition−Fragmentation Chain Transfer (RAFT) Agent (3) with AIBN Initiator at 60 °C for 24 h

$[\mathbf{3}]_0$ (M)	$[styrene]_0/[\mathbf{3}]_0 \times 10^{-2}$	$\bar{M}_n^{Calc}$ [b] (g mol^{-1})	$\bar{M}_n$ [c] (g mol^{-1})	$\bar{M}_w/\bar{M}_n$[c]	convn[d] (%)
0.24	0.0872	4980	4610	1.27	48
0.049	0.436	1740	1850	1.20	84

[a] AIBN concentration = 7.69×10^{-2} M. [b] $\bar{M}_n^{Calc}$ was evaluated using eq 9 with $\bar{X}_n^{Calc}$ from eq 7. [c] Number-average molecular weight ($\bar{M}_n$) and polydispersity ($\bar{M}_w/\bar{M}_n$) determined by gel permeation chromatography. [d] Conversion from ^{1}H NMR spectroscopy.

This equation can, in principle, be solved numerically to provide estimates of C_{tr} and C_{-tr}. If the rate of the reverse reaction between R• and the polymeric RAFT agent (**11**) is negligible (low C_{-tr} and/or low [**11**]) and if chains are long, this expression simplifies to an expression (eq 2) that describes conventional chain transfer and the transfer constant can be evaluated from the slope of a plot of log[**1**] vs log[M].

$$\frac{d[\mathbf{1}]}{d[M]} \approx C_{tr}\frac{[\mathbf{1}]}{[M]} \quad (2)$$

$$C_{tr} \approx \frac{d(\log[\mathbf{1}])}{d(\log[M])} \quad (3)$$

Values of C_{tr} ($=k_{tr}/k_p$) reported in this paper (Table 3) have been estimated using eq 3 and should therefore be considered as apparent transfer constants for the given reaction conditions rather than transfer constants and be taken as minimum values pending further investigation over a wider range of RAFT agent concentrations. The linearity of the double log plots (log[**1**] vs log[M]) or Mayo plots is consistent with the fact, but does not prove, that the reaction between R• and the polymeric RAFT agent (**11**) is negligible. We have found in other work[42] that the reverse transfer constant C_{-tr} ($=k_{-tr}/k_i$) is frequently very large and results in a nonlinear dependence of the apparent C_{tr} evaluated using eq 3 on RAFT agent concentration. Nonetheless, values of apparent C_{tr} obtained with eq 3, *when based on experiments with similar RAFT agent concentrations*, provide a useful measure of the relative effectiveness of RAFT agents.[40,42]

Scheme 6. General Scheme for RAFT Polymerization

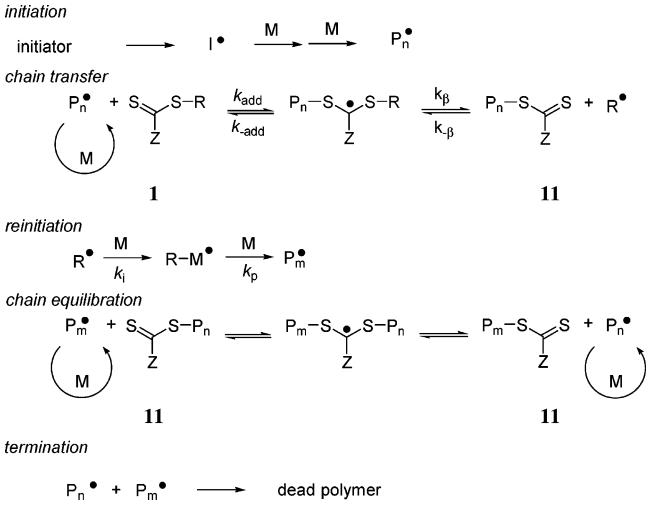


Table 3. Apparent Transfer Constants for Reversible Addition−Fragmentation Chain Transfer (RAFT) Agents in the Thermal Polymerization of Styrene at 110 °C Evaluated with Eq 3

RAFT agent	C_{tr}
3	7.5
4	8.2
5	23
12	18[40]
9	>100

In chain transfer by addition−fragmentation (Scheme 6), the rate coefficient for chain transfer (k_{tr}) is given by the following expression (eq 4).[43]

$$k_{tr} = k_{add} \times \frac{k_\beta}{k_{-add} + k_\beta} \quad (4)$$

Similarly, the rate coefficient reverse reaction (k_{-tr}) is given by eq 5.

$$k_{-tr} = k_{-\beta} \times \frac{k_{add}}{k_{-add} + k_\beta} \quad (5)$$

In this work, the concentration of residual RAFT agent in the reaction mixtures has, where possible, been determined

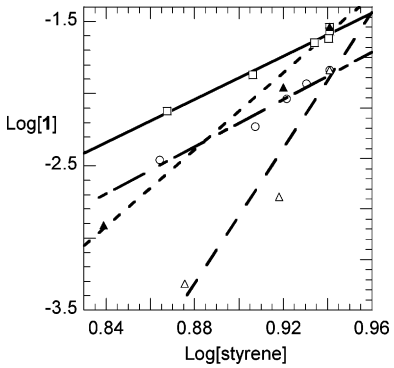
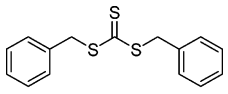


Figure 2. Plot of log[RAFT agent (**1**)] vs log[styrene] for thermal polymerizations of styrene at 110 °C. The residual reversible addition fragmentation chain transfer (RAFT) agent was determined by ^{1}H NMR spectroscopy. Specific RAFT agents were **3** (□), **4** (○), **5** (△), and **12**(▲). Slopes from linear regression analysis provide the apparent transfer constants shown in Table 3.

directly by NMR analysis. The ^{1}H NMR resonance associated with the S−C**H**$_2$−N methylene of phthalimido RAFT agents **3**−**5** appears at δ 5.64 where there is no interference from other signals. The signals due to RAFT agents (**1**) were compared with those due to the residual monomer to give the ratio ([**1**]/[M])$_t$. Thus, since the monomer concentration ([M]$_t$) is known independently from the conversion, the concentration [**1**] can be easily calculated.

Plots of log[**1**] vs log[M] for thermal polymerization of styrene at 110 °C for the RAFT agents **3**−**5** are shown in Figure 2. The apparent transfer constants evaluated from the slopes summarized in Table 3. The values for **3**−**5** are of the same magnitude as that previously determined for dibenzyl trithiocarbonate (**12**) under similar reaction conditions[40] but are significantly lower than that for butyl 1-phenylethyl trithiocarbonate (**9**). For the case of the latter RAFT agent (**9**) residual was not detectable even at the first conversion point. This indicates that the transfer constant of **9** in styrene polymerization under these conditions is >100.



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The RAFT agent **5** has a higher apparent transfer constant than either **3** or **4** (Figure 2, Table 3). Electron-withdrawing Z enhances the transfer constant of RAFT agents.[40,44,45] Thus, **5**, where Z is an electrophilic phthalimidomethyl group, is expected to have a higher transfer constant than **3** or **4**, where Z is a simple alkyl group. The RAFT agent **5** might also be expected to have a higher transfer constant than **13**, with one phthalimidomethyl substituent, or the polymeric RAFT agent **19** with none. This may account for some departure from linearity in the double log plot of [**5**] vs [styrene] (Figure 2). Note that the chemical shift of S−C**H**$_2$−N methylene is the same in RAFT agents **5** and **13**. The apparent transfer constant of **5**, taking only the first two data points is 37.

The trithiocarbonate **9** (with phenylethyl as leaving group) has a much higher transfer constant than any of **3**−**5** or **12**. This follows from the observations (a) that it is fully consumed (undetectable by NMR spectroscopy) at the first time−conversion point and (b) the rapidity with which the molecular weight distribution narrows with monomer conversion (compare Figure 1a−c with Figure 1d). Previous findings[42] for dithiobenzoate RAFT agents indicate that the polystyryl radical should be a significantly better leaving group than phenylethyl radical. The relative rate constants for fragmentation of RAFT intermediates (polystyrene-S−C(•)(Ph)S−R) to R = polystyrene propagating radical, cumyl radical and benzyl radicals were in the ratio ∼29:5:1. The relative rate constant for fragmentation to phenylethyl radical is expected to be between that of cumyl and benzyl radicals.

The polystyrene propagating radical (**17**) should therefore be substantially better homolytic leaving group than either the phthalimidomethyl radical (**16**). Thus, the intermediate **14** formed from the polymeric RAFT agent **13** should preferentially lose **17** and give extension of the existing polystyrene chain rather than lose a phthalimidomethyl radical (**16**) to initiate a new chain and form the di(polystyrene) trithiocarbonate **19**. Direct evidence for this polymer growth mechanism comes from thermolysis experiments (see later discussion). This provides an additional explanation for a slow rate of disappearance of the S−C**H**$_2$−N methylene signal in the NMR spectrum for a departure from linearity in the double log plot of [**5**] vs [styrene] (Figure 2).

The scale-up of styrene polymerization using **3** has been investigated for number-average molecular weights ranging from 1000 to 100000 g mol^{-1} and polymer yields of ∼100−300 g. The results are shown in Table 4. These polymerizations were conducted with the slightly impure RAFT agent **3** referred to above. The impurities, the compounds **7** and **8**, were <10% by ^{1} H NMR spectroscopy) and are expected to be inert and have no significant effect on the outcome of the polymerization (vide infra). Slightly broader molecular weight distribution were observed for the higher molecular weight polymers. This might in part be attributed to the increased scale of the polymerizations which may compromise the control over reaction conditions (degassing, temperature). However, the main cause is likely to be the greater contribution of chains formed by thermal initiation, and hence of chains terminated by radical−radical reaction, to the molecular weight distribution.[46]

If the initial RAFT agent is completely consumed then for the case of polymerization initiated by AIBN or other initiator the calculated degree of polymerization ($\bar{X}_n^{Calc}$) is given by eq 6, which simplifies to eq 7 if initiator-derived chains are neglected.

$$\bar{X}_n^{Calc} = \left(\frac{[\text{styrene}]_0 \times \text{convn}}{[\mathbf{1}]_0 + df([\text{I}]_0 - [\text{I}]_t)}\right) \quad (6)$$

$$\bar{X}_n^{Calc} = \left(\frac{[\text{styrene}]_0 \times \text{convn}}{[\mathbf{1}]_0}\right) \quad (7)$$

where f is the initiator efficiency, d is number of chains produced by radical−radical termination ($d \sim 1.0$ for styrene) and $df([\text{I}]_0 - [\text{I}]_t)$ is the number of initiator-derived chains.[42]

For thermal styrene polymerization we need some other means of estimating the number of chains formed by the thermal initiation process. If we assume that the rate of thermal initiation of styrene (by the Mayo mechanism) is not affected by the presence of the RAFT agent, then we can use eq 8.

$$\bar{X}_n^{Calc} = \left(\left(\frac{[\text{styrene}]_0 \times \text{convn}}{[\mathbf{1}]_0}\right)^{-1} + \frac{1}{\bar{X}_{n0}}\right)^{-1} \quad (8)$$

where $\bar{X}_{n0}$ is the degree of polymerization obtained in the absence of the RAFT agent.

The calculated molecular weight is then

$$\bar{M}_n^{Calc} = \bar{X}_n^{Calc} \times m + r \quad (9)$$

Table 4. Molecular Weights and Polydispersities for Polystyrene Obtained in Large Scale Thermal Polymerizations of Bulk Styrene in the Presence of RAFT Agent (3) at 110 °C for 24 h

$[\mathbf{3}]_o$ (M)	$[\text{styrene}]_0/[\mathbf{3}]_0 \times 10^{-2}$	$\bar{M}_n^{Calc}$ [a] (g mol^{-1})	$\bar{M}_n$ [b] (g mol^{-1})	$\bar{M}_w/\bar{M}_n$ [b]	convn[c] (%)	polymer[d] (g)
0.419	0.208	1220	1370	1.18	49	133.1
0.127	0.689	4810	4770	1.17	66	142.1
0.0289	3.02	13 300	13 600	1.24	44	218.0
0.0145	6.00	36 100	35 200	1.23	66	313.9
0.00288	30.3	122 000	124 000	1.37	68	276.3

[a] $\bar{M}_n^{Calc}$ was evaluated using $\bar{X}_n^{Calc}$ from eq 8. The degree of polymerization obtained in the absence of the RAFT agent ($\bar{X}_{n0}$) is ~280000 g mol^{-1} for thermal polymerization of styrene at 110 °C (Table 1). [b] Number-average molecular weight ($\bar{M}_n$) and polydispersity ($\bar{M}_w/\bar{M}_n$) determined by gel permeation chromatography. [c] Monomer conversion. [d] Mass of isolated polymer.

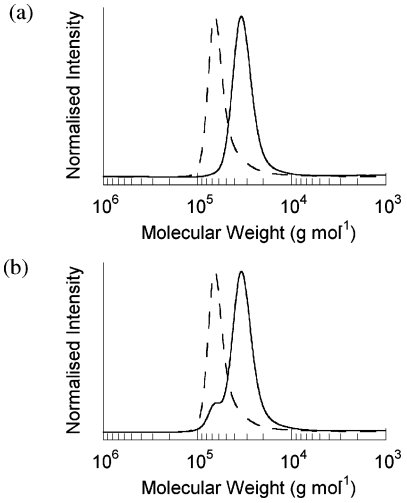


Figure 3. Molecular weight distributions (*y*-axis is normalized signal intensity observed in gel permeation chromatogram) for bis(polystyrene) trithiocarbonate **20** ($\bar{M}_n$ 51100 g mol^{-1}, $\bar{M}_w/\bar{M}_n$ 1.17) (− − −) and the reaction product (—) which arises from the radical-induced reduction with either (a) tributylstannane (**21**, $\bar{M}_n$ 30000 g mol^{-1}, $\bar{M}_w/\bar{M}_n$ 1.11, refer Scheme 8) or (b) tris(trimethylsilyl)silane ($\bar{M}_n$ 31500 g mol^{-1}, $\bar{M}_w/\bar{M}_n$ 1.17).

where *m* is the monomer molecular weight and *r* is the molecular weight of the RAFT agent.

Trithiocarbonate Group Removal from RAFT-Synthesized Polystyrene. A key feature of RAFT polymerization is that the thiocarbonylthio groups, present in the original RAFT agent, are retained in the polymeric product. The retention of these groups is responsible for the polymers' living character. In the present work, we required a primary amino-functional polymer which we choose to introduce in protected form as a phthalimidomethyl group. The transformation of the phthalimidomethyl to aminomethyl by hydrazinolysis would also be expected to transform the thiocarbonylthio groups to thiol or other functionality and would lead to byproducts. Thus, it was important to convert the trithiocarbonate groups in our polymer to inert groups prior to deprotection of the phthalimido functionality.

The chemistry of the thiocarbonylthio group is well-known from small molecule chemistry[47,48] and much of this knowledge has shown applicable to the thiocarbonylthio groups in RAFT-synthesized polymers.[22] Thiocarbonylthio groups undergo reaction with nucleophiles and ionic reducing agents (e.g. amines,[24,39,49−53] hydroxide,[54,55] borohydride[56,57]) to provide thiols. They also react with various oxidizing agents[22,58−60] (including NaOCl, H_2O_2, tBuOOH, peracids) and are sensitive to UV irradiation.[61,62] These reactions may leave reactive functionality and thus were considered unsuitable in the present work.

Radical-induced reactions (reduction,[24,63,64] termination[65]) offer more promise since these processes provide desulfurization

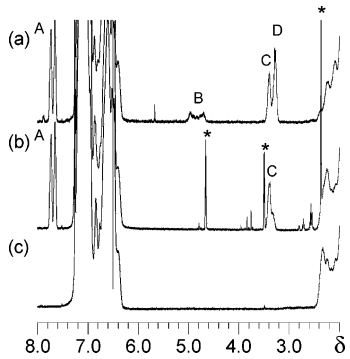


Figure 4. Region δ 2−8 of ^{1}H NMR spectra of (a) polystyrene **10** ($\bar{M}_n$ 1970 g mol^{-1}, $\bar{M}_w/\bar{M}_n$ 1.17), (b) α-(phthalimidomethyl)polystyrene **21** after reduction with tributylstannane, and (c) α-(aminomethyl)-polystyrene **22** formed following hydrazinolysis. Signals are assigned as follows: A, phthalimide Ar−**H**; B, −C**H**(Ph)S(C═S)SCH$_2$C$_3$H$_7$; C, C**H**$_2$−phthalimide; D, −CH(Ph)S(C═S)SC**H**$_2$C$_3$H$_7$. Sharp peaks in spectrum b labeled with an asterisk are due to instrumental artifacts or impurities.

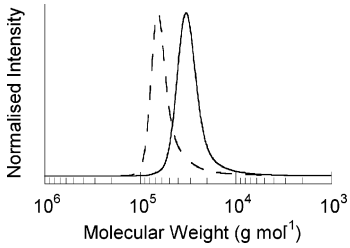


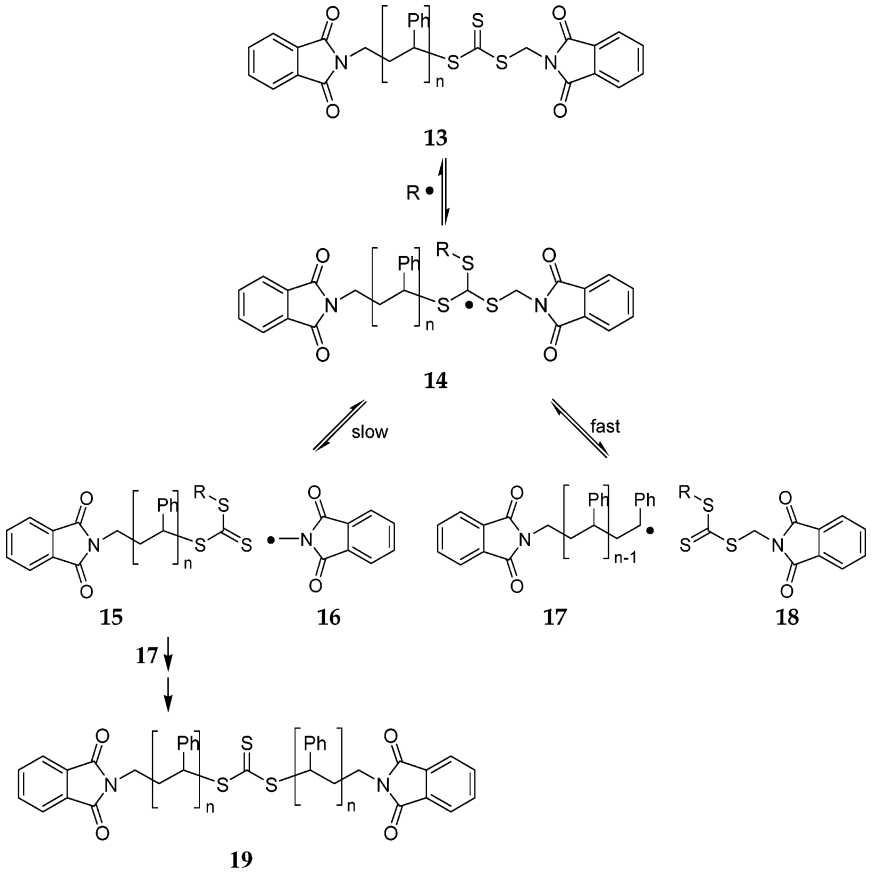
Figure 5. Molecular weight distributions (*y*-axis is normalized signal intensity observed in gel permeation chromatogram) for bis(polystyrene) trithiocarbonate (**20**) ($\bar{M}_n$ 51100 g mol^{-1}, $\bar{M}_w/\bar{M}_n$ 1.17) (− − −) and product **24** ($\bar{M}_n$ 27100, $\bar{M}_w/\bar{M}_n$ 1.17) (refer to Scheme 12) (—) from thermolysis under nitrogen.

by complete end group removal/transfer. In recent communications,[24,36] we reported that thermolysis provides another solution to this dilemma. Here we provide further details of this work.

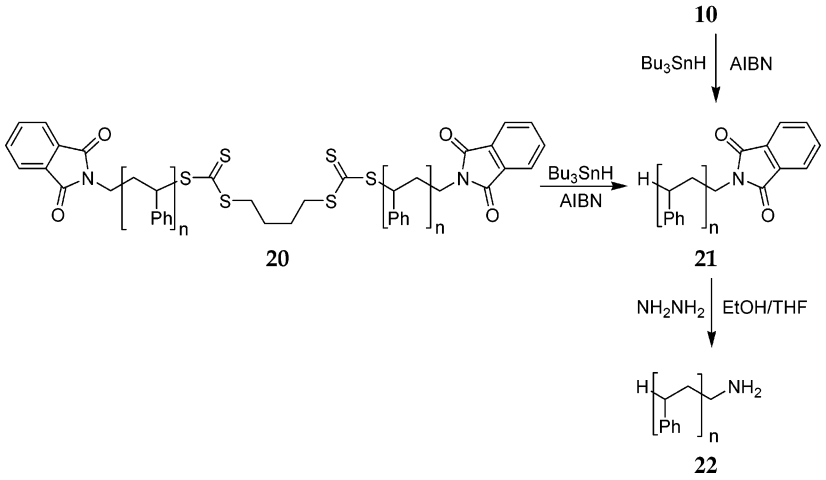
For lower molecular weight polymers, end group transformations can be conveniently followed by ^{1}H NMR spectroscopy. The polystyrene methine hydrogen adjacent to the thiocarbonylthio appears as a broad "doublet" at δ 4.7 in the ^{1}H NMR spectrum of the polystyrenes formed with (**3**−**5**). However, for the case of the polymers formed with the symmetrical trithiocarbonate RAFT agents **4** and **5**, it is also possible to follow the process by GPC since removal of the thiocarbonylthio groups effectively cleaves the polymer in two. Before/after GPC traces for the processes are shown in Figure 3 and Figure 5.

Radical-induced reduction of thiocarbonylthio compounds is well-known.[66] The radical-induced reduction with tributylstannane of dithiobenzoate-terminated poly(acenaphthalene) was recently reported by Chen et al.[63,64] We applied this method to reduce polystyrenes **10** and **20**. In the case of high molecular weight polystyrene **20** ($\bar{M}_n$ 51100 g mol^{-1}, $\bar{M}_w/\bar{M}_n$ 1.17) GPC

Scheme 7. Reaction Pathways for RAFT Intermediate



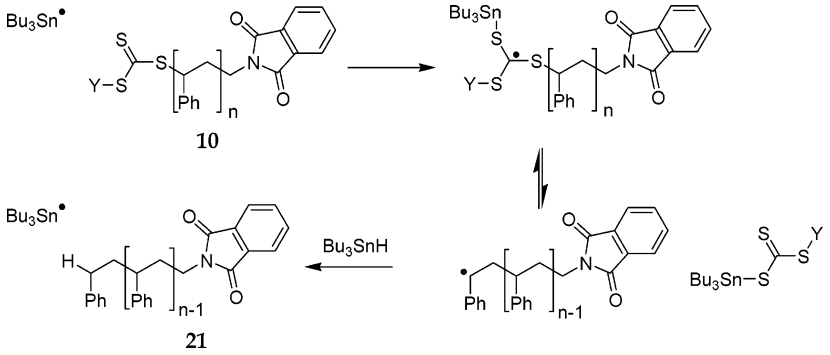
Scheme 8. Synthesis of Primary Amine Functional Polystyrene



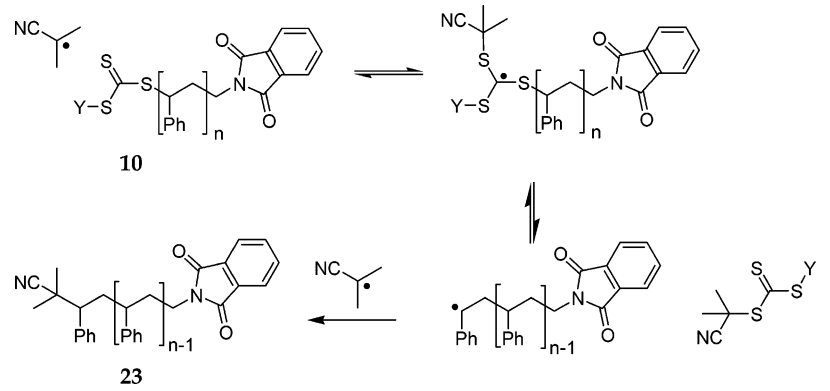
analysis showed that radical-induced reduction with tributylstannane appears to cleanly remove trithiocarbonate groups from the polymer. The product polystyrene **21** ($\bar{M}_n$ 30000 g mol^{-1}, $\bar{M}_w/\bar{M}_n$ 1.11) has a molecular weight half that of the precursor polymer (Figure 3a). This experiment also shows that the two polystyrene chains of **20** are equivalent and therefore that the two trithiocarbonate groups of the bis-RAFT agent **4** have reacted equally during polymerization. It also shows that the stannane is a good radical trap and that no significant radical−radical coupling accompanied reduction. For the case of low molecular weight polystyrene **10** ($\bar{M}_n$ 1970 g mol^{-1}, $\bar{M}_w/\bar{M}_n$ 1.17), the ^{1}H NMR spectrum demonstrates the clean removal of the thiocarbonylthio group and the retention of the phthalimido end group (Figure 4). No significant change in molecular weight occurred and a color change (pale yellow → colorless) for the polymer was observed. The data are thus consistent with tributylstannane reduction polystyrenes **10** and **20** providing an α-(phthalimidomethyl)polystyrene **21** as shown in Scheme 8. The proposed mechanism is shown in Scheme 9. A drawback of the process is that removal of excess tributylstannane and derived byproducts of the reduction is problematic in that traces of stannane-derived byproducts remained after several precipitations.

Various alternatives to tin hydrides have been reported in the literature.[66] Radical-induced reduction of polystyrene **20** ($\bar{M}_n$ 51100 g mol^{-1}, $\bar{M}_w/\bar{M}_n$ 1.17) with tris(trimethylsilyl)silane (TTSS) was also briefly investigated using similar experimental conditions (Figure 3b). TTSS was a less effective reducing agent as evidenced by a high molecular weight shoulder in the GPC trace of the product. This may be due to incomplete reduction

Scheme 9. Idealized Mechanism for Trithiocarbonate Group Removal by Radical-Induced Reduction



Scheme 10. Idealized Mechanism for Trithiocarbonate Group Removal by Reaction with Cyanoisopropyl Radicals



or some termination by radical−radical coupling competing with silane reduction of the intermediate polystyryl radicals. However, the process was not examined further.

Recently Perrier et al.[65] have recommended radical exchange process as a method of end group removal from RAFT-synthesized polymers. In earlier work[46] we demonstrated radical exchange as a method of RAFT agent synthesis. Thus, cyanoisopropyl dithioacetate[40] and dithiobenzoate[42] were synthesized from cumyl dithioacetate and dithiobenzoate respectively by heating with an excess of AIBN (a source of cyanoisopropyl radicals). However, benzyl dithiobenzoate appeared essentially inert under similar conditions.[42] The effectiveness of the method thus depends strongly on the leaving group ability of the "R" group relative to that of the initiator-derived radical. As a method of end group removal, the process appears very effective for poly(methyl methacrylate) (PMMA). The PMMA propagating radical is a very good leaving group, ~100-fold better than the polystyrene propagating radical.[67] For acrylic polymers[33] and polystyrene we have found that a very large excess of AIBN is required and it is difficult to achieve complete end group removal. Polystyrene **10** ($\bar{M}_n$ 1370 g mol^{-1}, $\bar{M}_w/\bar{M}_n$ 1.18) was heated with 20 wt % AIBN in toluene at 80 °C for 2.5 h was shown by ^{1}H NMR analysis to retain 5% of residual trithiocarbonate ends. A slight increase in molecular weight ($\bar{M}_n$ 1556 g mol^{-1}, $\bar{M}_w/\bar{M}_n$ 1.16) may be indicative of some termination by coupling between polystyrene propagating radicals. However, polystyrene **23** arising from coupling between polystyrene propagating radicals and cyanoisopropyl radicals is the major product (Scheme 10). The ratio of rate constant for termination by combination vs disproportionation for the reaction of 1,3-diphenylpropyl radicals (a model for polystyrene propagating radicals) with cyanoisopropyl radicals at 90 °C is reported to be 0.61.[68] Other work demonstrates that the reaction of polystyrene propagating radicals with cyanoisopropyl radicals at 60 °C involves mainly combination with a small yet detectable amount of disproportionation.[69]

Table 5. Molecular Weight and Functionality of α-Phthalimidomethyl, α-Aminomethyl, and TAI-Derivatized α-Aminomethylpolystyrene[38]

$\bar{M}_n^{Calc\ a}$ (g mol^{-1}) (**24**)	$\bar{M}_n^{GPC\ b}$ phthalimido (**24**)	amino (**25**)	TAI (**31**)	$[NH_2]^c$ (μequiv/g)	$f_n^{Calc\ d}$	f_n^e
1220	1320	*f*	1660	5.58	1.00	1.06
4810	4870	900	4990	1.29	0.98	0.97
13 300	14 400	6020	13 800	0.57	0.95	0.99
36 100	37 000	26 800	35 000	0.1_9	0.87	0.9_0
122 000	121 000	108 000	114 000	0.03_7	0.56	0.4_8

[a] Expected molecular weight of polystyrene **24** based on the polymerization conditions and the concentrations of RAFT agent used and applying eq 8 to determine the degree of polymerization $\bar{X}_n^{Calc}$. The experiments correspond to those in Table 4. [b] Molecular weight determined by gel permeation chromatography (GPC). [c] Concentration of amine functionality in microequivalents per gram determined by eq 10, where *m* is the molar mass of the monomer unit.

$$[NH_2] = \frac{\dfrac{1}{\bar{M}_n^{NMR}}}{m} 10^6 \qquad (10)$$

[d] Number of functional groups per chain estimated using eq 11, where $\bar{M}_n^{GPC}$ is the molecular weight of the polymer determined by GPC (phthalimido or TAI), and $\bar{M}_n^{NMR}$ is the apparent molecular weight determined by comparing the integral of the TAI resonance with that for the backbone ArH in the ^{1}H NMR spectrum.

$$f_n^{Calc} = \frac{\bar{M}_n^{GPC}}{\bar{M}_n^{NMR}} \qquad (11)$$

[e] Anticipated functionality after allowing for fraction of chains formed by radical−radical termination. [f] Low molecular weight broad bimodal distribution observed.

Olefin formation by pyrolysis of esters and xanthates (the Chugaev reaction[70]) is well-known[71] and we have previously examined elimination of benzoate end groups from polystyrene by thermolysis.[72,73] Thermolysis has a clear advantage over other methods mentioned above in that no chemical treatment is

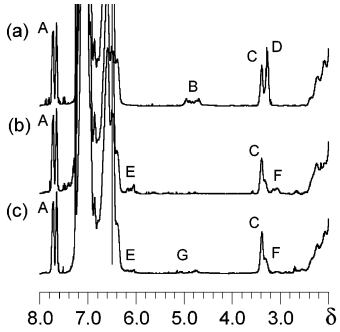


Figure 6. ^{1}H NMR spectrum (400 MHz) of (a) polystyrene **10** with $\bar{M}_n$ 1850 g mol^{-1} ($\bar{M}_n^{NMR}$ 1950 g mol^{-1}), $\bar{M}_w/\bar{M}_n$ 1.20 (b) thermolysis product (**24**) with $\bar{M}_n$ 1740 g mol^{-1} ($\bar{M}_n^{NMR}$ 1860 g mol^{-1}), $\bar{M}_w/\bar{M}_n$ 1.18 and (c) copper mediated thermolysis product (**24** plus **30**) with $\bar{M}_n$ 2339 g mol^{-1} ($\bar{M}_n^{NMR}$ 1990 g mol^{-1}), $\bar{M}_w/\bar{M}_n$ 1.36. Signals are assigned as follows: A, phthalimide Ar−**H**; B, −C**H**(Ph)S(C═S)-$SCH_2C_3H_7$; C, CH_2−phthalimide; D, −CH(Ph)S(C═S)SC$H_2C_3H_7$; E, PhC**H**═C**H**−CH(Ph)−; F, PhCH═CH−C**H**(Ph)−; G, −CHPhCH_2C-(Ph)═CH_2. Thermolyses were performed under a nitrogen atmosphere.

required. The method does, however, require that the polymer and any desired functionality are stable to the thermolysis conditions.

Our first experiments in this area have been published in communication form.[24,36] These initial investigations presented details on the thermolysis of polystyrene synthesized with RAFT agents **3** or **4**. Small scale thermolysis was carried out using a thermogravimetric balance. On heating the polystyrene **10** ($\bar{M}_n$ 1850 g/mol $\bar{M}_w/\bar{M}_n$ 1.20) from 50 to 600 °C at 10 ° min^{-1} under nitrogen a mass loss step was observed between 200 and 270 °C that corresponds to 7.5% of total mass (vs 9.0% expected for $C_5H_{10}S_3$). Isothermal thermolysis at temperatures in the range 210−250 °C cleanly eliminates the butyl trithiocarbonate group from the yellow polystyrene to provide a colorless product.

The thermolysis product was analyzed by GPC and by ^{1}H NMR and mass spectroscopy. The polystyrene **10** had $\bar{M}_n$ 1850 g/mol $\bar{M}_w/\bar{M}_n$ 1.20 ($\bar{M}_n^{NMR}$ 1950 g/mol) and thermolysis product **24** had $\bar{M}_n$ 1740 g/mol $\bar{M}_w/\bar{M}_n$ 1.18 ($\bar{M}_n^{NMR}$ 1860 g/mol). The ^{1}H NMR spectrum of the low molecular weight polymer (Figure 6b) is consistent with the polymer possessing predominantly 1,3-diphenylpropenyl end groups [PhCH═CH−CH(Ph)-] at the ω-chain end indicating that the trithiocarbonate group has been eliminated to give polystyrene **24**. The electrospray ionization (ESI) mass spectrum[74] (Figure 7) supports this finding. The interpeak distance corresponds to the mass of the styrene repeat unit. The major peak positions correspond to 160.04 (phthalimidomethyl) + $n \times$ 104.06 (styrene) + 103.05 (phenylethenyl) + 23.99 (Na^+). We propose that the dominant process is a concerted elimination mechanism (Scheme 12) analogous to that involved in the pyrolysis of esters and xanthates. The eliminated trithiocarbonic acid is expected to readily lose carbon sulfide to form the corresponding thiol. Thus, thermolysis of polystyrene **19** should produce a mixture of polystyrenes **24**, with an unsaturated end group **26** with a thiol end group. However, the NMR spectrum of the thermolysis product does not provide any evidence for the formation of **26** and shows that polystyrene **24** is the main product. It is possible that polystyrene **26** is formed but eliminates hydrogen sulfide under the thermolysis conditions to form **24**.

Closer analysis of the ^{1}H NMR spectrum shows a small amount (∼10%) of macromonomer end groups [−CH(Ph)-CH_2C(Ph)═CH_2] of polystyrene **30**. Addition of copper powder caused loss of the trithiocarbonate at a lower temperature (onset temperature lowered to 165 °C) and the thermolysis mechanism was modified such that the macromonomer **30** (^{1}H NMR signals

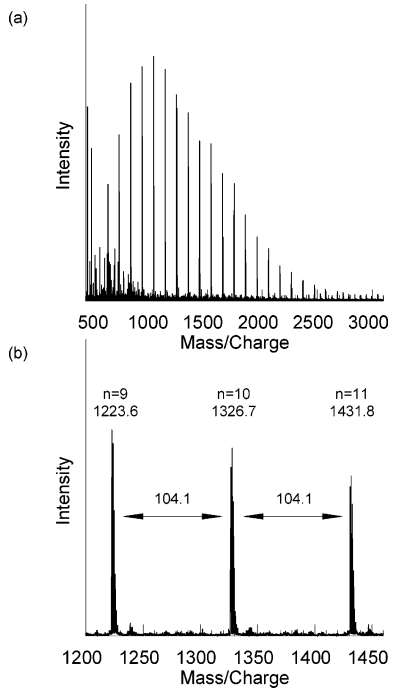


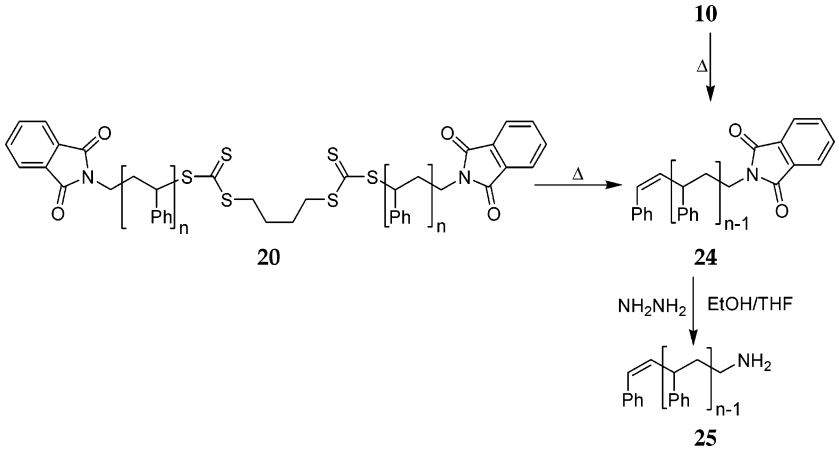
Figure 7. Electrospray ionization (ESI) mass spectrum of polystyrene **24** ($\bar{M}_n$ (GPC) 1740 g/mol, $\bar{M}_w/\bar{M}_n$ 1.18) and (b) an expanded region of the spectrum obtained by thermolysis of polystyrene **10** ($\bar{M}_n$ 1850 g mol^{-1}, $\bar{M}_w/\bar{M}_n$ 1.20) at 240 °C under nitrogen. The major peaks are labeled with their measured molecular weights and the number of styrene repeat units (n).

at δ 4.8 and 5.1) was the major product (Figure 6c). The products were identified by comparison with authentic samples prepared by homopolymerization of styrene or copolymerization styrene with α-methylstyrene respectively with catalytic chain transfer.[75,76] It is proposed that the copper-catalyzed process involves homolysis of the C−S bond to the trithiocarbonate group to give a polystyrene propagating radical (**27**) which can then decay by backbiting (to give **28**) followed by scission (to give **30**) as shown in Scheme 13. It can be noted that thermolysis of an analogous poly(butyl acrylate) (without copper) provides predominantly polymer with macromonomer chain ends [-CH(CO_2Bu)CH_2C(CO_2Bu)═CH_2] by a similar mechanism.[33,36] The presence of some coupled product and oligomers (derived from **29**) in the GPC trace is also consistent with this mechanism.

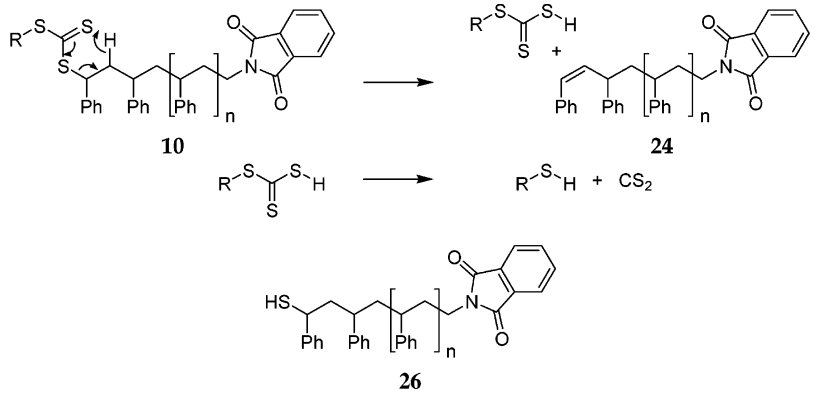
The thermolysis experiments also provide information on the mechanism of RAFT polymerization. For the case of polystyrene **20** prepared with RAFT agent **4**, GPC analysis clearly shows that thermolysis cleanly cleaves the polymer in half (Figure 5). A decrease in molecular weight of ∼50% is seen for high conversion samples. This indicates that the two polystyrene chains of **20** are equivalent and therefore that the two trithiocarbonate groups of the bis-RAFT agent **4** are equivalent during polymerization. Comparisons of peak and weight-average molecular weight of polystyrene synthesized with RAFT agent **20** before and after thermolysis are shown in Figure 8. In the early stages of the polymerization, the ratio of the initial chain lengths and final chain lengths after thermolysis ($\bar{M}_p^i/\bar{M}_p^f$) is close to 1 for very low conversion (%) but rapidly increases to approach 2 at ∼60% conversion. $\bar{M}_p$ and $\bar{M}_w$ were used in this analysis because $\bar{M}_n$ is not reliable for very low molecular weight samples where it is difficult to resolve the polystyrene from solvent peaks in the GPC.

In contrast, samples of polystyrene prepared with low monomer conversion (below 20%) or short reaction time with

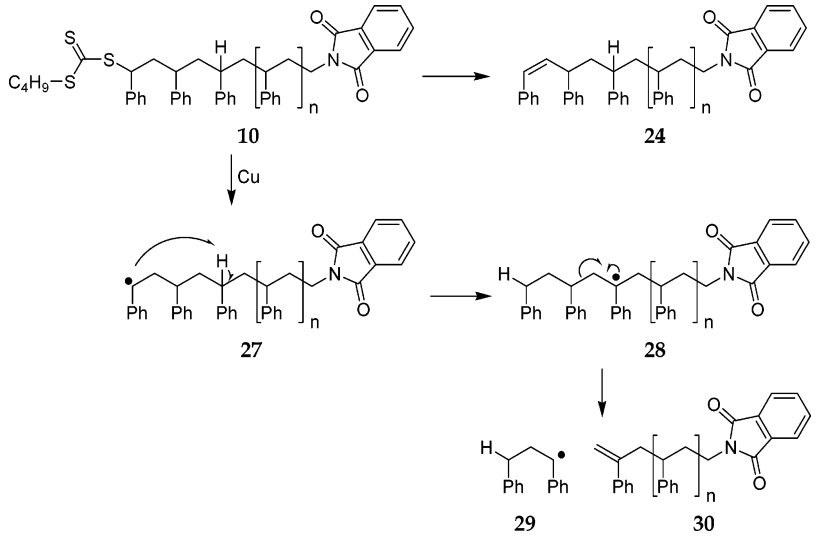
Scheme 11. Synthesis of Primary Amine Functional Polystyrene



Scheme 12. Concerted Mechanism for Trithiocarbonate Group Elimination



Scheme 13. Mechanism for Trithiocarbonate Group Elimination in the Presence of Copper



RAFT agent **5** showed little change in molecular weight or molecular weight distribution on thermolysis. Only those samples prepared with higher monomer conversions (above 20%) or longer time showed a significant reduction in molecular weight on thermolysis (Figure 9). This suggests that, at low monomer conversions, the product is mainly **13** and that **19** becomes the dominant product only after more than 20% of the monomer has been converted (Scheme 7)**.** This is rationalized as a consequence of the polystyrene propagating radical being a substantially better homolytic leaving group than the phthalimidomethyl radical in the case of the intermediate polymer RAFT agent **13** (vide infra).

Larger scale thermolysis of polystyrene **10** was carried out in a Kugelrohr at 220 °C (samples mentioned in Table 5). ^{1}H NMR analysis showed that elimination of the trithiocarbonate groups was complete within 3.5 h. The crude product in each case was odorous due to contamination with butanethiol which was removed by precipitation of the polymer. These samples were used for the synthesis of primary amine end-functional polystyrene.

The byproducts of thermolysis of **10** are butanethiol, butyl trithiocarbonic acid (that dissociates to butanethiol and carbon disulfide) and small amounts of dibutyl trithiocarbonate (**7**), which is believed to arise by a thiol exchange reaction between

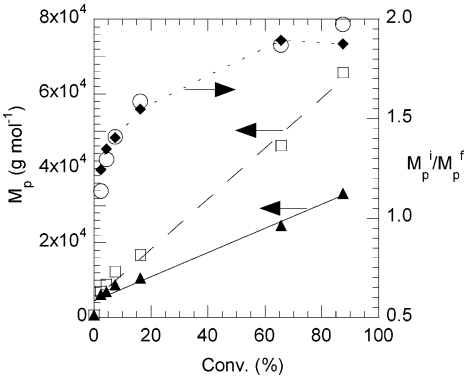


Figure 8. Comparison of peak molecular weight of polystyrene **20** synthesized with RAFT agent **4** before (M_p^i, □, − − −) and after (M_p^f, ▲, —) thermolysis under nitrogen and ratio of peak molecular weights (M_p^i/M_p^f, ◆, - - -) or weight-average molecular weights ($\bar{M}_w^i/\bar{M}_w^f$, ○).

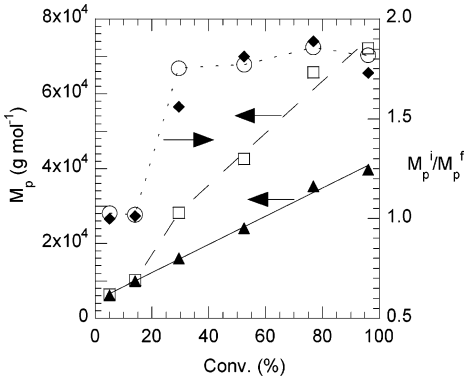


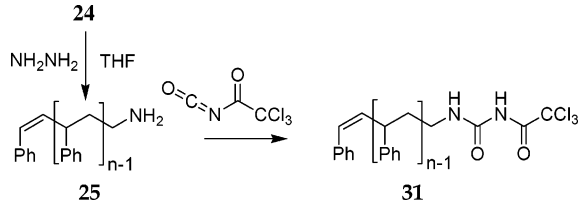
Figure 9. Comparison of peak molecular weight of polystyrene synthesized with RAFT agent **5** before (M_p^i, □, − − −) and after (M_p^f, ▲, —) thermolysis and ratio of peak molecular weights (M_p^i/M_p^f, ◆, - - -) or weight-average molecular weights ($\bar{M}_w^i/\bar{M}_w^f$, ○).

butanethiol with **10**. All are removed by precipitation of the polymer.

Primary Amine End-Functional Polystyrene. Hydrazinolysis of the phthalimido group of α-phthalimidopolystyrene **21** or **24** afforded polystyrene with the desired α-monoamino functionality (Scheme 8 and Scheme 11 respectively). The deprotection step was realized by treating the α-phthalimidopolystyrene with hydrazine either in DMF at 80 °C for 12 h or THF/ethanol under reflux for 2 h. We have previously used DMF as solvent in hydrazinolysis of analogous polymers prepared by ATRP.[29] The use of DMF as solvent has the advantage that both hydrazine monohydrate and polystyrene are soluble. However, isolation of the polystyrene postreaction free of residual solvent is difficult. This problem is overcome by using THF/ethanol as solvent. The amount of ethanol should be chosen to dissolve the hydrazine monohydrate yet maintain the polystyrene in solution.

Quantitative conversion to the primary amine group was confirmed by derivatization with trichloroacetyl isocyanate (TAI) and ^{1}H NMR spectroscopy.[37,38] TAI reacts rapidly with amine (and other protic end groups) to provide a derivative **31** as shown in (Scheme 14). The ^{1}H NMR chemical shifts of the α-methylene, amidic and imidic hydrogens of the end group are diagnostic and appear as broad "doublets" at δ 3.2, 7.5 and 8.2, respectively. TAI derivatization also aids with GPC analysis of the low molecular weight amine functional polymers which were found to give severe line broadening and an apparent shift to lower molecular weight when analyzed under standard conditions for polystyrene analysis (THF solvent). Details of the characterization of the polymers shown in Table 5 has been

Scheme 14. Derivatization with Trichloroacetyl Isocyanate



published elsewhere.[38] The level of functionality achieved (f_n) is in excellent agreement with that expected (f_n^{Calc}) and indicating that the conversion of the phthalimido group to the primary amine group is quantitative.

Conclusion

In this paper we have shown that trithiocarbonates with "R" = phthalimidomethyl are effective RAFT agents for the control of styrene polymerization. The activity of the phthalimidomethyl trithiocarbonates in RAFT polymerization of styrene appears similar to those of analogous benzyl trithiocarbonates. With removal of the trithiocarbonate group, the phthalimidomethyl groups can be efficiently converted to primary amines. Thus, RAFT polymerization provides an effective route to narrow polydispersity α-aminomethyl polystyrenes. Several processes for removal of a trithiocarbonate chain end from RAFT-synthesized polystyrene have been compared. Most effective are radical-induced reduction with tributylstannane and thermolysis at 200 °C.

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