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Thiocarbonylthio End Group Removal from RAFT-Synthesized Polymers by Radical-Induced Reduction

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ABSTRACT: The removal of thiocarbonylthio groups from polymers synthesized by radical polymerization with reversible addition−fragmentation chain transfer (RAFT) by radical-induced reduction has been studied. The efficiency of reduction is strongly dependent on the H-donor and the polymer. The effectiveness of the H atom donors studied increases in the series toluene $\ll$ 2-propanol $<$ triethylsilane $<$ triphenylsilane $\ll$ tris(trimethylsilyl)-silane $\sim$ *N*-ethylpiperidine hypophosphite $<$ tributylstannane. The end groups of the (meth)acrylic polymers, e.g., poly(butyl acrylate) and poly(methyl methacrylate), are more readily reduced than those of polystyrene. With poor H-donors such as toluene or 2-propanol radical−radical reaction between propagating radicals competes with reduction even when they are used in vast excess as a solvent for the process. Thiocarbonylthio groups of polymers prepared with dithiobenzoate or trithiocarbonate RAFT agents can be replaced by hydrogen by radical-induced reduction with hypophosphite salts, in particular, *N*-ethylpiperidine hypophosphite. Their use overcomes issues of reagent toxicity and ease of workup associated with the use of stannane and silane H-donors.

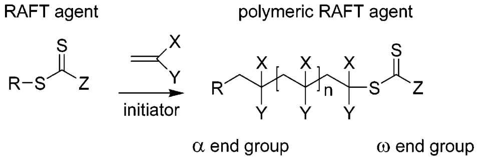
Introduction

Control of radical polymerization with the addition of thiocarbonylthio compounds that serve as reversible addition fragmentation chain transfer (RAFT) agents was first reported in 1998.[1,2] Since that time much research carried out in these laboratories and elsewhere[3−6] has demonstrated that polymerization with reversible addition−fragmentation chain transfer (RAFT) is an extremely versatile process that satisfies most of the established criteria for a living polymerization.[7] It can be applied to form narrow polydispersity polymers or copolymers from most monomers amenable to radical polymerization. With appropriate choice of reaction conditions it is possible to take RAFT polymerizations to high conversion and achieve commercially acceptable polymerization rates. Polymerizations can be successfully carried out in heterogeneous media (emulsion, miniemulsion, suspension). There is compatibility with a wide range of functionality in monomers, solvents and initiators. Stars, blocks, microgel, and hyperbranched structures, supramolecular assemblies and other complex architectures are accessible and can have high purity.

The overall RAFT process involves insertion of monomer units into the C−S bond of a suitable thiocarbonylthio compound (the RAFT agent) as shown in Scheme 1.

A key feature of the process is that the thiocarbonylthio groups, present in the initial RAFT agent, are retained in the polymeric product(s). This means that the polymeric products are themselves RAFT agents and are a dormant form of the propagating radical. The feature is responsible for the polymerization's living character and makes the process eminently suitable for synthesizing block copolymers and end functional polymers.

Scheme 1



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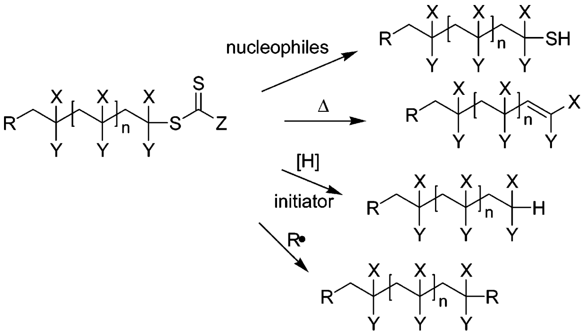
Scheme 2. Processes for End Group Removal ([H] = H Atom Donor)



However, the presence of the thiocarbonylthio groups in the polymer also means that the polymers may be colored. This color may range from violet through red to pale yellow depending on the absorption spectrum of the particular thiocarbonylthio chromophore. The polymers may also, in some cases, release an odor over time due to decomposition of the thiocarbonylthio groups and the evolution of volatile sulfur-containing compounds. The presence of such color and odor can be disadvantageous in some applications. Even though these issues may be largely mitigated or overcome by more appropriate selection of the initial RAFT agent, there has nonetheless been some incentive to develop effective methods for treatment of RAFT-made polymer to remove the thiocarbonylthio end groups post polymerization. In some circumstances, it is also necessary or desirable to deactivate thiocarbonylthio groups because of their reactivity or to transform them for use in subsequent processing.

The chemistry of the thiocarbonylthio group is well-known from small molecule chemistry[8−11] and much of this knowledge has been shown applicable to transforming the thiocarbonylthio groups present in RAFT-synthesized polymers.[1] Some of the methods used for end group removal/transformation are summarized in Scheme 2. Thiocarbonylthio groups undergo reaction with nucleophiles and ionic reducing agents (e.g., amines,[12−23] hydroxide,[22,24,25] borohydride[22,26−28]) to provide thiols. They also

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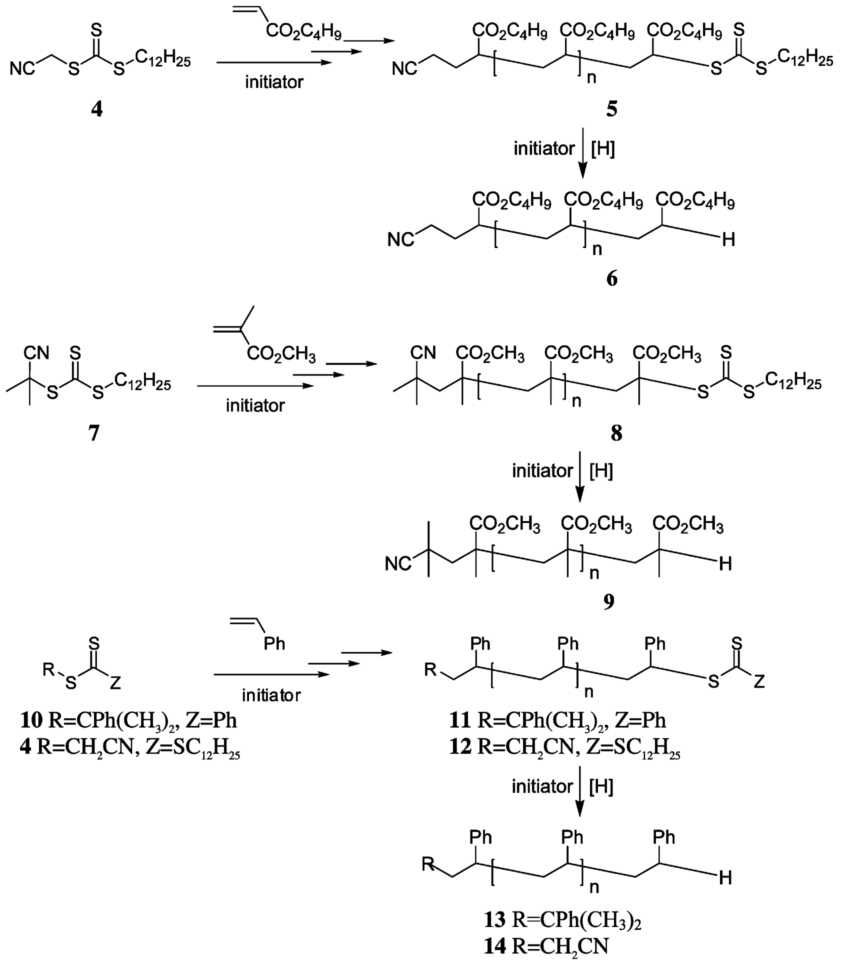
Scheme 3. Overall Process for RAFT Polymerization and End Group Removal



4 **5** **6** **7** **8** **9**

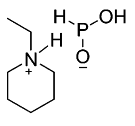
10 R=CPh$(CH_3)_2$, Z=Ph
4 R=CH_2CN, Z=$SC_{12}H_{25}$

11 R=CPh$(CH_3)_2$, Z=Ph
12 R=CH_2CN, Z=$SC_{12}H_{25}$

13 R=CPh$(CH_3)_2$
14 R=CH_2CN

react with various oxidizing agents[1,29−31] (including NaOCl, H_2O_2, tBuOOH, peracids, ozone) and are sensitive to UV irradiation.[32,33] However these reactions may leave reactive end group functionality and thus are not appropriate in all circumstances. Thermolysis[12,34−39] and radical-induced reactions (such as reduction[12,35,39−42] or termination[43]) provide another solution and can provide complete desulfurization.

Radical-induced reduction of low molecular weight thiocarbonylthio compounds is well-known.[44] Radical-induced reduction of xanthates is the basis of the Barton-McCombie reaction for deoxygenation of secondary alcohols (where the xanthate *O*-alkyl is a good homolytic leaving group).[45−47] Hypophosphite salts,[48−50] including *N*-ethylpiperidine hypophosphite (EPHP, **3**),[50] have been recommended for use as an alternative to stannanes in this process.

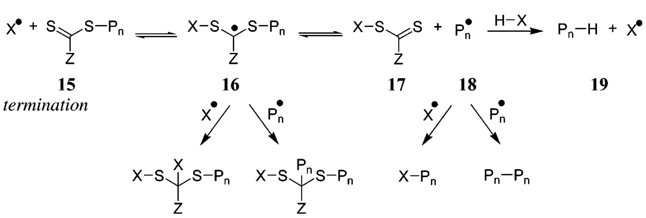


EPHP (**3**)

Radical-induced reduction has also been applied to desulfurization of low molecular weight xanthates when the *O*-alkyl is a poor homolytic leaving group—e.g., primary alkyl.[51,52] Radical-induced reduction has been shown to be applicable to end group removal for RAFT-synthesized polymers.[12,35,40,53] Radical-induced reductions with tributylstannane of poly(acenaphthalene)[40,53] or polystyrene[12,35] prepared with dithiobenzoate or trithiocarbonate RAFT agents respectively have been reported. However, residual stannane and stannane-derived byproducts may be toxic and can be difficult to remove and hence the process is unlikely to be industrially acceptable. The use of less active H atom donors (e.g., 2-propanol,[39] silanes[35]) has been reported but these reagents are not always appropriate since coupling of propagating radicals and other side reactions may compete with H atom transfer (vide infra). There is also reference in the patent literature to end group removal by radical-induced processes.[54−56]

In this paper, we further explore the application of radical-induced reduction to the removal of end groups for poly(butyl acrylate) (PBA), poly(methyl methacrylate) (PMMA) and polystyrene with either trithiocarbonate or dithioester chain ends. We demonstrate that radical-induced reduction, with hypophosphite salts as the H atom source, is an effective method for replacing the thiocarbonylthio groups of a range of polymers synthesized with trithiocarbonate or dithioester RAFT agents.[42,56,57] The process has the advantage that excess reagent and reaction

Scheme 4. Radical-Induced Reduction of Thiocarbonylthio Compounds



15 **16** **17** **18** **19**

Table 1. Results of Radical-Iinduced Reduction of RAFT-Synthesized Polymers in Toluene or Toluene/2-Propanol with Dibenzoyl Peroxide (BPO) or Didodecanoyl Peroxide (LPO) Initiator

			conditions[a]			product	
precursor	$\bar{M}_n$[b] (g/mol)	PD[c]	solvent/peroxide	[polymer][d] (M)	[peroxide] (M)	MWD	end group removal[e]
5	1930	1.12	tol/BPO	0.20	0.62	Figure 1	complete
5	47 400	1.08	tol/BPO	0.010	0.031	Figure 1	complete
5	90 900	1.09	tol/BPO	0.005	0.011	Figure 1	complete
5	1930	1.12	tol-iPOH/BPO	0.098	0.32	Figure 1	complete
5	47 400	1.08	tol-iPOH/BPO	0.0032	0.012	Figure 1	complete
5	90 900	1.09	tol-iPOH/BPO	0.0025	0.070	Figure 1	complete
5	1930	1.12	tol/LPO	0.20	0.050	Figure 1	complete
5	47 400	1.08	tol/LPO	0.010	0.030	Figure 1	complete
5	90 900	1.09	tol/LPO	0.0050	0.0015	Figure 1	complete
8	3400	1.18	tol-iPOH/BPO	0.050	0.176	Figure 2	complete
11	1550	1.08	tol/LPO	0.1	0.2	Figure 3	complete
11	50 200	1.11	tol/LPO	0.0050	0.011	Figure 3	complete
11	1550	1.08	tol-iPOH/BPO	0.10	0.31	Figure 3	complete
11	50 200	1.11	tol-iPOH/BPO	0.0033	0.010	Figure 3	complete
12	4470	1.06	tol/BPO	0.05	0.15	7400/1.11	complete
12	4470	1.06	tol-iPOH/BPO	0.05	0.15		complete

[a] Reactions at 90 °C for 1 h (LPO) or 100 °C for 1.25 h (BPO). Abreviations: tol, toluene; tol-iPOH, 1:1 (v/v) toluene:2-propanol. [b] $\bar{M}_n$ is number-average molecular weight in polystyrene equivalents. [c] PD ($=\bar{M}_w/\bar{M}_n$) is the polydispersity, the ratio of the weight-average to the number-average molecular weight. [d] Polymer concentration based on precursor molecular weight shown. [e] The extent of end group removal for lower molecular weight samples ($\bar{M}_n$ <5000 g mol^{-1}) is based on ^{1}H NMR spectroscopic assessment of the disappearance of signals associated with the thiocarbonylthio end group (see Experimental Section). For higher molecular weight samples ($\bar{M}_n$ > 40000 g mol^{-1}) evidence of end group removal is provided by decolorization and the observed changes in the molecular weight distribution.

Table 2. Transfer Constants (C_{tr}) and Rate Constants for Transfer to Solvent (k_{tr}) in Radical Polymerization at 80 °C

	monomer					
	ethyl acrylate		methyl methacrylate		styrene	
solvent	C_{tr} ($\times 10^4$)[a]	k_{tr}[b] (M^{-1}s^{-1})	C_{tr} ($\times 10^4$)[a]	k_{tr}[b] (M^{-1}s^{-1})	C_{tr} ($\times 10^4$)[a]	k_{tr}[b] (M^{-1} s^{-1})
toluene	2.6	11.3	0.3−0.9	0.078	0.2−0.8	0.033
2-propanol	28.7	125	1.9	0.25	4	0.27

[a] The transfer constant (C_{tr}) is the ratio of the rate constant for hydrogen transfer from the solvent (k_{tr}) to that for propagation in radical polymerization (k_p). Values are taken from the Polymer Handbook.[60] [b] Values of k_{tr} calculated from the median value of C_{tr} shown using values of k_p for bulk polymerization at 80 °C.[61]

Table 3. Results of Radical-Induced Reduction of Thiocarbonylthio Compounds with Silanes

RAFT agent	silane/initiator[a]	[RAFT]$_o$	[silane]$_o$	[I]$_o$	T/time[b] (°C/h)	reaction[c]
4	triethylsilane/AIBN	0.090	0.13	0.043	70/2	none
4	triethylsilane/ACHN	0.090	0.13	0.029	90/2 90/18	<20% complete
4	triphenylsilane/AIBN	0.090	0.14	0.043	60/2 70/2	nonenone
4	triphenylsilane/ACHN	0.090	0.13	0.029	90/2 90/18	<20% complete
21	triphenylsilane/ACHN	0.11	0.17	0.029	90/2	none
					100/4	none
4	tris(trimethylsilyl)silane/AIBN	0.090	0.13	0.043	60/2	complete
21	tris(trimethylsilyl)silane/AIBN	0.14	0.23	0.043	80/2	complete
22	tris(trimethylsilyl)silane/AIBN	0.071	0.14	0.043	80/4.5	partial
12[d]	tris(trimethylsilyl)silane/AIBN	0.05	0.099	0.029	80/4	complete

[a] Initiator (I), AIBN = azobis(isobutyronitrile), ACHN = azobis(cyclohexanenitrile). [b] Reactions carried out in a 5 mm NMR tube in benzene-d_6 solvent at the temperature (T) and reaction time indicated. [c] Extent of reaction based on ^{1}H NMR analysis. [d] RAFT-synthesized polystyrene (**12**) with number-average molecular weight ($\bar{M}_n$) 4470 and polydispersity ($\bar{M}_w/\bar{M}_n$) 1.06—refer to Figure 4.

byproducts are water-soluble and thus readily separated from the polymer.

Results and Discussion

The overall process of RAFT polymerization and end group removal by radical-induced reduction as applied in this paper is shown in Scheme 3.

The process of radical-induced reduction makes use of the property of thiocarbonylthio compounds to undergo facile reaction with radicals by addition−fragmentation. A general mechanism for the process is shown in Scheme 4. A radical (X$^\bullet$) adds to the thiocarbonyl group of the macro RAFT agent (**15**) to generate an intermediate **16** which fragments to provide the propagating radical (**18**) and a new thiocarbonylthio compound (**17**). Reaction of the propagating radical **18** with a H atom donor (H−X) then gives the desired product in which the thiocarbonylthio group has been replaced with hydrogen. The reaction is a radical chain reaction and is catalytic in X$^\bullet$. The steps involving reaction between radical species constitute the termination step. Not shown is the initiation step for generation of radicals.

A variety of side reactions can complicate the process, these include the various termination reactions. Shown in Scheme 4 are reactions of the intermediate **16** or the propagating radical **18** with other radical species (initiator-derived radicals, transfer agent-derived radicals, propagating radicals). The reactions are shown to proceed by combination. However, reaction by disproportionation is also likely, the extent dependent on the

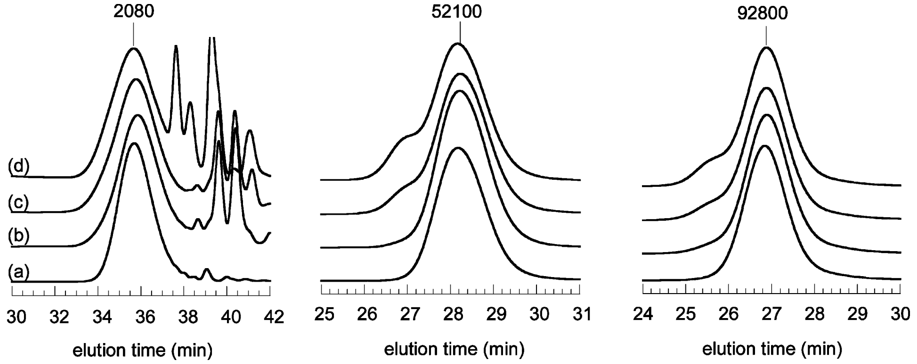
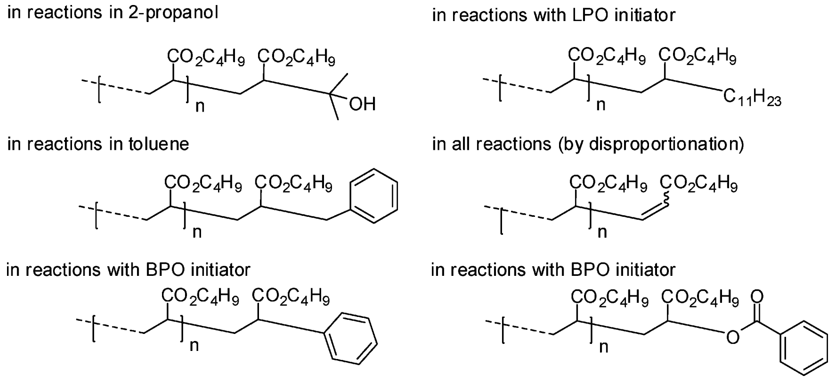


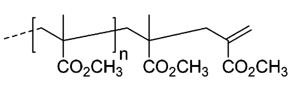
Figure 1. Gel permeation chromatograms for three samples of (a) poly(butyl acrylate) **5** of differing molecular weight prepared with RAFT agent **4** and the products obtained by their reduction in (b) 2-propanol/toluene (1:1) or (c) toluene as H-donor/solvent and with dibenzoyl peroxide (BPO) as initiator (100 °C, 1.25 h) or in (d) toluene with didodecanoyl peroxide (LPO) as initiator (90 °C, 1 h). Peak molecular weights in polystyrene equivalents are indicated on the chromatograms. Details of polymers and the experimental conditions are provided in Table 1.

Scheme 5. Possible End Groups Formed by Reaction of the Poly(butyl acrylate) Propagating Radical with Small Radicals



species involved. Termination reactions will be favored by a high radical flux which is usually associated with a high initiator concentration.

The presence of these side reactions means that the loss of the thiocarbonylthio groups alone is not a suitable measure of the efficiency of radical-induced reduction. Reaction between propagating radicals by combination (termination is mainly by combination for PBA and polystyrene propagating radicals)[58] will be manifest as formation of higher molecular weight polymer (approximately twice that of the propagating radical) and will usually be evident in the gel permeation chromatogram (GPC chromatogram) if the precursor polymer has a sufficiently narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n$ <1.2). For polymers with $\bar{M}_w/\bar{M}_n \geq 1.2$, any broadening of the molecular weight distribution as a consequence of termination by combination is likely to be obscured.[59] If termination is by disproportionation (termination is substantially by disproportionation for PMMA propagating radicals)[58] the incidence of termination may not be observable in the GPC chromatogram. In this case, the presence of olefinic resonances in the ^{1}H NMR spectrum can provide a measure of the incidence of termination (e.g., of end groups **20** in the case of PMMA).



20

Radical-Induced End Group Removal in Toluene or Toluene—2-Propanol. Destarac et al.[39] have decribed xanthate end group removal from poly(acrylic acid) ($\bar{M}_n$ 2000, $\bar{M}_w/\bar{M}_n$ 1.48) by radical-induced reduction in 2-propanol with either didodecanoyl peroxide (LPO) at 80 °C or di-*tert*-butylcyclohexyl percarbonate at 60 °C as initiator. Reduction was reported to be quantitative, and the molecular weight and polydispersity were said to be unchanged by the process.

In our initial experiments dibenzoyl peroxide (BPO) or LPO were chosen as initiators over azonitriles (e.g., azobis(isobutyronitrile) (AIBN), azobis(cyclohexanenitrile) (ACHN)). Benzoyloxy or phenyl radicals (from BPO) and undecyl radicals (from LPO) are poor homolytic leaving groups and this should favor the intermediate (**16**) formed by addition of the initiator-derived radicals partitioning on the side of the propagating radicals. In each case the concentration of peroxide used was a 2−3-fold excess over the end group concentration. The experiments conducted are summarized in Table 1.

The results of radical-induced-reduction of PBA (**5**) in either toluene or toluene/2-propanol (1:1) as solvent and with BPO or LPO as initiator are illustrated by GPC chromatograms in Figure 1. With toluene as solvent, the products, except for the very low molecular weight sample, had a bimodal molecular weight distribution. The formation of a high molecular weight shoulder (with peak molecular weight approximately twice that of the precursor polymer) is indicative of ineffective radical trapping (vide infra). The shoulder was more pronounced when LPO was used as initiator. With toluene/2-propanol as solvent, the reduction was more effective and only slight broadening of the molecular weight distribution was observed. This is in accord with 2-propanol being ~10-fold more effective as a hydrogen donor toward the PBA propagating radical. The transfer constants in radical polymerization ($C_{tr} = k_{tr}/k_p$) of toluene and 2-propanol provide an indication of the relative ability of toluene

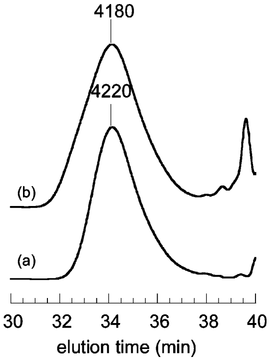


Figure 2. Gel permeation chromatogram for PMMA **8** prepared with RAFT agent **7** and the product obtained by its reduction in 2-propanol/toluene (1:1) as H-donor/solvent and with BPO as initiator. Peak molecular weights are indicated on the chromatograms. Details of the experimental conditions are provided in Table 1.

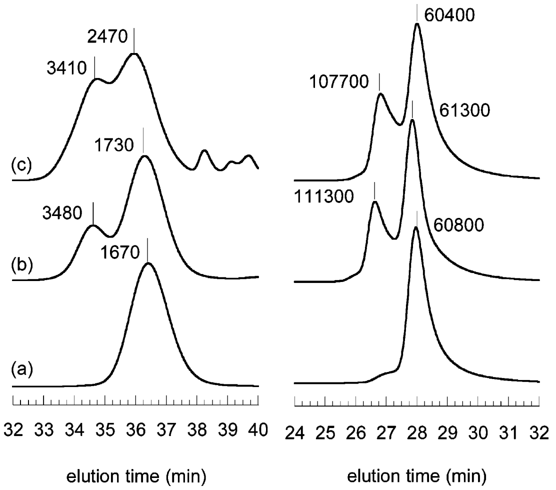


Figure 3. Gel permeation chromatograms for two samples of (a) polystyrene **11** of differing molecular weight prepared with RAFT agent **10** and the product obtained by its reduction in (b) toluene with LPO initiator or (c) 2-propanol/toluene (1:1) with BPO as initiator. Peak molecular weights are indicated on the chromatograms. Details of polymers and the experimental conditions are provided in Table 1.

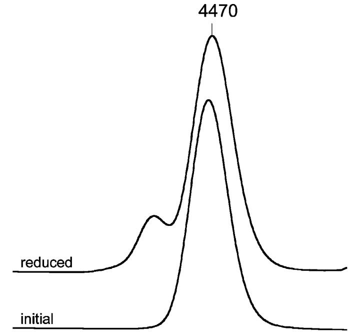


Figure 4. Gel permeation chromatograms of polystyrene **12** (0.05 M) and the product obtained by its reduction in toluene with tris(trimethylsilyl)silane (0.099 M) and azobis(isobutyronitrile) (0.029 M) at 80 °C for 4 h. Peak molecular weights are indicated on the chromatograms.

and 2-propanol to act as H-donors toward propagating radicals (Table 2).

The NMR spectra of the products of radical induced reduction, while confirming complete end group removal, were complex indicating that reactions other than the desired replacement of the dodecyl trithiocarbonate end group with hydrogen have taken place. A high radical flux is desirable to achieve a reasonable reaction rate but this also increases the likelihood of the propagating radicals terminating. A high radical flux also increases the likelihood that termination will involve reaction with a small radical rather than another propagating radical. If all that is required is desulfurization by replacement of the thiocarbonylthio group, this need not seen as a detrimental side reaction.

The end groups that may be formed by reaction of the PBA propagating radical with small radicals include those shown in Scheme 5. These radicals include benzyl radicals (from toluene), 2-hydroxyprop-2-yl radicals (from 2-propanol) undecyl radicals (from LPO), phenyl and benzoyloxy radicals (from BPO). It is also possible that the PBA propagating radical could rearrange by backbiting prior to undergoing further reaction.

A variety of low molecular weight byproducts were also formed. Some are clearly evident in the GPC chromatograms (Figures 1−3). The initial low molecular weight byproducts were expected to be various dodecyl trithiocarbonates ($X-S(C{=}S)SC_{12}H_{25}$) or dithiobenzoates ($X-S(C{=}S)Ph$; refer to Scheme 4). Complete or partial decolorization of the reaction mixtures was observed in all cases indicating that these compounds undergo further reaction under the process conditions. As well as those derived from the cleaved end group, we anticipated various initiator-derived byproducts, by cage recombination or transfer to initiator, and compounds from reactions between the various small radicals formed in the process either as initiator derived species or as a consequence of transfer to solvent. No attempt was made to further characterize these materials. Differences in the relative size of the impurity peaks seen in the GPC chromatograms of the low molecular weight examples in Figures 1−3 is attributed to differences in the intensity of the polymer peaks and differences in reagent concentrations used rather than a difference in the amount of impurities formed. The chromatograms in each case are for the polymer product obtained by evaporation of solvent so all nonvolatile byproducts derived from the initiator and end groups may be observed.

Perrier et al.[43] have reported a process that involves decomposition of a large excess of a free radical initiator in the presence of a RAFT-synthesized polymer as a means of end group removal. In the example detailed in their communication,[43] PMMA with dithiobenzoate end groups was treated with AIBN initiator in toluene solvent to produce a polymer with cyanoisopropyl end groups and cyanoisopropyl dithiobenzoate. The process was also reported[43] to be successful for polystyrene, poly(methyl acrylate) and other acrylic polymers with various thiocarbonylthio end groups. A recent attempt to apply this strategy to polystyrene with butyl trithiocarbonate end groups under the recommended conditions gave incomplete (95%) end group removal.[35] The large excess of initiator (∼20-fold excess, typically AIBN or ACHN) is required to avoid the formation of products from termination between macro-RAFT agent derived propagating radicals. For example, in a similar experiment with PMMA and a lower, 10-fold excess, of initiator, unsaturated end groups, proposed to arise from termination by disproportionation, were observed.[43]

The formation of product of twice the molecular weight could, in principle, be formed by coupling of propagating radicals **18** or it could result from reactions involving intermediate **16**. These reactions include coupling of **16** (where X is low molecular weight) with a propagating radical (**18**) and coupling of the intermediate **16** (where X is a polymer chain) with a low molecular weight radical or a H-donor (X−H). We have found

Table 4. Results of Radical-Induced Reduction of Polymers with *N*-Ethylpiperidine Hypophosphite (EPHP)

				conditions				product		
entry	precursor	$\bar{M}_n$[a] (g/mol)	PD[b]	*T*/time[c] (°C/h)	[EPHP] (M)	[P][d] (M)	[I] (M)	$\bar{M}_n$[a] (g/mol)	PD[b]	end group removal[e]
1	**5**	1930	1.12	80/2	0.31	0.1	0.030	1830	1.14	∼50%
2	**5**	1930	1.12[f]	100/1	0.42	0.08	0.021	1665	1.14[f]	complete[g]
3	**5**	3090	1.09	100/2	0.25	0.05	0.016	2850	1.09	complete
4	**8**	3400	1.18[f]	100/2	0.25	0.05	0.016	3380	1.16[f]	complete
5	**12**	4480	1.06	100/2	0.25	0.05	0.016	4460	1.09	∼50%
6	**12**	4240	1.08	100/16	1.0	0.05	0.020	4100	1.10	complete
7	**12**	4480	1.06	110/4	0.5	0.05	0.020	3970	1.19	complete
8	**12**	4240	1.08[h]	110/4	1.0	0.05	0.020	4120	1.10[h]	complete
9	**11**	1550	1.08[h]	110/4 × 2[i]	0.74	0.05	0.027	1590	1.12[h]	complete[i]
10	**11**	333	1.14	110/4	1.26	0.05	0.028	310	1.19	complete

[a] $\bar{M}_n$ is number-average molecular weight in polystyrene equivalents. [b] PD ($\bar{M}_w/\bar{M}_n$) is the polydispersity, the ratio of the weight-average to the number-average molecular weight. [c] Reactions in toluene solvent at the temperature (T) and reaction time indicated with azobis(cyclohexanenitrile) (ACHN) initiator (I) for experiments at ≥100 °C or azobis(isobutyronitrile) (AIBN) for experiments at 80 °C. [d] Concentration of polymer. [e] Extent of end group removal assessed by ^{1} H NMR spectroscopy. [f] See Figure 6. [g] See Figure 5. [h] See Figure 7. [i] Incomplete reduction after first 4 h. Furthermore, EPHP and ACHN were added and the reaction continued for a further 4 h to provide complete end group removal.

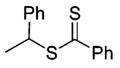
no direct evidence for reactions involving intermediate **16** in this work.

Radical-induced reduction of PMMA with dodecyl trithiocarbonate end groups in toluene/2-propanol (1:1) with BPO initiator was successful in cleaving the end groups and producing a polymer with a similar molecular weight distribution to that of the precursor (Figure 2). However, signals at δ 6.2 and 5.5, characteristic of the olefinic hydrogens of chain end (**20**) as might be formed by termination by disproportionation, were visible in the ^{1}H NMR spectrum of the product.

Radical induced-reduction of polystyrene with either dithiobenzoate (**11**) or dodecyl trithiocarbonate end groups (**12**) in toluene with LPO initiator or toluene/2-propanol (1:1) with BPO initiator gave a polymer with a markedly bimodal molecular weight distribution (e.g., Figure 3 for results with polystyrene **11**). Similar results were obtained when LPO was used as the initiator.

The use of toluene or 2-propanol as a H atom source in radical induced reduction would have some advantages, in terms of cost and convenience, since they can also be used as the solvent for the reaction. However, they are relatively poor H atom donors toward polystyrene and PMMA propagating radicals (Table 3).

Radical-Induced Reduction with Silanes. The use of various silanes was explored as H-donors in radical-induced reduction. The silane was used in ∼50% molar excess with respect to end groups. Initial experiments were carried out with RAFT agents **21** (electron rich "R" , model for polystyrene chain), **22** (tertiary "R"), or **4** (electron deficient "R") as model compounds showed that tris(trimethylsilyl)silane was substantially more effective as a H donor than poly(methylhydrosilane), triphenylsilane or triethylsilane (Table 3) which is consistent with the literature.[44] The latter reagents gave no or incomplete reaction under conditions where use of tris(trimethylsilyl)silane gave quantitative reduction at 80 °C after 2 h. Although use of tris(trimethylsilyl)silane in the reduction of polystyrene with dodecyl trithiocarbonate ends (80 °C, 4 h) gave end group removal, the product had a bimodal molecular weight distribution (Figure 4) indicating that the silane was a poor H-donor to the polystyrene propagating radical under the reaction conditions.



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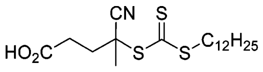

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Similar results (end group removal but product with a bimodal molecular weight distribution similar to that shown in Figure 4) have recently been reported for the use of this reagent for polystyrene with butyl trithiocarbonate ends.[35] In that work,[35] it was found that reduction with tributylstannane gave quantitative end group removal and a product with a monomodal molecular weight distribution.

Radical-Induced Reduction with *N*-Ethylpiperidine Hypophosphite. The outstanding feature of the hypophosphite salts is that they, and byproducts formed from the hypophosphite, are water-soluble and can be removed from the polymer by a simple water wash. This has seen them exploited in organic synthesis as alternative to stannanes and silanes for which the reaction byproducts have often proved difficult to remove. Thus, the use of *N*-ethylpiperidine hypophosphite (EPHP, **3**) was explored as a H-donor in radical-induced reduction of the RAFT agents **4** and **21** and for PMMA, PBA, and polystyrene produced by RAFT polymerization. Results for reduction of RAFT-synthesized polymers with EPHP are summarized in Table 4.

RAFT agent **4** was completely decolorized with excess EPHP (∼3 mol equiv) and AIBN in benzene-d_6 at 80 °C after 2 h or at 60 °C after 4 h and the ^{1}H NMR analysis indicated quantitative formation of acetonitrile. When 1-phenylethyl dithiobenzoate **21** (a simple model for polystyrene **11**) was subjected to these conditions, while the EPHP was consumed, the RAFT agent was little changed. Reaction at 100 °C with ∼5 fold excess EPHP and ACHN initiator gave a complex mixture. The poor reduction efficiency with **21** is attributed to the 1-phenylethyl radical being both a relatively poor homolytic leaving group and a poor H atom abstractor.

Reaction byproducts are complex and were not characterized. As anticipated those derived from EPHP were removed by a simple water wash. The mechanism shown in Scheme 4 suggests that the thiocarbonylthio end group should be converted to a low molecular weight byproduct (**17**) which still contains the thiocarbonylthio group. The observation of decolorization suggests that **17** might react further under the reaction conditions. The NMR of the final products of polymers with $-C(=S)SC_{12}H_{25}$ end groups after work up by water wash (e.g Figure 5) contain signals that are attributed to dodecanethiol ($HSC\mathbf{H}_2C_{11}H_{23}$ at 2.5 ppm).

Reduction of PBA with dodecyl trithiocarbonate end groups at 100 °C with excess EPHP and ACHN initiator proceeded smoothly. Complete end group removal after 2 h was demonstrated by ^{1}H NMR spectrum (Figure 5). GPC analysis showed that there was no significant change in the molecular weight distribution and the expected small drop in molecular weight

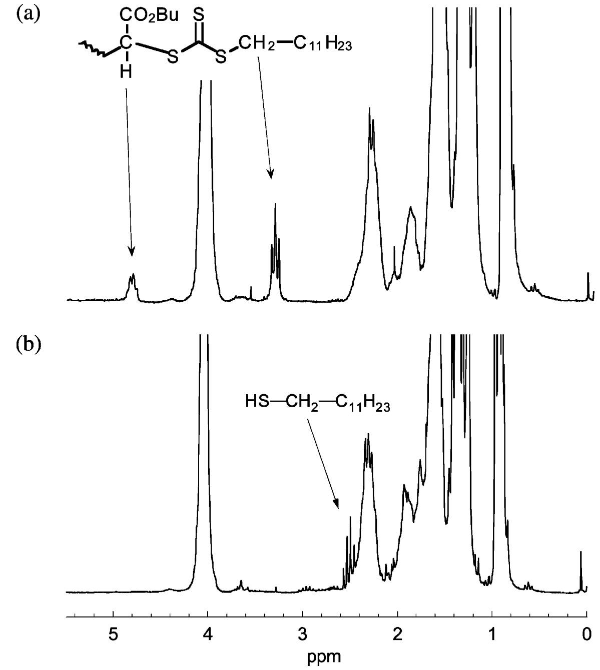

Figure 5. NMR spectra (0−5.5 ppm, 400 MHz, $CDCl_3$) of (a) poly(butyl acrylate) **5** prepared with RAFT agent **4** and (b) the product **6** obtained by its reduction with *N*-ethylpiperidine hypophosphite showing that signals at 4.8 ppm [-C**H**(COOBu)SC(S)S-] and 3.3 ppm [-SC(S)-SC**H**$_2$C$_{11}$H$_{23}$] associated with the dodecyl trithiocarbonate end group are removed on reduction and water extraction.

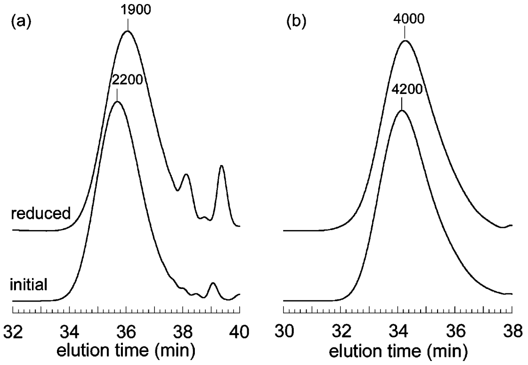

Figure 6. GPC chromatograms for (a) poly(butyl acrylate) **5** prepared with RAFT agent **4** and (b) poly(methyl methacrylate) **8** prepared with RAFT agent **7** and the products obtained by their reduction with *N*-ethylpiperidine hypophosphite (100 °C/ 2 h). Peak molecular weights in polystyrene equivalents are indicated on the chromatograms. Further details of experiments are shown in Table 4 as entries 2 and 4 respectively).

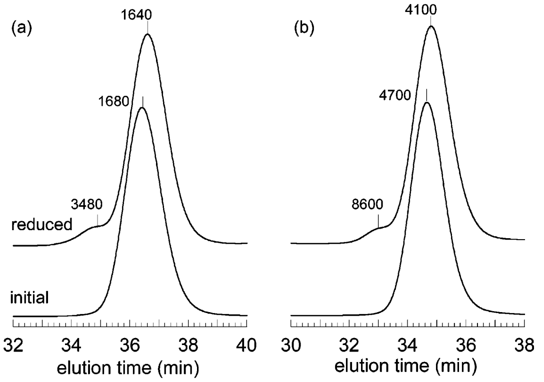

Figure 7. Gel permeation chromatograms for (a) polystyrene with dithiobenzoate or (b) dodecyl trithiocarbonate end groups and the products of their reduction with *N*-ethylpiperidine hypophosphite (110 °C/4 h or 110 °C/8 h, respectively). Peak molecular weights are indicated on the chromatograms. Further details of experiments are shown in Table 4 as entries 9 and 8, respectively.

associated with end group loss (Figure 6a). Efficient reduction was also observed for PMMA with dodecyl trithiocarbonate ends (Figure 6b). No signals in the olefinic region of the ^{1}H NMR spectrum, which would be evidence for termination by disproportionation (vide infra) could be detected. The reaction temperature was found to be important, attempted reduction of PBA **5** at 80 °C with excess EPHP and AIBN initiator gave only ~50% reduction.

As predicted on the basis of the model compound study, the radical induced reduction of polystyrene end groups required slightly more forcing conditions than those used for PBA or PMMA to achieve complete reduction. Incomplete removal of dodecyl trithiocarbonate end groups (~50%) and a product with bimodal molecular weight distribution was obtained under the conditions shown to be successful for PBA and PMMA (100 °C/2 h). Nonetheless the end groups for PS with dodecyl trithiocarbonate or dithiobenzoate ends were completely removed at 110 °C after 4 h with a higher concentration of *N*-ethylpiperidine hypophosphite. Under these conditions trapping of the propagating radicals with EPHP is not completely efficient even with a large 20-fold excess of EPHP as indicated by the appearance of a small high molecular weight shoulder on the molecular weight distribution (Figure 7).

Conclusions

The effectiveness of the hydrogen-donors increases in the series toluene ≪ 2-propanol < triethylsilane < triphenylsilane ≪ tris(trimethylsilyl)silane ~ *N*-ethylpiperidine hypophosphite < tributylstannane. With poor H-donors such as toluene or 2-propanol radical−radical reaction between propagating radicals competes with reduction even when they are used in vast excess as the solvent for the reaction. This is manifest in the product as a bimodal molecular weight distributions (PBA, polystyrene) and/or unsaturated end groups (PMMA). Tris(trimethylsilyl)silane and EPHP are more effective H atom donors in radical-induced reduction and EPHP has the advantage that the reaction byproducts are innocuous and water-soluble thus reaction workup is simplified.

Irrespective of the hydrogen-donor used, reduction of the thiocarbonyl end groups of polystyrene is less efficient than reduction of similar end groups of acrylic polymers (PBA or PMMA). This is attributed to the polystyrene propagating radical being a relatively poor H atom abstractor.

Experimental Section

General Data. Solvents were of AR grade and were distilled before use. Monomers, butyl acrylate (BA), methyl methacrylate (MMA) and styrene, were obtained from Aldrich and were filtered through neutral alumina (70−230 mesh), fractionally distilled under reduced pressure, and redistilled under reduced pressure immediately before use. Initiators AIBN and ACHN (VAZO-64 and VAZO-88 respectively from DuPont) and BPO and LPO were purified by crystallization from chloroform/methanol. Dodecanethiol (Aldrich, >98%), chloroacetonitrile (Aldrich, 99%), carbon disulfide (Aldrich, >99.9%), sodium hydride (Aldrich, 60% in oil), tris(trimethylsilyl)silane (Aldrich, 97%), and *N*-ethylpiperidine hypophosphite (Aldrich, 95%) were used as received. NMR spectra were obtained with a Bruker AC200, AC400 or DRX500 spectrometer. Chemical shifts are reported in ppm from external tetramethylsilane. High-resolution electron impact (HREI) mass spectra (MS) were obtained with a ThermoQuest MAT95XL mass spectrometer. GPC was performed on a Waters Associates liquid chromatograph equipped with differential refractometer and 3×Mixed C columns and (7.5 mm × 300 mm, 5 μ particle size, linear molecular weight range 2×10^2 to 2×10^6 g mol^{-1}) and one mixed E PLgel column (7.5 mm × 300 mm, 3 μ particle size, linear molecular weight range up to 3×10^5 g mol^{-1}) from Polymer Laboratories. Tetrahydrofuran (flow rate of 1.0 mL/min) was used as eluent at ambient temperature (22 ± 2 °C). The columns were calibrated with narrow polydispersity polystyrene standards (Polymer Laboratories). A third-order polynomial was used to fit the log M vs time calibration curve, which appeared approximately linear across the molecular weight range 2×10^2 to 2×10^6 g mol^{-1}.

RAFT Agents. The syntheses of 1-phenylethyl dithiobenzoate (**21**),[62] 4-cyano-4-(dodecylsulfanylthiocarbonyl)sulfanyl pentanoic acid (**22**),[12] and cumyl dithiobenzoate (**10**)[62] have been reported previously.

Cyanomethyl Dodecyl Trithiocarbonate (4). Dodecane-1-thiol (15.38 g, 75.99 mmol) was added over 10 min to a stirred suspension of sodium hydride (60 wt % in oil, 3.15 g, 78.7 mmol) in diethyl ether (150 mL) while the reaction temperature was maintained between 5 and 10 °C. A vigorous evolution of hydrogen gas was observed and the gray sodium hydride was converted to a thick white slurry of sodium thiododecylate. The reaction mixture was then cooled to 0 °C and carbon disulfide (6.0 g, 78.9 mmol) was added. The resulting thick yellow precipitate was isolated by filtration to give sodium dodecyl trithiocarbonate in quantitative yield.

Chloroacetonitrile (1.1 g, 14.6 mmol) was added to a suspension of sodium dodecyl trithiocarbonate (4.4 g, 14.7 mmol) in diethyl ether (50 mL) at room temperature. The resulting mixture was allowed to stir for 1 h. Water (50 mL) was then added and the bright yellow ether layer which separated and dried over anhydrous magnesium sulfate. After removal of solvent, the product cyanomethyl dodecyl trithiocarbonate (**4**) was obtained as a yellow solid (4.2 g, 90% yield). ^{1}H NMR (CDCl$_3$): δ 0.86 (t, 3H, C$\mathbf{H}_3$CH$_2$); 1.28 (br s, 18H, (C$\mathbf{H}_2$)$_6$); 1.71 (m, 2H. C$\mathbf{H}_2$CH$_2$S); 3.40 (t, 2H, CH$_2$C$\mathbf{H}_2$S); 4.15 (s, 2H, (CN)C$\mathbf{H}_2$S). MS (HREI): m/z 317.1313 (M$^+$) (C$_{15}$H$_{27}$NS$_3$ requires 317.1300).

2-Cyanopropan-2-yl Dodecyl Trithiocarbonate (7). Iodine (6.3 g, 0.025 mol) was added portionwise to a suspension of sodium dodecyl trithiocarbonate (14.6 g, 0.049 mol) in diethyl ether (100 mL). The resultant mixture was then stirred at room temperature for 1 h when the white sodium iodide which settled was removed by filtration. The yellow−brown filtrate was washed with aqueous sodium thiosulfate, to remove excess iodine, and water, dried over sodium sulfate and evaporated to leave a residue of bis(dodecylsulfanylthiocarbonyl) disulfide (13.6 g, ∼100%), mp 33−35 °C. ^{1}H NMR (CDCl$_3$): δ 0.89 (t, 6H, C$\mathbf{H}_3$CH$_2$); 1.30 (br s, 36H, (C$\mathbf{H}_2$)$_6$); 1.71 (m, 4H, C$\mathbf{H}_2$CH$_2$S); 3.29 (t, 4H CH$_2$C$\mathbf{H}_2$S).

A solution of AIBN (1.0 g, 0.006 mol) and bis(dodecylsulfanylthiocarbonyl) disulfide (2.2 g, 0.004 mol) in ethyl acetate (20 mL) was heated at reflux for 18 h. After removal of the volatiles in vacuo, *n*-hexane was added to the crude product to precipitate some of the unreacted AIBN and tetramethylsuccinodinitrile. The hexane solution was subjected to column chromatography (Kieselgel-60, 70−230 mesh), with *n*-hexane:ethyl acetate (1:49) as eluent to afford 2-cyanopropan-2-yl dodecyl trithiocarbonate (**4**) as a pale yellow oil (1.65 g, 60% yield), which solidified when stored in the freezer (−15 °C) but remelted at room temperature. ^{1}H NMR (CDCl$_3$): δ 0.89 (t, 3H, C$\mathbf{H}_3$CH$_2$); 1.28 (br s, 18H, (C$\mathbf{H}_2$)$_6$); 1.72 (m, 2H, C$\mathbf{H}_2$CH$_2$S); 1.85 (s, 6H, (C$\mathbf{H}_3$)$_2$C(CN)-; 3.40 (t, 2H, CH$_2$C$\mathbf{H}_2$S). MS (HREI): m/z 340.1622 (M$^+$) (C$_{17}$H$_{21}$NS$_3$ requires 340.1613).

RAFT Polymerization. Butyl Acrylate Polymerization [NCCH$_2$—PBA—SC(=S)SC$_{12}$H$_{25}$] (**5**). A solution containing BA (6.0 mL), the RAFT agent **4** (400 mg, 0.126 M), AIBN (2.2 mg, 0.0013 M), and benzene (4.0 mL) was placed in an ampule, degassed with three freeze−evacuate−thaw cycles, sealed and heated at 60 °C for 5 h. Removal of the volatiles under reduced pressure provided a yellow polymer (3.4 g, 63% conversion $\bar{M}_n$ 3080, $\bar{M}_w/\bar{M}_n$ 1.09). The ^{1}H NMR spectrum of the polymer showed the presence of protons on carbon next to sulfur at 4.8 ppm [−C**H**(COOBu)SC(S)S−] and 3.3 ppm [−SC(S)SC$\mathbf{H}_2$C$_{11}$H$_{23}$].

A similar procedure was used to prepare PBA **5**,[4] 0.126 M, [AIBN] 0.0060 M, polymerization time 4 h, 37.5% conversion, $\bar{M}_n$ 1930, $\bar{M}_w/\bar{M}_n$ 1.12; polymerization time 3 h, 45% conversion, $\bar{M}_n$ 47400, $\bar{M}_w/\bar{M}_n$ 1.08; polymerization time 3 h, 47% conversion $\bar{M}_n$ 90900, $\bar{M}_w/\bar{M}_n$ 1.09 were also prepared with use of the appropriate RAFT agent concentration.

Methyl Methacrylate Polymerization [(CH$_3$)$_2$C(CN)—PMMA—SC(=S)SC$_{12}$H$_{25}$] (**8**). A solution of the RAFT agent **7** (685 mg, 0.198 M) and ACHN (10.5 mg, 0.0043 M) in methyl methacrylate (7.0 mL) and benzene (3.0 mL) was placed in an ampule, degassed with three freeze−evacuate−thaw cycles, sealed and heated at 90 °C for 6 h. Removal of the volatiles under reduced pressure afforded a yellow polymer (5.3 g, 81% conversion) of $\bar{M}_n$ 3400, $\bar{M}_w/\bar{M}_n$ 1.18. The methylene hydrogens next to sulfur [−SC(S)SCH_2C$_{11}$H$_{23}$] appeared 3.2 ppm in the ^{1}H NMR spectrum.

Styrene Polymerization [(CH$_3$)$_2$C(Ph)—PS—SC(=S)Ph] (11). A solution of RAFT agent **10** (995 mg, 0.18 M), ACHN (16 mg, 0.0033 M) in styrene (16.0 mL) and benzene (4.0 mL) was placed in an ampule, degassed with three freeze−evacuate−thaw cycles, sealed and heated at 90 °C for 16 h.

Removal of the volatiles under reduced pressure afforded a red polymer (2.2 g, 15% conversion, $\bar{M}_n = 333$, $\bar{M}_w/\bar{M}_n = 1.14$). The end group protons on carbon next to sulfur [−CH(Ph)SC(S)Ph] appeared in the ^{1}H NMR spectrum as a complex signal between 4.5 and 5.0 ppm. The aromatic protons ortho to the C=S group produced a signal at 7.9 ppm.

A similar procedure was used to prepare other samples of polystyrene **11** as follows:[10] 0.092 M, [ACHN] 0.0033 M, 16 h, 21% conversion; $\bar{M}_n = 1550$, $\bar{M}_w/\bar{M}_n = 1.08$;[10] 0.0055 M, [ACHN] 0.0016 M, 16 h, 42% conversion; $\bar{M}_n = 50\,200$, $\bar{M}_w/\bar{M}_n = 1.11$.

Styrene Polymerization [NCCH$_2$—PS—SC(=S)SC$_{12}$H$_{25}$] (12). A solution of RAFT agent **4** (584 mg, 0.092 M), ACHN (16 mg, 0.0033 M) in styrene (16.0 mL), and benzene (4.0 mL) was placed in a ampule, degassed with three freeze−evacuate−thaw cycles, sealed under vacuum, and heated at 90 °C for 16 h. Removal of the volatiles under reduced afforded a yellow polymer (8.4 g, 58% conversion, $\bar{M}_n$ 4475, 1.06). The ^{1}H NMR spectrum showed the end group methine [−C**H**(Ph)SC(S)S−] as a broad signal between 4.6 and 5.1 ppm and the dodecyl methylene [−SC(S)SC$\mathbf{H}_2$C$_{11}$H$_{23}$] at 3.25 ppm.

Reduction in Toluene or Toluene/2-Propanol. The following procedure is typical. A sample of PBA **5** ($\bar{M}_n$ 1970, $\bar{M}_w/\bar{M}_n$ 1.12, 190 mg, 0.096 mmol) and BPO (78 mg, 0.32 mmol) was placed in an ampule and in toluene (5 mL) and 2-propanol (5 mL) was added. The solution was through three freeze−evacuate−thaw cycles, sealed, and heated at 100 °C for 1.25 h. The ampule was opened and solvent was removed by evaporation prior to analysis by GPC (Figure 1) and^1 H NMR. The details of this and similar experiments are summarized in Table 2.

Reduction with Silanes. The following procedure is typical. A sample of polystyrene **12** ($\bar{M}_n$ 4470, $\bar{M}_w/\bar{M}_n$ 1.06, 225 mg, 0.05 mmol), tris(trimethylsilyl)silane (24.5 mg, 30 μL, 0.99 mmol) and AIBN (5 mg, 0.03 mol) was dissolved in toluene (1 mL) and transferred to an ampule. The solution was through three freeze−evacuate−thaw cycles, sealed, and heated at 80 °C for 4 h. The ampule was opened and solvent was removed by evaporation prior to analysis by GPC (Figure 4) and^1 H NMR spectroscopy. The details of this and similar experiments are summarized in Table 3.

Reduction with *N*-Ethylpiperidine Hypophosphite. The following procedures are typical. The details of these and similar experiments are summarized in Table 4.

Preparation of NCCH$_2$—PBA—H (6). A mixture of the PBA **5** ($\bar{M}_n$ 3080, $\bar{M}_w/\bar{M}_n$ 1.09, 154 mg, 0.05 mmol), *N*-ethylpiperidine hypophosphite (45 mg, 0.25 mmol) and ACHN (4 mg, 0.016 mmol) in toluene (1 mL) was placed in a ampule, degassed with three freeze−evacuate−thaw cycles, sealed under vacuum and heated at 100 °C for 2 h. The solution was extracted with water and the toluene removed to give a colorless polymer. GPC analysis showed the polymer to have $\bar{M}_n$ 2850, $\bar{M}_w/\bar{M}_n$ 1.09 (Figure 6).

The ^{1}H NMR spectrum of the product demonstrated the absence of the signals at 4.8 and 3.3 ppm attributable to the protons on the carbon adjacent to sulfur in **5** (Figure 5). The NMR spectrum also demonstrated the absence of signals attributable EPHP or *N*-ethylpiperidine. Signals attributed to dodecanethiol appeared at 2.5 ppm ($HSC\mathbf{H}_2C_{11}H_{23}$). Identity of this compound was confirmed by spiking the NMR solution with dodecanethiol.

Preparation of $CH_3)_2C(CN)$—PMMA—H (9). A mixture of the above PMMA **8** ($\bar{M}_n$ 3400, $\bar{M}_w/\bar{M}_n$ 1.18, 170 mg, 0.05 mmol), *N*-ethylpiperidine hypophosphite (45 mg, 0.25 mmol) and ACHN (4 mg, 0.016 mmol) in toluene (1 mL) was placed in a ampule, degassed with three freeze−evacuate−thaw cycles, sealed under vacuum and heated at 100 °C for 2 h. The solution was extracted with water and the toluene removed to give a colorless polymer $\bar{M}_n$ 3380, $\bar{M}_w/\bar{M}_n$ 1.16.

The ^{1}H NMR spectrum of the product showed that the signals attributable to the dodecyl trithiocarbonate end group were no longer present. Signals attributed to dodecanethiol appeared at 2.5 ppm ($HSC\mathbf{H}_2C_{11}H_{23}$).

Preparation of $CH_3)_2C(Ph)$—PS−H (13). A mixture of the above polystyrene **11** ($\bar{M}_n = 333$, $\bar{M}_w/\bar{M}_n = 1.14$, 170 mg, 0.5 mmol), *N*-ethylpiperidine hypophosphite (450 mg. 2.5 mmol) and ACHN (10 mg, 0.04 mmol) in toluene (2 mL) was placed in a ampule, degassed with three freeze−evacuate−thaw cycles, sealed under vacuum and heated at 110 °C for 4 h. The solution was diluted with ethyl acetate (5 mL), extracted with water and the organic phase evaporated to give a near-colorless polymer of $\bar{M}_n$ 310, $\bar{M}_w/\bar{M}_n$ 1.19 by GPC analysis. The ^{1}H NMR spectrum of the product demonstrated the absence protons associated with the dithiobenzoate end group at 4.5−5.0 and 7.9 ppm.

Preparation of $NCCH_2$−PS−H (14). A solution of the above polystyrene **12** ($\bar{M}_n$ 4475, $\bar{M}_w/\bar{M}_n$ 1.06, 224 mg, 0.05 mmol) *N*-ethylpiperidine hypophosphite (90 mg, 0.5 mmol), ACHN (5 mg, 0.02 mmol) in toluene (1 mL) was placed in a ampule, degassed with three freeze−evacuate−thaw cycles, sealed under vacuum and heated at 110 °C for 4 h. The mixture was diluted with ethyl acetate (10 mL), extracted with water and the organic phase evaporated. This produced a colorless polymer $\bar{M}_n$ 3970, $\bar{M}_w/\bar{M}_n$ 1.10. The ^{1}H NMR spectrum demonstrated the absence of signals at 4.6 − 5.1 and 3.25 ppm associated with the dodecyl trithiocarbonate end group. Signals attributed to dodecanethiol appeared at 2.5 ppm ($HSC\mathbf{H}_2C_{11}H_{23}$).

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