Thiocarbonylthio Compounds [S=C(Ph)S−R] in Free Radical Polymerization with Reversible Addition-Fragmentation Chain Transfer (RAFT Polymerization). Role of the Free-Radical Leaving Group (R)

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ABSTRACT: Radical polymerization with reversible addition−fragmentation chain transfer (RAFT polymerization) can be used to synthesize a wide range of polymers of controlled architecture and narrow molecular weight distribution. The polymerizations use addition−fragmentation chain transfer agents (RAFT agents) that possess high transfer coefficients in free radical polymerization and confer living character on the polymerization. This paper explores the effect of the substituents R of dithiobenzoate RAFT agents [S=C(Ph)S−R] on the outcome of polymerizations of styrene, methyl methacrylate (MMA) and butyl (BA) or methyl acrylate (MA). In MMA polymerization at 60 °C, effectiveness depends strongly on R decreasing in the order where R is: $-C(Alkyl)_2CN \sim -C(Me)_2Ar > -C(Me)_2C(=O)O(alkyl) > -C(Me)_2C(=O)NH(alkyl) > -C(Me)_2CH_2C(Me)_3 \geq -C(Me)HPh > -C(Me)_3 \sim -CH_2Ph$. Of these, only the compounds with R = $-C(Me)_2Ph$ and $-C(Me)_2CN$ provided polymers with substantially narrowed polydispersities in batch polymerization and gave molecular weight control of the form expected for a living polymerization. These compounds have high transfer coefficients in MMA polymerization (transfer coefficient >20 for 0.003 M RAFT agent in bulk MMA). Reagents with R = $-C(Me)_2C(=O)O(alkyl)$, $C(Me)_2C(=O)NH(alkyl)$, $-C(Me)_2CH_2C(Me)_3$, $-C(Me)HPh$, $-C(Me)_3$, and $-CH_2Ph$ appear relatively ineffective in MMA polymerization because they have much lower transfer coefficients (ca. 1.7, 0.7, 0.4, 0.15, 0.03, and 0.03 respectively). In polymerizations of styrene or acrylates at 60 °C, transfer coefficients of RAFT agents are several orders of magnitude higher and all compounds in the above series yield narrow polydispersity polymers. The transfer coefficients of benzyl dithiobenzoate in styrene and methyl acrylate polymerization at 60 °C are ca. 50 (0.0093 M RAFT agent in bulk monomer) and 105 (with 0.003−0.006 M RAFT agent in 4.43 M monomer), respectively. The rate constant for addition to the thiocarbonyl group does not depend strongly on R. Differences in activity depend on the properties of R and the propagating chain as free radical leaving groups and on the partitioning of $R^•$ between adding to monomer (to reinitiate) and adding to polymeric RAFT agent. When the reaction of $R^•$ with the polymeric RAFT agent to reform the initial RAFT agent is significant, the transfer coefficient may reduce with concentration of RAFT agent and with conversion. In these circumstances, the activity of RAFT agents is best characterized by two transfer constants associated with the forward and reverse reactions. Steric factors, polar factors, and the stability of $R^•$ all appear to play an important role in determining the transfer coefficient and the effectiveness of RAFT agents.

Introduction

In recent years, considerable effort[1−7] has been expended to develop free radical polymerizations that display the essential characteristics of living polymerizations.[8] One driving force behind this work has been to achieve the level of control associated with living polymerization while retaining as much as possible of the scope and versatility of the free radical process.

Recently, we described a new method for achieving living free radical polymerization[9,10] (RAFT polymerization) that involves, as the key step, reversible addition−fragmentation chain transfer.[11−20] The more effective RAFT agents are certain thiocarbonylthio compounds (**1**) where Z is a group that modifies the reactivity of the thiocarbonyl group toward free radical addition and R is a free radical leaving group.[14−16] With appropriate choice of the RAFT agent and reaction conditions, RAFT polymerization can be successfully used to produce narrow polydispersity polymers with molecular weights predetermined by the conversion and RAFT agent concentration.[14,16−20] Moreover, the polymers obtained by the RAFT process can be chain extended or used as precursors to block copolymers by the addition of further monomer(s).[15,16,18,19,21−23] RAFT polymerization also provides a route to stars and more complex architectures.[16,19,24−26]

We and others have also reported that the effectiveness of RAFT agents (**1**) strongly depends on the nature of the groups Z and R, the monomer and the polymerization conditions.[15,18−20,27−34] In this paper, we examine in greater detail the effect of varying the free radical leaving group, R, of dithiobenzoate derivatives (**2**, Scheme 1) on polymerizations of several monomers: styrene, methyl methacrylate (MMA), and methyl or butyl acrylate (MA or BA).[35] In the accompanying paper,[36] we report on the influence of the reactivity-modifying group, Z, in a similar manner.

Experimental Section

General Data. Tetrahydrofuran (THF) used in synthesis was freshly distilled from sodium benzophenone. Reagent chemicals were obtained from Aldrich and used without purification unless otherwise indicated. Solvents used for column chromatography were of AR grade and were distilled. Petroleum spirits refers to the fraction with bp 40−60 °C. The silica was Kieselgel-60 (Merck), 70−230 mesh. Nuclear magnetic resonance (NMR) spectra were obtained with a Bruker

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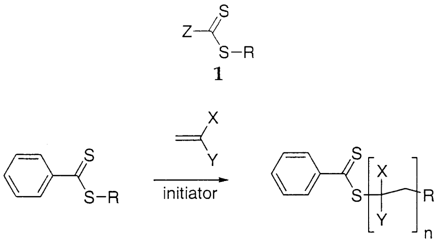
Scheme 1. Overall Reaction[a]



[a] Key: **2a**, $R = C(CH_3)_2Ph$; **2b**, $R = C(CH_3)_2C_6H_4Cl$; **2c**, $R = CH(CH_3)Ph$; **2d**, $R = CH_2Ph$; **2e**, $R = C(CH_3)_2CN$; **2f**, $R = C(CH_3)(CN)CH_2CH_2CH_2OH$; **2g**, $R = C(CH_3)_2C(=O)OC_2H_5$; **2h**, $R = C(CH_3)_2C(=O)NHCH_2CH_2OH$; **2i**, $R = C(CH_3)_2CH_2C(CH_3)_3$; **2j**, $R = C(CH_3)_3$; **2k**, $R = SC(CH_3)_3$; **2l**, $R = [C(CH_3)(CO_2CH_3)]_n-R'$; **2m**, $R = [CH(Ph)]_n-R'$; **2n**, $R = [CH(CO_2C_4H_9)]_n-R'$.

AC200 spectrometer on samples dissolved in deuteriochloroform. Chemical shifts are reported in ppm from tetramethylsilane. High-resolution mass spectra were obtained with either a JEOL JMS DX303 mass spectrometer (chemical ionization, CI) or a Bruker Bio Apex Fourier transform mass spectrometer (electron impact, EI). Methane was used as reagent gas for the CI mass spectra.

Cumyl Dithiobenzoate (2a). The synthesis of cumyl (or 2-phenylprop-2-yl) dithiobenzoate is described elsewhere.[19]

2-(4-Chlorophenyl)prop-2-yl Dithiobenzoate (2b). Dithiobenzoic acid[19] (6.3 g, 0.041 mol) and 4-chloro-α-methylstyrene (6 g, 0.039 mol) were combined, and the mixture was heated at 70 °C for 16 h. The residue was subjected to column chromatography on silica with *n*-hexane as eluent to give the title compound (**2b**) as a purple solid (4.3 g, 34.2% yield), mp 77−78 °C. ^{1}H NMR, δ: 1.97 (s, 6H, 2 × C*H*$_3$), 7.20−7.52 (m, 7H, Ar*H*) and 7.86 (d, 2H, *o*-Ar*H*). ^{13}C NMR, δ: 28.4 (2 × *C*H$_3$), 55.7 (*C*(CH$_3$)$_2$C$_6$H$_4$Cl), 126.5 (phenyl-*C3* and 4-chlrophenyl-*C3*), 128.1 (phenyl-*C2* and 4-chlrophenyl-*C2*), 131.9 (phenyl-*C4*), 132.4 (4-chlorophenyl-*C4*), 142.8 (4-chlorophenyl-*C1*), 146.0 (phenyl-*C1*). The signal due to C=S was not observed. EI mass spectrum: found, 306.0304 (M^+); $C_{16}H_{15}S_2Cl$ requires 306.0298.

1-Phenylethyl Dithiobenzoate (2c). Dithiobenzoic acid[19] (9.9 g, 0.064 mol), styrene (10 mL 0.087 mol) and carbon tetrachloride (30 mL) were combined and the mixture heated at 70 °C for 4 h. The resultant mixture was concentrated on a rotary evaporator and the residue subjected to column chromatography on alumina (activity III) with, petroleum spirits as eluent to give 1-phenylethyl dithiobenzoate (**2c**) (7.2 g, 43.4%). ^{1}H NMR, δ: 1.92 (d, 3H, CH−C*H*$_3$); 5.39 (q, 1H, C*H*-CH$_3$); 7.34−7.62 (m, 8H, Ar*H*), 8.08 (d, 2H, *o*-Ar*H* of dithiobenzoate). EI mass spectrum: EI found, 258.0531 (M^+); $C_{15}H_{14}S_2$ requires 258.0537.

Benzyl Dithiobenzoate (2d). The one-pot procedure described by Meijer and Vermeer[37] was modified as follows. A solution of phenylmagnesium bromide (from bromobenzene (62.8 g, 0.40 mol) and magnesium turnings (10 g, 0.42 mol) in dry tetrahydrofuran (300 mL) was warmed to 40 °C, and carbon disulfide (30.4 g, 0.41 mol) was added over 15 min at such a rate that the reaction temperature was maintained at 40 °C. Benzyl bromide (77 g, 0.45 mol) was then added to the resultant dark brown mixture over 15 min, after which the reaction temperature was raised to 50 °C and maintained at that temperature for a further 45 min. Ice-cold water (1.5 L) was added and the mixture extracted with diethyl ether (total 2 L). The combined ethereal extracts were washed with water (1 L) and brine (500 mL) and dried over anhydrous magnesium sulfate. After removal of solvent, vacuum distillation of the residue gave benzyl dithiobenzoate (**2d**) as a red oil (60.2 g, 61.7%), bp 152 °C (0.02 mmHg) [lit.[38] bp 179−180 °C (3 mmHg)]. ^{1}H NMR, δ: 4.60 (s, 2H, C*H*$_2$−Ph), 7.30−7.60 (m, 8H, Ar*H*), 8.02 (m, 2H, Ar*H*).

2-Cyanoprop-2-yl Dithiobenzoate (2e). A solution of cumyl dithiobenzoate (**2a**)[19] (2.0 g, 0.0074 mol) and an excess of AIBN (2.4 g, 0.0146 mol) in benzene (20 mL) was heated under reflux for 20.5 h. The solution was cooled and the solvent removed in vacuo to afford 2.5 g of crude product which was chromatographed on silica with hexane:diethyl ether (9:1) as the eluent. The isolated yield of pure 2-cyanoprop-2-yl dithiobenzoate (**2e**) was 1.6 g (92%). The ^{1}H NMR spectrum was identical with that of the sample prepared from the reaction bis(thiobenzoyl) disulfide with AIBN.[19]

4-Cyano-1-hydroxypent-4-yl Dithiobenzoate (2f). A solution of di(thiobenzoyl) disulfide (0.73 g, 2.4 mmol) and 4,4′-azobis(4-cyano-1-pentanol)[39] (0.50 g, 2 mmol) in ethyl acetate (10 mL) was prepared. The mixture was degassed and heated to 70 °C in a sealed vessel for 24 h. The volatiles were removed under reduced pressure and the residue chromatographed on silica with ethyl acetate/petroleum spirits/acetonitrile (6:14:1) as eluent to give the title compound (**2f**) (0.49 g, 46%). ^{1}H NMR, δ 1.90 (3H, C*H*$_3$), 2.10 (2H, CH$_2$C*H*$_2$CH$_2$OH), 2.30 (2H, C*H*$_2$CH$_2$ CH$_2$OH), 3.75 (2H, CH$_2$CH$_2$C*H*$_2$OH), 7.40, 7.50, 7.90 (m, 5H, Ar*H*).

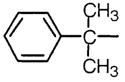
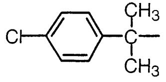
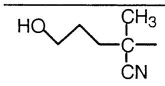
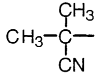
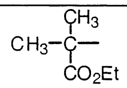
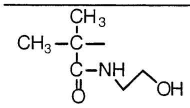
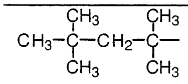
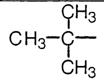
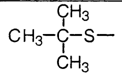
2-(Ethoxycarbonyl)prop-2-yl Dithiobenzoate (2g). Phenylmagnesium bromide was prepared from bromobenzene (6.28 g, 0.04 mol) and magnesium turnings (1 g, 0.041 mol) in dry THF (30 mL). The solution was warmed to 40 °C and carbon disulfide (3.05 g, 0.04 mol) was added over 15 min while maintaining the reaction temperature at 40 °C. Ethyl α-bromoisobutyrate (7 g, 0.036 mol) was added to the resultant dark brown solution and the reaction temperature then raised to 80 °C and maintained for 60 h. Ice-cold water (50 mL) was added, and the organic products were extracted with diethyl ether (3 × 50 mL). The combined organic extracts were washed with water and brine and dried over anhydrous magnesium sulfate. After removal of solvent and purification by column chromatography on silica with *n*-hexane/diethyl ether (9:1) as eluent. 2-(ethoxycarbonyl)prop-2-yl dithiobenzoate (**2g**) was obtained as a red oil (4.52 g, 42.2% yield). ^{1}H NMR, δ: 1.25 (t, 3H, CH$_2$C*H*$_3$), 1.77 (s, 6H, 2 × C*H*$_3$), 4.17 (q, 2H, OC*H*$_2$CH$_3$), 7.35 (dd, 2H, *m*-Ar*H*), 7.52 (dd, 1H, *p*-Ar*H*), 7.95 (d, 2H, *o*-Ar*H*). CI mass spectrum: found, 269.0675 ($M + 1$); $C_{13}H_{16}S_2O_2$ requires 269.0670.

2-[*N*-(2-Hydroxyethyl)carbamoyl]prop-2-yl Dithiobenzoate (2 h). A solution of di(thiobenzoyl) disulfide (0.61 g, 2 mmol) and 4,4′-azobis(2-methyl-*N*-(2-hydroxyethyl)propionamide) (0.87 g, 3 mmol, Wako) in ethyl acetate (20 mL) and ethanol (10 mL) was degassed at reflux for 24 h. The volatiles were removed under reduced pressure and the residue chromatographed on silica with ethyl acetate as eluent to give the title compound (**2h**) (0.1 g, 18%). ^{1}H NMR, δ: 1.74 (6H, 2 × C*H*$_3$), 1.89 (br s, 1H, O*H*), 3.34 (m, 2H, N−C*H*$_2$), 3.64 (m, 2H, O−C*H*$_2$), 6.74 (br s, 1H, N*H*), 7.35, 7.51, 7.92 (m, 5H, Ar*H*). EI mass spectrum: found, 283.0695 (M^+); $C_{13}H_{17}S_2O_2N$ requires 283.0701.

2,4,4-Trimethylpent-2-yl Dithiobenzoate (2i). A mixture of dithiobenzoic acid (5 g, 0.032 mol), 2,4,4-trimethylpentene (7.3 g, 0.065 mol), and carbon tetrachloride (25 mL) was heated at 70 °C for 2 days. The volatiles were removed under reduced pressure, and the residue was chromatographed on silica with petroleum spirits as eluent to give 2,4,4-trimethylpent-2-yl dithiobenzoate (**2i**) (2.74 g, 31.7% yield) as a dark purple oil. ^{1}H NMR, δ: 1.08 (s, 9H, C(C*H*$_3$)$_3$), 1.77 (s, 6H, 2 × C*H*$_3$), 2.20 (s, 2H, CC*H*$_2$C(CH$_3$)$_3$), 7.35 (dd, 2H, *m*-Ar*H*), 7.49 (dd, 1H, *p*-Ar*H*), 7.85 (d, 2H, *o*-Ar*H*). ^{13}C NMR, δ: 28.3 (SC(*C*H$_3$)$_2$CH$_2$), 31.5 (CH$_2$C(*C*H$_3$)$_3$), 32.8 (CH$_2$*C*(CH$_3$)$_3$), 50.5 (SC(CH$_3$)$_2$*C*H$_2$), 57.7 (S*C*(CH$_3$)$_2$CH$_2$), 126.6 (*o*-Ar*C*), 128.1 (*m*-Ar*C*), 131.5 (*p*-Ar*C*), 147.9 (Ar-*C1*). The signal due to C=S was not observed. EI mass spectrum: found, 266.1157 (M^+); $C_{15}H_{22}S_2$ requires 266.1163.

***tert*-Butyl Dithiobenzoate (2j).** *tert*-Butyl mercaptan (6.15 g, 0.068 mol) was added dropwise to a solution of benzoyl chloride (10.5 g, 0.075 mol) in pyridine (6 g). The resulting mixture was allowed to stir for 2 h at room temperature then poured onto ice−water and the mixture extracted with diethyl ether. The organic extract was washed with dilute HCl, water, and brine and finally dried over anhydrous sodium sulfate. After removal of solvent and vacuum distillation, *S*-*tert*-butyl thiobenzoate was obtained (6.64 g, 50.1% yield), bp 86 °C (0.8 mmHg). ^{1}H NMR, δ: 1.60 (s, 9H, C(C*H*$_3$)$_3$), 7.41 (m, 2H, *m*-Ar*H*), 7.54 (m, 1H, *p*-Ar*H*), 7.94 (d, 2H, *o*-Ar*H*). ^{13}C NMR,

Table 1. Molecular Weight and Conversion Data for Polymerization[a] of MMA at 60 °C in the Presence of Dithiobenzoate Derivatives

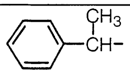
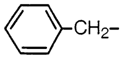
R	time (h)	M_n	M_w / M_n	Conv.[b] (%)	[**2**]$_0$ M	Cs
control	2.2	238320	1.93	20	0	
 **2a**	2	9800	1.27	14(15)	0.0116	(5.9)
	4	18000	1.19	27(27)		
	8	29800	1.15	52(50)		
	16	56200	1.12	95(96)		
 **2b**	2	8800	1.25	15(15)	0.0116	(6.6)
	4	16200	1.17	31(27)		
	8	30400	1.13	63(50)		
	16	52760	1.14	>95(96)		
 **2f**	3	11200	1.14	17(20)	0.0116	-
	16	55300	1.05	92(96)		
 $CH_3-\overset{CH_3}{\underset{CN}{C}}-$ **2e**	2	9200	1.26	16(15)	0.0116	(6.8)[c]
	4	16900	1.19	39(27)		
	8	30300	1.17	69(50)		
	16	52300	1.16	>90(96)		
 $CH_3-\overset{CH_3}{\underset{CO_2Et}{C}}-$ **2g**	2	29900	1.89	23(15)	0.0116	1.7
	4	35100	1.72	37(27)		(1.8)[c]
	8	39900	1.66	67(50)		
	16	52900	1.48	95(96)		
 **2h**	4	106300	1.69	37(27)	0.0112	-
	16	113600	1.65	95(96)		
 $CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-$ **2i**	0.5	87100	2.35	4(6)	0.0116	0.4
	2.2	125300	2.00	20(16)		(0.44)[c]
	4	132800	1.83	29(27)		
	16	130500	1.89	95(96)		
 $CH_3-\overset{CH_3}{\underset{CH_3}{C}}-$ **2j**	2	210900	2.03	18(15)	0.0116	(0.03)[c]
	4	267400	1.79	41(27)		
 $CH_3-\overset{CH_3}{\underset{CH_3}{C}}-S-$ **2k**	16	92100	1.34	63	0.0116	-

[a] Reaction medium: 75% (v/v) MMA in benzene ([MMA]$_0$ 7.02 M, [AIBN]$_0$ 6.10 × 10^{-3} M). [b] Numbers in parentheses are calculated conversions based on the molecular weights shown. [c] Transfer coefficients based on single point Mayo analysis are shown in parentheses (see text).

δ: 29.8 (SC(CH_3)$_3$), 48.0 (SC(CH_3)$_3$), 126.8 (*o*-Ar*C*), 128.3 (*m*-Ar*C*), 132.7 (*p*-Ar*C*), 138.6 (Ar-C1), 192.9 (C(=O)S). A mixture of *S*-*tert*-butyl thiobenzoate (1.94 g, 0.01 mol) and Lawesson's reagent (2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane-2,4-disufide) (2.43 g, 0.006 mol) in anhydrous toluene (10 mL) was refluxed for 25 h. After cooling to room temperature, the reaction mixture was concentrated and the residue subjected to column chromatography on silica with petroleum spirits/diethyl ether 19:1 as eluent. The title compound (**2j**) was obtained as a purple oil, 1.37 g (65.5%). ^{1}H NMR, δ: 1.69 (s, 9H, C(C*H*$_3$)$_3$), 7.36 (m, 2H, *m*-Ar*H*), 7.50 (m, 1H, *p*-Ar*H*), 7.88 (d, 2H, *o*-Ar*H*). ^{13}C NMR, δ: 28.2 (SC(CH_3)$_3$), 52.2 (SC(CH_3)$_3$), 126.6 (*o*-Ar*C*), 128.1 (*m*-Ar*C*), 131.7 (*p*-Ar*C*), 147.0 (Ar-C1). The signal due to C=S was not observed.

***tert*-Butyl Trithioperbenzoate (2k).** The procedure described by Aycock and Jurch[40] was applied. The crude reaction product was subjected to column chromatography on silica with *n*-hexane as eluent to give *tert*-butyl trithioperbenzoate (**2k**) as a dark purple oil in 60% yield. ^{1}H NMR, δ: 1.32 (s, 9H, C(C*H*$_3$)$_3$), 7.45 (m, 3H, *m*, *p*-Ar*H*), 8.00 (m, 2H, *o*-Ar*H*).

Table 2. Molecular Weight and Conversion Data for Bulk Polymerization of MMA at 60 °C in the Presence of Dithiobenzoate Derivatives[a]

R	M_n	M_w / M_n	Conv.(%)	$[\mathbf{2}]_o$ M	Cs
	244000	2.13	12	0	0.15
	232000	1.76	12	0.00167	
2c	199000	1.87	11	0.00465	
	165000	1.88	11	0.0122	
	262000	2.29	15	0	<0.03
	228000	1.87	14	0.0207	
2d	202000	1.94	13	0.0395	
	199000	1.82	13	0.0827	

[a] Reaction time 1 h, [AIBN] = 0.012 M.

Table 3. Molecular Weights and Conversions Observed in the Polymerization of MMA at 60 °C in the Presence of Cumyl Dithiobenzoate (2a)

$[\mathbf{2a}]_o$ (M × 10^2)	$[\mathrm{AIBN}]_o$ (M × 10^2)	reaction time (h)	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	convn (%)	convn (CTA)[a] (%)
2.900	5.67	0.5	5610	1.32	11	58
2.900	5.67	1	8570	1.28	22	75
2.900	5.67	2	14 700	1.24	88	
2.900	5.67	4	34 400	1.25	99	
2.910	0.556	1.5	4280	1.35	8.6	60
2.910	0.556	3	6940	1.29	19	85
2.910	0.556	9	11 900	1.23	42	
2.893	0.572	1	3500	1.38	5.4	45
2.893	0.572	4	9110	1.26	29	
2.893	0.572	16	30 300	1.22	>99	
2.883	0.0549	1	1790	1.35	1.1	5
2.883	0.0549	4	3230	1.36	5.2	47
2.883	0.0549	16	8110	1.26	26	
0.586	0.0587	2	12 800	1.43	6.1	75
0.586	0.0587	4	19 100	1.33	12	96
0.586	0.0587	8	33 700	1.20	22	

[a] Conversion of transfer agent evaluated using eq 6 with M_n(calcd) from eq 7.

Table 4. Molecular Weights and Conversions Observed in the Polymerization of MMA at 60 °C in the Presence of 2-Cyanoprop-2-yl Dithiobenzoate (2e)

$[\mathbf{2e}]_o$ (M × 10^2)	$[\mathrm{AIBN}]_o$ (M × 10^2)	reaction time (h)	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	convn (%)	convn (CTA)[b] (%)
2.901	4.405[a]	1	6710	1.26	20	95
2.901	4.405[a]	4	29 100	1.27	>99	
2.901	4.405[a]	16	31 000	1.29	>99	
2.937	0.462[a]	1	3380	1.41	6.5	65
2.937	0.462[a]	4	8500	1.20	28	
2.937	0.462[a]	16	31 900	1.23	>99	
2.941	0.589	1	3510	1.39	7.1	68
2.941	0.589	4	9000	1.19	32	
2.941	0.589	16	28 100	1.29	>99	
2.901	0.570	0.333	2550	1.50	1.5	20
2.901	0.570	0.667	3040	1.46	4.1	46
2.901	0.570	2	5200	1.32	14	86
2.931	0.0546	1	2660	1.40	1	13
2.931	0.0546	4	3850	1.38	7	61
2.931	0.0546	16	10 100	1.18	36	
0.576	0.577	1	13 900	1.39	7.2	82
0.576	0.577	2	26 600	1.59	15	
0.576	0.577	4	49 000	1.55	31	
0.576	0.577	8	152 300	3.32	97	
0.578	0.0585	0.75	8500	1.74	1.4	28
0.578	0.0585	1.5	9600	1.73	3.2	56
0.578	0.0585	3	13 600	1.51	7.1	85
0.578	0.0585	4	17 400	1.37	9.8	92
0.581	0.0585	1	9700	1.54	2.4	41
0.581	0.0585	2	12 400	1.42	5.4	71
0.581	0.0585	4	14 200	1.40	6.6	75
0.581	0.0585	8	30 000	1.29	18	

[a] Initiator: AIBMe, azobis(methyl isobutyrate). [b] Conversion of transfer agent evaluated using eq 6 with M_n(calcd) from eq 7.

Polymerizations. Monomers (Styrene Aldrich 99%, MMA Aldrich 99%, BA Aldrich 99+%, MA Aldrich 99%) were purified by filtration through neutral alumina (to remove inhibitors), fractionated under reduced pressure and flash distilled immediately prior to use. Azobis(isobutyronitrile) (AIBN) was obtained from Tokyo Kasei and recrystallized twice from chloroform−methanol. All concentrations are relate to an ambient temperature of 22 ± 2 °C. Unless stated otherwise, conversions were determined gravimetrically following drying to constant weight under vacuum and relate the total mass of product to the mass of monomer used. In applying these numbers in calculations these numbers were reduced by the initial amount of RAFT agent used. Gel permeation chromatography (GPC) was performed on a Waters Associates liquid chromatograph equipped with differential refractometer and a set of six Ultrastyragel columns (10^6, 10^5, 10^4, 10^3, 500, and 100 Å). Tetrahydrofuran (flow rate of 1.0 mL/min) was used as eluent at 22 ± 2 °C. The columns were calibrated with narrow polydispersity polystyrene or poly(methyl methacrylate) standards (data in Tables 3 and 4) obtained from Polymer Laboratories. Poly(butyl acrylate) molecular weights are reported in polystyrene equivalents. No precipitation or other form of fractionation was performed prior to analysis.

MMA Polymerizations. The following procedure is typical. A stock solution comprising MMA (15 mL), AIBN (20 mg), cumyl dithiobenzoate (**2a**) (60.7 mg), and benzene (5 mL) was prepared. Aliquots (4 mL) were transferred to four ampules, degassed with three freeze−evacuate−thaw cycles and sealed. The ampules were heated at 60±1 °C in a thermostated oil bath for the times indicated in Table 1. The excess monomer and solvent removed by evaporation at ambient temperature under vacuum and the residues analyzed directly by GPC.

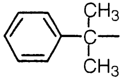
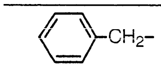
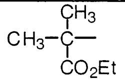
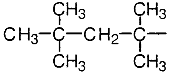
The conditions used and results of MMA polymerizations are shown in Tables 1−4.

Styrene Polymerizations. The following procedure is typical. A stock solution comprising styrene (60 mL) and AIBN (16.9 mg) was prepared. Aliquots (5 mL) were removed and transferred to ampules containing benzyl dithiobenzoate (**2d**) (11.4 mg). The ampules were degassed with three freeze−evacuate−thaw cycles, sealed and heated at 60 ± 1 °C for the periods of time indicated in Table 5. The excess monomer and solvent removed by evaporation at ambient temperature under vacuum and the residues analyzed directly by GPC.

The conditions used and results of styrene polymerizations are summarized in Table 5.

Polymerizations of Acrylate Esters. The following procedure is typical. Two stock solutions were prepared (a) comprising AIBN (13.4 mg) in benzene (50 mL) and (b) comprising benzyl dithiobenzoate (**2d**) (9.62 mg) in benzene (10 mL). Aliquots of these solutions (4 mL of solution a and 2

Table 5. Molecular Weight and Conversion Data for Bulk[a] Polymerization of Styrene at 60 °C in the Presence of Dithiobenzoate Derivatives

R	time (h)	$\bar{M}_n$	$\bar{M}_w / \bar{M}_n$	Conv. (%)	$[\mathrm{AIBN}]_o$ M	$[\mathbf{2}]_o$ M
control	1	164000	1.83	1.6	0.0017	
 **2a**	1	833	1.12	0.5	0.0017	0.0083
	4	4510	1.09	4		
	20	21500	1.14	19		
	50	40000	1.17[a]	37		
	100	52000	1.18[a]	57		
 **2d**	1	1500	1.36	0.7	0.0017	0.0093
	2	2260	1.27	1.5		
	4	3630	1.24	3.5		
	8	6020	1.21	6.9		
	12	8900	1.16	11		
	16	11800	1.16	14		
	20	14400	1.13	17		
	30	18500	1.12	22		
	50	25200	1.17[b]	32		
	100	33400	1.13[b]	42		
 $CH_3-C(CH_3)(CO_2Et)-$ **2g**	2	1630	1.13	2	0.0017	0.0084
	4	3500	1.12	4		
	20	24200	1.15	26		
 $CH_3-C(CH_3)_2-CH_2-C(CH_3)_2-$ **2i**	2	495	1.13	0.6	0.0017	0.0084
	4	1180	1.14	1.2		
	20	17400	1.19	19		

[a] Bulk [styrene] = 8.728 M. [b] Bimodal distribution observed.

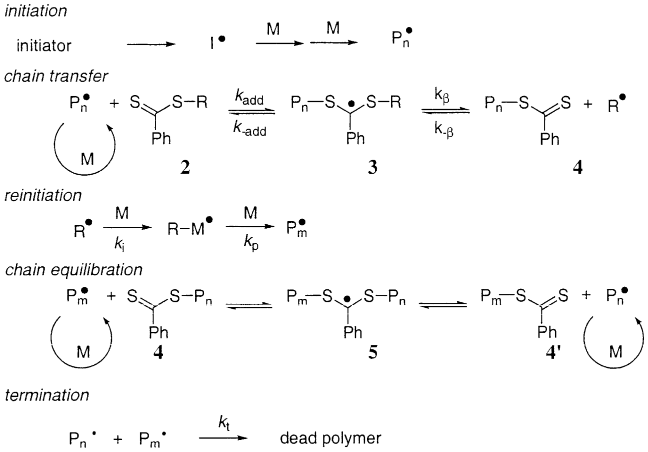
mL of solution b) were transferred to ampules containing BA (2 mL). The ampules were degassed with three freeze−evacuate−thaw cycles, sealed, and heated at 60 ± 1 °C for the periods of time indicated. The excess monomer and solvent removed by evaporation under vacuum and the residues analyzed directly by GPC. The results of this and related polymerizations are summarized in Table 6.

ω-(Thiobenzoylthio)polystyrene. The ω-(thiobenzoylthio)polystyrene was prepared as follows: A solution comprising AIBN (28 mg) and cumyl dithiobenzoate (**2a**) (228 mg) styrene (100 mL) was prepared, transferred to an ampule, degassed, and sealed. The solution was heated at 60 °C for 30.5 h. The ω-(thiobenzoylthio)polystyrene isolated by evaporation of the residual monomer under reduced pressure (18.8 g, 21% conversion) had $\bar{M}_n$ 20 300, $\bar{M}_w/\bar{M}_n$ 1.15.

Polymerization of Methyl Methacrylate in the Presence of ω-(Thiobenzoylthio)polystyrene. The above ω-(thiobenzoylthio)polystyrene (0.5 g) was dissolved in tetrahydrofuran and the solution transferred to an ampule. The tetrahydrofuran was removed under reduced pressure, and AIBN (3.88 mg) and MMA (2 mL) were added. The solution was degassed, sealed in an ampule, and heated at 60 °C for 3.8 h. After removal of the unreacted styrene, the product was analyzed by GPC, and the mixture comprised apparently unchanged ω-(thiobenzoylthio)polystyrene and poly(methyl methacrylate): $\bar{M}_n$ 290 000, $\bar{M}_w/\bar{M}_n$ 2.63 (conversion ca. 70%).

Polystyrene-*block*-poly(4-methylstyrene). ω-(Thiobenzoylthio)polystyrene (0.5 g, $\bar{M}_n$ 20 300, $\bar{M}_w/\bar{M}_n$ 1.15, prepared as described above), 4-methylstyrene (2 mL), AIBN (2.5 mg), and benzene (0.5 mL) were transferred to an ampule. The resulting solution was degassed, sealed, and heated at 60 °C for 3 h. Volatiles were removed under reduced pressure to give polystyrene-*block*-poly(4-methylstyrene) (0.81 g, 17.1% conversion, $\bar{M}_n$ 25 400, and $\bar{M}_w/\bar{M}_n$ 1.19).

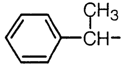
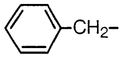
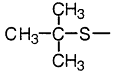
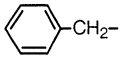
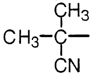
Scheme 2. Mechanism of RAFT Polymerization



Polystyrene-*block*-poly(*N*,*N*-dimethylacrylamide). ω-(Thiobenzoylthio)polystyrene (0.2 g, $\bar{M}_n$ 20 300, $\bar{M}_w/\bar{M}_n$ 1.15, prepared as described above), *N*,*N*-dimethylacrylamide (2 mL), AIBN (0.5 mg), and benzene (8 mL) was transferred to an ampule. The resulting mixture was degassed, sealed and heated at 60 °C for 1 h. The volatiles were removed in vacuo to give polystyrene-*block*-poly(*N*,*N*-dimethylacrylamide) at 0.4 g, 10.4% conversion, with $\bar{M}_n$ 43 000 and $\bar{M}_w/\bar{M}_n$ 1.24 (GPC with *N*,*N*-dimethylformamide eluent at 1 mL/min).

Polymerization of Styrene in the Presence of ω-(Thiobenzoylthio)poly(methyl methacrylate). The ω-(thiobenzoylthio)(methyl methacrylate) was prepared as follows: A solution comprising AIBN (53 mg), cumyl dithiobenzoate (**2a**) (160 mg) MMA (40 mL), benzene (13 mL) was prepared and

Table 6. Molecular Weight and Conversion Data for Polymerization of Acrylate Esters[a] at 60 °C in the Presence of Dithiobenzoate Derivatives

Monomer	R	time (h)	M_n[d]	M_w/M_n	Conv. (%)
BA[a] 2.79 M	 **2c** 0.0016 M	2	33600	1.13	-
BA[a] 2.79 M	 **2d** 0.0016 M	2	26200	1.12	11
		8	91700	1.14	40
BA[a] 2.79 M	 $CH_3-C(CH_3)_2-S-$ **2k** 0.0016 M	2	12700	1.12	7
		8	78400	1.07	41
		16	117600	1.14[f]	61
		40	174000	1.24[f]	82
MA 4.45 M	control	1	> 1640000[e]	-	22
MA[b] 4.45 M	 **2d** 0.0037 M	1	1470 (1240)	1.30	0.64
		2	3260 (2440)	1.20	2.3
		3	5340 (4350)	1.16	4.6
		16	43100	1.10	29
		24	56700	1.14[f]	39
		48	84700	1.18[f]	57
		64	94400	1.25[f]	64
MA[c] 4.43 M	**2d** 0.006 M	1	980 (750)	1.29	0.67
		2	1480 (1150)	1.29	1.4
		3	2120 (1660)	1.29	2.4
MA[b] 4.45 M	 $CH_3-C(CH_3)(CN)-$ **2e** 0.0037 M	1	420 (230)	1.34	0.41
		2	3200 (2490)	1.14	2.4
		3	6300 (5160)	1.09	4.6
		4	9700 (8000)	1.07	7.4

[a] Reaction medium: 40% (v/v) BA in benzene ($[BA]_0$ = 2.79 M, $[AIBN]_0$ = 0.00032 M, and $[\mathbf{2}]_0$ = 0.0016 M. [b] $[MA]_0$ = 4.45 M, [AIBN] = 0.00033 M, and $[\mathbf{2}]_0$ = 0.0037 M. [c] $[MA]_0$ = 4.43 M, [AIBN] = 0.00033 M, and $[\mathbf{2}]_0$ = 0.006 M. [d] Values in parentheses from universal calibration with Mark Houwink constants for poly(methyl acrylate): K = 0.000261 and α = 0.659.[76] [e] Part of the molecular weight distribution exceeds upper exclusion limit of column set. [f] Bimodal distribution observed.

transferred to an ampule, which was degassed and sealed. The solution was heated at 60 °C for 4 h. The ω-(thiobenzoylthio)-poly(methyl methacrylate) was isolated by evaporation of the solvent and residual monomer under reduced pressure (10.3 g, 25% conversion) had $\bar{M}_n$ 14 700, $\bar{M}_w/\bar{M}_n$ 1.21).

The reaction time was chosen to give an approximate doubling of the molecular weight under conditions similar to those used in styrene homopolymerization. The above poly(methyl methacrylate) (1.7 g) was dissolved in ethyl acetate and the solution transferred to an ampule. The ethyl acetate was removed under reduced pressure, and AIBN (2.82 mg) and styrene (10 mL) were added. The solution was degassed, sealed in an ampule, and heated at 60 °C for 20 h. After removal of volatiles, poly(methyl methacrylate)-*block*-polystyrene was obtained (3.9 g, 23.5% conversion) with $\bar{M}_n$ 35 000, $\bar{M}_w/\bar{M}_n$ 1.24. No residual poly(methyl methacrylate) was apparent in the GPC chromatogram.

Kinetic Simulation. Kinetic simulation was performed by directly solving the differential equations associated with the mechanism as defined in Scheme 2 and using the method of moments as described in an earlier publication.[41] In the present work, numerical integration was performed using the Mathematica 4.1 (Wolfram Research Inc.) function NDSolve.

For the kinetic simulation of styrene polymerization, it was assumed that k_{add} does not depend on R and is $12000k_p$ M^{-1} s^{-1}. This value is based on the value of C_{tr} of ~6000 estimated by Goto et al.[30] for **2m** ($\bar{M}_n$ ~ 2000) at 60 °C. The rate constant ($k_{-\beta}$) for benzyl or cumyl adding to the polymeric RAFT agent has been taken as $12000k_i$ M^{-1} s^{-1}.[42] Differences in the transfer coefficient for the various RAFT agents are then due to differences in the partition coefficient (1:1 for the polystyryl propagating radical, 1:29 for benzyl, and 1:5 for cumyl). The polymerization kinetics are insensitive to $k_\beta > 10$ s^{-1}. A lower k_β causes a broadening of the molecular weight distribution for low conversions and much lower values lead to retardation. A value of $k_\beta = 1000$ s^{-1} was used; the actual value may be higher or lower than this. Other rate constants used in the simulation are $k_p = 340$ M^{-1} s^{-1},[43] $k_t = 1.08 \times 10^8$ M^{-1} s^{-1},[44]

$k_{tc}/(k_{tc} + k_{td}) = 1$, $k_d = 9.65 \times 10^{-6}$ M^{-1} s^{-1},[4] and $f = 0.6$, and k_i (for benzyl, cumyl, and 2-cyanoprop-2-yl) was as shown in Table 10.

Molecular Orbital Calculations. Semiempirical molecular orbital calculations were performed with MOPAC 6.0 using the ChemBats3D Ultra package on an Apple Macintosh computer as the graphical user interface. For each compound a complete energy minimization was carried out using the keyword "PRECISE". For radical species the keyword "UHF" was specified. Multiple conformations were used a starting points for geometry optimization to ensure a global minimum was achieved.

The AM1 Hamiltonian was used for all calculations reported in this paper. Use of the PM3 Hamiltonian was also briefly explored. The trend in LUMO energies was the same. The AM1 was finally selected over the PM3 Hamiltonian as it provides better heat of formation data for free radical species.[45]

Results and Discussion

Transfer Coefficient Estimation. The Mayo equation[46] may be used to estimate transfer coefficients of dithiobenzoates in circumstances where the consumption of dithiobenzoate and monomer are negligible. For the case of the less active dithiobenzoates, these conditions are easily met in low conversion polymerizations. We have used this method to estimate transfer coefficients of the less active dithiobenzoates in MMA polymerization (Table 2). For the case of the more active dithiobenzoates, which provide very narrow polydispersities, and where the molecular weight is seen to increase with conversion even at very low conversion, direct application of the Mayo method will underestimate the transfer coefficient and a different approach is required.

In the case of reversible chain transfer, the rate of consumption of the transfer agent depends on two transfer coefficients, C_{tr} ($=k_{tr}/k_p$) and C_{-tr} ($=k_{-tr}/k_i$), which describe the reactivity of the propagating radical ($P_n^\bullet$), and the expelled radical ($R^\bullet$) respectively (see eq 1).[47]

$$\frac{d[\mathbf{2}]}{d[M]} \approx C_{tr} \frac{[\mathbf{2}]}{[M] + C_{tr}[\mathbf{2}] + C_{-tr}[\mathbf{4}]} \quad (1)$$

In chain transfer by addition–fragmentation (Scheme 2), the rate constant for chain transfer (k_{tr}) is given by the following expression (eq 2).[48]

$$k_{tr} = k_{add} \times \frac{k_\beta}{k_{-add} + k_\beta} \quad (2)$$

Similarly (eq 3)

$$k_{tr} = k_{-\beta} \times \frac{k_{-add}}{k_{-add} + k_\beta} \quad (3)$$

These relationships assume that adduct **3** undergoes no reactions other than fragmentation.

If the rate of the reverse reaction between $R^\bullet$ and the polymeric RAFT agent (**4**) is negligible, and chains are long, this expression (eq 1) simplifies to eq 4 that also describes conventional chain transfer.[49]

$$\frac{d[\mathbf{2}]}{d[M]} \approx C_{tr} \frac{[\mathbf{2}]}{[M]} \quad (4)$$

$$C_{tr} = \frac{k_{tr}}{k_p} \approx \frac{[M]\, d[\mathbf{2}]}{[\mathbf{2}]\, d[M]} = \frac{d(\ln[\mathbf{2}])}{d(\ln[M])} \quad (5)$$

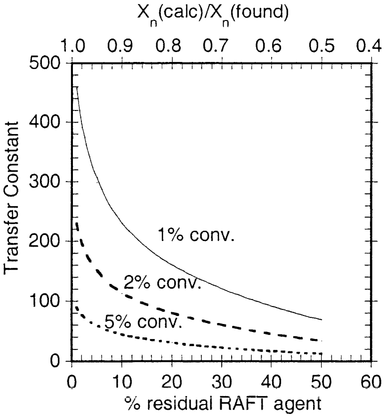


Figure 1. Relationship between transfer constant and the amount of residual RAFT agent for various monomer conversions.

In this case, the slope of a plot of ln[M] vs ln[**2**] yields the transfer coefficient. If the rate of the reaction of $R^\bullet$ with the polymeric RAFT agent (**4**) is not negligible, the transfer coefficient obtained from such a plot will be lower than the actual transfer constant. The fit of experimental data to eq 5 or the Mayo equation does not prove that the reaction of $R^\bullet$ with the polymeric RAFT agent (**4**) is negligible. For this reason the term transfer coefficient has been adopted rather than transfer constant to refer to numbers obtained by either the Mayo method or by application of eq 5.

A simple method of evaluating the conversion of transfer agent is based on a comparison of found and calculated molecular weights (eq 6).

$$\text{conversion of } \mathbf{2} = \frac{[\mathbf{2}]_o - [\mathbf{2}]_t}{[\mathbf{2}]_o} = \left\{\frac{[M]_o - [M]_t}{[\mathbf{2}]_o}\right\} \Big/ \left\{\frac{[M]_o - [M]_t}{[\mathbf{2}]_o - [\mathbf{2}]_t}\right\} = \frac{\bar{X}_n(\text{calcd})}{\bar{X}_n(\text{found})} \quad (6)$$

where $\bar{X}_n$(calcd) is the expected number-average degree of polymerization assuming complete consumption of transfer agent and $\bar{X}_n$(found) is the measured number-average degree of polymerization. In some cases, a small correction is needed to allow for initiator-derived chains (see below).

It is useful to at least place a lower limit on the value of the transfer constant in circumstances where the found and calculated molecular weights agree (or are within experimental error) at the first conversion time point. If the found and calculated degrees of polymerization (or molecular weights) agree, it suggests that the transfer agent is completely consumed (no residual RAFT agent). With eqs 5 (or 1), it is possible to predict the dependence of the amount of residual transfer agent on the transfer coefficient for a given monomer conversion. Figure 1 shows this dependence for three different monomer conversions (1%, 2%, and 5%) estimated using eq 5.

In principle, transfer coefficients of RAFT agents may also be estimated from the rate at which the polydispersity or weight-average molecular weight reduces with conversion/time. Kinetic simulation shows that these parameters are more sensitive to variations in the transfer coefficient than is the number-average molecular weight. Polydispersities depend on the transfer coefficients of *both* the initial RAFT agent (**2**) and those of the polymeric species (**4**) formed during polymeriza-

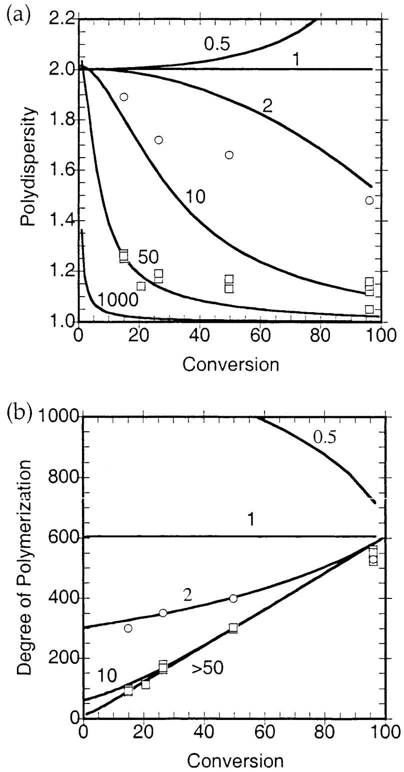
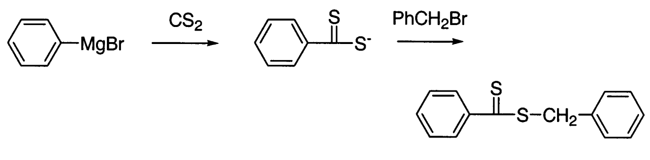


Figure 2. Predicted dependence of (a) polydispersity and (b) degree of polymerization on conversion in polymerizations involving reversible chain transfer as a function of the chain transfer constant. Predictions are based on equations proposed by Mueller et al.[50,51] with $\alpha = 10^{-7}$, β as indicated, and $\gamma = 605$. Experimental data points are for methyl methacrylate polymerization in the presence of dithiobenzoate esters PhC(=S)SR (0.0116 M) where R = $-C(Me)_2CO_2Et$ (**2g**) (○) and R = $-C(Me)_2Ph$ (**2a**) (□). For reaction conditions, see Table 1.

tion. Recent work of Goto et al.[30] suggests that ω-(thiobenzoylthio)poly(methyl methacrylate) (**2l**) and ω-(thiobenzoylthio)polystyrene (**2m**) have transfer coefficients of >6000 and ca. 140 at 60 °C in styrene and MMA polymerizations, respectively. The transfer coefficients of other polymeric dithiobenzoates are unknown. However, for the systems included in the present study, the transfer coefficient of the polymeric RAFT agents (in the monomer from which they are formed) do not appear to be a limiting factor. We have used polydispersities predicted by kinetic simulation to estimate C_{tr} and C_{-tr} for benzyl and cumyl dithiobenzoates in styrene polymerization (see below).

There has been some use of equations derived by Mueller et al.[50,51] to describe polymerization with reversible chain transfer to predict molecular weights and polydispersities in RAFT polymerization (Figure 2).[52,53] Use of these equations requires an assumption that the rate of consumption of the initial RAFT agent (**2**) is not kinetically significant and that there is no radical–radical termination (or other side reactions). Full kinetic simulations carried out based on numerical integration of the appropriate differential equations (i.e. including initiation and radical–radical termination) using methods described previously[41] demonstrate the validity of these equations and indicate they provide a reasonable estimate of the molecular weight and polydispersity for low monomer conversions (<20% for MMA polymerization, <5% for styrene polymerization under the reaction conditions used in this work) as long as $C_{-tr}(\mathbf{2})$ is negligible. It is also clear from Figure 2 that for high $C_{tr}(\mathbf{2})$ polydispersities are more sensitive to the value of the transfer coefficient than are the number-average molecular weights. The simulations also show that, with $C_{tr}(\mathbf{4}) \gg C_{tr}(\mathbf{2})$ and $C_{-tr}(\mathbf{2})$ negligible, the predicted polydispersities are independent of the precise value of $C_{tr}(\mathbf{4})$ and are indicative of the value of $C_{tr}(\mathbf{2})$. Polydispersities predicted with these equations can therefore be useful for placing a lower limit on the transfer coefficient and for initial parameter estimation. A finding that polydispersities reduce with conversion at a rate greater than suggested by these equations is evidence that $C_{-tr}(\mathbf{2})$ is not negligible.

Scheme 3



Scheme 4

Calculated Molecular Weights. Molecular weights in RAFT polymerizations were calculated using eq 7.

$$\bar{M}_n(\text{calcd}) = \frac{[\mathrm{M}]_o - [\mathrm{M}]_t}{[\mathbf{2}]_o + df([\mathrm{I}]_o - [\mathrm{I}]_t)}\,m \qquad (7)$$

where m is the monomer molecular weight.

$df([\mathrm{I}]_o - [\mathrm{I}]_t)$ is the number of initiator-derived chains produced and

$$[\mathrm{I}]_o - [\mathrm{I}]_t = [\mathrm{I}]_o(1 - e^{-k_d t}) \qquad (8)$$

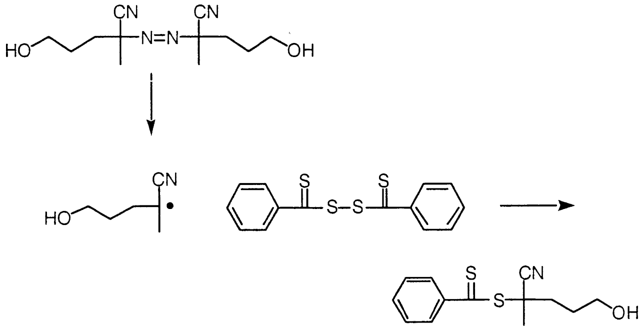
where k_d is the rate constant for initiator decomposition, f is the initiator efficiency (for AIBN at 60 °C,[4] $k_d = 9.65 \times 10^{-6}$ M^{-1} s^{-1}, and $f = 0.6$) and d is the number of chains produced from radical–radical reaction ($d = 1.67$ for MMA and $d = 1.0$ for styrene). These parameters should generally hold for low conversions <50%. For higher conversions use of these parameters will overestimate the number of initiator-derived chains and it is necessary to allow for the decrease in the initiator efficiency with conversion.[54] In many experiments (those with short reaction times or low initiator concentrations) the term $df([\mathrm{I}]_o(1 - e^{-k_d t})$ is small with respect to $[\mathbf{2}]_o$ and can be neglected.

Synthesis of Dithiobenzoate Derivatives. Dithiobenzoate derivatives are available in moderate to excellent yields by a variety of methods. For a summary of the literature on dithioester synthesis see review.[55] Sudalai et al.[56] have described a method based on the use of phosphorus pentasulfide which reportedly provides dithiobenzoates in high yields. The four methods have been used in this work are summarized below.

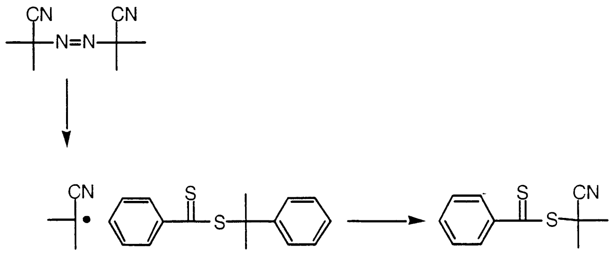
(a) The first is sequential treatment of a phenyl Grignard reagent with carbon disulfide and an alkylating agent (typically an alkyl bromide) in a "one pot" procedure (Scheme 3).[37] This process was used to prepare benzyl dithiobenzoate (**2d**) (62% yield), 2-(ethoxycarbonyl)prop-2-yl dithiobenzoate (**2g**) (42% yield) and 2-cyanoprop-2-yl dithiobenzoate (**2e**)[19] (43% yield).

(b) Second is addition of dithiobenzoic acid across an olefinic double bond (Scheme 4).[57] Dithiobenzoic acid is readily prepared by oxidation of benzyl chloride with

Scheme 5



Scheme 6



elemental sulfur.[58] Dithiobenzoic acid is unstable and should be used immediately or stored at low temperature (<−20 °C). The process was used to prepare cumyl dithiobenzoate (**2a**) from α-methylstyrene (33% yield),[19] 1-phenylethyl dithiobenzoate (**2c**) from styrene (43% yield), 2-(4-chlorophenyl)prop-2-yl dithiobenzoate (**2b**) from 4-chloro-α-methylstyrene (34% yield), and 2,4,4-trimethylpent-2-yl dithiobenzoate (**2i**) (32% yield). It (Scheme 4) cannot be used to prepare tertiary dithiobenzoates from electrophilic monomers (e.g. MMA, MAN) where the primary dithiobenzoate is formed preferentially.[57]

(c) Third is radical-induced decomposition of bis(thiobenzoyl) disulfide (Scheme 5). The procedure was used to prepare 4-cyano-1-hydroxypent-4-yl dithiobenzoate (**2j**) (46% yield) and 2-[*N*-(2-hydroxyethyl)carbamoyl]prop-2-yl dithiobenzoate (**2h**) (18% yield) with the corresponding azo-compound as the source of free radicals. This route is described in a recent communications and appears to be the method of choice for preparing functional tertiary dithiobenzoates.[21,59,60]

(d) Finally there is radical-induced ester exchange. Treatment of a dithiobenzoate ester with a source of free radicals can result in ester exchange as shown in Scheme 6. The reaction was used to prepare 2-cyanoprop-2-yl dithiobenzoate (**2e**) from cumyl dithiobenzoate (**2a**) (>90% yield) with AIBN as the source of free radicals. The R group of the precursor dithiobenzoate should be a good free radical leaving group with respect to desired R group. For example, benzyl dithiobenzoate appears not to react with the 2-cyanoprop-2-yl radical (though it may react reversibly). It appears essentially unchanged (NMR) after heating with AIBN in benzene at 80 °C.

All RAFT agents were purified by column chromatography, crystallization and/or distillation as appropriate and their purity established by NMR analysis and thin-layer chromatography prior to use. The yields quoted are for the isolated and purified products, reaction conditions have not been optimized. Confirmation of identity in the case of novel compounds also came from high-resolution chemical ionization mass spectrometry.

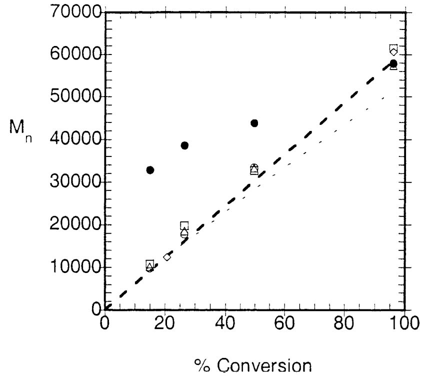


Figure 3. Evolution of molecular weight with conversion for polymerization of methyl methacrylate (7.02 M in benzene) at 60 °C with AIBN initiator (0.0061 M) in the presence of dithiobenzoate esters PhC(=S)SR (0.0116 M) where R = $-C(Me)_2CO_2Et$ (**2g**) (●), R = $-C(Me)_2Ph$ (**2a**) (□), R = $-C(Me)_2C_6H_4Cl$ (**2b**) (○), R = $-C(Me)_2CN$ (**2e**) (△), or R = $-C(Me)(CN)CH_2CH_2CH_2OH$ (**2f**) (◇). For experimental details, see Table 1. Key: calculated molecular weights assuming no initiator-derived chains (− −); calculated molecular weight including initiator-derived chains (- - -) based on *df* = 1.0.

Influence R Substituent on the Activity of Dithiobenzoate Derivatives. To examine the effect of the R substituent on RAFT polymerization in greater detail, polymerizations of MMA, styrene, and MA or BA have been carried out in the presence of a series of dithiobenzoate derivatives (**2**). Polymerizations were conducted at 60 °C either in bulk or in benzene solution for various reaction times and conversions. For MMA and styrene polymerization, the concentration of RAFT agent was chosen to be sufficiently low to avoid the substantial retardation that may be observed when high concentrations of RAFT agents are used (*e.g.* cumyl dithiobenzoate—see further discussion below).[19] The rate of polymerization of butyl acrylate, and other acrylates, is significantly retarded by dithiobenzoate derivatives.[19] The results (values of molecular weight and polydispersity vs conversion) obtained are summarized in Tables 1−6.

MMA Polymerization. Data for MMA polymerizations carried out in the presence of a series of dithiobenzoates (**2**) under a standard set of reaction conditions (60 °C, 7.02 M in benzene solvent) are shown in Table 1 and Figures 3 and 4. Under these conditions, the ability of dithiobenzoate derivatives [**2**, S=C(Ph)S−R] to give narrow polydispersity and molecular weight control decreases in the order where R is $-C(CH_3)(CH_2CH_2CH_2OH)CN > -C(Me)_2CN \sim -C(Me)_2Ar > -C(Me)_2C(=O)OEt > -C(Me)_2C(=O)NH\text{-}(alkyl) > -C(Me)_2CH_2C(Me)_3, \geq -C(Me)HPh > -C(Me)_3 \sim -CH_2Ph$.

Of the compounds listed, only the tertiary cyanoalkyl (**2e**,**f**) and cumyl dithiobenzoates (**2a**,**b**) give substantially narrowed polydispersities under the present reaction conditions. The close correspondence between found and calculated molecular weights (see Figure 3) indicates that the RAFT agent is largely consumed at the first time point (<15% conversion of monomer) and therefore these data do not permit a direct estimate of the transfer coefficient. Relatively high transfer coefficients (>10) are also indicated by the narrow polydispersity polymers (<1.3) that are obtained even at the first conversion point (Figure 2). The transfer coefficients of compounds **2a** and **2e** were evaluated in separate experiments where the polymerization was

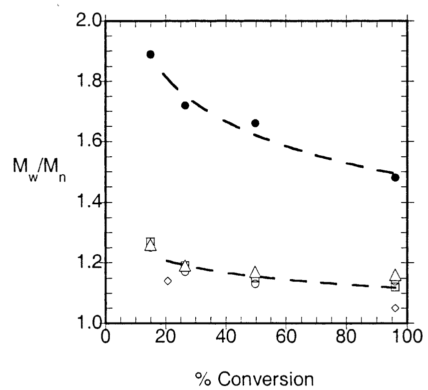


Figure 4. Evolution of polydispersity with conversion for polymerization of methyl methacrylate (7.02 M in benzene) at 60 °C with AIBN initiator (0.0061 M) in the presence of dithiobenzoate esters PhC(=S)SR (0.0116 M) where R = $-C(Me)_2CO_2Et$ (**2g**) (●), R = $-C(Me)_2Ph$ (**2a**) (□), R = $-C(Me)_2C_6H_4Cl$ (**2b**) (○), R = $-C(Me)_2CN$ (**2e**) (△), or R = $-C(Me)(CN)CH_2CH_2CH_2OH$ (**2f**) (◇). For experimental details, see Table 1.

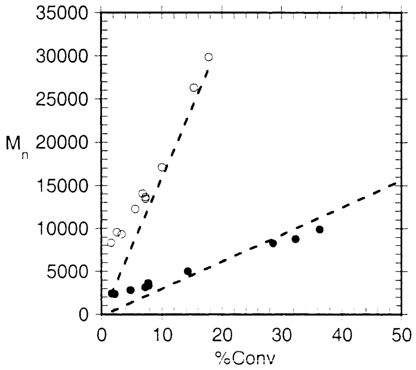


Figure 5. Plot of molecular weight vs conversion for polymerization of methyl methacrylate in the presence of PhC(=S)-$SC(Me)_2CN$ (**2e**).[47] Data are for bulk MMA polymerization at 60 °C with AIBN initiator in the range 0.0005−0.04 and 0.0058 M (●) or 0.029 M (○) cumyl dithiobenzoate as RAFT agent. For additional details, see Table 4.

carried out in bulk and some experiments were carried to relatively low conversions of monomer and RAFT agent (Tables 3 and 4, respectively). A plot of molecular weight vs conversion shows that the transfer agent is not fully consumed to at least 20% conversion (for **2e**, see Figure 5). For these compounds the transfer coefficients (obtained by direct use of eq 5) depend on RAFT agent concentration (see Figures 6 and 7; apparent $C_{tr} = 9$ with 0.029 M **2a**, 25 with 0.0058 M **2a**; apparent $C_{tr} = 13$ with 0.029 M **2e**, 21 with 0.0058 M **2e**). In these circumstances, the rate of consumption of RAFT agent is determined by eq 1. This equation can be solved numerically and $C_{tr} = 56$, $C_{-tr} = 2500$ for **2a**[61] and $C_{tr} = 25$, $C_{-tr} = 450$ for **2e** (bulk MMA, 60 °C) provides a good fit to the experimental data (see Figures 6 and 7). This means that 2-cyanoprop-2-yl dithiobenzoate (**2e**), even though it has a lower C_{tr}, is more effective than cumyl dithiobenzoate (**2a**) for high concentrations of RAFT agent. Both reagents are highly effective when using low RAFT agent concentrations (≤0.03 M) to make higher molecular weight polymers.

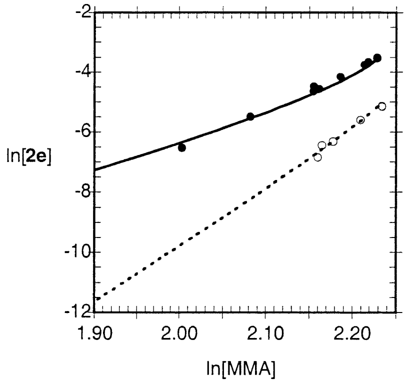


Figure 6. Double log plot of transfer agent concentration vs monomer concentration for polymerization of methyl methacrylate in the presence of $PhC(=S)SC(Me)_2Ph$ (**2a**).[47] Data are for bulk MMA polymerization at 60 °C with AIBN initiator in the range 0.0005−0.04 and 0.0058 M (●) or 0.029 M (○) **2a** as RAFT agent. For additional details, see Table 3. Lines are those predicted by eq 1 with $C_{tr} = 56$ and $C_{-tr} = 2500$.

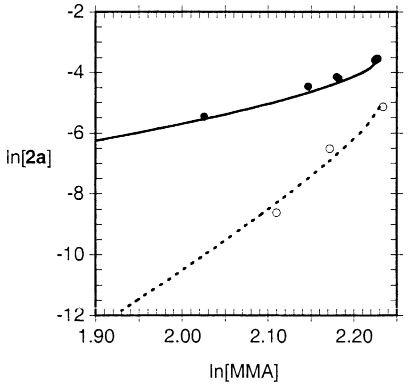


Figure 7. Double log plot of transfer agent concentration vs monomer concentration for polymerization of methyl methacrylate in the presence of $PhC(=S)SC(Me)_2CN$ (**2e**).[47] Data are for bulk MMA polymerization at 60 °C with AIBN initiator in the range 0.0005−0.04 and 0.0058 M (●) or 0.029 M (○) **2e** as RAFT agent. For additional details, see Table 4. Lines are those predicted by eq 1 with $C_{tr} = 25$ and $C_{-tr} = 450$.

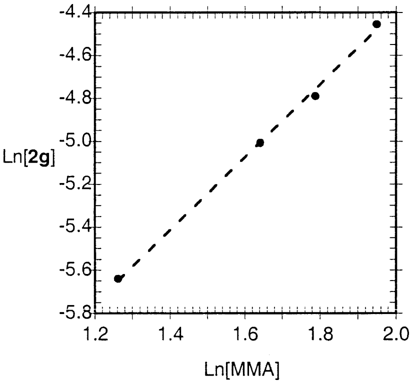


Figure 8. Double log plots of transfer agent concentration vs monomer concentration for polymerization of methyl methacrylate (7.02 M in benzene) at 60 °C with AIBN initiator (0.0061 M) in the presence of $PhC(=S)SC(Me)_2CO_2Et$ (0.0116 M **2g**). For additional experimental details, see Table 1. Line of best fit is −7.792 +1.6981 ln[M]; correlation coefficient = 0.99877.

When R = $-C(Me)_2CO_2Et$ (**2g**) the polydispersity reduces with conversion to a final value of $\bar{M}_w/\bar{M}_n = 1.5$ (Figure 4). The molecular weights predicted for low conversions are significantly higher than those expected based on complete consumption of the RAFT agent (see Figure 8). The difference between found and calculated molecular weights enables the conversion of transfer agent to be estimated (from eq 5) and a plot of ln[**2g**] vs ln[M] suggests a transfer coefficient of ca. 1.7 at 60 °C (Figure 8).

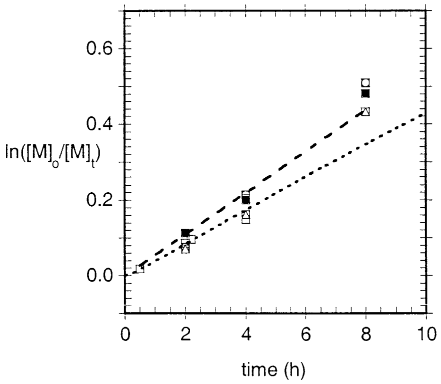


Figure 9. Kinetic plot for polymerization of methyl methacrylate (7.02 M in benzene) at 60 °C with AIBN initiator (0.0061 M) in the presence of dithiobenzoate esters PhC(=S)-SR, where R = $-C(Me)_2CO_2Et$ (**2g**) (●), R = $-C(Me)_2Ph$ (**2a**) (□), R = $-C(Me)_2C_6H_4Cl$ (**2b**) (○), R = $-C(Me)_2CN$ (**2e**) (△), or R = $-C(Me)(CN)CH_2CH_2CH_2OH$ (**2f**) (◇). For experimental details see Table 1. Key: (— —) a line of best fit; (- - -) result of kinetic simulation.

The dithiobenzoates with R = $-C(Me)_2CH_2C(Me)_3$ (**2i**), $-C(Me)HPh$ (**2c**), $-C(Me)_3$ (**2j**), and $-CH_2Ph$ (**2d**) appear ineffective as RAFT agents in MMA polymerization. No significant narrowing of the molecular weight distribution was observed (see Tables 1 and 2). No molecular weight control of the form expected for a living polymerization was obtained. There is only a small (≤2-fold) decrease in molecular weight with respect to the control. These poor results are attributed to these compounds having relatively low transfer coefficients in MMA polymerization. The transfer coefficients of **2i**, **2c**, **2j**, and **2d** at 60 °C were determined either using the conventional Mayo method or by analysis of the rate of RAFT agent consumption and are estimated to be ca. 0.4, 0.15, 0.03, and 0.03, respectively.

The compound with R = $-StBu$ (**2k**) provides a narrow polydispersity product suggesting a high transfer coefficient. However, molecular weights are significantly higher than expected based on the concentration of RAFT agent. This is attributed to the instability of the trithioperbenzoate under the reaction conditions causing the concentration of the reagent to be lower than expected.

The effectiveness of dithiobenzoate derivatives in promoting living polymerization of MMA thus depends strongly on the nature of R.

For the polymerizations reported in Table 1, the rate of polymerization shows no marked dependence of the particular dithiobenzoate derivative used (Figure 9), and while the rate of polymerization is slow with respect to the rate of polymerization expected in the absence of RAFT agent, it appears slightly accelerated when compared to the rate expected in the absence of a gel effect (that predicted by kinetic simulation with low conversion propagation and termination rate constants). For the polymerizations reported in Tables 3 and 4, a plot of log[initial rate of polymerization] vs log[AIBN] shows the (initial) rate of polymerization to be 0.5 order in initiator (as expected for conventional radical polymerization initiated by AIBN) and over a 5-fold range of RAFT agent concentrations (0.0006−0.003 M of **2a** or **2e**) and the rate of polymerization seems independent of the RAFT agent concentration (Figure 10)[19] with slight retardation apparent only for the highest concentration of **2a**. For higher concentrations of **2a,** polymerization may be strongly retarded.[61]

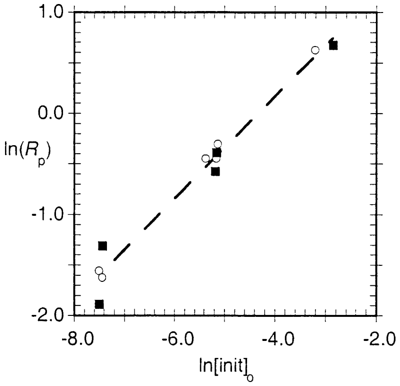


Figure 10. Plot of log (initial R_p) vs log (initial initiator concentration). Data are for bulk MMA polymerization at 60 °C with AIBN initiator (0.0005−0.04 M) and either cumyl (■) or 2-cyanoprop-2-yl dithiobenzoate (○) as RAFT agent 0.006−0.03 M. A least-squares fit provides slope 0.507, $R = 0.98655$.

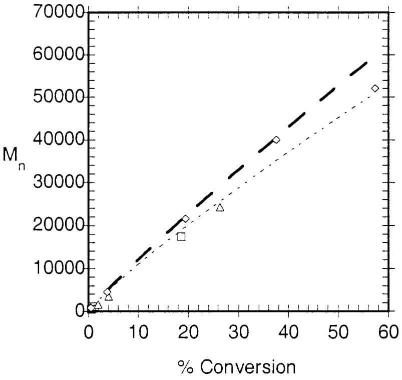


Figure 11. Evolution of molecular weight with conversion for bulk polymerization of styrene 60 °C with AIBN initiator (0.0017 M) in the presence of dithiobenzoate esters PhC(=S)-SR, where R = $-C(Me)_2Ph$ (**2a**) (◇), $-C(Me)_2CO_2C_2H_5$ (**2g**) (△), or $-C(CH_3)_2CH_2C(CH_3)_3$ (**2i**) (□). For experimental details, see Table 3. Key: calculated molecular weights assuming no initiator-derived chains (— —); calculated molecular weight including initiator-derived chains (- - -) based on $df = 1.4$.

Styrene Polymerizations. In styrene polymerization, all of the dithiobenzoates (**2**) tested were found to give both narrowed polydispersities and good molecular weight control (see Table 5 and Figures 11 and 12). In the case of dithiobenzoates with R = $-C(Me)_2Ph$, (**2a**), $-C(Me)_2CO_2Et$ (**2g**), or $-C(Me)_2CH_2C(Me)_3$ (**2i**), narrow polydispersities were evident at the first time/conversion point (≤1.13 at ≤2% conversion, Figure 12), and the correspondence between found and calculated molecular weight indicates complete consumption of the initial RAFT agent. Complete (>95%) utilization of the initial RAFT agent at <2% conversion suggests $C_{tr} > 150$ (Figure 1). Furthermore, to attain a polydispersity of 1.13 at <2% conversion, a substantially higher transfer coefficient ($C_{tr} > 500$) is required (Figure 2a). The transfer coefficient of the ω-(thiobenzoylthio)polystyrene (**2m**) in bulk styrene polymerization has been determined to be ≥6000.[30] Kinetic simulation with $C_{tr} = 2000$ and a $C_{-tr} = 10\,000$ with $k_\beta \geq 10$ provides an acceptable fit to the observed variation of molecular weight and polydispersity with conversion for RAFT agent **2a** (Figure 12). Additional experiments are required to refine these values.

The rate of polydispersity narrowing with conversion/time was lower with benzyl dithiobenzoate (**2d**) than with the other dithiobenzoates examined (see Figure 12). When using this reagent (**2d**), the molecular

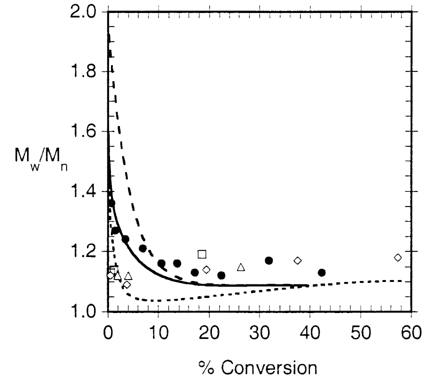


Figure 12. Evolution of polydispersity with conversion for bulk polymerization of styrene with AIBN initiator (0.0017 M) in the presence of dithiobenzoate esters PhC(=S)SR, where R = −CH$_2$Ph (0.0093 M **2d**) (●), R = −C(Me)$_2$Ph (0.0083 M **2a**) (◇), −C(Me)$_2$CO$_2$C$_2$H$_5$ (0.0084 M **2g**) (△), or −C(CH$_3$)$_2$CH$_2$C(CH$_3$)$_3$ (0.0084 M **2i**) (□). For experimental details, see Table 3. Lines come from the results of kinetic simulation with C_{tr} = 50 and C_{-tr} = 0 (− −), C_{tr} = 400 and C_{-tr} = 11 600 (—), or C_{tr} = 2000 and C_{-tr} = 10 000 (- - -). Other kinetic parameters are provided in the Experimental Section.

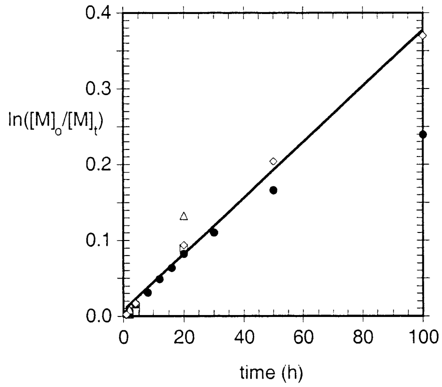


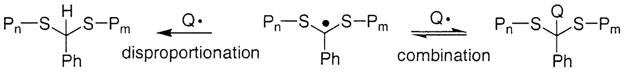
Figure 13. Kinetic plot for polymerization of styrene in the presence of dithiobenzoate esters PhC(=S)SR, where R = −CH$_2$Ph (0.0093 M **2d**) (●), R = −C(Me)$_2$Ph (0.0083 M **2a**) (◇), −C(Me)$_2$CO$_2$C$_2$H$_5$ (0.0084 M **2g**) (△), or −C(CH$_3$)$_2$CH$_2$C(CH$_3$)$_3$ (0.0084 M **2i**) (□). For experimental details, see Table 3. The line comes from the results of kinetic simulation with kinetic parameters provided in the Experimental Section.

weights observed for short reaction times are higher than those expected on the basis of the monomer conversion assuming complete utilization of the RAFT agent (Table 5). Analysis of the latter result suggests a C_{tr} for **2d** of ca. 50 (if C_{-tr} = 0) under the reaction conditions (by application of eq 5). However, the rate of narrowing of the polydispersity is consistent with a transfer coefficient that is significantly higher (Figure 10). Kinetic simulation shows that C_{tr} = 400 and a C_{-tr} = 11 600 provides an acceptable fit to the variation of both molecular weight and polydispersity with conversion (Figure 12).

The rate of styrene polymerization with cumyl dithiobenzoate (**2a**) as RAFT agent is, under these conditions, similar to that expected for styrene polymerization in the absence of a gel effect—Figure 13). In contrast, styrene polymerization with benzyl dithiobenzoate (**2d**) appears slightly retarded (conversions are lower for the same reaction time).

We[19] along with Monteiro and de Brouwer,[62] Barner-Kowollik et al.,[63] and Kwak et al.[64] have recently reported on retardation in styrene polymerization caused by dithiobenzoate derivatives. We reported[19] that there was marked retardation (manifest as a slow initial rate of polymerization) for very high concentrations of cumyl dithiobenzoate (0.018 M **2a**, at 110 °C 50% w/w styrene in toluene). Much less retardation was observed[19] with 2-cyanoprop-2-yl dithiobenzoate (**2e**) under these conditions or (in accord with the present work) with **2a** at lower concentrations (0.003 M **2a**). Monteiro and de Brouwer[62] use relatively high RAFT agent concentrations (0.04−0.06 M) as do Kwak et al.[64] (0.1 M). Thus, we have no reason to believe there is any inconsistency between our and their results. Our current findings appear in contrast with recent work of Barner-Kowollik et al.[63] who found that bulk styrene polymerization with cumyl dithiobenzoate at 60 °C is strongly retarded. Conditions differ, however: their[63] concentration range for **2a** (0.0025−0.033 M) spans that used in the present work (0.0084 M), and their initiator concentration ([AIBN] 0.0035 M) is 2-fold higher than ours ([AIBN] 0.0017 M). It is not clear why they should find strong retardation with their lower RAFT agent concentrations.

Scheme 7. Potential Side Reactions



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The rate of polymerization observed with **2d** appears consistent with a ca. 4-fold higher termination rate constant. Attempts to model the conversion time profile by including side reaction of the intermediates **3** or **5** (as shown in Scheme 7) did not give the observed conversion time profile. It can also be noted that, the development of a bimodal molecular weight distribution was observed for high conversions (>50%) with either **2a** or **2d** with the appearance of a high molecular weight shoulder with peak $\bar{M}_n$ ca. twice that of the principal peak (see discussion below).

Acrylate Polymerization. Molecular weight, polydispersity, and conversion data for polymerizations of BA or MA in the presence of several dithiobenzoates (**2**) are shown in Table 6. All reagents were effective in controlling the molecular weight and provided narrow polydispersity. These reagents include those that were ineffective in controlling MMA polymerization (R = −C(Me)HPh (**2c**), −CH$_2$Ph (**2d**). The correspondence between found and calculated molecular weights and the fact that very narrow polydispersities are obtained even at low conversion (≤1%) suggests that the transfer coefficients of the RAFT agents are very high. Where **2d** is used, molecular weights are higher than calculated for low conversions (residual **2d** was also detected in the NMR spectrum of the reaction mixtures − signal at 4.66 ppm for CH_2Ph). The slope of the plot of ln [**2d**] vs ln [MA] suggests a C_{tr} of ca. 105 for **2d** in MA polymerization (Figure 14) assuming C_{-tr} is negligible.

The kinetic plot shows that the rate of polymerization was strongly retarded compared to that observed in the absence of RAFT agent or that observed in the presence of other RAFT agents (e.g. benzyl dithioacetate[65]) but does not depend markedly on R (Figure 15). This is consistent with our previous findings.[19] The rate of polymerization reduces when the RAFT agent concentration is increased (Table 5). Despite this, polymerizations do proceed to high conversions after long reaction times (Table 6). The results suggest that retardation under these conditions are mainly due to a property of the polymeric RAFT agent. We have previously shown

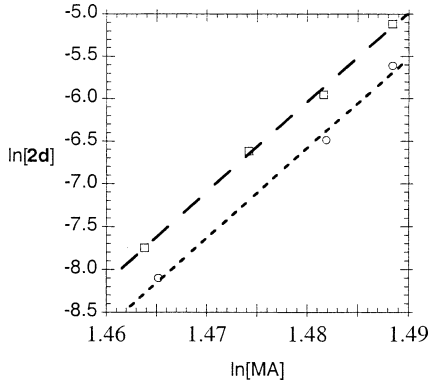


Figure 14. Double log plot of transfer agent concentration vs monomer concentration for polymerization of methyl acrylate ($[MA]_o = 4.45$ M) in benzene at 60 °C with AIBN initiator (0.00033 M) in the presence of PhC(=S)SCH$_2$Ph $[\mathbf{2d}]_0 = 0.006$ M (□) and 0.0037 M (○). For additional experimental details see Table 5. Lines of best fit are $-162.16 + 105.13 \ln[M]$, correlation coefficient 0.99665 (– –), and $-162.08 + 105.43$, correlation coefficient 0.99877 (- - -).

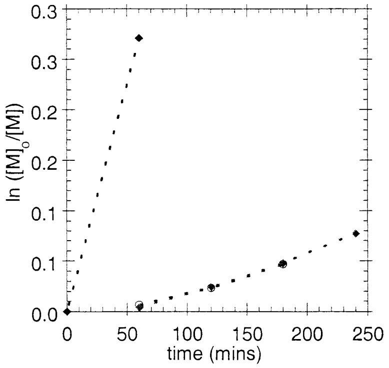


Figure 15. Kinetic plot for polymerization of methyl acrylate ($[MA]_o = 4.45$ M) in benzene at 60 °C with AIBN initiator (0.00033 M) in the absence (○) or presence of dithiobenzoate esters PhC(=S)SR, where R = $-$CH$_2$Ph (0.0037 M **2d**) (□) or R = $-$C(Me)$_2$CN (0.0037 M **2e**) (♦). For experimental details, see Table 6. The lines are lines of best fit through the experimental points.

that in polymerization of acrylate esters, the adduct radicals (**3** and **5**) are present in high concentration relative the propagating radical.[66]

As in the case of styrene polymerization, the appearance of a high molecular weight shoulder on the molecular weight distribution with peak molecular weight approximately twice that of the principal peak was observed for high conversions. The high molecular weight shoulder might, in part, be attributed to the product formed by bimolecular termination between polystyrene propagating radicals. Another process that may contribute to the formation of this peak is the reaction of adduct (**5**) with a small radical or a propagating radical (Q$^\bullet$) by combination or disproportionation (Scheme 7).[20,62] However, the molar yield of product from any of these processes cannot exceed the molar concentration of radicals generated. We have found in related polymerizations, by GPC with UV analysis, that the high molecular weight peak retains the thiocarbonylthio chromophore.[65] This observation, and size of the peak, which is substantially greater than that anticipated on the basis of the above considerations, suggests that some other mechanism(s) is responsible for the formation of the major part the high molecular weight shoulder. An observation of bimodal molecular weight distributions was recently reported for *N*,*N*-dimethylacrylamide (DMA) polymerization.[32] DMA was polymerized in the presence of a series of four dithiobenzoate RAFT agents. Retardation (manifest as an inhibition period) was observed with **2a** and **2d** (most severe with **2a**). Bimodal distributions were observed and were pronounced in the case of benzyl dithiobenzoate (**2d**). Inefficient transfer due to poor reinitiation efficiencies by the expelled benzyl radicals (R$^\bullet$) was suggested[32] as a possible explanation. This should not apply in MA polymerization. The reported value of k_i for benzyl radical is high and approximately 2.5 times that for cyanoisopropyl radical (Table 10).[67] Even though **2d** has a lower transfer coefficient (than **2e**), it is consumed rapidly and there is little difference in the rate of MA polymerization with **2d** and **2e** (Figure 15).

The possible origins of bimodal molecular weight distributions in high conversion RAFT polymerization are discussed elsewhere.[65]

Origin of Substituent Effects. The sequence of events for a polymerization carried out in the presence of dithiobenzoates (**2**) can be envisioned as follows (Scheme 2).[14] Propagating radicals are generated as in a conventional free radical polymerization. A propagating radical (P$_n^\bullet$) adds to the dithiobenzoate derivative (**2**) to form an adduct (**3**) which can fragment to form a polymeric dithiobenzoate (**4**) and a radical (R$^\bullet$). The liberated radical (R$^\bullet$) then reacts with monomer to form a new propagating radical (P$_m^\bullet$).

Chain extension of the polymeric dithiobenzoate (**4**) involves the same process. The reversible addition–fragmentation sequence in which the S=C(Ph)S– moiety is transferred between dormant and active chains, thus maintaining the living character of the polymerization. The formation of intermediates (**3** and **5**) during polymerizations of BA or styrene in the presence of cumyl dithiobenzoate (**2a**) has recently been confirmed by electron spin resonance spectroscopy under conditions of high radical flux.[66]

This mechanism of RAFT polymerization (Scheme 2) should not be confused with the "iniferter" mechanism first described by Otsu et al.[3] That process relies on reversible photodissociation of the C–S bond of a dithiocarbamate derivative to provide a mechanism for chain activation and deactivation (Scheme 8). Although it was originally considered that reversible chain transfer might occur during these polymerizations,[3] subsequent work has shown that the transfer coefficient of *N*,*N*-dialkyldithiocarbamates in polymerizations of methacrylates and styrenes are very low ($\ll 1$).[17,36,68–70] The thermal dissociation of the dithiobenzoates (**2**) analogous to Scheme 8 is not detectable under our reaction conditions as demonstrated by control experiments that

Scheme 8

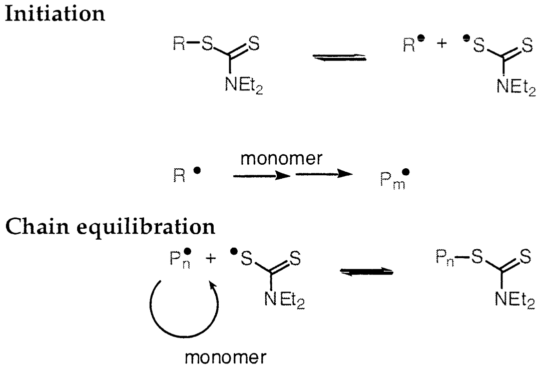


Table 7. Rate Constants for Formation for Radicals CTUV·

radical substituents T,U,V	rel C_{tr} in MMA[a]	reaction			
		Me• abs[b]	tBuO• abs[b]	Me• addn[c]	azo dec[d]
Me,Me,Ph	370	3.2	5.0	0.8	48
Me,Me,CN	170			2.1	2.4
Me,Me,CO_2Me(Et)	11			1.4	2.1
Me,H,Ph	1.0	1.0	1.0	1.0	1.0
Me,Me,Me_3CCH_2	3				0.006
H,H,Ph	0.2	0.2	0.3		0.0009
Me,Me,Me	0.2	0.9	1.2		0.0000009

[a] Relative transfer coefficient of dithiobenzoate in MMA polymerization. [b] Relative rate constant for hydrogen atom abstraction from C(TUV)−H at 60 °C.[77] [c] Relative rate constant for methyl radical addition to $CH_2{=}CUV$ at 65 °C.[78] [d] Relative rate constant for decomposition of azo compound C(TUV)−N=N−C(TUV) at 60 °C.[79]

showed no polymer is formed in the absence of added initiator.

On the basis of the addition−fragmentation chain transfer mechanism (Scheme 2), at least four factors can be seen to influence the effectiveness of the dithiobenzoates (**2**) as RAFT agents: (a) the rate constant of reaction of **2** with the propagating (or initiator-derived radicals) (k_{add}); (b) the partitioning of the adduct (**3**) between starting materials and products (determined by the relative magnitude of (k_{-add} and k_β); (c) the values of the rate constants for fragmentation of the intermediate radicals (**3** and **5**); (d) the ability of the expelled radicals (R•) to reinitiate polymerization.

Factors a and b should be directly reflected in the magnitude of the transfer coefficient of **2**. Factor c should not directly affect the transfer coefficient. However, if fragmentation is particularly slow (i.e., both k_{-add} and k_β are small) or reinitiation of polymerization is slow with respect to propagation, then polymerization may be retarded and the likelihood of the radicals **3** and/or R• undergoing side reactions leading to some degree of inhibition is increased. Retardation may be observed in RAFT polymerization with certain dithiobenzoate derivatives when relatively high concentrations of reagent are used.[19]

Since chain transfer is reversible, the rate of consumption of the RAFT agent (**2**) and the transfer coefficient depend on the reinitiation rate constant k_i and the partitioning of the radical R• between adding to monomer and reacting with the polymeric RAFT agent (**4**). The expelled radical R• may also react with the initial RAFT agent (**2**). However, this process is degenerate, involving no overall change.

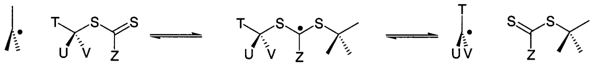
We have previously reported that chain transfer activity of reagents **1** is a function of the substituents R and Z and the particular propagating radical.[14−16,20] The rate of addition to the thiocarbonyl group (C=S) of **1** should not be dramatically affected by the nature of the group R since that group is remote from the C=S double bond and not directly conjugated with it. Thus, the magnitude of the transfer coefficient should reflect the partitioning of the intermediate between starting materials and products and the relative leaving group ability of R and the propagating radical. We therefore sought to establish if there was a correlation between the transfer coefficient (in MMA polymerization) and the properties of the radical R•

It has been stated that rates of free radical processes are determined by a "complex interplay of steric, polar, and bond strength terms".[67,71,72] In Table 7, the relative transfer coefficient of the dithiobenzoate derivatives in MMA polymerization are compared with the relative rate constants of other reactions that generate radicals •CTUV. In all reactions the rate constants decrease in the series where the radical is $C(Me)_2Ar > -C(Me)HPh > -CH_2Ph$ and $-C(Me)_2CH_2C(Me)_3 > -C(Me)_3$. However, there is no general correlation between the rate constants for the various reactions and there is also no general correlation with the stability of R•. This could reflect the different steric demands of the transition states for the various processes, a greater or lesser influence of polar terms, and perhaps other factors.

Table 8. Bond Dissociation Energies for Compounds CTUV−H

substituents T,U,V	D_{C-H}[80] (kJ mol^{-1})	D_{C-H}[81] (kJ mol^{-1})
Me,Me,Ph	365	
Me,H,Ph	378	
H,H,Ph		375
Me,Me,CN	385	
Me,Me,CO_2Me(Et)	388	
Me,Me,Me_3CCH_2		
Me,Me,Me	401	400

Scheme 9



The C−H bond dissociation energies provide one measure of radical stability. Values for C−H bond dissociation energies for compounds H−CTUV (=H−R) are summarized in Table 8. For tertiary dithiobenzoates Ph(C=S)S−R even though there is no direct correlation there is nonetheless a trend for the transfer coefficients to increase according to the stability of R. If the transfer coefficients were to reflect the stability of the free radicals formed (R•) it would be anticipated, for example, that **2d** (R = $-CH_2Ph$) or **2c** (R = $-CH(CH_3)Ph$) would have higher transfer coefficients than, for example, either **2i** (R = $-C(CH_3)_2CCH_2(CH_3)_3$) or **2g** (R = $-C(CH_3)_2CO_2Et$). The experimental data indicate that, in polymerizations of styrene and MMA, benzyl dithiobenzoate (**2d**) has a substantially lower transfer coefficient.

Steric effects come into play because of the B-strain engendered by the change from sp^3 to sp^2 hybridization when the adduct (**7**) fragments to form the radical (**8**) (Scheme 9). Steric interactions between T, U, and V groups will be greater for a tetrahedral configuration (in **7**) than for a planar configuration (in **8**) due to the closer proximity of those groups. The strain relieved on rehybridization should increase in the series tertiary > secondary > primary. We also expect on this basis, that oligomeric or polymeric radicals should be better leaving groups than monomeric species. This offers an explanation for the finding that **2g** (R = $-C(CH_3)_2CO_2Et$) is a poor RAFT agent in MMA polymerization, with $C_{tr} \sim 2$, even though it resembles the RAFT agent (**2l**) derived from the MMA propagating radical for which C_{tr} is approximately 2 orders of magnitude higher (∼140 at 60 °C).[30] Such steric factors have been previously invoked to rationalize the transfer coefficients of methacrylate macromonomers in RAFT polymerization and provide one explanation for the very low transfer coefficient of "MMA dimer" ($C_{tr} \sim 0.005$ at 60 °C) in relation to those of higher macromonomers ($C_{tr} \sim 0.04$ for $n \geq 3$); the ratio C_{tr}(isobutyrate):C_{tr}(oligo/polymeric species) is of similar magnitude for these two systems.[48]

Table 9. HUMO and LUMO Energies, Partial Charges on Sulfur for Dithiobenzoates PhC(═S)S−R (In Order of Decreasing LUMO Energy) and Relative Heats of Reaction for Addition of Methyl Radical

	energy (eV)		atomic charge				$\Delta\Delta H_r$[c] (kJ mol^{-1})
R	HOMO	LUMO	═S[a]	−S[a]	═S[b]	−S[b]	
Ph(Me)$_2$C	−8.45	−1.07	−0.06	0.25	0.01	0.29	−4.68
(Me)$_2$C	−8.46	−1.06	−0.05	0.24	0.01	0.28	−7.99
Ph(Me)CH	−8.67	−1.14	−0.05	0.26			−2.54
Me	−8.71	−1.17	−0.03	0.27	0.03	0.32	0
PhCH$_2$	−8.70	−1.18	−0.04	0.27	0.02	0.32	0
(CO$_2$Me)(CH$_3$)$_2$C	−8.71	−1.28	−0.02	0.28	0.04	0.32	4.06
CN(Me)2C	−8.81	−1.38	−0.02	0.27	0.04	0.31	3.70

[a] Milliken charge. [b] Atomic charge. [c] Relative heat of reaction = ΔH_f (**2**) − ΔH_f (**3**) (referenced to R = Me).

Such steric factors also help us to understand why *tert*-butyl dithiobenzoate (**2j**) and benzyl dithiobenzoate (**2d**) have significantly lower transfer coefficients than isooctyl dithiobenzoate (**2i**). We can also note that **2f** (R = $-C(CH_3)(CH_2CH_2CH_2OH)CN$ is more effective than **2e** (R = $-C(CH_3)_2CN$). Of the compounds studied, **2f** is the most effective RAFT agent in MMA polymerization under our experimental conditions (based on the polydispersity at a given conversion).

We indicated that for a series of dithiobenzoates **2**, variation in the reactivity of the C═S toward free radical addition should be small and the magnitude of the transfer coefficient should be dependent primarily on the leaving group ability of the radical $R^{\bullet}$. To provide a qualitative assessment of the effect of the group R on the rate constant for addition of radicals to dithiobenzoates **2**, we calculated the LUMO and HOMO energies of a series of dithiobenzoates using semiempirical molecular orbital calculations. These data are provided in Table 9. The rate constant for addition of a given radical should be highest for the compound with the lowest LUMO energy.[36] For RAFT agents with different Z substituents and common R, there is a reasonable correlation between ln(C_{tr}) and the LUMO energies estimated using semiempirical calculations or higher level ab initio calculations.[36] The calculations suggest that the rate of addition to the C═S is favored by alkyl or phenyl substitution of the α-carbon but disfavored by polar groups (nitrile or ester). The LUMO energy for the 2-cyanoprop-2-yl dithiobenzoate (**2e**) is lower than that of cumyl dithiobenzoate (**2a**) and on this basis should be less reactive toward addition. The lower C_{tr} for **2e** vs. **2a** may in part be due to a lower k_{add}. However, the differences in LUMO (and HOMO) energies are small with respect to the error inherent in the calculations (and when considered in relation to those calculated for different Z groups).[36] This is consistent with a hypothesis that the R group does not significantly affect the rate of addition.

Another factor to consider is the ability of the radicals $R^{\bullet}$ to reinitiate polymerization. As in conventional chain transfer, the rate of reinitiation should be equal to or greater than the rate of propagation to avoid retardation. In RAFT polymerization, it is also necessary to consider the rate of reinitiation in relation to the rate of reaction of $R^{\bullet}$ with the polymeric RAFT agent. If the rate of reinitiation is small, the rate of consumption of the initial RAFT agent will be reduced and this, in turn, may cause the transfer coefficient to be dependent on RAFT agent concentration and conversion. The transfer coefficients of cumyl dithiobenzoate (**2a**) and 2-cyanoprop-2-yl dithiobenzoate (**2e**) in MMA polymerization depend on the RAFT agent concentration (see above). The data show that while cumyl dithiobenzoate (**2a**) has a higher transfer coefficient, for high concentrations of RAFT agent (when making low molecular weight polymers) the 2-cyanoprop-2-yl derivative (**2e**) is the more effective RAFT agent. This is attributable to the very high reactivity of cumyl radicals toward the RAFT agent. For high concentrations of **2a** (greater than the concentrations used in the present experiments) substantial retardation may be observed in each MMA,[61,73] styrene,[19,62,63] and BA,[19] polymerization. For MMA and styrene polymerization with 2-cyanoprop-2-yl dithiobenzoate (**2e**) as the RAFT agent, this retardation is absent or much diminished.[19,61,73]

Literature data suggest no marked difference in k_i in MMA polymerization with $^{\bullet}C(CH_3)_2CN$,[74] $^{\bullet}C(CH_3)_2Ph$,[75] and $^{\bullet}CH_2Ph$[75] as the initiating species (see Table 10). The rate constants k_i for $^{\bullet}C(CH_3)_3$ and other alkyl radicals are several orders of magnitude higher. The rate constants for the reaction of these radicals with the polymeric RAFT agents are unknown. However, the similarity in k_i values suggests that the different behaviors of 2-cyanoprop-2-yl and cumyl dithiobenzoates are due to the rate constant ($k_{-\beta}$) for $^{\bullet}C(CH_3)_2CN$ being lower than that for $^{\bullet}C(CH_3)_2Ph$. Our molecular orbital calculations provide some support for this hypothesis.

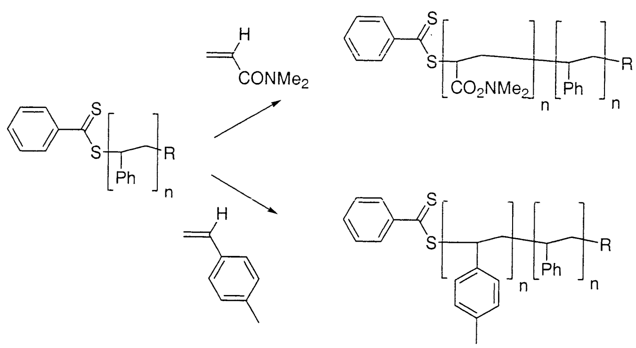
Relevance in Block Copolymer Synthesis. In a communication,[15] we reported that it is critical when making styrene-MMA block copolymers to prepare the poly(methyl methacrylate) block first. Attempted block copolymer syntheses involving polymerization of MMA in the presence of *ω*-(thiobenzoylthio)polystyrene (**2m**) in a batch polymerization were unsuccessful. Thus, an experiment using conditions similar to those used for the other MMA polymerizations mentioned above—see

Table 10. Absolute Rate Constants for Radical Addition to Various Monomers

		rate constant (M^{-1} s^{-1})				
monomer		$^{\bullet}C(CH_3)_3$[75,82] (300 K)	$^{\bullet}C(CH_3)_2CO_2Me$[83] (294 K)	$^{\bullet}C(CH_3)_2CN$[74] (315 K)	$^{\bullet}C(CH_3)_2Ph$[75] (296 K)	$^{\bullet}CH_2Ph$[75] (296 K)
MMA	a	660 000	3170	1590	2700	2100
	b		-	-	10 225	-
	c	952 970	9722	3291	7829	8348
MA	a	110 000	1150	367	800	430
	b		3129	-	-	2134
	c	1523800	3412	865	2650	2042
styrene	a	132 000	5500	2410	1100	1200
	b	226 622	12 508	4041	3803	4557
	c	224 850	13 455	4896	3802	4685

[a] Value provided in original paper for temperature indicated. [b] Value at 60 °C calculated using Arrhenius parameters provided in the reference indicated (- indicates no Arrhenius parameters given). [c] Value at 60 °C calculated using log *A* 7.5 (tertiary radicals) or log *A* 8.5 (benzyl radical) and activation energy as reported.[67]

Scheme 10



Experimental Section—provided poly(methyl methacrylate) with molecular weight and polydispersity values similar to those obtained in the absence of added **2m**.

Other block copolymers where the B-block is composed of a monosubstituted acrylic or styrenic monomer (e.g., *N*,*N*-dimethylacrylamide or 4-methylstyrene) were successfully prepared from this same ω-(thiobenzoylthio)polystyrene in a batch polymerization process (Scheme 10).[15] For details, see the Experimental Section.

Polymerization of styrene in the presence of ω-(thiobenzoylthio)poly(methyl methacrylate) (**2l**) ($\bar{M}_n$ 17408, $\bar{M}_w/\bar{M}_n$ 1.20) was successful in giving a narrow polydispersity block copolymer $\bar{M}_n$ 35 000, $\bar{M}_w/\bar{M}_n$ 1.24) with complete (>95%) incorporation of the precursor polymer.

It appears that the polystyrene propagating species ($-P_n = -[CH_2-CHPh]_n$ in Scheme 2), like the 1-phenylethyl radical, is a very poor free radical leaving group with respect to the poly(methyl methacrylate) propagating species ($-P_n = -[CH_2-C(Me)(CO_2Me)]_n$ in Scheme 2). Thus, for synthesis of poly(methyl methacrylate)-*block*-polystyrene under batch polymerization conditions, it is necessary to make the poly(methyl methacrylate) block first in order to make a narrow polydispersity block copolymer.

We anticipate that since the transfer coefficient of ω-(thiobenzoylthio)polystyrene (**2m**) should be ≥ 0.15 (transfer coefficient of phenylethyl dithiobenzoate **2c**), it should be possible to prepare block copolymers from this starting material using an appropriate feed addition protocol. We have successfully prepared poly(methyl methacrylate)-*block*-polystyrene from a ω-(thioacetylthio)polystyrene by a feed emulsion polymerization where the concentration of RAFT agent with respect to that of monomer is maintained at a low (approximately constant) level.[19] Feed emulsion polymerization has also been successful in other circumstances when the transfer coefficient of the RAFT agent is low. For example, narrow polydispersity methacrylate block copolymer can be prepared from methacrylate macromonomers (the transfer coefficients of methacrylate macromonomers in MMA polymerization are <0.5).[12,13]

Conclusions

In MMA polymerization, the ability of the RAFT agents [S═C(Ph)S−R] to promote living radical polymerization depends strongly on the nature of R. In polymerizations of styrene and BA, a much wider range of R groups is available. A major factor determining the transfer coefficient of dithiobenzoate derivatives is the way the intermediate **3** partitions between starting materials and products which is in turn determined by the relative leaving group ability of $R^{\bullet}$ and the propagating radical. Steric factors, radical stability, and polar factors all appear important in determining the leaving group ability of $R^{\bullet}$ (more stable, more electrophilic, more bulky radicals are better leaving groups). The partitioning of $R^{\bullet}$ between adding to monomer (to reinitiate) and adding to polymeric RAFT agent can also have a significant effect on the rate of consumption of RAFT agent. The propensity of benzylic radicals to add RAFT agent rather than monomer may explain why certain reagents (e.g., cumyl dithiobenzoate **2a**) are less effective RAFT agents when used in high concentrations to make lower molecular weight polymers.

Note Added in Proof. Two papers on retardation in acrylate polymerization using dithiobenzoate esters have recently appeared.[84]

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