Use of Substituted Allylic Sulfides To Prepare End-Functional Polymers of Controlled Molecular Weight by Free-Radical Polymerization

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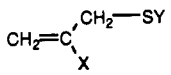
ABSTRACT: Substituted allylic sulfides **1b–f** and **2d** were utilized as chain-transfer agents to prepare low molecular weight polystyrene and poly(methyl methacrylate) capped with carboxy, hydroxy, trialkoxysilyl, or amino groups. End-functional polymers, prepared with ethyl α-(((carboxymethyl)thio)methyl)acrylate (**2b**) or α-(((carboxymethyl)thio)methyl)acrylic acid (**11b**), were capped with both a carboxy group and an acrylate moiety. Low molecular weight α,ω-dicarboxypolystyrene or poly(methyl methacrylate) were readily obtained by chain transfer with **11b**. α-Hydroxy-ω-carboxy- and α,ω-dihydroxy-terminated polystyrene, poly(methyl methacrylate), and poly(butyl acrylate) were prepared with α-(((2-hydroxyethyl)thio)methyl)-acrylic acid (**11d**) and 2-hydroxyethyl α-(((2-hydroxyethyl)thio)methyl)acrylate (**12d**), respectively, while *N*-phthalimidoethyl α-(((2-hydroxyethyl)thio)methyl)acrylate (**13d**) was used to prepare polymers terminated at one end with hydroxy and at the other with a phthalamido group. ^{1}H NMR or IR spectroscopy, titration, or derivatization was used to confirm the presence of the end groups.

We have recently reported that the CSIRO-patented allylic sulfides **1a**, **2a**, and **3a** are useful chain-transfer agents in the free-radical polymerization of styrene and methyl methacrylate.[1] These unsaturated sulfides react with propagating macroradicals by free-radical addition to give the intermediate radicals **4a–6a**, which fragment[2] to expel *tert*-butylthiyl radical **10**, which then initiates further polymerization (Scheme I).[3] Evidence obtained by ^{1}H NMR spectroscopy indicates that the fragmentations of **4a–6a** are efficient and that there is no discernible copolymerization with styrene or methyl methacrylate. A consequence of this process is that the low molecular weight polymers **7a–9a** contain end groups derived from the chain-transfer agent. We now report experiments demonstrating that the introduction of appropriately placed functional substituents on compounds of the general formula **1**, **2**, **11**, **12**, and **13** can lead to mono- or di-end-functional



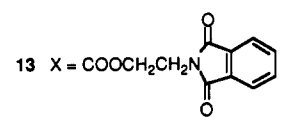
1 X = Ph — **b** Y = CH_2COOH

2 X = COOEt — **c** Y = CH_2CH_2COOH

11 X = COOH — **d** Y = CH_2CH_2OH

12 X = $COOCH_2CH_2OH$ — **e** Y = $CH_2CH_2NH_2$

f Y = $(CH_2)_3Si(OCH_3)_3$



13 X = $COOCH_2CH_2N$

polymers, which are useful as building blocks for block, segmented, and network copolymers.[5–7] It is particularly noteworthy that some of these chain-transfer agents allow the preparation of di-end-functional polymers by free-radical means. Previously, free-radical techniques were based primarily on the use of high concentrations of a functional initiator (i.e. "dead-end" polymerization).[8] However, "dead-end" polymerization gives satisfactory incorporation of functionality only with monomers that undergo termination predominantly by primary radical termination or by combination (e.g., styrene). An alternative means of producing di-end-functional polymers and oligomers is through the use of chain-transfer agents, such as carbon tetrachloride or substituted disulfides, that do not transfer a hydrogen atom during the chain-transfer process.[8] This procedure, however, is not widely utilized because the range of suitable chain-transfer agents is very limited and, with many monomers, the chain-transfer constants are unfavorable and consequently lead to a broad distribution of molecular weights in batch polymerizations. Other methods of preparing α,ω-difunctional polymers, such as living anionic polymerization, are used more frequently but require rather more stringent conditions[8] and are restricted to few monomers.

Experimental Section

General Procedures. Methyl methacrylate and styrene were passed through a short column of neutral alumina (activity I; Merck catalog no. 1077) and fractionally distilled under reduced pressure. The ^{1}H NMR spectra of polymers were recorded on a Bruker WM-250 spectrometer in carbon tetrachloride/acetone-d_6 (4:1) and are referenced to the central peak of acetone-d_5, which was set at δ 2.04. Other ^{1}H NMR spectra were recorded on a Varian EM-390 (90 MHz) instrument in chloroform-*d* solution, and chemical shifts are quoted relative to TMS. Mass spectra were determined on a Finnigan 3300 spectrometer, and the IR spectra of polymers (KBr pellets) were recorded with a Perkin-Elmer Model 577 grating spectrophotometer. Melting points were determined on an Electrothermal apparatus in capillary tubes. Analytical GPC was performed on a Waters instrument with six μ-Styragel columns (10^6-, 10^5-, 10^4-, 10^3-, 500-, and 100-Å pore size). Tetrahydrofuran was used as the eluent at a flow rate of 1 mL min^{-1}, and the system was calibrated with narrow-distribution polystyrene standards (for polystyrene and poly(butyl acrylate)). Molecular weights of poly(methyl methacrylate) samples were determined relative to narrow-distribution poly(methyl methacrylate) standards. Preparative GPC was carried out with an Altex Model 110A pump connected to Polymer Laboratories 50- and 500-Å columns (each column having dimensions of 600 × 25 mm). The eluent was tetrahydrofuran at a flow rate of 10 mL min^{-1}.

α-(((Carboxymethyl)thio)methyl)styrene (1b). A solution of α-(bromomethyl)styrene (20 g, 102 mmol) in methanol (6 mL) was added to a stirred suspension of sodium acetate (2.3 g, 28 mmol) and thioglycolic acid (2.5 g, 28 mmol) in methanol (12

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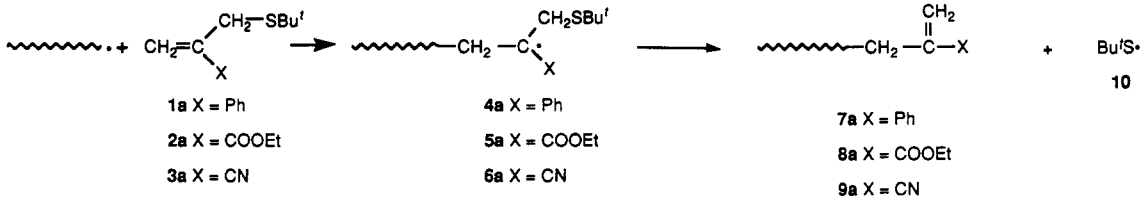
Scheme I



mL). The mixture was allowed to stir for 4 days and then was poured into a mixture of water and saturated $NaHCO_3$ solution (1:1). The aqueous basic layer was washed with ether, adjusted to pH 1 with hydrochloric acid, and extracted with diethyl ether. The organic phase was then dried ($MgSO_4$). After removal of the solvent, **1b** (5.0 g, 86%) was obtained: mp 74–76 °C (from CCl_4); ^1H NMR ($CDCl_3$) δ 3.20 (2 H, s, SCH_2COOH), 3.70 (2 H, s, allylic CH_2S), 5.25 (1 H, s, olefinic proton), 5.50 (1 H, s, olefinic H), 7.20–7.50 (5 H, m, aromatic H), 10.80 (1 H, br s, COOH); MS (CH_4) m/z (relative intensity) 209 (MH^+, 100), 191 (50), 163 (91), 117 (96); accurate mass m/z 208.0574. $C_{11}H_{12}O_2S$ requires m/z 208.0558.

α-(((Carboxyethyl)thio)methyl)styrene (1c). Similar treatment of α-(bromomethyl)styrene with 3-mercaptopropionic acid and sodium acetate in methanol afforded **1c**: mp 47–49 °C (from CCl_4); ^1H NMR ($CDCl_3$) δ 2.60–2.90 (4 H, m, SCH_2CH_2COOH), 3.60 (2 H, s, allylic CH_2S), 5.25 (1 H, olefinic H), 5.45 (1 H, s, olefinic H), 7.20–7.50 (5 H, m, aromatic H), 8.35 (1 H, br s, COOH); IR (Nujol) 2300–3300 (br), 1710, 1250, 910 cm^{-1}; MS (CH_4) m/z (relative intensity) 223 (MH^+, 59), 205 (100), 117 (37); accurate mass m/z 223.0795. $C_{12}H_{15}O_2S$ requires m/z 223.0793.

α-(((2-Hydroxyethyl)thio)methyl)styrene (1d). This compound was prepared from α-(bromomethyl)styrene, 2-hydroxyethanethiol, and potassium carbonate in methanol in 90% yield after chromatography on silica gel (EtOAc/petroleum spirit). ^1H NMR ($CDCl_3$) δ 2.35 (1 H, br s, OH), 2.65 (2 H, t, J = 7 Hz, SCH_2CH_2OH), 3.60 (2 H, s, allylic CH_2S), 3.68 (2 H, t, J = 7 Hz, SCH_2CH_2OH), 5.30 (1 H, s, olefinic H), 5.45 (1 H, s, olefinic H), 7.20–7.50 (5 H, m, aromatic H); ^{13}C NMR ($CDCl_3$) δ 34.4, 36.1, 60.2, 115.3, 126.3, 128.0, 128.4, 139.0, 143.6; MS m/z (relative intensity) 195 (MH^+, 40), 177 (100), 149 (69), 135 (42), 119 (87); accurate mass m/z 195.0864. $C_{11}H_{15}SO$ requires m/z 195.0844.

α-(((2-Aminoethyl)thio)methyl)styrene (1e). A solution of α-(bromomethyl)styrene (0.5 g, 2.6 mmol) in methanol (2 mL) was added to a cold, stirred solution of 2-aminoethanethiol (0.2 g, 2.6 mmol) and sodium methoxide (0.17 g, 3 mmol) in methanol (3 mL). After 15 min at 0 °C, the mixture was allowed to stir at room temperature for a further 1 h. The resulting mixture was then poured into water, acidified with dilute hydrochloric acid, and washed with ether to remove traces of the unreacted bromide. The acidic layer was then neutralized with 5% potassium hydroxide solution and extracted immediately with ether (3×). The combined ether extracts were dried (Na_2SO_4) and the solvent was removed to give **1e** (0.42 g, 85%) as a brownish liquid: ^1H NMR ($CDCl_3$) δ 1.75 (2 H, br s, NH_2), 2.45–2.85 (4 H, m, $SCH_2CH_2NH_2$), 3.55 (2 H, m, allylic CH_2S), 5.15 (1 H, m, olefinic H), 5.40 (1 H, m, olefinic H), 7.20–7.50 (5 H, m, aromatic H); MS m/z (relative intensity) (CH_4) 194 (MH^+, 6), 177 (100), 149 (54); accurate mass m/z 194.0995. $C_{11}H_{16}NS$ requires m/z 194.1003.

α-[((3-(Trimethoxysilyl)propyl)thio)methyl]styrene (1f). This compound was prepared in 94% yield from (3-mercaptopropyl)trimethoxysilane, potassium carbonate, and α-(bromomethyl)styrene in methanol. The compound was purified by column chromatography on silica gel (EtOAc). ^1H NMR ($CDCl_3$) δ 0.75 (2 H, t, J = 7 Hz, CH_2Si), 1.75 (2 H, m, $SCH_2CH_2CH_2Si$), 2.55 (2 H, t, J = 7 Hz, $SCH_2CH_2CH_2Si$), 3.60 (2 H, s, allylic CH_2S), 5.20 (1 H, s, olefinic H), 5.45 (1 H, s, olefinic H), 7.2–7.5 (5 H, m, aromatic H).

Ethyl α-(((Carboxymethyl)thio)methyl)acrylate (2b). Thioglycolic acid (2.0 g, 22 mmol) was added slowly to a stirred suspension of ethyl 1,3-dibromopropane-2-carboxylate (6.0 g, 22 mmol) and potassium carbonate (3 g, 22 mmol) in absolute ethanol (25 mL). After 2 h of stirring at ambient temperature, the mixture was poured into saturated aqueous $NaHCO_3$ and washed with ether. The aqueous layer was acidified with dilute HCl and then extracted repeatedly with ether. The combined ether extracts were dried over anhydrous Na_2SO_4. After the solvent was removed, distillation of the crude product afforded pure **2b** (1.3 g, 29%) as a slightly yellow liquid, bp 122–130 °C (0.5 mmHg), which solidified on cooling in the freezer. ^1H NMR ($CDCl_3$) δ 1.30 (3 H, t, J = 7.0 Hz, OCH_2CH_3), 3.20 (2 H, s, SCH_2COOH), 3.55 (2 H, s, allylic CH_2S), 4.25 (2 H, q, J = 7.0 Hz, OCH_2CH_3), 5.65 (1 H, s, olefinic H), 6.25 (1 H, s, olefinic H), 10.55 (1 H, br s, exchangeable, COOH); IR (film) 2400–3700 (br), 1715 (br), 1630, 1420, 1330, 1305, 1200, 1020, 960 cm^{-1}; MS (CH_4) m/z (relative intensity) 205 (MH^+, 12), 187 (23), 159 (83), 131 (41), 93 (100); accurate mass m/z 205.0544. $C_8H_{13}SO_4$ requires m/z 205.0535.

Ethyl α-(((2-Hydroxyethyl)thio)methyl)acrylate (2d). This compound was prepared by a similar method to that used for **2b**. The crude product was purified by column chromatography on silica gel (benzene/methanol) to give a colorless oil (0.86 g, 23%): ^1H NMR ($CDCl_3$) δ 1.34 (3 H, t, J = 7.5 Hz, CH_3), 2.71 (3 H, m, CH_2S, OH), 3.44 (2 H, s, CH_2S), 3.77 (2 H, t, J = 6 Hz, CH_2OH), 4.27 (2 H, q, J = 7.5 Hz, CH_2O), 5.71 (1 H, s, olefinic H), 6.23 (1 H, s, olefinic H); MS (CH_4) m/z (relative intensity) 191 (MH^+, 6), 173 (44), 145 (100); accurate mass m/z 191.0754. $C_8H_{15}O_3S$ requires m/z 191.0742.

α-(((Carboxymethyl)thio)methyl)acrylic Acid (11b). This compound was prepared from **2b** (0.5 g, 2.45 mmol) and 4% aqueous KOH (20 mL). The mixture was allowed to stir at room temperature overnight and then brought to pH 1 with hydrochloric acid. The resultant mixture was extracted 5 times with ether. The combined extracts were then dried over anhydrous Na_2SO_4, and the solvent was removed to afford **11b** (0.42 g, 97%): mp 121–125 °C; ^1H NMR (CD_3OD) δ 3.20 (2 H, s, SCH_2COOH), 3.50 (2 H, s, allylic H), 4.90 (2 H, br s, 2 × COOH), 5.70 (1 H, s, olefinic H), 6.20 (1 H, s, olefinic H); IR (KBr) 2500 (br), 1700, 1680 cm^{-1}; MS (CH_4) m/z (relative intensity) 177 (MH^+, 5), 159 (47), 131 (100); accurate mass m/z 177.0209. $C_6H_9SO_4$ requires m/z 177.0222.

11b was also prepared directly from 1,3-dibromopropane-2-carboxylic acid as follows: Thioglycolic acid (1.08 g, 11 mmol) was added to a stirred suspension of 1,3-dibromopropane-2-carboxylic acid (3.08 g, 13 mmol) and potassium carbonate (3.04 g, 22 mmol) in absolute ethanol (15 mL). The mixture was stirred overnight at room temperature, then brought to pH 1 with dilute hydrochloric acid, and extracted 5 times with ether. The combined extracts were washed with water and dried over anhydrous sodium sulfate to give crude **11b** (2.18 g), which was recrystallized from toluene to afford the pure acid (0.87 g, 45%): mp 120–125 °C.

α-(((2-Hydroxyethyl)thio)methyl)acrylic Acid (11d). A solution of 1,3-dibromopropane-2-carboxylic acid (5 g, 20 mmol) in dry dichloromethane was treated with triethylamine (6.3 g, 62 mmol) and stirred under argon at ambient temperature. After 6 h, 2-hydroxyethanethiol (1.8 g, 22 mmol) was added and the stirring continued for 16 h. The reaction mixture was poured with stirring into a chilled mixture of water (50 mL), 2 M H_2SO_4 (100 mL), and ammonium sulfate (40 g) and the organic phase was separated. After the aqueous phase was extracted 3 times with ethyl acetate, the combined organic phases were washed with brine and dried (Na_2SO_4). Removal of solvent and recrystallization of the product from toluene yielded **11d** (2.03 g, 62%): mp 79–81 °C. ^1H NMR ($CDCl_3/CD_3OD$) δ 2.65 (2 H, t, J = 7 Hz, CH_2S), 3.40 (2 H, s, CH_2S), 3.72 (2 H, t, J = 7 Hz, CH_2OH), 4.57 (2 H, br s, OH, COOH), 5.68 (1 H, s, olefinic H), 6.24 (1 H, s, olefinic H); MS (CH_4) m/z (relative intensity) 163 (MH^+, 15), 203 (26), 191 (59), 145 (100), 117 (15). Anal. Calcd for $C_6H_{10}O_3S$: C, 44.4; H, 6.21; S, 19.8. Found: C, 44.3; H, 6.5; S, 20.2.

Table I
Molecular Weight and Conversions for Polymerizations Carried Out in the Presence of Various Chain-Transfer Agents (CTA)

entry	CTA	monomer	10^3[CTA]/[monomer]	% conversion[a]	$\bar{M}_n$	entry	CTA	monomer	10^3[CTA]/[monomer]	% conversion[a]	$\bar{M}_n$
1	**1b**	St	0	8.2	125 000	47	**2d**	St	2.44	2.9	23 100
2	**1b**	St	1.11	7.5	54 700	48	**2d**	St	4.90	2.7	14 200
3	**1b**	St	2.21	7.3	33 800	49	**2d**	St	9.79	2.2	8 480
4	**1b**	St	3.34	6.5	26 300	50	**2d**	MMA	0	12.6	264 000
5	**1b**	MMA	0	12.9	252 000	51	**2d**	MMA	2.70	12.1	51 600
6	**1b**	MMA	1.02	10.0	68 000	52	**2d**	MMA	7.12	10.9	23 400
7	**1b**	MMA	2.04	10.2	36 100	53	**2d**	MMA	11.4	11.2	16 700
8	**1b**	MMA	4.07	8.5	20 200	54	**2d**	BA	0	19.0	355 000
9	**1c**	St	0	8.2	114 000	55	**2d**	BA	5.43	17.0	15 400
10	**1c**	St	0.93	7.5	56 800	56	**2d**	BA	10.11	16.4	9 820
11	**1c**	St	1.82	7.2	47 900	57	**2d**	BA	18.7	16.0	5 210
12	**1c**	St	3.63	6.5	30 000	58	**11d**	St	0	1.5	32 100[b]
13	**1d**	St	0	8.2	117 000	59	**11d**	St	2.97	1.2	11 100[b]
14	**1d**	St	1.17	8.3	57 900	60	**11d**	St	5.76	1.2	7 600[b]
15	**1d**	St	2.38	8.0	38 400	61	**11d**	St	11.3	1.1	4 330[b]
16	**1d**	St	3.54	7.6	28 900	62	**11d**	MMA	0	5.6	227 000[b]
17	**1d**	MMA	0	12.5	306 000	63	**11d**	MMA	3.33	4.6	49 300[b]
18	**1d**	MMA	1.08	10.8	64 000	64	**11d**	MMA	6.47	4.4	34 400[b]
19	**1d**	MMA	2.20	10.9	38 700	65	**11d**	MMA	13.4	2.8	23 900[b]
20	**1d**	MMA	4.37	10.0	20 300	66	**11d**	BA	0		316 000
21	**1e**	St	0	8.0	134 000	67	**11d**	BA	5.49	16.4	14 600
22	**1e**	St	1.24	7.4	60 800	68	**11d**	BA	11.3	15.6	6 890
23	**1e**	St	2.40	7.2	39 900	69	**11d**	BA	22.5	14.8	3 800
24	**1e**	St	5.03	6.9	21 900	70	**12d**	St	0	3.3	128 000
25	**1e**	MMA	0	12.6	208 000	71	**12d**	St	4.42	3.0	21 000
26	**1e**	MMA	1.30	10.2	55 700	72	**12d**	St	8.95	2.8	13 500
27	**1e**	MMA	2.32	9.0	36 500	73	**12d**	MMA	0	9.5	369 000
28	**1e**	MMA	4.53	9.6	21 700	74	**12d**	MMA	2.60		55 200
29	**1f**	St	0	8.0	96 000	75	**12d**	MMA	5.61	8.4	32 100
30	**1f**	St	29.5	4.8	8 200	76	**12d**	MMA	10.3	6.5	22 500
31	**2b**	St	0	7.9	114 000	77	**12d**	BA	0	19.6	484 000
32	**2b**	St	1.2	7.6	37 500	78	**12d**	BA	4.49	12.5	12 000
33	**2b**	St	2.4	7.3	20 900	79	**12d**	BA	8.87	12.0	6 950
34	**2b**	St	4.5	6.9	12 100	80	**12d**	BA	17.5	7.3	3 810
35	**2b**	MMA	0	12.1	184 000	81	**13d**	St	0	3.0	126 000
36	**2b**	MMA	1.02	12.3	83 000	82	**13d**	St	1.44	2.7	26 100
37	**2b**	MMA	2.24	12.1	50 200	83	**13d**	St	2.82	2.4	15 600
38	**11b**	St	0	8.3	53 400	84	**13d**	St	5.56	2.2	9 190
39	**11b**	St	1.32	7.5	28 200	85	**13d**	MMA	0	11.0	409 000
40	**11b**	St	2.64	7.7	19 700	86	**13d**	MMA	1.58	10.6	71 700
41	**11b**	St	5.24	7.4	12 100	87	**13d**	MMA	3.29	10.4	35 600
42	**11b**	MMA	0	12.2	172 000	88	**13d**	MMA	6.40	10.1	20 700
43	**11b**	MMA	1.21	12.5	78 100	89	**13d**	BA	0		2,840 000
44	**11b**	MMA	2.43	12.2	46 000	90	**13d**	BA	2.72	18.8	30 700
45	**11b**	MMA	4.82	13.0	27 400	91	**13d**	BA	5.48	11.0	12 900
46	**2d**	St	0	3.3	135 000	92	**13d**	BA	10.6	8.0	6 680

[a] Determined from the yield of polymer after one precipitation in methanol (polystyrene) or pentane (poly(methyl methacrylate)). [b] Cosolvent (ethyl acetate) used in polymerization.

2-Hydroxyethyl α-(((2-Hydroxyethyl)thio)methyl)acrylate (12d). α-(((2-Hydroxyethyl)thio)methyl)acrylic acid (**11d**) (1.72 g, 10.6 mmol) was dissolved in ethanol (20 mL) and then treated with cesium carbonate (1.92 g, 53 mmol) in water (10 mL) with stirring. After the evolution of CO_2 had subsided (10–15 min), the solution was evaporated to dryness. The remaining water was removed azeotropically with benzene, and then the solvent was removed by evaporation. Dry dimethylformamide (40 mL) was added to the residue, and 2-chloroethanol (5.5 mL, 80 mmol) was added under argon. The reaction mixture was stirred for 8 h under argon at 110 °C. After dilution with benzene, the reaction mixture was filtered and the filtrate was evaporated to dryness. Subjection of the crude product to chromatography on silica gel (toluene/CH_2Cl_2/MeOH, 2:7:1) yielded pure **12d** (1.19 g, 55%) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 2.69 (4 H, br s, SCH_2 and OH), 3.44 (2 H, s, CH_2S), 3.77 (4 H, m, 2 × CH_2OH), 4.32 (2 H, m, $CH_2OC(O)$), 5.68 (1 H, s, olefinic H), 6.22 (1 H, s, olefinic H); IR (film) 3350 (s), 1710 (s) cm^{-1}; MS (CH_4) m/z (relative intensity) 247 (M + 41, 30), 235 (M + 29, 63), 207 (M + 1, 6), 205 (8), 189 (68), 145 (100); accurate mass m/z 207.0686. $C_8H_{15}O_4S$ requires m/z 207.0691.

***N*-Phthalimidoethyl α-(((2-Hydroxyethyl)thio)methyl)acrylate (13d).** This ester was prepared by a similar procedure to that described above for **12d** except that (bromoethyl)phthalimide was substituted for 2-chloroethanol. Recrystallization from petroleum ether (40–60 °C) gave **13d** in 39% yield as white crystals: mp 58–59 °C; ^{1}H NMR ($CDCl_3$) δ 2.63 (2 H, t, J = 6 Hz, CH_2S), 3.34 (2 H, s, CH_2S), 3.70 (2 H, t, J = 6 Hz, CH_2OH), 4.02 (2 H, t, J = 5 Hz, CH_2N), 4.41 (2 H, t, J = 5 Hz, $CH_2OC(O)$), 5.65 (1 H, s olefinic H), 6.19 (1 H, s, olefinic H), 7.76 (4 H, m, aromatic H); MS (CH_4) m/z (relative intensity) 376 (M + 41, 5), 364 (M + 29, 9), 318 (72), 192 (92), 174 (100).

General Procedure for Carrying Out Polymerizations. Azobis(isobutyronitrile) (AIBN) (49.5 mg) was dissolved in freshly distilled inhibitor-free methyl methacrylate (25 mL). An aliquot (5 mL) was removed and added to an ampule containing the amount of the chain-transfer agent required to produce the concentration shown in Table I. The contents of the ampule were then degassed by three freeze–evacuate–thaw cycles and sealed under vacuum (10^{-3} Torr). The mixtures were then polymerized at 60 °C for 1 h. The volatiles were then removed and the polymers were dried in vacuo to constant weight and examined by GPC. Polymerizations with styrene were carried out similarly except that the AIBN concentration was 8.4 mM. The polymerization time for styrene was 3 h, except for the experiments listed in entries 46–49, 58–61, 70–73, and 82–85 in

Table I; in these cases, the polymerization was carried out at 60 °C for 1 h. Samples of poly(butyl acrylate) were prepared by polymerizing a mixture of inhibitor-free butyl acrylate (10 mL), the chain-transfer agent, and thiophene-free benzene (40 mL) in the presence of AIBN (5.1 mg) at 60 °C for 1 h. The conversions of the polymerizations were determined from the mass of polymer isolated after precipitation in methanol (for styrene) or pentane (for poly(methyl methacrylate)). The conversions of the butyl acrylate polymerizations were determined by weighing of the residue obtained after removal of the volatiles in vacuo and after subtracting the mass of the chain-transfer agent. All polymers of styrene and methyl methacrylate prepared for spectral analysis were synthesized as described above and isolated by precipitation in pentane or methanol. The polymers were then further purified by subjection to either preparative GPC or two further precipitations. With preparative GPC, cuts were carefully taken so as to include the whole of the polymer sample but to exclude any low molecular weight nonpolymeric material. The resulting polymer was dried in vacuo to constant weight. The ^{1}H NMR spectrum showed that all traces of the chain-transfer agent had been removed.

Reaction of Carboxy-Terminated Polymers with Diazomethane. A solution of diazomethane in ether [prepared from *N*-methyl-*N*-nitrosotoluene-*p*-sulfonamide (1 g)][9] was added dropwise to a solution of polystyrene ($\bar{M}_n \approx 8560$) (117 mg) in THF (10 mL) at 0 °C until the yellow color persisted. After 1 h of further stirring at 0 °C, the excess diazomethane was destroyed by the dropwise addition of a 5% solution of acetic acid in ether. The volatiles were then removed by rotary evaporation, and a portion of the residue was purified by preparative GPC and examined by ^{1}H NMR spectroscopy.

Estimation of Carboxy Groups in Polystyrene Prepared with 1b.[10] A sample of polystyrene prepared with **1b** was purified by precipitation in methanol (3 times) to remove the unreacted chain-transfer agent. The molecular weight ($\bar{M}_n$) after precipitation was 7700. A portion (331 mg) was dissolved in a mixture of freshly distilled tetrahydrofuran (3 mL) and boiled distilled water (1 mL). Phenolphthalein indicator (1% in ethanol/water (8:2); 5 drops) was added, and the polymer was titrated with 0.01 M NaOH solution. After the results of two similar titrations were averaged, the mean functionality per polymer chain ($\bar{F}_n$) was found to be 1.05 (±0.14). The titration of a sample of polystyrene ($\bar{M}_n$ = 5350) prepared with **11b** was conducted similarly, except that the pH was measured throughout the titration and the end point was determined graphically. This titration was not carried out in duplicate, due to a lack of material. The titration indicated that the mean functionality per polymer chain was 2.02.

Estimation of Amine Groups in Polystyrene Prepared with 1e. (a) A sample of polystyrene purified as above ($\bar{M}_n$ = 4460) (502.2 mg) in 30 mL of freshly redistilled tetrahydrofuran was titrated with 0.0104 M aqueous HCl. The pH was recorded throughout the titration and the end point was determined graphically. By averaging the results of two titrations the mean functionality per polymer chain was found to be 0.71 (±0.01). (b) Commercial poly(acrylic acid) ($\bar{M}_n \approx$ 500 000–1 000 000; Fluka) (1.15 g) was refluxed with thionyl chloride (7 mL) for 1 h. After this time, the excess thionyl chloride was removed in vacuo. Triethylamine (5 mL) was then added, followed by a solution of polystyrene ($\bar{M}_n$ = 5510, prepared with **1e**) (506 mg) and pyridine (4 mL). A further 1 mL of pyridine was used to wash in any remaining polystyrene residues, and the mixture was then boiled under reflux for 48 h. After this time, water (3 mL) was added and the mixture was stirred for 2 h. It was then poured into water and extracted 3 times with ether/ethyl acetate (1:1). The combined organic phases were washed successively with water, dilute hydrochloric acid, water, saturated sodium bicarbonate solution (3 times), and brine. After removal of the solvent from the dried organic layer, a residue (38.5 mg, 8% of the original sample mass) was obtained, which was shown to be low molecular weight polystyrene by GPC and ^{1}H NMR spectroscopy. The reactive functionality estimated by this method was, therefore, 92%.

Reaction of Hydroxy-Terminated Polystyrene Prepared in the Presence of 1d with *tert*-Butyldimethylsilyl Chloride.[11] Hydroxy-terminated polystyrene ($\bar{M}_n$ = 6100) (197 mg) prepared in the presence of **1b** was added to a stirred mixture of *tert*-butyldimethylsilyl chloride (348 mg), imidazole (300 mg), and dimethylformamide (2 mL).[9] After 24 h of stirring at 40 °C, the mixture was diluted with water and extracted with ethyl acetate. The extracts were washed with water and dried ($MgSO_4$), and the solvent was removed to afford 299 mg of crude material, which was taken up into ethyl acetate (ca. 2 mL) and precipitated in methanol (30 mL). A portion of the resultant polymer (total yield = 166 mg) was purified by preparative GPC and examined by ^{1}H NMR spectroscopy. Polystyrene prepared with **12d** was derivatized similarly.

Results and Discussion

When samples of styrene were polymerized (AIBN, 60 °C, in bulk) in the presence of various amounts of α-(((carboxymethyl)thio)methyl)styrene (**1b**), the resultant polymers were of markedly lower molecular weight than a sample prepared in the absence of **1b** (Table I, entries 1–4). The chain-transfer constant (C_x), calculated with the Mayo equation,[12] was 0.95. This value is close to the optimum of 1.0 for obtaining polymers of low polydispersity in batch polymerizations at moderate to high conversions.[13]

The thioether **1b** also was useful for lowering molecular weight in methyl methacrylate polymerizations (entries 5–8). The chain-transfer constant was 1.13 at 60 °C.

Although there was a decrease in the yields[14] of the precipitated polymers as the concentration of **1b** increased in both methyl methacrylate and styrene polymerizations (see Table I, % conversion column), it is clear that the lowering of molecular weight is predominantly by true chain *transfer*, rather than by termination of growing polymer chains without reinitiation (i.e., retardation or degradative chain transfer). If degradative chain transfer were the major pathway responsible for the lowering of molecular weight by **1b**, significantly lower conversions would be obtained.

To obtain evidence for the presence of the end groups, low molecular weight polymers were prepared with higher concentrations of the chain-transfer agents than those reported in Table I. The resulting polymers were examined by ^{1}H NMR or IR spectroscopy or by titration, after either a single precipitation and purification by preparative GPC, or after repeated precipitation. These steps were necessary to remove all traces of unreacted chain-transfer agent that otherwise would interfere with the analyses.[15]

The IR spectrum of polystyrene of $\bar{M}_n$ = 2600, prepared with **1b**, showed absorptions at 2500–3000 (broad), 1710, and 1300 cm^{-1}, due to the presence of carboxylic acid end groups. Additional proof as to the incorporation of carboxyl groups was provided by reaction of the polymer with diazomethane, which is well-known to convert carboxylic acids into their corresponding methyl esters.[16] The ^{1}H NMR spectrum then showed a signal at δ 3.7, due to methyl ester groups. By relating the GPC-derived number-average molecular weight with the relative integrals of the methyl ester signal and the aromatic protons of the polymer, the degree of functionality ($\bar{F}_n$) was calculated to be 0.85 (±~10%) (Table III). A further determination of the carboxylic acid end group content of the polymer was carried out by titration[10] of a sample of polystyrene prepared with **1b** and purified by precipitation. From an average of three titrimetric determinations, the mean functionality per polymer chain ($\bar{F}_n$) was calculated to be 1.05 (±13%). To ascertain whether the unsaturated end groups of the polymer (see Scheme I) underwent significant copolymerization at polymerizations taken to higher conversion, a polymerization of styrene in the presence of **1b** was also carried out for an extended period (64 h). This

Table II
Chain-Transfer Constants (C_x) Derived for Styrene, Methyl Methacrylate, and Butyl Acrylate Polymerizations

CTA	C_x		
	styrene	methyl methacrylate	butyl acrylate
1b	0.95	1.13	nd[a]
1c	0.68	nd	nd
1d	0.77	1.04	nd
1e	0.79	0.91	nd
1f	0.4[b]	nd	nd
2b	1.72	0.65	nd
2d	1.15	0.49	1.28
11b	1.27	0.64	nd
11d	1.81	0.27	1.49
12d	0.77	0.40	1.88
13d	1.87	0.72	1.83

[a] nd = not determined. [b] Determined on the basis of one experiment from precipitated polymer.

Table III
Polymer Functionality ($\bar{F}_n$) As Determined by ^{1}H NMR Spectroscopy[a]

CTA	monomer	$\bar{M}_n$	after treatment	$\bar{F}_n$	type of functionality
1b	St	7780	CH_2N_2 esterification	0.9	CO_2CH_3
1d	St	6780	*tert*-butyldimethylsilylation	1.1	$(CH_3)_2SiO$
2d	St	9090	none	0.8	CH_2OH
2d	St	9090	none	1.1	SCH_2CH_2OH
11d	St	6150	none	1.2	CH_2OH
11d	St	5920	none	1.0	CH_2OH
11d	St	6060	CH_2N_2 esterification	1.3	$CH_3OC(O)$
12d	St	5340	none	2.1	$CH_2OH \times 2$
12d	St	5310	*tert*-butyldimethylsilylation	2.4	$(CH_3)_2SiO \times 2$
12d	MMA	3350	none	1.4	$CH_2OC(O)$
12d	BA	5770[b]	none	0.9	$CH_2OC(O)$
13d	St	6910	none	1.0	CH_2OH
13d	MMA	5940	none	1.2	phthalamido

[a] The precision of measurement depends largely on the accuracy of integration of the ^{1}H NMR spectra. Each spectrum was retransformed, rephased, and reintegrated 5 times and average values were used. In favorable cases, the reproducibility was ca. ±5%. In some cases, the uncertainty could be 15% or greater, especially when the integrated signals were broad or where the spectrum was difficult to phase. [b] Accurate GPC calibration for poly(butyl acrylate) was unavailable. The molecular weight quoted is the "PSt-equivalent" molecular weight.

resulted in a conversion of 43%. The GPC trace of the resulting polymer showed no broadening or asymmetry, as would be expected from partial copolymerization of the macromonomer-like polymer. Titration of the polymer indicated a carboxylic acid functionality of 1.1 and also implied that copolymerization of the polymer (which would lead to greater average functionalities), if it occurred, was a minor reaction at this level of conversion. This apparent low reactivity, of course, does not preclude the use of these materials as macromonomers with comonomers of greater reactivity or in ionic copolymerizations.

A sample of poly(methyl methacrylate) ($\bar{M}_n$ = 3300 after precipitation from petroleum ether), also prepared with **1b**, was examined by ^{1}H NMR spectroscopy. The spectrum showed signals at δ 7.22, due to the aromatic hydrogens of the incorporated chain-transfer agent, and signals at δ 5.15 and 4.95, ascribed to the terminal double bond, and at δ 3.1, due to the methylene protons of the SCH_2COOH moiety.

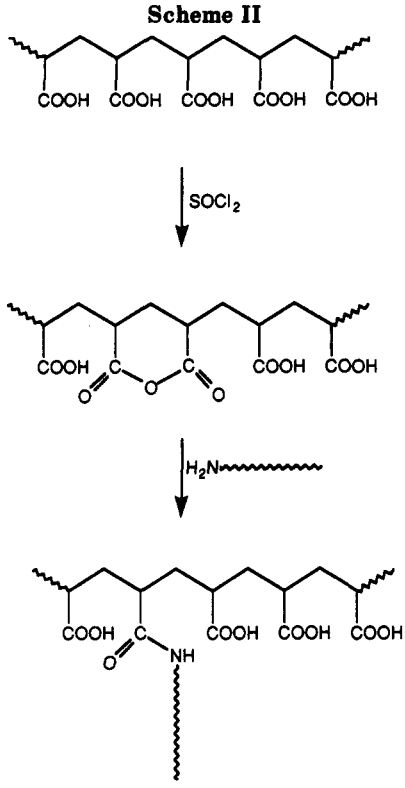
The carboxy thioether **1c** was also prepared and shown to be effective as a chain-transfer agent (C_x = 0.68 for styrene at 60 °C), although evidence for the functionality of the resulting polymer was not sought.

Figure 1. ^{1}H NMR spectrum of polystyrene ($\bar{M}_n$ = 6300) prepared in the presence of **1d**.

Low molecular weight hydroxy-terminated polymers were readily prepared with the allylic sulfide **1d**, which had a chain-transfer constant of 0.77 for styrene and 1.04 for methyl methacrylate polymerizations (Table II). A purified sample of hydroxy-terminated polystyrene ($\bar{M}_n$ = 6300), prepared with **1d**, showed absorptions at δ 3.35–3.55 in the ^{1}H NMR spectrum (Figure 1), confirming the presence of the hydroxymethylene group, and at δ 4.7–4.8 and 5.0–5.1, due to the double bond. Treatment of this sample with *tert*-butyldimethylsilyl chloride in the presence of imidazole[11] led to the polymer being capped with a (*tert*-butyldimethylsilyl)oxy group, the methyl groups of which were clearly visible by ^{1}H NMR spectroscopy. By comparing the degree of polymerization (determined by GPC) with the relative integrals of the dimethylsilyl signal (δ 0.0–0.1) and the aromatic signals from the polystyrene backbone, we estimated that the average functionality per polymer chain ($\bar{F}_n$) was 1.1 (see Table III).

The thioether **1e** was shown to be useful for introducing amine end groups. It had a chain-transfer constant of 0.79 for polymerizations of styrene and 0.91 for polymerizations of methyl methacrylate. Evidence for the amine functionality in polystyrene of $\bar{M}_n$ = 6300, prepared with **1e**, was obtained from the ^{1}H NMR spectrum, which showed a signal at δ 2.6, consistent with a methylene adjacent to an amino group. A signal at δ 3.0 was assigned to the amine protons. The average amine functionality was shown by titration with hydrochloric acid to be 0.7. This result, however, may be unreliable because the titration was complicated by precipitation of the polymer and the end point was difficult to determine. The functionality of a similarly prepared sample of polystyrene

Scheme II



($\bar{M}_n$ = 5510) was also estimated by a grafting reaction onto an excess of poly(acrylic acid) that had previously been treated with thionyl chloride. This grafting reaction is illustrated in Scheme II. The acrylic acid based graft copolymer was then separated from any unreacted polystyrene by washing with aqueous sodium bicarbonate. Provided the conditions of the grafting reaction were sufficiently vigorous to graft all of the functionalized polymer, as we believe was the case (see Experimental Section), the fraction of the polymer remaining in the organic phase is indicative of the extent of nonfunctional material in the original sample. The use of a large excess of poly(acrylic acid) was necessary to avoid the possible complication of a highly grafted copolymer sequestering nonfunctional polystyrene. With a low graft density (because of the excess of poly(acrylic acid)), this was considered to be far less likely. The amine functionality of the polystyrene sample estimated by this method was 0.92.

The trimethoxysilyl-substituted allylic sulfide **1f** lowered the molecular weight in a polymerization with styrene; an apparent chain-transfer constant of 0.4 was estimated from entries 29 and 30 in Table I. This compound did, however, retard the polymerization. The allylic sulfide **1f** was expected to introduce a potentially reactive trimethoxysilyl end group. On keeping, however, a sample crosslinked; this behavior was consistent with a trimethoxysilyl-containing polymer in the presence of moisture.[17] The allylic sulfide **2b**, which contained a thioglycolic acid group and an acrylate moiety, had favorable chain-transfer constants (Table II). Polystyrene of $\bar{M}_n$ = 4000 prepared with **2b** showed ^{1}H NMR signals at δ 1.15, 3.9–4.1, 5.0–5.1, and 5.8–5.9, confirming the presence of the ethyl ester end group and the terminal double bond. The IR spectrum of this polymer showed absorptions at 3500–2300 (broad), 1705, and 1295 cm^{-1}, indicating the presence of the carboxylic acid end group. The ester end group is hydrolyzable to a carboxylic acid group, and the polymer could be used as a precursor to α,ω-dicarboxypolystyrene. However, α,ω-dicarboxy polymers are directly produced

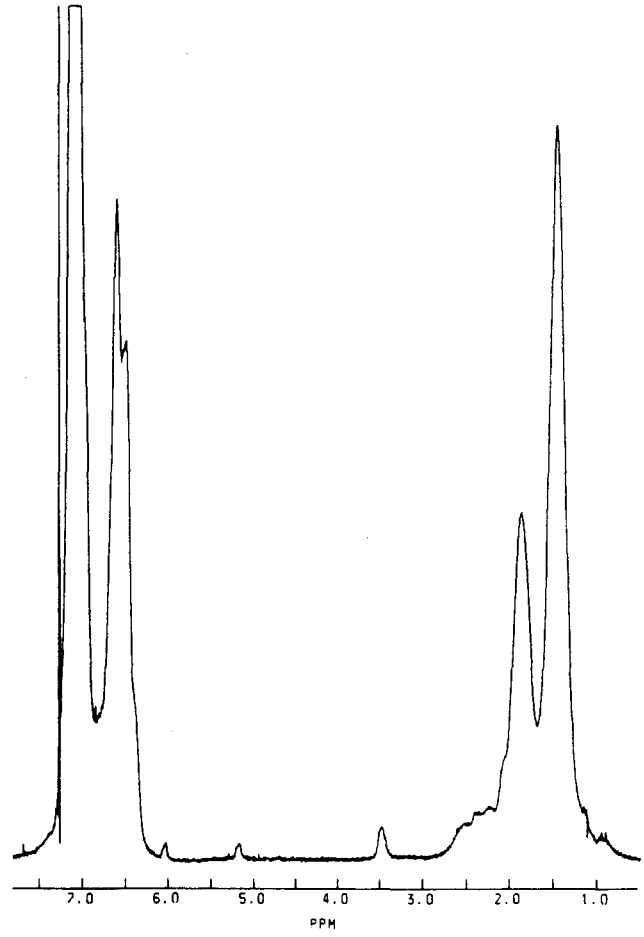


Figure 2. ^{1}H NMR spectrum of polystyrene ($\bar{M}_n$ = 5920) prepared in the presence of **11d**.

with the acrylic acid derivative **11b**, which has a chain-transfer constant of 1.27 for styrene polymerizations and 0.64 for methyl methacrylate polymerizations. The IR spectrum of low molecular weight ($\bar{M}_n$ = 12 000) polystyrene showed absorptions at 1735 and at 1700 cm^{-1}, due to the saturated and α,β-unsaturated carboxylic acid end groups. Titration of a sample of polystyrene ($\bar{M}_n$ = 5350) prepared with **11b** with sodium hydroxide solution indicated that the carboxy functionality was 2.0.

The hydroxy-containing ethyl acrylate derivative **2d** was used to prepare low molecular weight hydroxy end-functional polystyrene, poly(methyl methacrylate), and poly(butyl acrylate). The chain-transfer constants in each case were favorable (see Table II). In the case of a sample of polystyrene of $\bar{M}_n$ = 9090 prepared with **2d**, the ^{1}H NMR spectrum showed a signal at δ 3.42, indicative of a methylene adjacent to a hydroxyl group. The hydroxyl functionality determined by integration of this signal was 0.9 (see Table III). However, a signal at δ 2.58, due to methylenes adjacent to sulfur, was better resolved; integration of this signal gave a functionality of 1.1. Since this moiety is also expected to carry the hydroxyl group, this measurement also serves to confirm the high incorporation of hydroxy functionality.

The acrylic acid derivative **11d** was used to prepare low molecular weight α-hydroxy-ω-carboxypolystyrene and α-hydroxy-ω-carboxypoly(methyl methacrylate). The chain-transfer constants appear in Table II. The hydroxyl functionality was assayed by ^{1}H NMR spectroscopy, using the absorption at δ 3.5, assigned to the methylene protons adjacent to oxygen (Figure 2). The hydroxyl functionality measured in this way varied from 0.99 to 1.2 in two separately prepared batches of polystyrene (Table III).

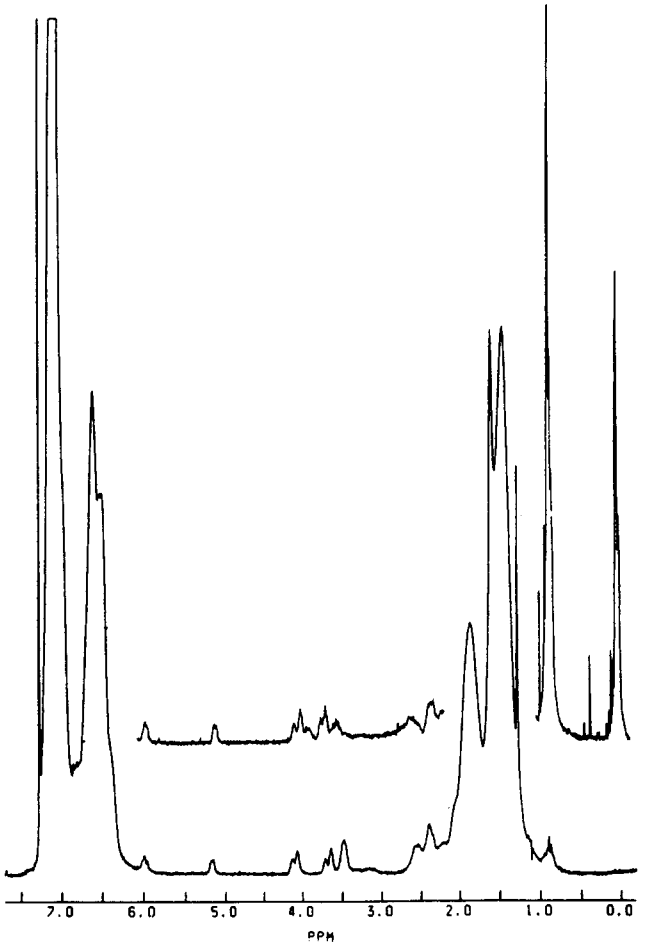


Figure 3. ^{1}H NMR spectra of polystyrene ($\bar{M}_n \approx 5300$) prepared in the presence of **12d** before (lower trace) and after derivatization with *tert*-butyldimethylsilyl chloride (upper trace).

The carboxyl functionality was estimated to be 1.3 by ^{1}H NMR spectroscopy (methyl ester signal) after treatment of the polymer with diazomethane.

The diol **12d** was used to prepare dihydroxy end-functional polystyrene and poly(methyl methacrylate). The chain-transfer constants (C_x = 0.77 with styrene and C_x = 0.40 for methyl methacrylate) indicated a lower activity in reducing molecular weight of poly(methyl methacrylate) than their non-hydroxy-containing counterparts. The allylic sulfide **12d** was also used to prepare low molecular weight α,ω-dihydroxypoly(butyl acrylate). The functionality that was incorporated into polystyrene was 2.1 as measured by integration of the methylene protons adjacent to oxygen in the ^{1}H NMR spectrum (Figure 3, lower trace). In addition, the polymer was treated with *tert*-butyldimethylsilyl chloride, and the methylsilyl signal (Figure 3, upper trace) of the silyl ether derivative was integrated; the functionality calculated by this method was 2.4. Calculation of functionality in the case of α,ω-dihydroxypoly(methyl methacrylate) prepared with **12d** was less straightforward and only a partial determination was made. The signals due to the methylenes adjacent to the hydroxyls were not readily integrated because of interference by the nearby methyl ester group. The incorporation of the ester group of **12d** (and presumably also the hydroxyl attached to it) was assayed by integration of the methylene protons adjacent to the ester group ($\bar{F}_n$ = 1.4). In the case of poly(butyl acrylate), integration of the methylene protons adjacent to the ester group of the end group derived from **12d** showed that $\bar{F}_n$ = 0.9.

The chain-transfer agent **13d**, which contains a phthalamido group, was moderately active (see Table II) and installed both hydroxyl and phthalamido groups onto styrene, methyl methacrylate, and butyl acrylate. It is expected that low molecular weight styrene prepared with **13d** would, after hydrolysis, contain both hydroxy and amino end groups. Evidence for the hydroxy groups in polystyrene was obtained by ^{1}H NMR spectroscopy ($\bar{F}_n$ = 1.0); integration of the phthalamido aromatics in a poly(methyl methacrylate) sample indicated that 1.2 phthalamido groups were present per polymer chain.

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(2) The fragmentation step is likely to be very fast since **4a**, **5a**, and **6a** do not copolymerize with methyl methacrylate or styrene;[1] the fragmentation may even be concerted with addition.
(3) An alternative route for chain transfer, namely, that of abstraction of the allylic hydrogens, can be discounted on the basis of the relatively low published transfer constants for allylic systems and methylene groups adjacent to sulfur, the expected inertness of the resulting stabilized allyl radical to undergo reinitiation, the known propensity of activated allylic sulfides to undergo S_H2 reactions with alkyl radicals,[4] and the inertness to chain transfer of allyl *tert*-butyl sulfide,[1] which is unactivated toward radical addition. In addition, the ^{1}H NMR spectra of the low molecular weight polymers prepared with **1a** show no evidence for methine protons adjacent to sulfur.
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(14) It is noteworthy that low molecular weight polymer fractions were not lost when the samples listed in entries 1–4 (Table I) were precipitated in methanol, since the filtrates, after evaporation, were shown by ^{1}H NMR spectroscopy to be free from polystyrene.
(15) The low molecular weights of the polymers that were prepared caused a substantial loss of material during the precipitations, and accordingly the number-average molecular weight of the purified product was greater than that predicted from the Mayo equation for chain transfer.
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