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Reversible Addition Fragmentation Chain Transfer Polymerization of Methyl Methacrylate in the Presence of Lewis Acids: An Approach to Stereocontrolled Living Radical Polymerization

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ABSTRACT: Reversible addition fragmentation chain transfer (RAFT) polymerization of methyl methacrylate (MMA) can be carried out in the presence of cyanoisopropyl methyl trithiocarbonate $[CH_3SC(=S)SC(CH_3)_2CN]$ and scandium triflate $[Sc(OTf)_3]$ to provide simultaneous RAFT-controlled (reversible addition-fragmentation chain transfer controlled) molecular weight and molecular weight distribution ($\bar{M}_w/\bar{M}_n < 1.3$ at >95% conversion), Lewis acid-controlled tacticity (*mm*:*mr*:*rr* = 12:44:44 for a mole ratio $Sc(OTf)_3$/MMA = 1:8.5 at 60 °C) and an enhanced rate of polymerization. The tacticities observed for poly(methyl methacrylate) (PMMA) are similar to those observed with scandium triflate in the absence of the RAFT agent. The stability of dithiobenzoate RAFT agents $[ZC(=S)SR]$ in the presence of scandium triflate is strongly dependent on both the Z and R substituent. 2-(ethoxycarbonyl)prop-2-yl dithiobenzoate $[PhC(=S)SC(CH_3)_2CO_2CH_3]$ and the polymeric RAFT agent $[PhC(=S)S-(CH_3)(CO_2CH_3)CH_2-PMMA]$ appear relatively stable. However, cumyl $[PhC(=S)SC(CH_3)_2Ph]$ and cyanoisopropyl dithiobenzoate $[PhC(=S)SC(CH_3)_2CN]$ are rapidly degraded and are therefore not appropriate for direct use in this application. These RAFT agents may, however, be used to synthesize stereoblock copolymers where the RAFT agent is first transformed to an oligomeric or polymeric RAFT agent in the absence of a Lewis acid. Cyanoisopropyl 1*H*-pyrrole-1-carbodithioate $[(C_4H_4N)C(=S)SC(CH_3)_2CN]$ is stable to Lewis acid-induced decomposition but slowly homolyzes at 60 °C (even in the absence of the Lewis acid) to initiate the RAFT polymerization of MMA.

Introduction

Reversible addition fragmentation chain transfer (RAFT) polymerization offers many benefits over conventional radical polymerization including the ability to exert control over the molecular weight and molecular weight distribution, prepare block copolymers or polymers with more complex architectures, and generate functionalized polymers (the features usually associated with living polymerizations).[1−5] RAFT polymerizations can be carried out in bulk, solvent, emulsion, or suspension, over a large temperature range, and are compatible with the functionality present in most monomers, initiators, and solvents. However, the RAFT process does not, by itself, exert any control over polymer chain stereochemistry. The tacticity of RAFT-synthesized polymers appears identical to those obtained by the conventional radical polymerization under similar experimental conditions.

Stereocontrol over the propagation step is achievable in anionic and coordination polymerization through the choice of solvent or complexing agents.[6,7] However, despite some significant advances,[8] effective stereocontrol over the propagation step in radical polymerization remains one of the holy grails of polymer science.[9,10]

Various approaches to stereocontrol of propagation in radical polymerization of methacrylic monomers are reported in the literature.[10] The most successful involve the use of modified monomers. Polymerization of methacrylates with bulky aromatic ester groups [e.g., triphenylmethyl methacrylate or 1-phenyldibenzosuberyl methacrylate (**1**)] provides isotactic polymers.[11−13] A preponderance of isotactic triads was also observed in the polymerization of the zinc coordination complex of methacrylic acid **2**.[14,15]

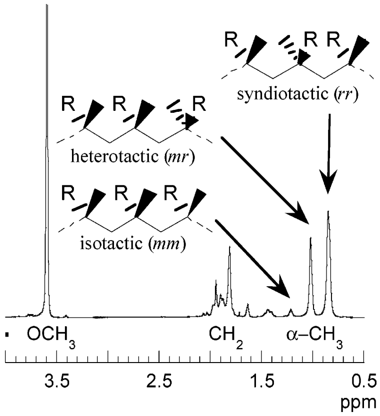
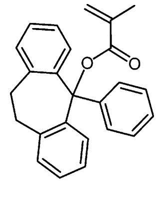


Figure 1. 400 MHz ^{1}H NMR spectrum ($CDCl_3$) of poly(methyl methacrylate) ($R = CO_2CH_3$) showing triad assignments.[37,38] Sample was prepared by polymerization of methyl methacrylate (7.01 M in benzene) with cumyl dithiobenzoate (9.3×10^{-3} M) and azobisisobutyronitrile (6.98×10^{-3}M) as the initiator for 16 h at 60 °C. Conversion 90%, $\bar{M}_n$ 62 000 (polystyrene equivalents), $\bar{M}_w/\bar{M}_n = 1.09$, *mm*:*mr*:*rr* = 3:34:63.



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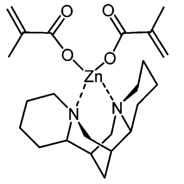

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Some modification of tacticity in radical polymerization of methyl methacrylate (MMA) and other simple methacrylate esters has been achieved through the use of fluorinated alcohols

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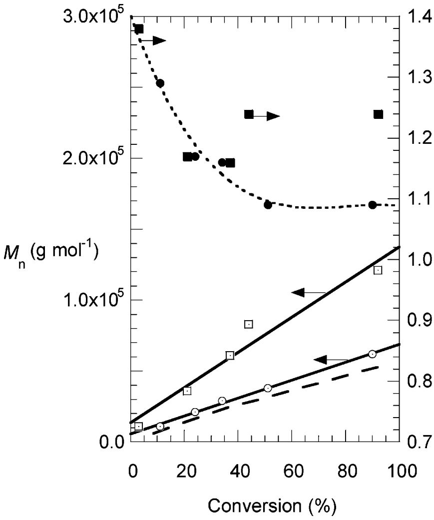


Figure 2. Evolution of number average molecular weight (polystyrene equivalents, open symbols) and polydispersity ($\bar{M}_w/\bar{M}_n$, filled symbols) with conversion during reversible addition fragmentation chain transfer polymerization of methyl methacrylate with cumyl dithiobenzoate (**3**) in the presence (□) and absence (○) of scandium triflate at 60 °C. The dashed line (− − −) indicates the theoretical molecular weight calculated using eq 1.

as a solvent for the polymerization[9,16] or by the addition of Lewis acids.[9,17] Isobe et al.[17] conducted a systematic study of the radical polymerization of MMA in the presence of a series of Lewis acids. They found that the largest change in tacticity for poly(methyl methacrylate) (PMMA) was induced by addition of scandium triflate (scandium trifluoromethanesulfonate, Sc(OTf)$_3$). Conventional radical polymerization of MMA in toluene provides a predominantly syndiotactic (*rr*) polymer with *mm*:*mr*:*rr* = 3:33:64 (2.4 M MMA in toluene at 60 °C).[17] MMA polymerization in the presence of scandium triflate produced polymers with a significantly higher fraction of isotactic (*mm*) and heterotactic triads (*mr*) than polymers prepared in the absence of scandium triflate. Thus, PMMA with *mm*:*mr*:*rr* = 14:46:40 was obtained for polymerization at 60 °C under similar conditions but with 0.2 M scandium triflate.[17]

Previous attempts to use the RAFT process to control MMA polymerization in the presence of a Lewis acid have been frustrated by RAFT agent instability (vide infra). Lutz et al.[18] found poor control over the molecular weight and distribution for the RAFT polymerization of MMA with cumyl dithiobenzoate in the presence of scandium triflate in toluene as the solvent. Better control over the molecular weight and distribution was achieved with use of methanol as the solvent; however, under these conditions the polymers synthesized did not display substantially modified tacticity. Isobe et al.[17] observed in earlier work that the degree of stereocontrol achieved with scandium triflate is solvent dependent.

Other RAFT polymerizations carried out in the presence of Lewis acids, with the aim of achieving tacticity control for homopolymers, monomer sequence control for copolymers, or simply rate enhancement have met with greater success.[19] RAFT polymerization of *N*-isopropylacrylamide (NIPAM) derivatives in the presence of Lewis acids and with either 1-phenylethyl or cumyl dithioacetate as the RAFT agent was reported by Okamoto and co-workers.[20−22] Mori et al.[23] studied RAFT polymerization of *N*-acryloyl-*l*-phenylalanine methyl ester with benzyl 1*H*-pyrrole-1-carbodithioate as the RAFT agent. Matyjaszewski and co-workers reported RAFT polymerization of *N*,*N*-dimethylacrylamide[24] and MMA[18] in the presence of Lewis acids with cumyl dithiobenzoate as the RAFT agent. They[25−27] also investigated RAFT copolymerization of styrene and MMA in the presence of Lewis acids to achieve alternating copolymers. The Lewis acid-induced alternating copolymerization of *β*-pinene with acrylonitrile in the presence of cyanoisopropyl dithiobenzoate has also been studied.[28,29] Very recently RAFT polymerization of butyl acrylate in the presence of alumina as a heterogeneous Lewis acid to give significant rate enhancement has been reported.[30]

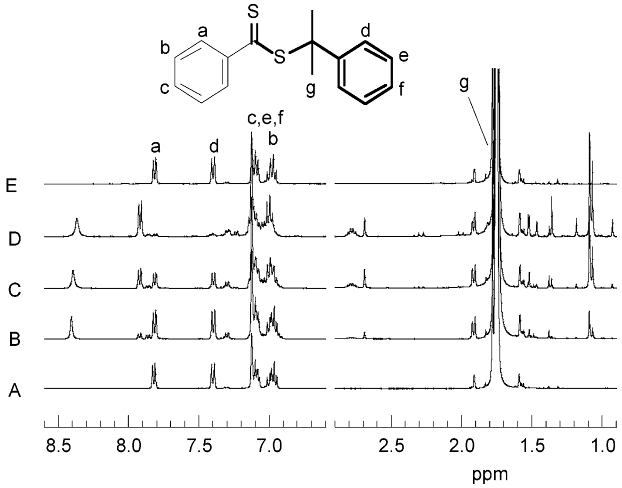


Figure 3. Regions of the 400 MHz ^{1}H NMR spectra of (A) cumyl dithiobenzoate (**3**, 0.089 M) in methyl methacrylate (2.27 M in benzene-d_6) without heating and without scandium triflate, with scandium triflate (0.081 M) after heating at 60 °C for (B) 1 h, (C) 4 h, and (D) 16 h, and (E) without scandium triflate after heating at 60 °C for 16 h. The singlet at 7.12 ppm is assigned to residual hydrogens of benzene-d_6. The large singlet at 1.75 ppm is assigned to the α-methyl hydrogens of methyl methacrylate, and the cumyl methyl hydrogens of **3**, "g", appear slightly downfield and are not completely resolved from this signal.

In this paper we report our investigations of the RAFT polymerization of MMA in the presence of scandium triflate carried out with the aim of finding RAFT agents that provide control over molecular weight and distribution of PMMA and which are stable in the presence of Lewis acid and thus offer the potential of simultaneous control over polymer chain tacticity and molecular weight.[31,32]

Experimental Section

General. Scandium triflate (Sc(OTf)$_3$) (Aldrich, 99%) was used as received. MMA (Aldrich, 99%) was purified by passage through activity I neutral alumina (to remove inhibitors) followed by fractional distillation and then flash distillation immediately prior to use. Azobisisobutyronitrile (AIBN, DuPont) was purified twice by crystallization from chloroform/methanol and stored at −14 °C. Gel permeation chromatography (GPC) was performed with a Waters Associates liquid chromatograph equipped with differential refractometer and 3 × mixed C and 1 × mixed E PLgel column (each 7.5 mm × 300 mm) from Polymer Laboratories. Tetrahydrofuran (flow rate of 1.0 mL/min) was used as the eluent at 22 ± 2 °C. The columns were calibrated with narrow polydispersity polystyrene standards (Polymer Laboratories). A third-order polynomial was used to fit the log M vs time calibration curve, which appeared approximately linear across the molecular weight range (2×10^2)−(2×10^6) g mol^{-1}. The molecular weights in this paper are reported as polystyrene equivalents. Samples for GPC analysis were isolated by evaporation of solvent and unreacted monomer. No precipitation or fractionation was performed prior to GPC analysis. Samples were further purified by precipitation into methanol for analysis by NMR spectroscopy. The NMR spectra were recorded on a Bruker AC200 (200 MHz for ^{1}H NMR) or Bruker Av400 spectrometer (400 MHz for ^{1}H NMR, 125 MHz for ^{13}C NMR) where indicated. Chemical shifts are quoted relative to (external) tetramethylsilane (TMS).

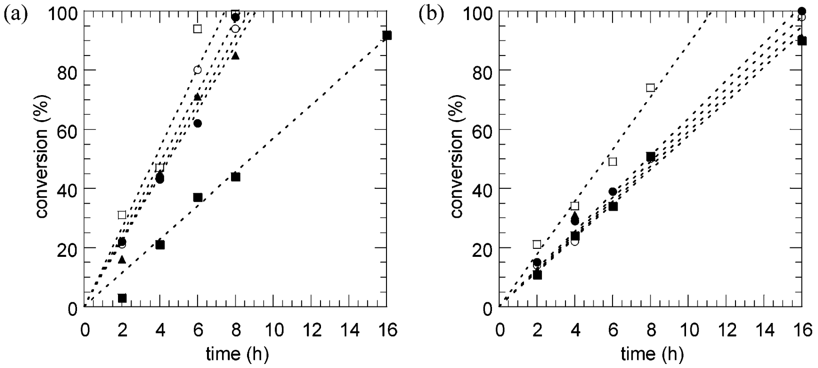


Figure 4. Rate of reversible addition fragmentation chain transfer polymerization of methyl methacrylate (7.01 M in benzene) (a) in presence of scandium triflate (~0.21 M) and (b) in the absence of scandium triflate. Polymerization at 60 °C with AIBN initiator (6.98×10^{-3} M) and with RAFT agent cumyl dithiobenzoate (**3**) (■), cyanoisopropyl dithiobenzoate (**4**) (▲), 2-(ethoxycarbonyl)prop-2-yl dithiobenzoate (**5**) (●), cyanoisopropyl 1*H*-pyrrole-1-carbodithioate (**6**) (□), and cyanoisopropyl methyl trithiocarbonate (**7**) (○).

Table 1. Effect of Scandium Triflate on Reversible Addition Fragmentation Chain Transfer Polymerization of Methyl Methacrylate (MMA) in the Presence of Dithiobenzoate RAFT Agents (3−5) and Azobis(isobutyronitrile) (AIBN) Initiator at 60 °C in Benzene[a]

RAFT agent	$[Sc(OTf)_3]$ (M)	time (h)	conversion %	*mm*	*mr*	*rr*	*m*	$\bar{M}_n$[b] (g mol^{-1})	$\bar{M}_n$ (theoret)[c] (g mol^{-1})	$\bar{M}_w/\bar{M}_n$[d]
3	0	2	11	5	33	62	22	11 000	7 900	1.29
3	0	4	24	4	33	63	21	21 000	16 500	1.17
3	0	6	34	4	33	63	21	29 000	22 500	1.16
3	0	8	51	3	34	63	20	38 000	32 700	1.09
3	0	16	90	3	34	63	20	62 000	51 700	1.09
3	0.218	2	3	5	34	61	22	11 000	2 160	1.38
3	0.218	4	21	4	33	63	21	36 000	14 500	1.17
3	0.218	6	37	4	33	63	21	61 000	24 500	1.16
3	0.218	8	44	4	36	60	22	83 000	28 200	1.24
3	0.218	16	92	5	37	58	24	121 000	52 800	1.24
4	0	2	12	3	34	63	20	13 000	8 500	1.23
4	0	4	31	4	33	63	21	22 000	21 000	1.12
4	0	8	51	3	34	63	20	31 000	33 200	1.09
4	0	16	91	4	34	62	21	47 000	52 000	1.06
4	0.211	2	16	4	34	62	21	34 800	11 800	1.23
4	0.211	4	45	4	34	62	21	75 000	31 200	1.16
4	0.204	6	71	6	38	56	24	96 500	47 200	1.15
4	0.206	8	85	7	38	55	24	129 000	54 500	1.26
5	0	2	15	4	33	63	21	38 000	9 990	1.56
5	0	4	29	4	33	63	21	41 000	18 600	1.51
5	0	6	39	4	33	63	21	43 000	24 100	1.50
5	0	8	51	4	33	63	21	48 000	30 600	1.43
5	0	16	100	4	33	63	21	60 000	54 400	1.32
5	0.206	2	22	5	34	61	22	34 000	14 700	1.52
5	0.206	4	43	5	35	60	23	39 000	27 600	1.47
5	0.206	6	62	4	36	60	22	46 000	38 400	1.38
5	0.206	8	98	6	37	57	25	61 000	58 800	1.27

[a] [MMA] = 7.01 M in benzene, [AIBN] = 6.98×10^{-3} M, [dithiobenzoate] = 9.3×10^{-3} M. [b] Number average molecular weight in polystyrene equivalents. [c] Calculated using eq 1. [d] Polydispersity = ratio of weight average and number average molecular weights.

RAFT Reagents. Cumyl dithiobenzoate (**3**),[33] cyanoisopropyl dithiobenzoate (**4**),[33] 2-(ethoxycarbonyl)prop-2-yl dithiobenzoate (**5**),[34] cyanoisopropyl 1*H*-pyrrole-1-carbodithioate (**6**),[35] and cyanoisopropyl methyl trithiocarbonate (**7**)[35] were prepared as described elsewhere.

Polymerization Procedure. Control MMA Polymerization. The following procedure is typical for all polymerizations in the absence of scandium triflate. In a 10 mL volumetric flask, a stock solution comprising MMA (7.5 mL, 7.01 M), AIBN (11 mg, 0.0066 M), cyanoisopropyl methyl trithiocarbonate (**7**) (0.023 g, 0.01 M) in benzene (2.5 mL) was prepared. Aliquots (0.5 mL) were transferred to ampules, degassed with three freeze−evacuate−thaw cycles and sealed. The ampules were heated at 60 ± 1 °C in a thermostatted oil bath for the times indicated. ^{1}H NMR (200 MHz) of the reaction mixture was taken before removal of the solvent to determine conversions. The excess monomer and solvent were removed by evaporation at ambient temperature under vacuum, and the residues were analyzed directly by GPC. Samples were then precipitated into methanol and dried prior to analysis by NMR spectroscopy to determine tacticity. The NMR spectrum of a control PMMA indicating triad assignments is shown in Figure 1.

Monomer conversions were established by comparing the intensity of ^{1}H NMR signals for the methoxyl hydrogens of MMA (δ 3.75) and PMMA (δ 3.59).

MMA Polymerizations with Scandium Triflate. The following procedure is typical for all polymerizations in the presence of scandium triflate. Aliquots (0.5 mL) of stock solution from the control experiment (prepared as described above) were transferred to ampules containing scandium triflate (0.05 g, to give 0.21 M), degassed with three freeze−evacuate−thaw cycles and sealed. The ampules were heated at 60 ± 1 °C in a thermostatted oil bath for the times indicated. NMR spectra of the reaction mixtures were obtained to determine conversions. The excess monomer and solvent were removed by evaporation at ambient temperature under vacuum, and the residues were analyzed directly by GPC. Samples were then reprecipitated into methanol and dried prior to analysis by NMR spectroscopy to determine tacticity

Results and Discussion

A series of RAFT agents comprising, dithiobenzoates (**3**−**5**), cyanoisopropyl 1*H*-pyrrole-1-carbodithioate (**6**), and cyano-

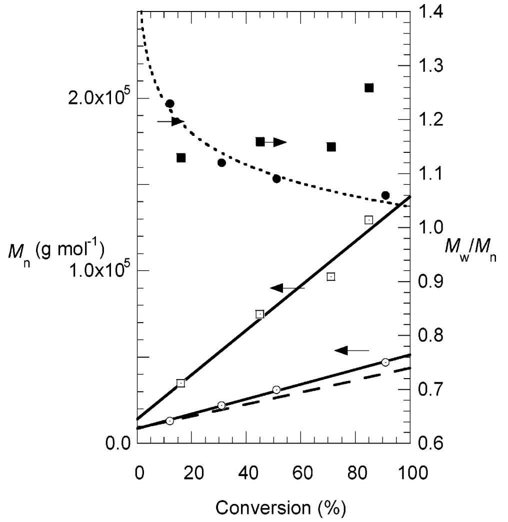


Figure 5. Evolution of number average molecular weight (polystyrene equivalents, open symbols) and polydispersity (filled symbols) with conversion during reversible addition fragmentation chain transfer polymerization of methyl methacrylate with cyanoisopropyl dithiobenzoate (**4**) in presence (□) and absence (○) of scandium triflate at 60 °C. The dashed line (— — —) indicates the theoretical molecular weight calculated using eq 1.

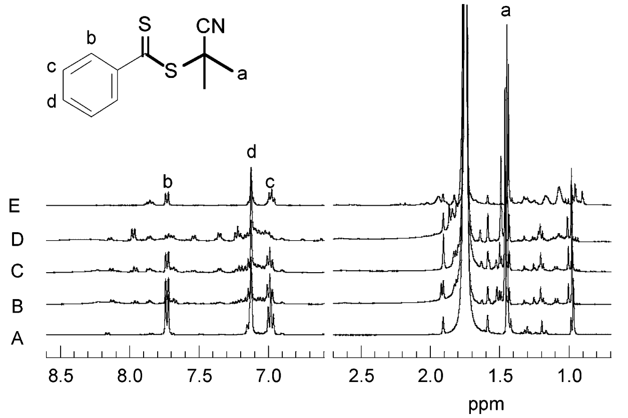
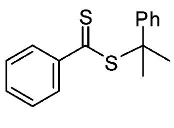


Figure 6. Regions of the 400 MHz ^{1}H NMR spectra of cyanoisopropyl dithiobenzoate (**4**, 0.11 M) in methyl methacrylate (2.50 M in benzene-d_6) (A) without heating and without scandium triflate, with scandium triflate (0.079 M) after heating at 60 °C for (B) 1 h, (C) 4 h, and (D)16 h, and (E) without scandium triflate after heating at 60 °C for 16 h. The singlet at 7.12 ppm that is incompletely resolved from signal "d" is assigned to residual hydrogens of benzene-d_6. The large singlet at 1.75 ppm is assigned to the α-methyl hydrogens of methyl methacrylate.



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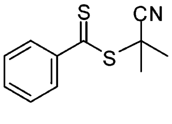

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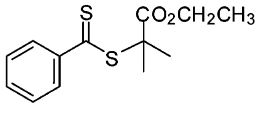

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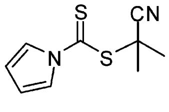

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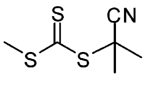

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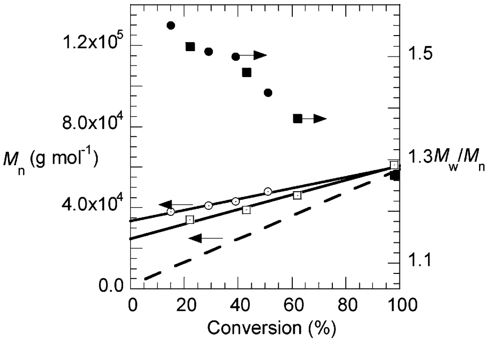


Figure 7. Evolution of number average molecular weight (polystyrene equivalents, open symbols) and polydispersity (filled symbols) with conversion during reversible addition fragmentation chain transfer polymerization of methyl methacrylate with 2-(ethoxycarbonyl)prop-2-yl dithiobenzoate (**5**) in presence (□) and absence (○) of scandium triflate at 60 °C. The dashed line (— — —) indicates the theoretical molecular weight calculated using eq 1.

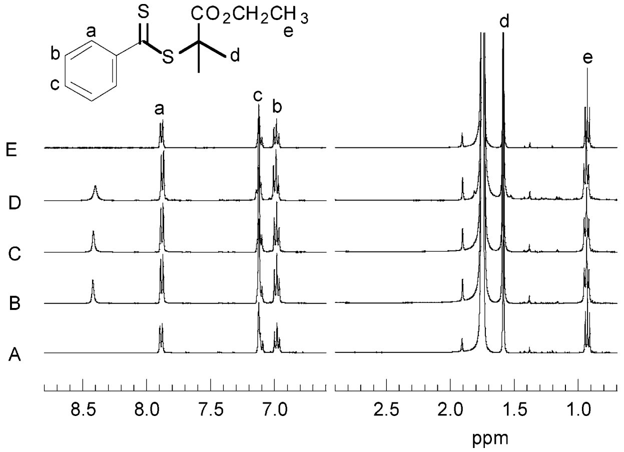


Figure 8. Aromatic region of the 400 MHz ^{1}H NMR spectra of 2-(ethoxycarbonyl)prop-2-yl dithiobenzoate (**5**, 0.079 M) in methyl methacrylate (2.59 M in benzene-d_6) (A) without heating and without scandium triflate, with scandium triflate (0.80 M) after heating at 60 °C for (B) 1 h, (C) 4 h, and (D)16 h, and (E) without scandium triflate after heating at 60 °C for 16 h. The singlet at 7.12 ppm that is incompletely resolved from signal "c" is assigned to residual hydrogens of benzene-d_6. Large singlet at ~1.75 ppm is assigned to the α-methyl hydrogens of methyl methacrylate.

isopropylmethyl trithiocarbonate (**7**) were investigated both with respect to their stability and their ability to control MMA polymerization in the presence of the Lewis acid, scandium triflate. The RAFT agents all have tertiary "R" groups (cumyl (**3**), cyanoisopropyl (**4**, **6**, **7**), or 2-(ethoxycarbonyl)prop-2-yl (**5**)). Polymerizations of MMA were carried out in the presence and absence of scandium triflate in benzene solvent at 60 °C and with AIBN as the initiator.

An indication of the instability of the RAFT agent is provided by molecular weights being higher than anticipated based on eq 1.[3]

$$\bar{M}_n = \frac{[M]_o - [M]_t}{[T]_o - [T]_t + df[I_2]_o(1 - \exp(-k_d t))} m_M + m_T \tag{1}$$

where m_M and m_T are the molecular weights of the monomer (MMA) and the initial RAFT agent (T), respectively, d is the number of chains produced in a radical−radical termination event ($d \sim 1.67$ for MMA polymerization), and k_d and f are the rate constants for initiator decomposition and the initiator efficiency, respectively (for AIBN at 60 °C, $k_d = 9.65 \times 10^{-6}$ M^{-1} s^{-1} and $f \sim 0.6$).[3,36] If the fraction of initiator-derived chains is small and the RAFT agent is rapidly converted to a polymeric RAFT agent, this equation simplifies to eq 2.

$$\bar{M}_n = \frac{[M]_o - [M]_t}{[T]_o} m_M + m_T \tag{2}$$

Table 2. Effect of Scandium Triflate on Reversible Addition Fragmentation Chain Transfer Polymerization of Methyl Methacrylate (MMA) in the Presence of Polymeric Dithiobenzoate RAFT Agent (8) and Azobis(isobutyronitrile) (AIBN) Initiator at 60 °C in Benzene

RAFT agent	$[Sc(OTf)_3]$ (M)	time (h)	conversion %	*mm*	*mr*	*rr*	*m*	$\bar{M}_n$[b] (g mol^{-1})	$\bar{M}_n$ (theoret)[c] (g mol^{-1})	$\bar{M}_w/\bar{M}_n$[d]
3[e]	0	4	22	4	33	63	20	15 300	15 400	1.24
8[f]	0	4 + 6	65	4	33	63	20	43 400	40 800	1.12
8[f,g]	+0.21	4 + 6	89	5	36	59	24	58 800	55 700	1.18

[a] $[MMA]_o = 7.01$ M in benzene, $[AIBN]_o = 6.31 \times 10^{-3}$ M. [b] Number average molecular weight in polystyrene equivalents. [c] Calculated using eq 1. [d] Polydispersity = ratio of weight average and number average molecular weights. [e] $[\mathbf{3}]_0$ 9.4×10^{-3} M. [f] Polymeric RAFT agent **8** is formed from **3** during first 4 h reaction time. [g] Scandium triflate added after 4 h.

Table 3. Effect of Scandium Triflate on Reversible Addition Fragmentation Chain Transfer Polymerization of MMA with Cyanoisopropyl 1*H*-pyrrole-1-carbodithioate (6) and Azobis(isobutyronitrile) (AIBN) Initiator at 60 °C[a]

Lewis acid	time (h)	conversion %	*mm*	*mr*	*rr*	*m*	$\bar{M}_n$[c] (g mol^{-1})	$\bar{M}_n$ (theoret)[d] (g mol^{-1})	$\bar{M}_w/\bar{M}_n$[e]
none	2	21	3	33	64	20	15 000	16 700	1.49
none	4	34	3	33	64	20	23 000	25 800	1.32
none	6	49	3	33	64	20	30 000	35 800	1.28
none	8	74	3	33	64	20	48 000	52 100	1.28
$Sc(OTf)_3$	2	31	4	35	61	22	32 000	24 700	1.75
$Sc(OTf)_3$	4	47	4	36	60	22	39 000	35 700	1.49
$Sc(OTf)_3$	6	94	6	38	56	25	65 000	68 600	1.31
$Sc(OTf)_3$	8	99	7	38	55	26	67 000	69 600	1.29

[a] $[MMA] = 7.01$ M, $[AIBN] = 6.98 \times 10^{-3}$ M, [cyanoisopropyl 1*H*-pyrrole-1-carbodithioate] = 9.5×10^{-3} M, $[Sc(OTf_3)] = 0.206$ M. [b] Number average molecular weight in polystyrene equivalents. [c] Calculated using eq 1. [d] Polydispersity = ratio of weight average and number average molecular weights.

Table 4. Effect of Scandium Triflate on the Reversible Addition Fragmentation Chain Transfer Polymerization of MMA with Cyanoisopropyl Methyl Trithiocarbonate (7) and Azobis(isobutyronitrile) (AIBN) Initiator at at 60 °C[a]

Lewis acid	time (h)	conversion %	*mm*	*mr*	*rr*	*m*[b]	$\bar{M}_n$[c] (g mol^{-1})	$\bar{M}_n$ (theoret)[d] (g mol^{-1})	$\bar{M}_w/\bar{M}_n$[e]
none	2	14	4	33	63	21	9 500	10 000	1.47
none	4	22	4	33	63	21	14 900	15 000	1.27
none	8	50	3	33	63	21	33 900	33 900	1.17
none	16	98	3	33	63	21	66 500	55 300	1.08
$Sc(OTf)_3$	2	21	5	34	62	21	24 600	15 000	1.54
$Sc(OTf)_3$	4	44	5	36	59	23	32 000	25 800	1.26
$Sc(OTf)_3$	6	80	6	37	58	24	57 400	52 100	1.19
$Sc(OTf)_3$	8	94	7	39	55	26	63 600	59 100	1.12

[a] Initial concentrations: $[MMA] = 7.01$ M, $[AIBN] = 6.98 \times 10^{-3}$ M, $[\mathbf{7}] = 9.5 \times 10^{-3}$ M, $[Sc(OTf_3)] = 0.206$ M. [b] Fraction of meso (*m*) dyads. [c] Number average molecular weight in polystyrene equivalents. [d] Calculated using eq 1. [e] Polydispersity = ratio of weight average and number average molecular weights.

For longer reaction times, this equation is not appropriate for the initiator concentration used in this work. Thus, the calculated molecular weights reported are calculated using eq 1 with the assumption that $[T]_t = 0$. Any affect of the Lewis acid on either k_d or f or of the variation of f with conversion is also neglected. High molecular weights for low conversions seen with, for example, **5** is due to slow utilization of the RAFT agent and $[T]_t \neq 0$. The precision of GPC molecular weights is considered to be ±5%. The data presented here also contain a systematic error and are ~5−10% high as they are reported in polystyrene equivalents.

The tacticity of PMMA is conveniently assessed by analysis of the ^1H NMR spectrum. A spectrum of PMMA indicating assignments[37,38] for the hydrogens of the α-methyl in isotactic, heterotactic, and syndiotactic triads is shown in Figure 1.

Experiments with Dithiobenzoates. The use of three dithioesters, cumyl dithiobenzoate (**3**), cyanoisopropyl dithiobenzoate (**4**), and 2-(ethoxycarbonyl)prop-2-yl dithiobenzoate (**5**), have been explored in the present work with respect to their ability to control radical polymerizations of MMA carried out in the presence of the Lewis acid, scandium triflate. The data obtained is summarized in Table 1. In the presence of 0.2 molar equiv of scandium triflate with respect to monomer, a small increase in the fraction of syndiotactic triads is observed which becomes more noticeable for higher monomer conversions. The magnitude of the effect does not depend on the particular dithioester and is similar to that seen in the absence of dithioester. However, with either cumyl dithiobenzoate (**3**) or cyanoisopropyl dithiobenzoate (**4**) as the RAFT agent, control over the molecular weight and molecular weight distribution is clearly impaired by the presence of the Lewis acid.

Experiments with Cumyl Dithiobenzoate (3). Cumyl dithiobenzoate (**3**) is readily synthesized[33] and is one of the most frequently utilized RAFT agents for controlling the polymerization of MMA and other methacrylic monomers.[1,33,34,39−42] The evolution of the molecular weight and molecular weight distribution with conversion of PMMA formed during AIBN initiated polymerization of MMA with **3** both in the presence and absence of scandium triflate in benzene at 60 °C is shown in Figure 2. The tacticity of the polymers determined by ^1H NMR analysis is shown in Table 1. In accord with our previous findings,[34] PMMA formed by RAFT polymerization in the absence of scandium triflate is well-defined having the predicted molecular weight and a narrow molecular weight distribution. The polymer chains formed in the presence of scandium triflate at high conversion contain a slightly higher fraction of isotactic (*mm*) and heterotactic (*mr*) triads and correspondingly a lower fraction of syndiotactic (*rr*) triads. Even though the evolution of molecular weight with conversion is linear, it is clear that the molecular weight of the PMMA synthesized in the presence

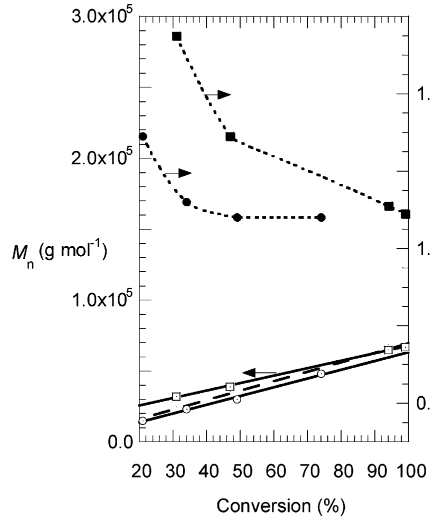


Figure 9. Evolution of number average molecular weight (polystyrene equivalents, open symbols) and polydispersity (filled symbols) with conversion during reversible addition fragmentation chain transfer polymerization of methyl methacrylate with cyanoisopropyl 1*H*-pyrrole-1-carbodithioate (**6**) in the presence (□) and absence (○) of scandium triflate at 60 °C. The dashed line (— — —) indicates the theoretical molecular weight calculated using eq 1.

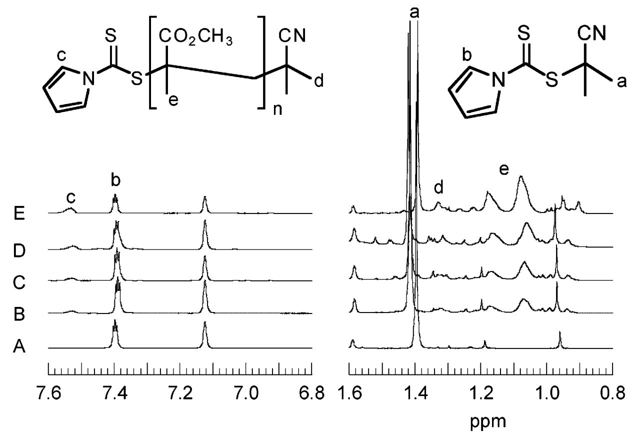


Figure 10. Regions 6.8−7.6 and 0.8−1.6 ppm of the 400 MHz ^{1}H NMRspectra of cyanoisopropyl 1*H*-pyrrole-1-carbodithioate (**6**, 0.12 M) in methyl methacrylate (2.49 M in benzene-d_6) (A) without heating and without scandium triflate, with scandium triflate (0.14 M) after heating at 60 °C for (B) 1 h, (C) 4 h, and (D)16 h, and (E) without scandium triflate after heating at 60 °C for 16 h. Signal intensities are normalized vs methyl methacrylate methoxy resonance. The two broad signals “e” in the region 1−1.2 ppm are assigned to PMMA α-methyl hydrogens. The singlet at 7.12 ppm is assigned to residual hydrogens of benzene-d_6.

of scandium triflate is substantially higher than the theoretical and that the molecular weight distribution is broader than that formed in its absence. Lutz et al.[18] proposed that poor control over molecular weight and polydispersity for polymers formed in the presence of scandium triflate and other Lewis acids was due to degradation of **3** caused by scandium triflate. Consistent with this hypothesis, we observed that the polymerization mixtures changed color from pink to orange after 8 h of heating at 60 °C.

To further test the hypothesis, we followed changes in the ^{1}H NMR spectrum of **3** on being heated in MMA (7.01 M in benzene-d_6) at 60 °C over 16 h (no AIBN initiator). The findings are shown in Figure 3. After 1 h, the RAFT agent has begun to degrade (spectrum B). This is evidenced by the appearance of new peaks and the disappearance of resonances associated with

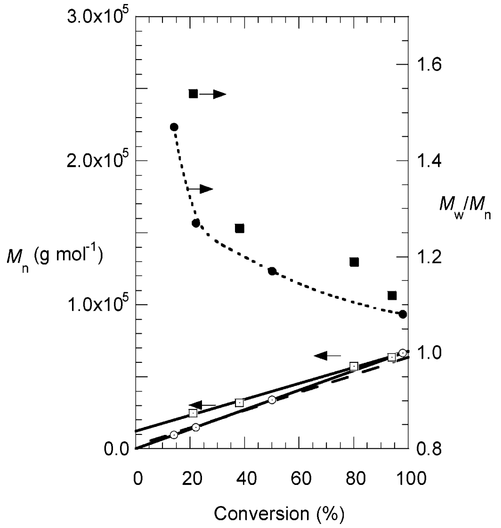


Figure 11. Evolution of number average molecular weight (polystyrene equivalents, open symbols) and polydispersity (filled symbols) with conversion during reversible addition fragmentation chain transfer polymerization of methyl methacrylate with cyanoisopropyl trithiocarbonate (**7**) in the presence (□) and absence (○) of scandium triflate at 60 °C. The dashed line (— — —) indicates the theoretical molecular weight calculated using eq 1.

3. After 16 h (spectrum D), the RAFT agent appears to be almost completely degraded. Under similar conditions, but in the absence of scandium triflate, essentially cumyl dithiobenzoate appears stable. The spectrum obtained after 16 h at 60 °C is unchanged (spectrum E).

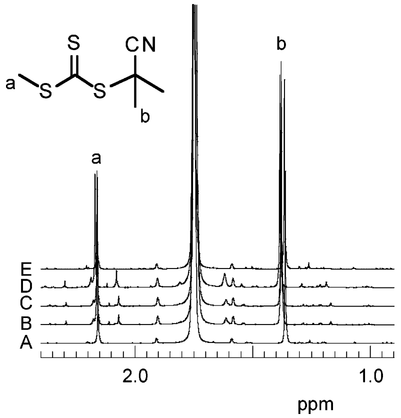


Figure 12. Region 0.9−2.4 ppm of the 400 MHz ^{1}H NMR spectra of cyanoisopropyl methyl trithiocarbonate (**7**, 0.12 M) in methyl methacrylate (2.59 M in benzene-d_6) (A) without heating and without scandium triflate, with scandium triflate (0.082 M) after heating at 60 °C for (B) 1 h, (C) 4 h, and (D) 16 h, and (E) without scandium triflate after heating at 60 °C for 16 h. Signal intensities are normalized vs methyl methacrylate methoxy resonance. Large singlet at ~1.75 ppm is assigned to the α-methyl hydrogens of methyl methacrylate.

The polymerizations carried out in the presence of scandium triflate show no significant rate enhancement with reference to the control experiment without Lewis acid. This is in marked contrast to polymerizations with all other RAFT agent studies where a significant rate enhancement is induced by the presence of the scandium triflate (Figure 4). Increased polymerization rates are also observed in conventional (non-RAFT) radical polymerization of MMA in the presence of Lewis acids.[17] It seems that the reaction of scandium triflate with **3** also deactivates the Lewis acid.

Cumyl dithiobenzoate (**3**) while stable at 60 °C in the absence of Lewis acid is clearly not suitable to be used in conjunction with scandium triflate.

Table 5. Effect of Scandium Triflate Concentration on Reversible Addition Fragmentation Chain Transfer Polymerization of Methyl Methacrylate (MMA) with Cyanoisopropyl Methyl Trithiocarbonate (7) and Azobis(isobutyronitrile) (AIBN) Initiator at 60 °C[a,32]

[MMA]/[Sc(OTf)$_3$][b]	time (h)[c]	conversion %	*mm*	*mr*	*rr*	*m*	$\bar{M}_n$[d] (g mol^{-1})	$\bar{M}_n$ (theoret)[e] (g mol^{-1})	$\bar{M}_w/\bar{M}_n$[f]
control[g]	8	50	4	33	63	21	33 900	29 300	1.17
control[g]	16	98	4	33	63	21	61 000	52 500	1.08
34:1	4	44	5	36	59	23	32 000	27 400	1.26
34:1	8	94	6	39	55	26	63 600	55 000	1.12
16:1	2	43	7	39	54	27	35 000	27 700	1.35
16:1	6	86	7	38	55	26	69 000	51 800	1.22
8.5:1	1	26	7	38	55	26	32 300	17 000	1.61
8.5:1	4	87	12	44	44	34	78 900	54 100	1.31

[a] [MMA] = 7.01 M, [**7**] = 0.106 M, [AIBN] = 0.0061 M. [b] Mole ratio. [c] Reaction times were chosen to provide ~50 and >90% conversion. [d] Number average molecular weights in polystyrene equivalents. [e] Calculated using eq 1. [f] Polydispersity = ratio of weight average and number average molecular weights. [g] Control experiment without scandium triflate.

Experiments with Cyanoisopropyl Dithiobenzoate. Cyanoisopropyl dithiobenzoate (**4**) is one of the preferred RAFT agents for use in RAFT polymerization of methacrylate esters.[34,39,43−46] As was observed with **3,** the PMMA formed by RAFT polymerization with cyanoisopropyl dithiobenzoate (**4**) in the presence of scandium triflate at high conversion contains a slightly higher fraction of isotactic (*mm*) and heterotactic (*mr*) triads and correspondingly a lower fraction of syndiotactic (*rr*) triads (Table 1). Again, the molecular weights of the PMMA synthesized in the presence of scandium triflate is substantially higher than predicted, and the molecular weight distributions are broader than those formed in the absence of scandium triflate, particularly for higher conversions (Figure 5). It was also observed that solutions containing both RAFT agent and scandium triflate change color from pink to orange on heating at 60 °C. These observations are indicative of degradation of the RAFT agent.

In the absence of scandium triflate, cyanoisopropyl dithiobenzoate (**4**) appears to slowly initiate RAFT polymerization when heated at 60 °C with MMA (2.50 M in benzene-d_6) (Figure 6). There is approximately 2% conversion of MMA and 20% consumption of **4** after 16 h. It is possible that this is due to the presence of a very small amount of AIBN present as a contaminant in the RAFT agent (AIBN is used in the synthesis of the RAFT agent). In the presence of scandium triflate, no PMMA is formed and **4** is degraded to unknown byproducts. There is substantial loss of **4** after only 1 h and little remains after 16 h (Figure 6).

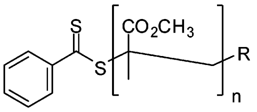
Degradation of the RAFT agent (**4**) in the presence of scandium triflate thus explains higher than expected molecular weights with reference to similar experiments without the Lewis acid (Figure 5). The molecular weights observed are consistent with a RAFT agent concentration ~40% of that actually used in the experiment. The fact that evolution of molecular weight with conversion remains linear suggests that the polymeric PMMA RAFT agent has greater stability than **4**. Nonetheless, we conclude cyanoisopropyl dithiobenzoate (**4**), like **3** is not suitable for use in conjunction with scandium triflate.

Experiments with 2-(Ethoxycarbonyl)prop-2-yl Dithiobenzoate (5). The results of RAFT polymerization of MMA with 2-(ethoxycarbonyl)prop-2-yl dithiobenzoate (**5**) in the presence and absence of scandium triflate in benzene at 60 °C are shown in Table 1 and Figure 7. The effect of added scandium triflate on tacticity is similar to that seen with other RAFT polymerizations. A significantly increased reaction rate of polymerization is observed in the presence of scandium triflate (Figure 4).

Our previous work[35] has shown that in RAFT polymerization of MMA, 2-(ethoxycarbonyl)prop-2-yl dithiobenzoate (**5**) provides poorer control over the molecular weight and molecular weight distribution than cumyl (**3**) or cyanoisopropyl dithiobenzoate (**4**). Molecular weights for low conversions are higher with respect to those calculated based on full utilization of the RAFT agent, and molecular weight distributions are broader. This can be attributed to **5** having a lower transfer constant and as a consequence being consumed relatively slowly. 2-Alkoxycarbonylprop-2-yl radicals are poor homolytic leaving groups with respect to either the cyanoisopropyl or cumyl radicals[35] and with respect to the PMMA propagating radicals.[35,47,48]

The level of control observed is not affected by the presence of scandium triflate. This suggests that dithiobenzoate **5** unlike **3** or **4** is relatively stable in the presence of scandium triflate. This is confirmed by ^{1}H NMR analysis (Figure 8) that shows the RAFT agent to be unchanged on heating for 16 h at 60 °C whether in the presence or absence of scandium triflate. Recent work by Xu et al. shows this RAFT agent to be stable to heating at 120 °C.[49]

Experiments with PMMA Dithiobenzoate (8). The results obtained with **5** suggest that the polymeric RAFT agent **8** (for which **5** can be considered a monomeric analogue) is also stable in the presence of scandium triflate. This is also suggested by the linear molecular weight conversion profiles observed in RAFT polymerizations with **3** and **4**. The stability of **8** in the presence of scandium triflate should not depend on the remote end group "R".



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To test this hypothesis, an experiment was conducted in which PMMA dithiobenzoate (**8**) was prepared with cumyl dithiobenzoate (**3**) as RAFT agent in the absence of scandium triflate. After 4 h reaction time (during which time the initial RAFT agent (**3**) was largely converted to **8**), scandium triflate was added to the polymerization mixture, the usual degassing procedure was applied and polymerization was continued for a further 6 h. The outcome of this experiment and that of a corresponding experiment without added Lewis acid are summarized in Table 2.

The results show that control over the polymerization process is retained (polydispersity remains narrow, molecular weight is as predicted by eq 1), some control over tacticity, manifested as an increased fraction of isotactic dyads (*m*), is evident and the polymerization rate is enhanced vs the similar experiment to which no scandium triflate was added. These findings are consistent with RAFT agent **8** being stable in the presence of scandium triflate and that the poor control observed with **3** relate only to the stability of the initial RAFT agent.

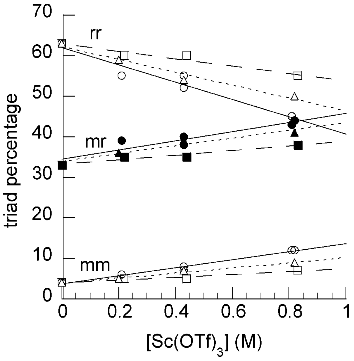

Figure 13. Triad percentages as a function of scandium triflate concentration during reversible addition fragmentation chain transfer polymerization of methyl methacrylate (7.01 M in benzene) at 60 °C with cyanoisopropyl methyl trithiocarbonate (**7**) (0.106 M) for 20−30% (— — — —), 40−50% (- - - -), and 85−95% monomer conversion (—).

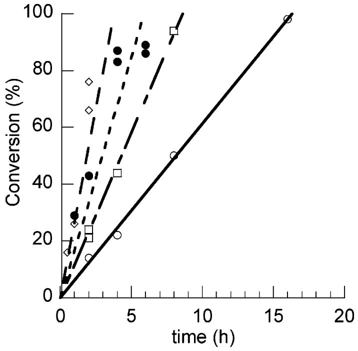

Figure 14. Rate of reversible addition fragmentation chain transfer polymerization of methyl methacrylate (MMA, 7.01 M in benzene) at 60 °C with cyanoisopropyl methyl trithiocarbonate (**7**) (0.106 M) in the absence (○, —) and presence of scandium triflate with [MMA]/[Sc(OTf)$_3$] = 8.5:1 (◇, — — —), 16:1 (●, - - - -), and 34:1 (□,— - — - —).

The results show that, even though cumyl dithiobenzoate (**3**) is unstable and not appropriate for use in experiments with added Lewis acid, The RAFT agent may be used to prepare what might be considered stereoblock copolymers where the Lewis acid is added after the initialization period during which **3** has been converted to **8**.

Experiments with Cyanoisopropyl 1*H*-pyrrole-1-carbodithioate (6). Cyanoisopropyl 1*H*-pyrrole-1-carbodithioate (**6**) is also known to be an effective RAFT agent for MMA polymerization.[50] The results of RAFT polymerization of MMA with **6** in the presence and absence of scandium triflate in benzene at 60 °C are shown in Table 3 and Figure 9. The effect of added scandium triflate on tacticity is similar to that seen in other RAFT polymerizations. PMMA formed in the presence of scandium triflate have slightly higher molecular weights and slightly broader molecular weight distributions and rates of polymerization are enhanced with respect to those formed in the absence of scandium triflate (Figure 4).

The stability of the RAFT agent (**6**) was examined by ^{1}H NMR analysis (Figure 10). On heating, new peaks appear in the region 1.0−1.3 ppm and at 7.55 ppm. However, even after 16 h, the degree of degradation of **6** is still small. Moreover, heating **6** in the absence of scandium triflate for 16 h at 60 °C also causes changes in the spectrum indicating that the RAFT agent **6** is, by itself, unstable at 60 °C under these conditions. We have previously observed that **6** is unstable and undergoes homolysis during the RAFT polymerization of styrene at 110 °C.[35] The findings (a) that molecular weights observed for the experiments in the absence of scandium triflate are lower than those predicted by eq 1 (Table 3) and (b) that the rates of polymerization with RAFT agent **6** in the absence of scandium triflate are significantly higher than observed for polymerizations with similar concentrations of RAFT agents **3**−**5** or **7** (which are the same within experimental error, Figure 4) are also indicative of an additional source of chain initiation and are consistent with RAFT agent **6** being a source of radicals under the polymerization conditions. Notably degradation of **6** is not accelerated (and, indeed, appears retarded) by the presence of scandium triflate.

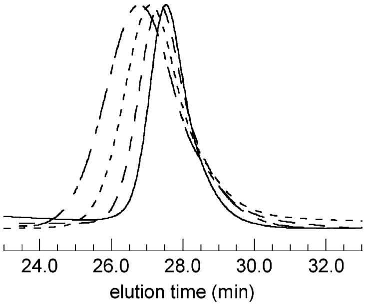

Figure 15. GPC traces for PMMA obtained in high conversion reversible addition fragmentation chain transfer polymerization of methyl methacrylate (MMA, 7.01 M in benzene) at 60 °C with cyanoisopropyl methyl trithiocarbonate (**7**) (0.106 M) in the absence (16 h, 98% conversion, —) presence of scandium triflate with [MMA]:[Sc(OTf)$_3$] = 34:1 (8 h, 94% conversion, — — —), 16:1 (6 h, 86% conversion, - - - -) and 8.5:1 (4 h, 87% conversion, — - — - —).

Thus, cyanoisopropyl 1*H*-pyrrole-1-carbodithioate (**6**) appears suitable for use in RAFT polymerization in the presence of scandium triflate.

Experiments with Cyanoisopropyl Methyl Trithiocarbonate (7). Tertiary cyanoalkyl trithiocarbonates are also able to control MMA polymerization and provide PMMA with a narrow molecular weight distribution.[3,5,32,51] Cyanoisopropyl methyl trithiocarbonate (**7**) has been used in this work because the compound has a simple ^{1}H NMR spectrum. It should be noted that the RAFT agent **7** and the derived polymers can become odorous most likely due to the formation of trace amounts of methanethiol. This issue can be circumvented by use of a trithiocarbonate based on a less volatile thiol[5,32] or by removal of the end group postpolymerization.[52,53]

The data shown in Table 4 and Figure 11 summarize the results of AIBN initiated RAFT polymerization of MMA with cyanoisopropyl methyl trithiocarbonate (**7**), in the presence and absence of scandium triflate in benzene at 60 °C. Polymers formed in the presence of scandium triflate show altered tacticity at high conversion, with the percentage of isotactic (*mm*) and heterotactic (*mr*) triads increasing and syndiotactic (*rr*) triads decreasing. Although molecular weights for low conversion are higher than calculated using eq 2 indicating **7** has a lower transfer constant than the similar dithiobenzoate (**4**), polymers formed in the presence and absence of scandium triflate appear equally well-defined with the predicted molecular weights and a narrow molecular weight distribution even at high conversion.

^{1}H NMR shows that trithiocarbonate **7** is comparatively stable for extended periods when heated in MMA (no initiator) at 60 °C with or without scandium triflate (Figure 12). Minimal loss of the RAFT agent and no PMMA were observed after 16 h. Previous findings indicated that trithiocarbonates are also more resistant to hydrolysis than analogous dithiobenzoate RAFT agents.[54,55] Even though the polydispersities are slightly higher than those obtained in control experiments for similar monomer conversions (Figure 11), the PMMA formed at high conversion

Table 6. ^{1}H and ^{13}C NMR Chemical Shifts (Benzene-d_6) for Methyl Methacrylate and Cyanoisopropyl Methyl Trithiocarbonate (7) with Addition of Scandium Triflate[a]

		chemical shift (ppm)[b]				
substrate	assignment	no $\mathrm{Sc(OTf)_3}$	0.07 mmol $\mathrm{Sc(OTf)_3}$	change	0.013 mmol $\mathrm{Sc(OTf)_3}$	change
		^{13}C NMR				
7	$\mathrm{S\mathit{C}(S)C}$	218.65	218.73	0.07	218.81	0.15
MMA	$\mathrm{\mathit{C}{=}O}$	167.28	167.90	0.63	168.37	1.10
MMA	$\mathrm{H_2C{=}\mathit{C}(CH_3)}$	136.75	136.58	−0.17	136.45	−0.30
solvent	ArC	128.26	128.26	0.00	128.26	0.00
solvent	ArC	128.02	128.02	0.00	128.02	0.00
solvent	ArC	127.77	127.77	0.00	127.78	0.00
MMA	$\mathrm{H_2\mathit{C}{=}C(CH_3)}$	124.99	125.62	0.63	126.09	1.10
7	$\mathrm{\mathit{C}N}$	120.13	120.16	0.03	120.20	0.07
MMA	$\mathrm{O\mathit{C}H_3}$	51.32	51.71	0.39	52.01	0.69
7	$\mathrm{\mathit{C}(CH_3)_2CCN}$	42.75	42.74	−0.01	42.74	−0.01
7	$\mathrm{(\mathit{C}H_3)_2CCN}$	26.64	26.58	−0.06	26.56	−0.08
7	$\mathrm{S\mathit{C}H_3}$	19.41	19.41	0.00	19.41	0.01
MMA	$\mathrm{C{=}C(\mathit{C}H_3)}$	18.28	18.20	−0.08	18.13	−0.16
		^{1}H NMR				
solvent	ArH	7.15	7.15	0.000	7.15	0.000
MMA	$\mathrm{\mathit{H}C{=}C}$	6.02	6.04	0.026	6.06	0.049
MMA	$\mathrm{\mathit{H}C{=}C}$	5.23	5.25	0.025	5.28	0.053
MMA	$\mathrm{OC\mathit{H}_3}$	3.40	3.44	0.041	3.48	0.078
7	$\mathrm{C\mathit{H}_3S}$	2.18	2.18	−0.002	2.18	0.004
MMA	$\mathrm{C{=}CC\mathit{H}_3}$	1.78	1.78	0.000	1.78	0.002
7	$\mathrm{(C\mathit{H}_3)_2CCN}$	1.38	1.39	0.007	1.40	0.016

[a] The ^{1}H (400 MHz) and ^{13}C NMR spectra (125 MHz) of MMA (2.14 mmol) and **7** (0.10 mmol) in benzene-d_6 (0.6 mL) were recorded. Subsequent spectra were obtained following addition of scandium triflate (0.07 and 0.131 mmol). Chemical shifts are based on the solvent (benzene-d_6) resonances being unaffected by addition of scandium triflate.

in the presence of scandium triflate and trithiocarbonate **7** has a significantly lower polydispersity ($\bar{M}_w/\bar{M}_n = 1.12$) than that seen with other RAFT agents in the presence of scandium triflate (compare data in Table 1). Therefore, the use of **7** was further examined in the presence of higher concentrations of scandium triflate.

Effect of Higher Concentrations of Scandium Triflate. Most of the experiments presented in this paper have been performed with the minimum concentration of scandium triflate required to see a discernible change in stereochemical outcome at high monomer conversion. This ratio of scandium triflate to MMA (~1:34, 0.2 M $\mathrm{Sc(OTf)_3}$) has little effect on the stereochemistry of the polymer formed at low conversion. This finding is in accord with the findings of Isobe et al.[17] Experiments performed with higher scandium triflate to MMA ratios are summarized in Table 5.

Increasing the concentration of scandium triflate results in larger changes in tacticity (Table 5, Figure 13). A predominantly syndiotactic polymer is obtained in the absence of scandium triflate with *mm:mr:rr* = 4:33:63. The fraction of isotactic triads increases progressively as the ratio of scandium triflate to MMA increases and as monomer conversion increases, with *mm:mr:rr* rising to 12:44:44 for a ratio of 1:8.5 at high conversion. Isobe et al.[17] have shown (for a conventional radical polymerization) that further increasing the ratio of scandium triflate to MMA to 1:3 in toluene results in a polymer with *mm:mr:rr* = 21:48:31. These results suggest that a process in which monomer is fed slowly to a polymerization mixture so as to maintain a high ratio of scandium triflate to MMA would provide a polymer with a higher fraction of isotactic triads. Such experiments are planned.

A 1:34 ratio of scandium triflate to MMA (0.2 M) significantly increases the rate of polymerization (Figure 4). Further increasing of the scandium triflate concentration, increases the rate of polymerization further (Figure 14). Without scandium triflate, it takes 16 h to obtain almost complete (98%) conversion. By increasing the ratio of scandium to MMA from 1:34 to 1:16 to 1:8.5, conversions of 94, 86, and 87% were obtained in 8, 6, and 4 h, respectively.

Increasing the concentration of scandium triflate modifies the stereospecificity at the expense of control over molecular weight and polydispersity (Table 5). Increasing the ratio of scandium triflate to MMA from 0 to 1:34 to 1:16 to 1:8.5 results in the molecular weight and polydispersity at high conversion increasing from 61 000 and 1.08 to 63 600 and 1.12 to 69 000 and 1.22 to 79 000 and 1.31, respectively, at high conversion (Figure 15). Broader polydispersity might indicate some instability of the RAFT agent with higher concentrations of Lewis acid. However, a broader molecular weight distribution may also be a consequence of a faster propagation rate and more monomer units being added to the chain during each activation cycle.

NMR Study of Interaction with Lewis Acid. The interaction of scandium triflate with cyanoisopropyl methyl trithiocarbonate (**7**) and MMA monomer in benzene-d_6 was studied by both ^{1}H and ^{13}C NMR. A summary of the assignments and the chemical shifts observed is provided in Table 6. The concentration of scandium triflate used was similar to that used by Isobe et al.[17] Note that the ratio of scandium triflate to **7** is ~20 times lower in these experiments than in the polymerizations reported above.

The largest change in chemical shift was observed for the carbonyl (+1.10 ppm), methylene (+1.10 ppm), and the methoxy carbon (+0.69 ppm) and the associated protons (+0.078 ppm) of MMA. A much smaller change was observed for the α-methyl carbon of MMA (+0.16 ppm). Isobe et al.[17] observed that scandium triflate caused changes in chemical shift of a similar magnitude with $\mathrm{CDCl_3}$ as the solvent.

Comparatively, small changes in chemical shift were observed for the $\mathrm{-(\mathit{C}H_3)_2CCN}$ carbons (−0.08 ppm) and protons (+0.016 ppm), the $\mathrm{-(CH_3)_2C\mathit{C}N}$ carbons (0.07 ppm) and the thiocarbonyl ($\mathrm{-S\mathit{C}(S)S-}$) carbon (+0.15 ppm) of **7**. The relatively small shifts for signals of cyanoisopropyl methyl trithiocarbonate (**7**) compared with the large shifts observed for signals from MMA is indicative of stronger interactions between the scandium triflate and MMA than between scandium triflate and **7**.

Conclusions

Stability of the RAFT agent in the presence of scandium triflate is the key to successfully synthesizing well-defined PMMA with Lewis acid-induced tacticity control. We have shown that both cumyl (**3**) and cyanoisopropyl dithiobenzoates (**4**) degrade in the presence of scandium triflate and are therefore unsuitable chain transfer agents for use in RAFT polymerization when scandium triflate is present. The RAFT agents, 2-(ethoxycarbonyl)prop-2-yl dithiobenzoate (**5**), cyanoisopropyl 1*H*-pyrrole-1-carbodithioate (**6**), and cyanoisopropyl methyl trithiocarbonate (**7**), and the derived polymeric RAFT agents (**8**) appear relatively stable in the presence of scandium triflate. Whether RAFT polymerization can be carried out successfully with **3** or **4** depends on the rate of conversion of these RAFT agents to a polymeric RAFT agent (**8**). This rate is relatively slow during MMA polymerization at 60 °C but can be rapid in other polymerizations (e.g., in polymerization of acrylamides).

RAFT polymerization of MMA in the presence of scandium triflate with cyanoisopropyl methyl trithiocarbonate (**7**) as the RAFT agent produces polymers with controlled molecular weights and narrow molecular weight distributions with tacticity control imposed by the Lewis acid. Increasing the ratio of scandium triflate to MMA produces a more isotactic polymer at the expense of poorer control over the molecular weight and molecular weight distribution. For RAFT polymerizations with RAFT agents **4**−**8**, the addition of a Lewis acid also provides a substantial enhancement in the rate of polymerization.

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