"Constrained Geometry" Titanium Complexes: Exceptionally Robust Systems for Living Polymerization of Methacrylates at High Temperature and Model Studies toward Chain Transfer Polymerization with Thiols

Bing Lian,[†] Christophe M. Thomas,[†] Christophe Navarro,[‡] and Jean-François Carpentier*[,†]

Catalyse et Organométalliques, UMR 6226, University of Rennes 1, 35042 Rennes Cedex, France, and Arkema, Lacq Research Center, PO Box 34, 64170 Lacq, France

Received September 13, 2006

The 1:1 combination of Ti{CGC}Me_2 (**1**; CGC = $Me_2Si(Me_4C_5)(t$BuN)) with $B(C_6F_5)_3$ was found to feature a so far unrevealed thermal robustness in methacrylate polymerization that enables it to operate in a broad temperature range (0−100 °C) with a living behavior. Highly effective (576 kg PMMA·mol $Ti^{-1}\cdot h^{-1}$) and productive (monomer-to-Ti ratio up to 5000) homopolymerization of methyl methacrylate (MMA) and effective diblock and triblock copolymerization of MMA with butyl methacrylate (BMA) were thus achieved at 80 °C. The robust "constrained geometry" titanium system has been used to investigate thiols as possible chain transfer agents in MMA polymerization. Neutral alkylthiolato and thiophenolato complexes [Ti{CGC}(X)(Y)] (**2**, X = Me, Y = *t*BuS; **3**, X = Me, Y = *o*-$MeOC_6H_4S$; **4**, X = Y = *i*PrS; **5**, X = Y = $PhCH_2S$) have been synthesized by protonolysis of **1** with thiols and shown to polymerize MMA once activated by a Lewis acid such as $B(C_6F_5)_3$. Combinations **1**/$B(C_6F_5)_3$/*t*BuSH polymerized quantitatively MMA in toluene to yield PMMAs with narrow polydispersity ($M_w/M_n \cong 1.10$), but no effective chain transfer was evidenced, whatever the conditions used. The stoichiometric reaction of *t*BuSH and *o*-$MeOC_6H_4SH$ with the cationic enolate complex [Ti{CGC}(O(O*i*Pr)C═CMe_2)(THF)]$^+$[$MeB(C_6F_5)_3$]$^-$ (**8**) revealed that thiols do cleave the Ti−O(enolate) bond of **8** to give the alkylthiolato and thiophenolato titanium cationic species; however, this pathway proceeds remarkably slowly in comparison with that with a similar Zr−O(enolate) bond.

Introduction

Methacrylate polymerization mediated by group 4 metal systems has attracted much attention in recent years.[1−3] Living polymerization of methyl methacrylate (MMA) with two-component Zr systems was first reported by Collins and co-workers in 1992 using [$Cp_2Zr(THF)Me$]$^+$[BPh_4]$^-$ and Cp_2ZrMe_2,[1a] and further by combination of the neutral enolate complex $Cp_2ZrMe[O(OMe)C{=}CMe_2]$ as initiator and cationic complex [$Cp_2Zr(THF)Me$]$^+$[BPh_4]$^-$ as catalyst.[1b,c] The isolation of the *neutral* zirconocene enolate in its pure form established unambiguously, via detailed kinetic studies, a group-transfer-type bimetallic propagating mechanism. Recently, Chen and co-workers have reported the isolation of the cationic *ansa*-zirconocene ester enolate complex [*rac*-(EBI)Zr(THF){O(O*i*Pr)C═CMe_2}]$^+$[$MeB(C_6F_5)_3$]$^-$ (EBI = ethylenebis(indenyl)) and the generation of the cationic "constrained geometry" Ti ester enolate complex [(CGC)Ti(THF){O(O*i*Pr)C═CMe_2}]$^+$[$MeB(C_6F_5)_3$]$^-$ (CGC = $Me_2Si(Me_4C_5)(t$BuN)), which were both shown to be highly active for the polymerization of MMA.[2h,i] The rate-limiting step in those monocomponent systems[4] involves either the intramolecular Michael addition[2i] or regeneration of the monomer-coordinated enolate active species via ring-opening of the resting eight-membered cyclic enolate.[2j] A major point of interest in these group 4 metal systems is the high degree of control, i.e., the livingness and stereochemistry of polymerization, they exhibit under suitable conditions. Particularly interest-

* Corresponding author. Fax: (+33)(0)223-236-939. E-mail: jean-francois.carpentier@univ-rennes1.fr.

[†] Université de Rennes 1.

[‡] Arkema.

(1) (a) Collins, S.; Ward, D. G. *J. Am. Chem. Soc.* **1992**, *114*, 5460−5462. (b) Collins, S.; Ward, D. G.; Suddaby, K. H. *Macromolecules* **1994**, *27*, 7222−7224. (c) Li, Y.; Ward, D. G.; Reddy, S. S.; Collins, S. *Macromolecules* **1997**, *30*, 1875−1883. (d) Nguyen, H.; Jarvis, A. P.; Lesley, M. J. G.; Kelly, W. M.; Reddy, S. S.; Taylor, N. J.; Collins, S. *Macromolecules* **2000**, *33*, 1508−1510. (e) Stojcevic, G.; Kim, H.; Taylor, N. J.; Marder, T. B.; Collins, S. *Angew. Chem. Int. Ed.* **2004**, *43*, 5523−5526.

(2) (a) Chen, E. Y.-X.; Metz, M. V.; Li, L.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1998**, *120*, 6287−6305. (b) Bolig, A. D.; Chen, E. Y.-X. *J. Am. Chem. Soc.* **2001**, *123*, 7943−7944. (c) Jin, J.; Chen, E. Y.-X. *Organometallics* **2002**, *21*, 13−15. (d) Jin, J.; Wilson, D. R.; Chen, E. Y.-X. *Chem. Commun.* **2002**, 708−709. (e) Bolig, A. D.; Chen, E. Y.-X. *J. Am. Chem. Soc.* **2002**, *124*, 5612−5613. (f) Chen, E. Y.-X.; Cooney, M. J. *J. Am. Chem. Soc.* **2003**, *125*, 7150−7151. (g) Mariott, W. R.; Chen, E. Y.-X. *J. Am. Chem. Soc.* **2003**, *125*, 15726−15727. (h) Bolig, A. D.; Chen, E. Y.-X. *J. Am. Chem. Soc.* **2004**, *126*, 4897−4906. (i) Rodriguez-Delgado, A.; Mariott, W. R.; A.; Chen, E. Y.-X. *Macromolecules* **2004**, *37*, 3092−3100. (j) Rodriguez-Delgado, A.; Chen, E. Y.-X. *Macromolecules* **2005**, *38*, 2587−2594. (k) Mariott, W. R.; Rodriguez-Delgado, A.; Chen, E. Y.-X. *Macromolecules* **2006**, *39*, 1318−1327. (l) Rodriguez-Delgado, A.; Mariott, W. R.; Chen, E. Y.-X. *J. Organomet. Chem.* **2006**, *691*, 3490−3497.

(3) (a) Deng, H.; Shiono, T.; Soga, K. *Macromolecules* **1995**, *28*, 3067−3073. (b) Cameron, P. A.; Gibson, V. C.; Graham, A. J. *Macromolecules* **2000**, *33*, 4329−4335. (c) Frauenrath, H.; Keul, H.; Höcker, H. *Macromolecules* **2001**, *34*, 14−19. (d) Batis, C.; Karanikolopoulos, G.; Pitsikalis, M.; Hadjichristidis, N. *Macromolecules* **2003**, *36*, 9763−9774. (e) Jensen, T. R.; Yoon, S. C.; Dash, A. K.; Luo, L.; Marks, T. J. *J. Am. Chem. Soc.* **2003**, *125*, 14482−14494. (f) Strauch, J. W.; Fauré, J.-L.; Bredeau, S.; Wang, C.; Kehr, G.; Fröhlich, R.; Luftmann, H.; Erker, G. *J. Am. Chem. Soc.* **2004**, *126*, 2089−2104. (g) Lian, B.; Toupet, L.; Carpentier, J.-F. *Chem. Eur. J.* **2004**, *10*, 4301−4307. (h) Stuhldreier, T.; Keul, H.; Höcker, H.; Englert, U. *Organometallics* **2000**, *19*, 5231−5234.

(4) For a DFT study see: Tomasi, S.; Weiss, H.; Ziegler, T. *Organometallics* **2006**, *25*, 3619−3630.

10.1021/om060838g CCC: $37.00
Publication on Web 11/30/2006

ing are the technologically significant olefin polymerization "constrained geometry" Ti{CGC} systems[5] that are used in forming methyl methacrylate (MMA) polymers (PMMAs) with a highly syndiotactic-enriched microstructure ([*rr*] = 82%, P_r = 0.90) at ambient temperature.[2i]

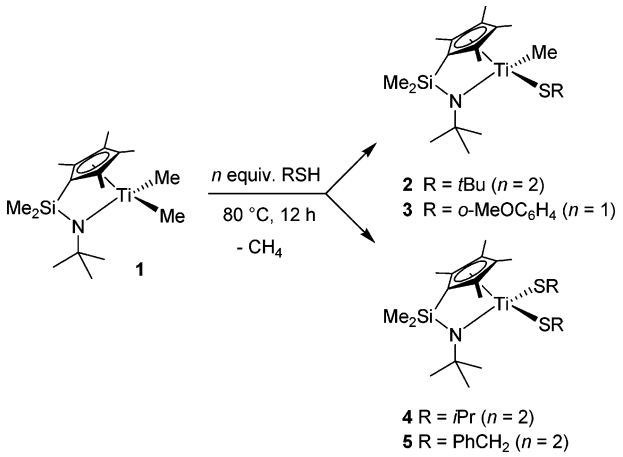
The use of a *stoichiometric* amount of metal complex per macromolecular chain remains, however, a major limitation of initiating polymerization systems. To transform *initiators* into true *catalysts*, the search for effective chain transfer agents (CTAs) is of high industrial relevance. In this process, three essential objectives must be achieved: (i) CTAs must cleave the growing PMMA chain, (ii) the resulting new cationic species must reinitiate polymerization of MMA, and (iii) an adequate kinetic regime must be reached. Organic acids such as enolizable ketones (or esters) and alkylthiols have been recently investigated for such purposes with neutral lanthanidocenes[6] and by both Chen's group[2k] and our group[7] with cationic zirconocenes.

Herein, we report some related studies using "constrained geometry" titanium systems. The first aim of this work was to investigate MMA polymerization mediated by Ti{CGC}Me_2/activator binary systems, especially the influence of temperature. It has been eventually evidenced that Ti{CGC} systems feature high efficiency and productivity, and a thus far unrevealed thermal robustness that enables them to operate in a broad temperature range (0−100 °C) while keeping a living behavior. The second and central aim of this work was to investigate the use of thiols as potential CTAs for MMA polymerization mediated by the robust Ti{CGC} systems. Results from polymerization experiments and stoichiometric studies with model alkylthiolato-, thiophenolato-, and enolato-Ti complexes are described.

Results and Discussion

Synthesis of Neutral Alkylthiolato- and Thiophenolato-Titanium Precursors [Ti{$Me_2Si(Me_4C_5)$(*t*BuN)}(X)(Y)] (X, Y = Me, RS). A series of neutral "constrained geometry" alkylthiolato- and thiophenolato-titanium complexes [Ti{CGC}-(X)(Y)] (**2**, X = Me, Y = *t*BuS; **3**, X = Me, Y = *o*-$MeOC_6H_4S$; **4**, X = Y = *i*PrS; **5**, X = Y = $PhCH_2S$) were synthesized by protonolysis of the dimethyltitanium precursor **1** with the desired alkylthiol or thiophenol (Scheme 1). The reaction of **1** with 2 equiv of *t*BuSH proceeded quantitatively at 80 °C to yield the mono-*tert*-butylthiolato complex **2**. Despite the presence of excess thiol, the bis-*tert*-butylthiolato complex was not detected, even after prolonged reaction times at this temperature. Combination of **1** with 1 equiv of *o*-$MeOC_6H_4SH$ proceeded

Scheme 1



quantitatively at 80 °C to yield also the corresponding mono-thiophenolato complex **3**. Interestingly, NMR monitoring of this reaction at 20 °C showed that a mixture formed within 2.5 h that consisted of **3** (42% NMR yield) and the alcoholysis product of the Ti−N(CGC) bond,[8] i.e., [Ti{$Me_2Si(Me_4C_5)$(*t*BuNH)}(*o*-$MeOC_6H_4S$)Me_2] (**3′**, 22% NMR yield); complex **3′** was completely converted to **3** within 12 h upon raising the temperature to 80 °C, re-forming the Ti{$C_5R_4SiMe_2N$*t*Bu} chelate ring via methane elimination.[8] Single crystals of **3** suitable for X-ray diffraction were grown from pentane (Table 1, Figure 1). As anticipated, the *o*-methoxy group coordinates to the Ti center, which is thus five-coordinated in the solid state showing a pseudo-pentahedral environment. The configuration of the {CGC}Ti moiety is similar to that reported previously for similar species,[5] indicative of a constrained geometry around the Ti center. The unit cell of **3** contains two different stereoisomers that originate from opposite chelation of the [*o*-$MeOC_6H_4S$]$^-$ group onto Ti.[9] The two stereoisomers feature slight differences in the bond angles, e.g., S(5)−Ti(1)−(41), 72.20(9)° vs S(4)−Ti(1)−O(51), 74.11(18)°; on the other hand, the Ti−O(thiophenolato) bonds are significantly different (Ti-(1)−O(41), 2.430(3) vs Ti(1)−O(51), 2.262(7) Å), while the Ti−S bonds are similar (Ti(1)−S(4), 2.4664(11) vs Ti(1)−S(5), 2.461(2) Å). In comparison with a Ti-ethylthiolato complex (Ti−S(1), 2.398(3) Å; Ti−S(1)−C(1), 108.2(3)°),[10] the latter Ti−S bonds are somewhat longer with narrower Ti−S−C bond angles (Ti(1)−S(4)−C(61A), 99.88(9)°; Ti(1)−S(5)−C(62A), 103.08-(11)°), reflecting the presence of a thiophenolato group and likely also the additional OMe group coordinated to the Ti center.

On the other hand, upon using 2 equiv of the less bulky thiols *i*PrSH or $PhCH_2SH$, the corresponding bis-alkylthiolato complexes **4** and **5** were obtained in 100% NMR yield. When the same reactions were performed with 1 equiv of these thiols,

(5) For the initial design of this ligand system see: (a) Shapiro, P. J.; Bunel, E.; Schaefer, W. P.; Bercaw, J. E. *Organometallics* **1990**, *9*, 867−869. (b) Piers, W. E.; Shapiro, P. J.; Bunel, E.; Bercaw, J. E. *Synlett* **1990**, *2*, 74−84. (c) Shapiro, P. J.; Cotter, W. D.; Schaefer, W. P.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1994**, *116*, 4623−4640. For selected examples see: (d) Stevens, J. C.; Timmers, F. J.; Rosen, G.; Knight, G. W.; Lai, S. Y. (Dow Chemical Co.) Eur. Pat. App., EP 0416815 A2, 1991. (e) Canich, J. A. (Exxon Chemical Co.) Eur. Pat. App., EP 0420436 A1, 1991. (f) Stevens, J. C. In *Studies in Surface Science and Catalysis*; Soga, K., Terano, M., Eds.; Elsevier: Amsterdam, 1994; Vol. 89, pp 277−284. (g) Chen, Y.-X.; Marks, T. J. *Organometallics* **1997**, *16*, 3649−3657. (h) Soga, K.; Uozomi, T.; Nakamura, S.; Toneri, T.; Teranishi, T.; Sano, T.; Arai, T. *Macromol. Chem. Phys.* **1996**, *197*, 4237−4251. (i) McKnight, A. L.; Waymouth, R. M. *Chem. Rev.* **1998**, *98*, 2587−2598. (j) Li, L.; Metz, M. V.; Li, H.; Chen, M.-C.; Marks, T. J.; Liable-Sands, L.; Rheingold, A. L. *J. Am. Chem. Soc.* **2002**, *124*, 12725−12741.

(6) (a) Nodono, M.; Tokimitsu, T.; Tone, S.; Makino, T.; Yanagase, A. *Macromol. Chem. Phys.* **2000**, *201*, 2282−2288. (b) Yanagase, A.; Tone, S.; Tokimitsu, T.; Nodono, M. (Mitsubishi Rayon) Eur. Pat. Appl. 0919569A1, 1999.

(7) Lian, B.; Lehmann, C. W.; Navarro, C.; Carpentier, J.-F. *Organometallics* **2005**, *24*, 2466−2472.

(8) (a) Key ^{1}H NMR data for **3′**: ^{1}H NMR (C_6D_6): δ 3.41 (s, 3H, OCH_3), 2.28 (s, 6H, CH_3C_5), 1.84 (s, 6H, CH_3C_5), 1.15 (s, 9H, $NC(CH_3)_3$), 1.03 (s, 6H, $Ti(CH_3)_2$), 0.57 (s, 6H, $Si(CH_3)_2$), resonances for Ph overlapped with those of **3** and unreacted *o*-$MeOC_6H_4SH$. (b) For a similar observation during the alcoholysis of {$SiMe_2(C_5R_4)$(N*t*Bu)}Ti complexes, see: Carpentier, J.-F.; Maryin, V. P.; Luci, J.; Jordan, R. F. *J. Am. Chem. Soc.* **2001**, *123*, 898−909. (c) For other reactions in which the {$SiMe_2(C_5R_4)$(N*t*Bu)}M chelate ring in constrained geometry complexes is cleaved see: Carpenetti, D. W.; Kloppenburg, L.; Kupec, J. T.; Petersen, J. L. *Organometallics* **1996**, *15*, 1572−1581. (d) Kloppenburg, L.; Petersen, J. L. *Organometallics* **1996**, *15*, 7−9.

(9) Stereoisomers **3A** and **3B** are not distinguished by NMR spectroscopy at room temperature in C_6D_6 solution.

(10) Calhorda, M. J.; Carrondo, M. A. A. F. C. T.; Dias, A. R.; Frazão, C. F.; Hursthouse, M. B.; Simões, J. A. M.; Teixeira. C. *Inorg. Chem.* **1988**, *27*, 2513−2518.

Table 1. Crystal Data and Structure Refinement for 3

empirical formula	$C_{23}H_{37}NOSSiTi$
fw	451.59 g·mol^{-1}
temperature/K	100 (2)
wavelength/Å	0.71073
cryst syst	orthorhombic
space group	*Pcab*
a/Å	14.7578(7)
b/Å	15.1980(7)
c/Å	20.8733(10)
α/deg	90
β/deg	90
γ/deg	90
volume/Å^3	4681.7(4)
Z	8
density (calcd)/Mg·m^{-3}	1.281
absorp coeff/mm^{-1}	0.520
F(000)	1936
cryst size/mm^3	0.4 × 0.35 × 0.1
θ range for data collection/deg	2.37 to 27.52
index ranges	$-19 \le h \le 19$, $-19 \le k \le 19$, $-27 \le l \le 19$
no. of reflns collected	45 743
no. of indep reflns	5378 [$R_{int} = 0.0408$]
completeness to $\theta = 26.40°$	99.9%
absorp corr	semiempirical from equivalents
refinement method	full-matrix least-squares on F^2
no. of data/restraints/params	5378/0/281
goodness-of-fit on F^2	1.066
final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0402$, $wR_2 = 0.0991$
R indices (all data)	$R_1 = 0.0502$, $wR_2 = 0.1037$
largest diff peak and hole/e Å^{-3}	0.367 and −0.330

mixtures of mono- and bis-alkylthiolato species were obtained, from which the complexes could not be efficiently separated.

Generation of Cationic Species [Ti{Me$_2$Si(Me$_4$C$_5$)(*t*BuN)}(SR)(L)$_n$]$^+$. Model reactions were attempted to characterize the cationic species [Ti{CGC}](SR)(L)$_n$]$^+$ (L = solvent, n = 0,1), putatively generated upon activation with an appropriate abstractor and which may act further as initiators toward methacrylate polymerization (vide infra). The reactions of neutral [Ti{CGC}(X)(Y)] complexes **2**, **4**, and **5** with B(C$_6$F$_5$)$_3$ or [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$] in THF-d_8 or toluene-d_8 solution at low temperature led invariably to complicated mixtures of products, as assessed by multinuclear NMR spectroscopy. We assume that this reflects the poor stability of the corresponding [Ti{CGC}(SR)(L)$_n$]$^+$ cationic species derived from aliphatic monodentate alkylthiolato ligands (*t*BuS, *i*PrS, and PhCH$_2$S, respectively). A more stable cationic species (**6**) was generated in ca. 95% NMR purity from the *o*-methoxythiophenolato complex **3** by methyl abstraction with 1 equiv of B(C$_6$F$_5$)$_3$ in THF-d_8 solution (Scheme 2). Alternatively, cationic complex **6-*d*$_8$** was also prepared by the methane elimination reaction between [Ti{CGC}(Me)(THF-d_8)]$^+$ (**7-*d*$_8$**) and 1 equiv of *o*-MeOC$_6$H$_4$SH in THF-d_8. The low-temperature (213 K) ^{1}H NMR spectrum of **6-*d*$_8$** in THF-d_8 shows resonances for an asymmetric structure on the NMR time scale, including four singlets for the C$_5$Me$_4$ methyl groups (Figure 2). Upon warming, those resonances coalesce and collapse to two singlets at room temperature. This fluxional behavior is consistent with either an exchange process between the coordinated THF molecule and [*o*-MeOC$_6$H$_4$S]$^-$ group and/or exchange of the thiophenolato and methoxy ligands within the latter chelated moiety, as observed in the solid state for **3** (vide supra). Complex **6** is stable in THF solution at low temperature but decomposes at room temperature within 3 days to form a new species, which could not be so far identified.[11]

Methacrylate Polymerization with [Ti{Me$_2$Si(Me$_4$C$_5$)(*t*BuN)}(X)(Y)] (X, Y = Me, SR)/Activator Systems. The newly prepared neutral alkylthiolato and thiophenolato complexes **2**−**5** were investigated for MMA polymerization after activation with 1 equiv of a molecular Lewis acid to generate in situ the corresponding cationic species (Scheme 3). For comparison purposes, the performances of the polymerization systems based on the dimethyl precursor **1** were first investigated.[2i]

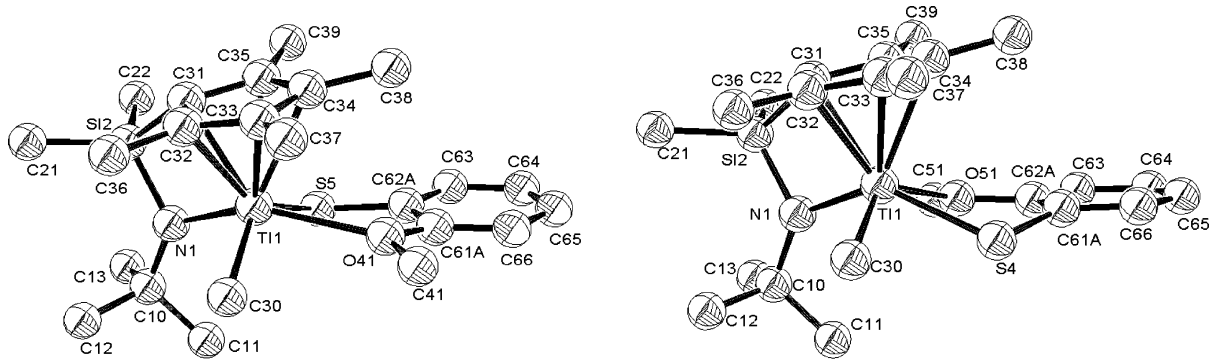
High-Temperature Living Polymerization of Methacrylates with Ti{CGC}Me$_2$/Activator Systems. Representative MMA polymerization results obtained from the simple dimethyltitanium precursor **1** in toluene solution are summarized in Table 2. As previously reported,[2i] combinations of **1** with usual molecular activators led to quantitative conversion of MMA at room temperature (entries 2−4). The PMMAs obtained under these conditions had a relatively narrow molecular weight distribution (M_w/M_n = 1.17−1.28) and a syndiotactic-enriched microstructure, the best results being observed with B(C$_6$F$_5$)$_3$ (entry 2). Decreasing the temperature to 0 °C proved deleterious in terms of control and initiation efficiency (entry 1). On the other hand, surprisingly good performances were obtained at higher temperatures (entries 5−17). The active cationic [Ti{CGC}(enolato-PMMA)(L)$_n$]$^+$ species, generated in situ from **1**, B(C$_6$F$_5$)$_3$ and MMA, remains stable at least up to 100 °C, yielding quantitatively PMMAs with an excellent match between experimental and calculated number average molecular weights considering a monometallic initiating system, along quite narrow polydispersities. The latter seem even to narrow as the temperature increases, suggesting a better control of the polymerization at high temperature. This is a rather counterintuitive observation for most chemists, who are used to lowering temperature to minimize side reactions, e.g., back biting, and achieve better control of the polymerization. In fact, "living-controlled" polymerizations of methacrylates with early transition metal systems are carried out at most at room temperature.[12] As expected, however, the syndiotacticity decreased to some extent from 80% *rr* at 20 °C to ca. 67% *rr* at 80 °C.

A series of experiments were carried out at 80 °C to investigate the influence of the MMA-to-Ti ratio (entries 7, 9−13). Full conversions were observed for monomer-to-initiator ratios up to 5000, yielding within short reaction times PMMAs with high molecular weight that fit well with the calculated M_n values and still with a very narrow polydispersity (Figure 3). It is noteworthy that similar performances were obtained when the polymerization was performed in bulk (entry 11). A kinetic monitoring established also that average number molecular weights increase linearly with MMA conversion (entries 13−17, Figure 4). In a separate experiment, MMA polymerization was performed for 10 min at 80 °C with [MMA]/[Ti] = 4000, giving a TOF value of 576 kg PMMA·mol Ti^{-1}·h^{-1}. All these results demonstrate the high productivity and degree of livingness of the **1**/B(C$_6$F$_5$)$_3$ system at 80 °C.

The livingness of the **1**/B(C$_6$F$_5$)$_3$ system in toluene at high temperature (80 °C) was further illustrated by sequential diblock PMMA-*b*-PBMA (BMA = *n*-butyl methacrylate) and triblock PMMA-*b*-PBMA-*b*-PMMA copolymerizations. Experiments were performed with [MMA]/[BMA]/[Ti] = 200:200:1 and [MMA]/[BMA]/[MMA]/[Ti] = 200:200:200:1, respectively.

(11) Key NMR data for the decomposition species from **6**: ^{1}H NMR (THF-d_8): δ 7.20 (m, Ph), 7.11 (m, Ph), 6.87 m, Ph), 3.80 (s, OC*H*$_3$), 2.29 (s, C*H*$_3$C$_5$), 2.27 (s, C*H*$_3$C$_5$), 2.06 (s, C*H*$_3$C$_5$), 2.05 (s, C*H*$_3$C$_5$), 1.28 (s, NC(C*H*$_3$)$_3$), 0.74 (s, Si(C*H*$_3$)$_2$), 0.75 (s, Si(C*H*$_3$)$_2$).

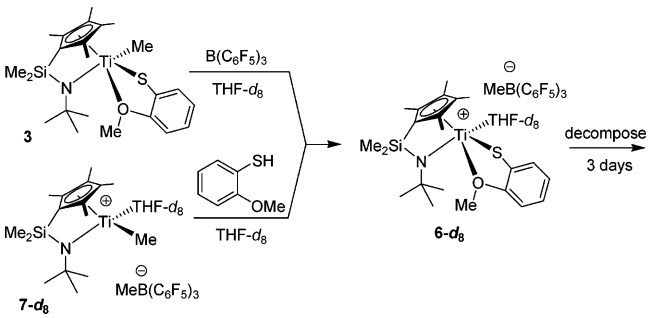
(12) Systems based on combinations of dialkyl zirconocenes with borane or borate co-activators have been used for bulk MMA polymerization at high temperature (155−190 °C), but offered PMMAs with relatively broad molecular weight distributions (PDI = 1.6 for Cp$_2$ZrMe$_2$ at 155 °C and 2.4 for (EBI)ZrMe$_2$ at 105 °C); see: Rhodes, L. F.; Goodall, B. L.; Collins, S. US Pat. 5668234, 1997.



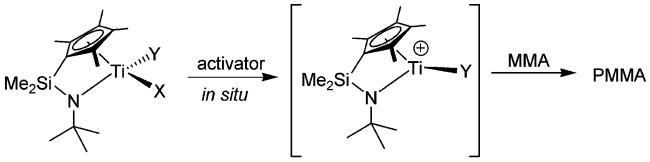
Molecule **3A** Molecule **3B**

Figure 1. The two independent molecules found in the solid-state structure of **3**. Selected bond lengths (Å) and angles (deg) (molecule **3B**): Ti(1)−N(1), 1.9506(17); Ti(1)−C(30), 2.157(2); Ti(1)−O(51), 2.262(7); Ti(1)−S(4), 2.4664(11); Ti(1)−C(31), 2.2884(19); Ti(1)−C(32), 2.368 (2); Ti(1)−C(33), 2.497(2); Ti(1)−C(34), 2.4908(19); Ti(1)−C(35), 2.3710(19); C(61A)−S(4), 1.865(3); N(1)−Ti(1)−C(30), 94.85(9); N(1)−Ti(1)−O(51), 93.47(16); C(30)−Ti(1)−O(51), 131.4(2); O(51)−Ti(1)−S(4), 74.11(18); C(30)−Ti(1)−S(4), 68.85(10); Ti(1)−S(4)−C(61A), 99.88(9); N(1)−Ti(1)−C_5Me_4(centroid C(31)−C(35), 107.63. Selected bond lengths (Å) and angles (deg) (molecule **3A**): Ti(1)−S(5), 2.461(2); Ti(1)−O(41), 2.430(3); O(41)−Ti(1)−S(5), 72.20(9), Ti(1)−S(5)−C(62A), 103.08(11).

Scheme 2



Scheme 3



1 X = Y = Me
2 X = Me, Y = *t*BuS
3 X = Me, Y = *o*-MeOC$_6$H$_4$S
4 X = Y = *i*PrS
5 X = Y = PhCH$_2$S

The results obtained are summarized in Table 3. In both cases, the final polymers recovered had narrow polydispersity, and M_n values in close agreement with the calculated values were obtained. Also, the ^{1}H NMR spectra of the copolymers showed composition of PMMA-to-PBMA as 1.16:1 and 2.10:1, respectively, which is very close to the starting monomer ratios. The GPC traces of intermediary and final polymers clearly evidence the living nature of the polymerizations (Figure 5).

Polymerization of Methacrylates with Ti{CGC}(SR)(Y)/Activator Systems. Representative polymerization results obtained with the new alkylthiolato and thiophenolato precursors are summarized in Table 4. Very high to quantitative MMA conversions were reached with the *tert*-butylthiolato precursor **2** provided the polymerization is carried out in toluene. In fact, both the yield and syndiotacticity of PMMA dramatically decreased when the polymerization is carried out in THF solution (entry 20), evidencing the detrimental influence of such a coordinating solvent. The syndiospecificity of systems based on **2** in toluene ([*rr*] = 75−81%) is comparable to that of the corresponding systems based on **1**, with triad distributions characteristic of chain-end control mechanism.[13] The reaction protocol proved very important with these alkylthiolato-Ti systems. Addition of a stabilizing base (THF or MMA; protocols B and C) to the highly sensitive, in situ generated ionic species was found to improve significantly polymerization control. Under such conditions, precursor **2** led to PMMAs with very narrow molecular weight distributions (M_w/M_n = 1.05−1.10) and experimental M_n values in good agreement with the calculated values (entries 24, 25). These data indicate that the corresponding *tert*-butylthiolato ionic complex [Ti{CGC}(S*t*Bu)]$^+$[anion]$^-$, despite its apparent thermal sensitivity (in the absence of MMA; vide supra), is an effective initiator.

On the other hand, whatever the activation protocol used, PMMAs with molecular weight much higher than that expected and bimodal distributions were obtained from the thiophenolato complex **3** in toluene (e.g., entry 26). We assume that the low efficiency of this system likely reflects the poor ability of the weakly basic thiophenolato group to undergo nucleophilic addition onto coordinated MMA and/or the instability of the in situ generated cationic species in a nonpolar solvent, as observed

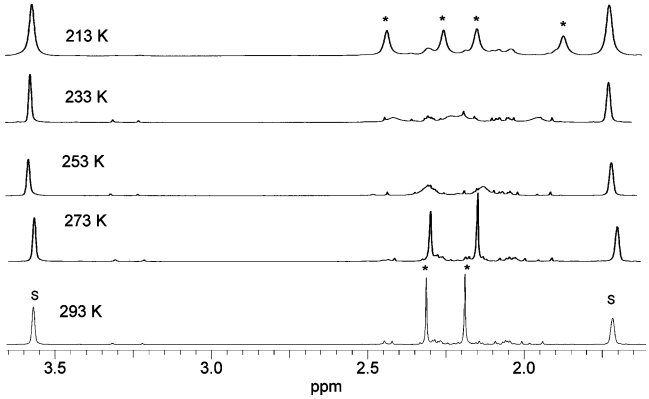


Figure 2. Selected region of the variable-temperature ^{1}H NMR spectra (300 MHz, THF-d_8) of [Ti{CGC}(*o*-OMeC$_6$H$_4$S)(THF-d_8)][MeB(C$_6$F$_5$)$_3$] (**6-*d*$_8$**). Descriptors * and "s" refer to (C*H*$_3$)$_4$C$_5$ and residual solvent resonances, respectively. The vertical expansion is different for each temperature.

(13) Triad distribution at 23 °C: 81% *rr*, 4% *mm*, 15% *mr*.

Table 2. Living Polymerization of MMA Mediated by Ti{CGC}Me_2 (1)/B(C_6F_5)$_3$ Systems[a]

entry	temp (°C)	[MMA]/[Ti]	time[b] (min)	yield (%)	$M_{n,cal}$[c] (g·mol^{-1})	$M_{n,exp}$[d] (g·mol^{-1})	M_w/M_n[d]	[*rr*][e] (%)
1	0	200	1440	95	19 000	28 600	1.54	73
2	20	200	1440	>99	20 000	24 700	1.17	80
3[f]	20	200	1440	96	19 200	24 000	1.23	78
4[g]	20	200	1440	93	18 600	31 400	1.28	74
5	40	200	1440	95	19 000	22 100	1.09	75
6	60	200	1440	96	19 200	17 600	1.07	71
7	80	200	30	96	19 200	20 000	1.06	69
8	100	200	1440	>99	20 000	21 200	1.06	60
9	80	400	30	98	39 200	37 200	1.05	67
10	80	1000	60	98	98 000	95 600	1.05	67
11[h]	80	1000	1080	96	96 000	92 600	1.13	64
12	80	2000	120	95	190 000	180 100	1.08	67
13	80	5000	1080	98	480 000	531 100	1.24	66
14	80	2000	3	15	30 000	35 400	1.05	nd
15	80	2000	6	45	90 000	82 600	1.05	nd
16	80	2000	10	65	130 000	113 800	1.06	nd
17	80	2000	20	96	192 000	175 700	1.06	67

[a] Polymerization conditions unless otherwise stated: [MMA] = 5.0 M in toluene; **1** and B(C_6F_5)$_3$ = 0.05 mmol; addition order of reagents: [Ti + activator], then MMA within 20 s. [b]Reaction time was not necessarily optimized; reactions carried out at 20 °C with [MMA]/[Ti] = 200 were usually completed within 6−8 h, while those carried out at 80 °C with [MMA]/[Ti] = 2000 required 10−15 min to go to completion. [c]Calculated M_n values from conv × [MMA]/[Ti] × 100 g·mol^{-1}. [d]Determined by GPC in THF vs PMMA standards. [e]Determined by ^{1}H NMR. [f][CPh_3][B(C_6F_5)$_4$] was used as activator. [g][$HNMe_2Ph$][B(C_6F_5)$_4$] was used as activator. [h]Bulk polymerization (i.e., <0.1 mL of toluene).

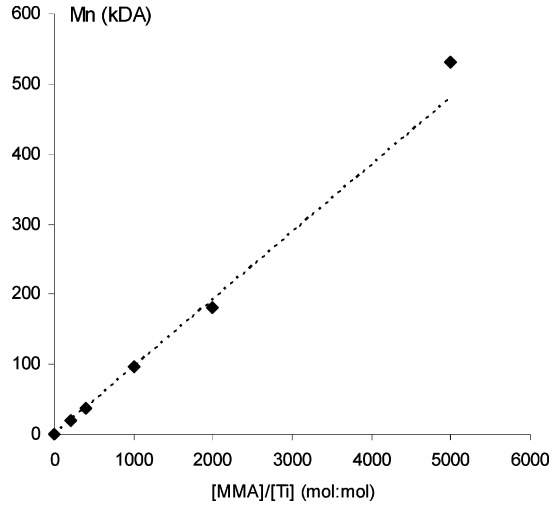


Figure 3. Dependence of M_n on monomer-to-titanium ratio in the polymerization of MMA promoted by **1**/B(C_6F_5)$_3$ in toluene at 80 °C (conversion >95%). ◆: M_n values determined by GPC vs PMMA standards; dashed line: calculated M_n values in a monometallic system.

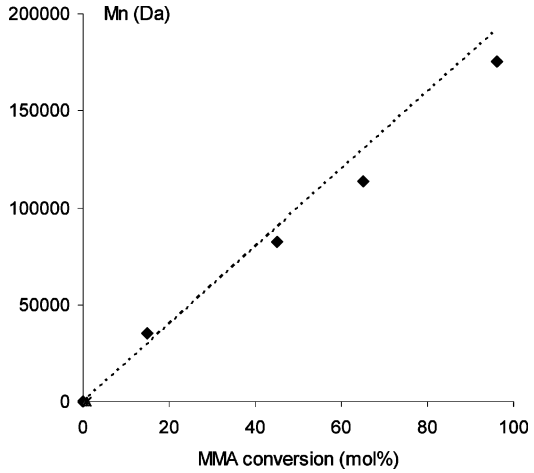


Figure 4. Dependence of M_n on monomer conversion in the polymerization of MMA promoted by **1**/B(C_6F_5)$_3$ in toluene at 80 °C. ◆: M_n values determined by GPC vs PMMA standards; dashed line: calculated M_n values in a monometallic system.

by NMR (vide supra). High polymerization yields were obtained with the bis(alkylthiolato)titanium complexes **4** and **5**, but also with somewhat larger molecular weight distributions and lower initiation efficiency (entries 27−30).

The above results confirm that [Ti{CGC}(enolate)$(L)_n$]$^+$ species are very effective methacrylate polymerization initiators. Their high activity and productivity, and so far unrevealed thermal robustness that enables them to operate in a broad temperature range (0−100 °C) with a living behavior, make them a good candidate for possible transfer agents. Also, combinations of a neutral [Ti{CGC}(SR)(Y)] precursor with a molecular activator can efficiently polymerize MMA, indicating that some in situ generated [Ti{CGC}(SR)$(L)_n$]$^+$ cationic species are good initiators. Further to our initial studies on the search for chain transfer agents with zirconocene systems,[7] we therefore investigated MMA polymerization with Ti{CGC}Me_2/activator systems in the presence of thiols.

Investigations of MMA Chain Transfer Polymerization Using Ti{CGC}Me_2/B(C_6F_5)$_3$/Thiols Systems. A series of alkylthiols and thiophenols varying in bulkiness and acidity have been investigated in terms of chemical compatibility and chain transfer activity toward Ti{CGC}Me_2 (**1**)/B(C_6F_5)$_3$ systems. Representative MMA polymerization experiments are summarized in Table 5. The active Ti species proved intolerant of an ester-functionalized alkylthiol ($HSCH_2CO_2CH_3$) since the addition of only 5 equiv (vs Ti) of it completely inhibited MMA polymerization (entry 44). Significantly decreased PMMA yields were observed in the presence of thiophenols (2-naphthylthiol, *p*-ClC_6H_4SH, and *o*-$MeOC_6H_4SH$) (entries 45−47). The addition of up to 5 equiv of other alkylthiols (*t*BuSH, *i*PrSH, $PhCH_2SH$, and CF_3CH_2SH) did not preclude the polymerization (entries 31−43), but an important decrease in the PMMA yield was observed when larger amounts (50 equiv) of *t*BuSH were used (entry 39). Intermediary results in terms of polymerization activity were observed in the presence of nC_4H_9SH (entry 41).

With all active combinations, the observed M_n values were always much higher than the calculated values, considering one polymer chain per added thiol; the molecular weight distributions remained in most cases quite narrow. Modification of the reaction conditions (temperature, solvent) using *t*BuSH as the thiol had a small influence on the polymerization results, although a slight, but noticeable, decrease of M_n values was

Table 3. Sequential Diblock and Triblock Copolymerization of MMA and BMA Mediated by the Ti{CGC}Me_2 (1)/B(C_6F_5)$_3$ System at 80 °C[a]

entry	polymer type	time (h)	yield (%)	$M_{n,cal}$ (g·mol^{-1})	$M_{n,exp}$[b] (g·mol^{-1})	M_w/M_n[b]	[*rr*][c] (%)
18	PMMA-*b*-PBMA	1 + 1	>99	48 400	49 500	1.06	65
19	PMMA-*b*-PBMA-*b*-PMMA	1 + 1 + 1	97	66 400	60 400	1.20	64

[a] **1** = 0.05 mmol; Ti/B(C_6F_5)$_3$ = 1; 200 equiv of monomer at each feed; toluene = 6 mL. [b]Determined by GPC in THF vs PMMA standards. [c]Determined by ^{1}H NMR.

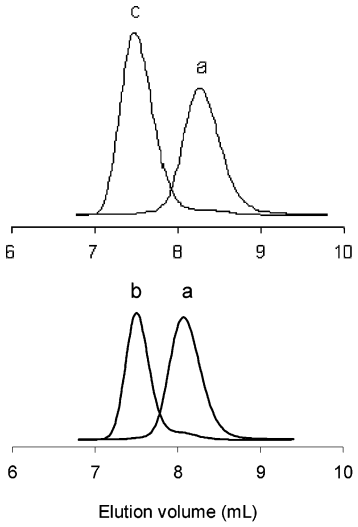


Figure 5. GPC traces (THF, 23 °C, flow rate 1 mL/min) of (bottom) PMMA-*b*-PBMA diblock copolymer and (top) PMMA-*b*-PBMA-*b*-PMMA triblock copolymer. Descriptors a, b, and c refer to PMMA, PMMA-*b*-PBMA, and PMMA-*b*-PBMA-*b*-PMMA, respectively.

observed with increasing temperature in the range 0−80 °C using the **1**/B(C_6F_5)$_3$/*t*BuSH system. This indicates that no effective chain transfer polymerization occurred under the above conditions.

Two possibilities can be envisioned to account for the inefficiency of thiols (e.g., *t*BuSH) to act as chain transfer agents: (a) thiols are inactive, i.e., they do not cleave growing PMMA chains from the Ti-enolate intermediate species during the time period necessary for complete conversion of MMA. (b) Thiols are extremely active, i.e., they are consumed by active Ti-enolate species in the early stage of the reaction. In the latter hypothesis, one should expect the formation of oligomers end-capped with alkylthiolato (*t*BuS) groups, which was observed neither by ^{1}H NMR analysis nor by MALDI-TOF mass spectrometry.

To support the validity of the first hypothesis, the stoichiometric reactivity of alkylthiols and thiophenols toward cationic Ti-enolate species was next investigated. The model species [Ti{CGC}(OC(O*i*Pr)═CMe_2)(THF)]$^+$[MeB(C_6F_5)$_3$]$^-$ (**8**), which mimics the propagating intermediate in the Ti-mediated polymerization of MMA,[2i] was selected for this purpose. Complex **8** reacts with 1 equiv of *t*BuSH in THF-d_8 at room temperature via protonolysis of the Ti−O(enolate) bond to yield the corresponding [Ti{CGC}(S*t*Bu)(THF)]$^+$ cationic species (**9**) with concomitant release of 1 equiv of isopropyl isobutyrate (Scheme 4). Although **9** is not stable at room temperature and slowly decomposes into an unidentified species (consistent with the aforementioned unsuccessful attempts to isolate such species from Ti{CGC}(S*t*Bu)Me (**2**)), this is the pathway expected to take place while using *t*BuSH as a transfer agent in the polymerization of MMA. However, cleavage of the Ti−O(enolate) bond in **8** by *t*BuSH proceeds remarkably slowly in comparison with that of the Zr−O(enolate) bond in the parent complex [ZrCp_2(OC(O*i*Pr)═CMe_2)(THF)]$^+$[MeB(C_6F_5)$_3$]$^-$ (**10**).[3h] In fact, the complete consumption of **8** and *t*BuSH, and concomitant generation of **9** and release of 1 equiv of isopropyl isobutyrate, requires 3 days, while it takes place within only 1 h with **10** under the same conditions.[7] The reaction of **8** with 1 equiv of the more acidic thiophenol *o*-$MeOC_6H_4SH$ in THF-d_8 was also investigated (Scheme 4). A ^{1}H NMR monitoring showed that **8** is consumed within 2 days to form **6** with concomitant release of 1 equiv of isopropyl isobutyrate. This reaction proceeds much faster in the weakly coordinating solvent CD_2Cl_2, but still requires 6 h. Reasons for this remarkably slow cleavage pathway are still unclear.[14]

Conclusions

We have shown that Ti{CGC}Me_2/activator combinations are highly effective and productive systems for living polymerization of methacrylates in an unexpected and exceptionally broad temperature range, from 20 °C up to 100 °C. To the best of our knowledge, this is the highest temperature reported for "living-controlled" polymerization of MMA mediated by an early transition metal system.[12]

In combination with a Lewis acid, "constrained geometry" alkylthiolato and thiophenolato titanium complexes (**2**−**5**) proved able to initiate the polymerization of MMA. The stoichiometric reactivity of thiols toward a model Ti-enolate species (**8**) revealed also that thiols do cleave the Ti−O(enolate) bond to yield the corresponding alkylthiolato and thiophenolato Ti cationic species. However, cleavage of the Ti−O(enolate) bond by thiols proceeds very slowly, which is likely the main reason to account for the poor efficiency of chain transfer polymerization with Ti{CGC}Me_2/abstractor/RSH systems.

Experimental Section

General Procedures. All experiments were carried out under purified argon using standard Schlenk techniques or a glovebox (<1 ppm O_2, 5 ppm H_2O). Hydrocarbon solvents, diethyl ether, and tetrahydrofuran were distilled from Na/benzophenone; toluene and pentane were distilled from Na/K alloy under nitrogen and degassed by freeze−thaw−vacuum prior to use. Chlorinated solvents were distilled from calcium hydride. Deuterated solvents were purchased from Eurisotop and purified before use. Methyl methacrylate (MMA, Acros) and *n*-butyl methacrylate (BMA, Acros) were distilled twice under argon over CaH_2. *t*BuSH, *i*PrSH, nC_4H_9SH, CF_3CH_2SH, $PhCH_2SH$, and $HSCH_2CO_2CH_3$ (all Aldrich) and thiophenols *p*-ClC_6H_4SH, 2-naphthylthiol, and *o*-$MeOC_6H_4$-SH (all Acros) were distilled before use. MeLi (1.6 M solution in diethyl ether, Acros), Ti{$Me_2Si(Me_4C_5)$(*t*BuN)}Cl_2 (Boulder Scientific Co.), [Ph_3C][B(C_6F_5)$_4$] (Boulder Scientific Co.), and [HNMe_2-

(14) A possible cleavage process of the Ti−O(enolate) bond in [Ti{CGC}(enolate)]$^+$ species by thiols includes initial THF dissociation, then thiol coordination, and finally generation of the [Ti{CGC}(SR)(L)$_n$]$^+$ species (Scheme 5). Preliminary decoordination of THF from Ti is supported by enhanced cleavage kinetics in a weakly coordinating solvent such as CD_2Cl_2, as compared to THF (vide supra). Similar observations have been made and conclusions drawn for cationic Zr systems; see ref 3g and: Piers, W. E.; Koch, L.; Ridge, D. S.; MacGillivray, L. R.; Zaworotko, M. *Organometallics* **1992**, *11*, 3148−3152.

Table 4. Polymerization of MMA Mediated by 2−5/Activator Systems[a]

entry	comp	activator	protocol[b]	yield (%)	$M_{n,cal}$[c] (g·mol^{-1})	$M_{n,exp}$[d] (g·mol^{-1})	M_w/M_n[d]	[*rr*][e] (%)
20[f]	**2**	$B(C_6F_5)_3$	A	35	7000	22 400	1.05	73
21	**2**	$B(C_6F_5)_3$	A	96	19 200	31 300	1.10	81
22	**2**	$[HNMe_2Ph][B(C_6F_5)_4]$	A	96	19 200	28 600	1.09	77
23	**2**	$[Ph_3C][B(C_6F_5)_4]$	A	95	19 000	28 800	1.10	75
24	**2**	$B(C_6F_5)_3$	B	95	19 000	18 500	1.07	75
25	**2**	$B(C_6F_5)_3$	C	96	19 200	22 000	1.09	78
26	**3**	$B(C_6F_5)_3$	B	>99	20 000	198 000[g]	1.18[g]	74
27	**4**	$[HNMe_2Ph][B(C_6F_5)_4]$	B	92	18 400	73 500	1.13	73
28	**5**	$[HNMe_2Ph][B(C_6F_5)_4]$	B	93	18 600	64 300	1.20	72
29	**5**	$B(C_6F_5)_3$	B	60	12 000	105 200	1.24	75
30	**5**	$[Ph_3C][B(C_6F_5)_4]$	B	97	19 400	33 800	1.23	73

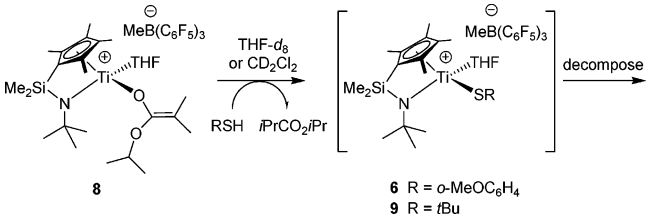
[a] Polymerization conditions unless otherwise stated: [MMA] = 5.0 M in toluene; Ti = 0.05 mmol; [Ti]/[activator]/[MMA] = 1:1:200, T = 20 °C; reaction time = 24 h (unoptimized). [b]Protocol A: precursor, then activator, then MMA; protocol B: precursor in THF, then activator, then dried, then MMA; protocol C: Precursor in 0.1 g of MMA, then activator, then rest of MMA. [c]Calculated M_n values from conv × [MMA]/[Ti] × 100 g·mol^{-1}. [d]Determined by GPC in THF vs PMMA standards. [e]Determined by ^{1}H NMR spectroscopy. [f]THF solvent. [g]A second distribution that accounts for ca. 5% of the sample was observed with M_n = 27 600 and M_w/M_n = 1.06.

Table 5. Polymerization of MMA Using Ti{CGC}Me$_2$ (1) Precursor in the Presence of Thiols as Potential Chain Transfer Agent (CTA)[a]

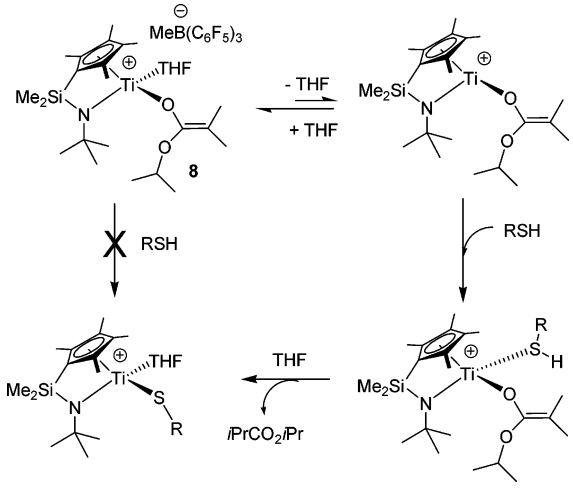
entry	thiol	CTA (equiv)	temp (°C)	yield (%)	$M_{n,calc}$[c] (g/mol)	$M_{n,exp}$[b] (g/mol)	M_w/M_n[b]
31	*t*BuSH	1	20	92	18 400	24 500	1.41
32[d]	*t*BuSH	5	20	7	1400	n.d.	n.d.
33	*t*BuSH	5	0	95	3800	28 600	1.54
34	*t*BuSH	5	20	92	3680	23 900	1.15
35[e]	*t*BuSH	5	20	96	3680	23 500	1.21
36	*t*BuSH	5	40	95	3800	21 800	1.08
37	*t*BuSH	5	60	96	3680	18 800	1.06
38	*t*BuSH	5	80	93	3720	19 200	1.06
39[f]	*t*BuSH	50	20	20	80	5800	1.20
40	*i*PrSH	5	20	85	3400	(40%) 52 900	1.19
						(60%) 16 000	1.06
41	nC_4H_9SH	5	20	38	1520	19 300	1.17
42	$PhCH_2SH$	5	20	92	3680	22 300	1.28
43	CF_3CH_2SH	5	20	95	3800	31 600	1.18
44	$HSCH_2CO_2CH_3$	5	20	<1			
45	2-naphthylthiol	5	20	5	200	12 000	1.14
46	*p*-ClC_6H_4SH	5	20	15	600	11 700	1.19
47	*o*-$MeOC_6H_4SH$	5	20	17	680	(60%) 91 200	1.03
						(40%) 15 100	1.19

[a] Polymerization conditions unless otherwise stated: toluene = 2 mL; **1** = 0.05 mmol; activator = $B(C_6F_5)_3$ (1 equiv vs **1**); [MMA]/[Ti] = 200; reaction time = 24 h (unoptimized); addition order of reagents: [Ti + activator], then [CTA + MMA] within 20 s. [b]Determined by GPC in THF vs PS standards. [c]Calculated M_n values considering one polymer chain per CTA. [d]CH_2Cl_2 as solvent. [e]$[CPh_3][B(C_6F_5)_4]$ as activator. [f]$[HNMe_2Ph][B(C_6F_5)_4]$ as activator.

Scheme 4



Scheme 5



Ph][$B(C_6F_5)_4$] (Boulder Scientific Co.) were used as received. $B(C_6F_5)_3$ (Boulder Scientific Co.) was sublimed twice before use. Complexes **1**[5d] and **8**[2i] were synthesized as previously reported.

NMR spectra were recorded on Bruker AC-200, AC-300, and AM-500 spectrometers in Teflon-valved NMR tubes at 23 °C unless otherwise stated. ^{1}H and ^{13}C NMR chemical shifts were determined using residual solvent resonances and are reported vs $SiMe_4$. Assignment of signals was made from ^{1}H−^{13}C HMQC and ^{1}H−^{13}C HMBC 2D NMR experiments. Coupling constants are given in hertz. Cationic Ti complexes containing $MeB(C_6F_5)_3^-$ are totally dissociated in THF-d_8 or CD_2Cl_2 solution, and the NMR resonances for this anion are almost identical (see below). Elemental analyses (C, H, N, S) were performed by the Microanalytical Laboratory at the Institute of Chemistry of Rennes and are the average of two independent determinations. Molecular weights of PMMA (or block copolymers) were determined by gel permeation chromatography (GPC) at room temperature on a Waters apparatus equipped with five PL gel columns (Polymer Laboratories Ltd), a Waters WISP 717 autosampler, and a Shimadzu RID 6A differential refractometer. THF was used as eluent at a flow rate of 1.0 mL·min^{-1}. PS or PMMA standards were used for molecular weight calibration. The microstructure of polymers was determined by ^{1}H NMR in $CDCl_3$.

NMR Data for the Free Anion $MeB(C_6F_5)_3^-$.[15] ^{1}H NMR (THF-d_8): δ 0.50 (br s, 3H, BCH_3). ^{1}H NMR (CD_2Cl_2): δ 0.54 (br s,

3H, BCH_3). $^{13}C\{^1H\}$ NMR (THF-d_8): δ 148.5 (dm, J_{C-F} = 252, *o*-C_6F_5), 137.4 (dm, J_{C-F} = 247, *p*-C_6F_5), 136.2 (dm, J_{C-F} = 229, *m*-C_6F_5), 129.7 (C_{ipso}), 9.7 (br, BCH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 148.3 (dm, J_{C-F} = 238, *o*-C_6F_5), 137.4 (dm, J_{C-F} = 257, *p*-C_6F_5), 136.4 (dm, J_{C-F} = 245, *m*-C_6F_5), 128.9 (C_{ipso}), 9.9 (br, BCH_3). ^{11}B NMR (THF-d_8): δ −14.8 (s, *B*CH_3). ^{11}B NMR (CD_2Cl_2): δ −14.9 (s, *B*CH_3). ^{19}F NMR (THF-d_8): δ −134.5 (d, $^3J_{C-F}$ = 21, 6F, *o*-F), −168.5 (t, $^3J_{F-F}$ = 21, 3F, *p*-F), −170.6 (m, $^3J_{F-F}$ = 18, 6F, *m*-F). ^{19}F NMR (CD_2Cl_2): δ −133.6 (d, $^3J_{F-F}$ = 18, 6F, *o*-F), −165.6 (t, $^3J_{F-F}$ = 22, 3F, *p*-F), −168.2 (t, $^3J_{F-F}$ = 22, 6F, *m*-F).

Ti{$Me_2Si(Me_4C_5)$(*t*BuN)}(S*t*Bu)Me (2). Ti{$Me_2Si(Me_4C_5)$-(*t*BuN)}Me_2 (**1**, 17.6 mg, 0.054 mmol) and *t*BuSH (9.7 mg, 0.11 mmol) were charged in a Teflon-valved NMR tube, and C_6D_6 (ca. 0.5 mL) was vacuum transferred. The tube was sealed and kept at 80 °C, and ^1H NMR spectroscopy was recorded periodically. Over 12 h, complex **2** formed quantitatively together with release of CH_4 (^1H NMR (C_6D_6): δ 0.16). Volatiles were removed under vacuum, the residue was washed with a minimal amount of cold pentane, and complex **2** was obtained as a red, oily solid (14 mg, 64%). NMR data for **2**: ^1H NMR (C_6D_6): δ 2.21 (s, 3H, CH_3C_5), 2.07 (s, 3H, CH_3C_5), 2.05 (s, 3H, CH_3C_5), 1.92 (s, 3H, CH_3C_5), 1.67 (s, 9H, SC(CH_3)$_3$), 1.53 (s, 9H, NC(CH_3)$_3$), 0.83 (s, 3H, TiCH_3), 0.50 (s, 3H, SiCH_3), 0.39 (s, 3H, SiCH_3). ^1H NMR (THF-d_8): δ 2.27 (s, 3H, CH_3C_5), 2.22 (s, 3H, CH_3C_5), 1.99 (s, 3H, CH_3C_5), 1.96 (s, 3H, CH_3C_5), 1.57 (s, 9H, SC(CH_3)$_3$), 1.40 (s, 9H, NC(CH_3)$_3$), 0.54 (s, 3H, SiCH_3), 0.53 (s, 3H, SiCH_3), 0.42 (s, 3H, TiCH_3). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 135.0 (C_5CH_3), 132.5 (C_5CH_3), 131.7 (C_5CH_3), 131.1 (C_5CH_3), 100.8 (C_5SiMe_2), 59.5 (S*C*(CH$_3$)$_3$), 57.5 (q, J = 97, Ti*C*H$_3$), 50.0 (N*C*(CH$_3$)$_3$), 36.4 (NC(*C*H$_3$)$_3$), 34.7 (SC(*C*H$_3$)$_3$), 15.4 (C_5CH_3), 15.1 (C_5CH_3), 13.9 (C_5CH_3), 12.0 (C_5CH_3), 6.4 (Si*C*H$_3$), 5.7 (Si*C*H$_3$). Anal. Calcd for $C_{20}H_{39}NSSiTi$ (401.55): C, 59.82; H, 9.79; N, 3.49; S, 7.99. Found: C, 59.1; H, 10.2; N, 3.8; S, 7.6.

Ti{$Me_2Si(Me_4C_5)$(*t*BuN)}(*o*-$OMeC_6H_4S$)(Me) (3). This product was prepared as described above for **2** starting from **1** (113.0 mg, 0.34 mmol) and *o*-$MeOC_6H_4SH$ (53.2 mg, 0.38 mmol) to give **3** as a red, oily solid (110 mg, 71%). Single crystals suitable for X-ray diffraction were obtained from a concentrated solution in pentane at −30 °C. ^1H NMR (C_6D_6): δ 7.58 (d, ^3J = 8.0, 1H, Ph), 6.97 (t, ^3J = 8.0, 1H, Ph), 6.79 (t, ^3J = 8.0, 1H, Ph), 6.51 (t, ^3J = 8.0, 1H, Ph), 3.38 (s, 3H, OCH_3), 2.15 (s, 3H, CH_3C_5), 2.04 (s, 3H, CH_3C_5), 1.99 (s, 3H, CH_3C_5), 1.96 (s, 3H, CH_3C_5), 1.42 (s, 9H, NC(CH_3)$_3$), 0.83 (s, 3H, TiCH_3), 0.53 (s, 3H, Si(CH_3)$_2$), 0.44 (s, 3H, Si(CH_3)$_2$). ^1H NMR (THF-d_8): δ 7.17 (d, ^3J = 8.0, 1H, Ph), 7.01 (t, ^3J = 8.0, 1H, Ph), 6.85 (t, ^3J = 8.0, 1H, Ph), 6.74 (t, ^3J = 8.0, 1H, Ph), 3.83 (s, 3H, OCH_3), 2.19 (s, 3H, CH_3C_5), 2.06 (s, 3H, CH_3C_5), 2.03 (s, 3H, CH_3C_5), 1.88 (s, 3H, CH_3C_5), 1.35 (s, 9H, NC(CH_3)$_3$), 0.55 (s, 3H, TiCH_3), 0.49 (s, 3H, Si(CH_3)$_2$), 0.46 (s, 3H, Si(CH_3)$_2$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 157.9 (Ph), 135.4 (C_5CH_3), 134.9 (Ph), 132.0 (Ph), 131.8 (C_5CH_3), 128.2 (Ph), 120.9 (Ph), 111.3 (Ph), 101.2 (C_5-Si(CH$_3$)$_2$), 59.9 (N*C*(CH$_3$)$_3$), 55.9(O*C*H$_3$), 53.6 (Ti*C*H$_3$), 33.6 (NC-(*C*H$_3$)$_3$), 15.6 (C_5CH_3), 12.0 (C_5CH_3), 5.9 (Si*C*H$_3$). Anal. Calcd for $C_{23}H_{37}NOSSiTi$ (451.56): C, 61.18; H, 8.26; N, 3.10; S, 7.10. Found: C, 61.50; H, 8.34; N, 2.94; S, 6.94.

Ti{$Me_2Si(Me_4C_5)$(*t*BuN)}(S*i*Pr)$_2$ (4). This product was prepared as described above for **2** starting from **1** (17.6 mg, 0.054 mmol) and *i*PrSH (8.4 mg, 0.11 mmol) to give **4** as a red oil (19 mg, 79%). ^1H NMR (C_6D_6): δ 4.10 (sept, ^3J = 6.6, 2H, C*H*(CH$_3$)$_2$), 2.19 (s, 6H, CH_3C_5), 2.15 (s, 6H, CH_3C_5), 1.60 (s, 9H, NC(CH_3)$_3$), 1.46 (d, ^3J = 6.6, 6H, CH(CH_3)$_2$), 1.44 (d, ^3J = 6.6, 6H, CH-(CH_3)$_2$), 0.52 (s, 6H, Si(CH_3)$_2$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 135.6 (C_5CH_3), 133.0 (C_5CH_3), 102.3 (C_5SiMe_2), 61.2 (N*C*(CH$_3$)$_3$), 41.9 (*C*H(CH$_3$)$_2$), 33.8 (NC(*C*H$_3$)$_3$), 28.3 (CH(*C*H$_3$)$_2$), 16.4 (C_5CH_3), 12.1 (C_5CH_3), 5.9 (Si*C*H$_3$). Anal. Calcd for $C_{21}H_{41}NS_2SiTi$ (447.64): C, 56.35; H, 9.23; N, 3.13; S, 14.33. Found: C, 57.1; H, 9.7; N, 3.3; S, 14.1.

Ti{$Me_2Si(Me_4C_5)$(*t*BuN)}$(SCH_2Ph)_2$ (5). This product was prepared as described above for **2** starting from **1** (18.2 mg, 0.056 mmol) and $PhCH_2SH$ (13.8 mg, 0.11 mmol) to give **5** as a red, oily solid (19.5 mg, 64%). ^1H NMR (C_6D_6): δ 7.43 (m, 4H, Ph), 7.13 (m, 6H, Ph), 4.74 (s, 2H, CH_2Ph), 4.73 (s, 2H, CH_2Ph), 2.12 (s, 6H, CH_3C_5), 2.09 (s, 6H, CH_3C_5), 1.59 (s, 9H, NC(CH_3)$_3$), 0.53 (s, 6H, Si(CH_3)$_2$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 143.3 (Ph), 135.7 (C_5CH_3), 133.6 (C_5CH_3), 129.1 (Ph), 128.8 (Ph), 126.3 (Ph), 103.4 (C_5SiMe_2), 62.2 (N*C*(CH$_3$)$_3$), 42.4 (*C*H$_2$Ph), 34.3 (NC(*C*H$_3$)$_3$), 16.1 (C_5CH_3), 12.6 (C_5CH_3), 5.9 (Si*C*H$_3$). Anal. Calcd for $C_{29}H_{41}NS_2$-SiTi (543.73): C, 64.06; H, 7.60; N, 2.58; S, 11.79. Found: C, 64.8; H, 7.9; N, 2.7; S, 11.4.

Generation of [Ti{$Me_2Si(Me_4C_5)$(*t*BuN)}(*o*-$MeOC_6H_4S$)(THF-d_8)][$MeB(C_6F_5)_3$] (6-d_8) from [Ti{$Me_2Si(Me_4C_5)$(*t*BuN)}Me-(THF-d_8)][$MeB(C_6F_5)_3$] (7-d_8). A solution of **1** (18.0 mg, 0.055 mmol) in THF-d_8 (ca. 0.5 mL) was prepared in a Teflon-valved NMR tube, and $B(C_6F_5)_3$ (28.1 mg, 0.055 mmol) was added at room temperature. The tube was sealed and agitated for 10 min, and ^1H NMR spectroscopy was recorded, showing quantitative conversion of **1** to **7-d_8**. ^1H NMR of **7-d_8** (THF-d_8): δ 2.42 (s, 3H, CH_3C_5), 2.15 (s, 3H, CH_3C_5), 2.09 (s, 3H, CH_3C_5), 2.01 (s, 3H, CH_3C_5), 1.48 (s, 9H, NC(CH_3)$_3$), 1.02 (s, 3H, TiCH_3), 0.72 (s, 3H, Si(CH_3)$_2$), 0.68 (s, 3H, Si(CH_3)$_2$). The NMR data of free anion $MeB(C_6F_5)_3^-$ were the same as those described above. To the above solution of **7-d_8**, *o*-$MeOC_6H_4SH$ (7.7 mg, 0.055 mmol) was added via microsyringe. The tube was sealed and ^1H NMR spectroscopy was recorded. The conversion of **7-d_8** to **6-d_8** was >95% after 2 h. NMR data for **6-d_8**: ^1H NMR (THF-d_8, 23 °C): δ 7.26 (t, ^3J = 8.0, 1H, Ph), 7.17 (d, ^3J = 8.0, 1H, Ph), 7.09 (d, ^3J = 8.0, 1H, Ph), 6.96 (t, ^3J = 8.0, 1H, Ph), 3.89 (s, 3H, OCH_3), 2.31 (s, 6H, CH_3C_5), 2.18 (s, 6H, CH_3C_5), 1.27 (s, 9H, NC(CH_3)$_3$), 0.77 (s, 6H, Si(CH_3)$_2$). ^1H NMR (THF-d_8, −60 °C): δ 7.34−6.81 (m, 5H, Ph), 3.84 (s, 3H, OCH_3), 2.45 (s, 3H, CH_3C_5), 2.31 (s, 3H, CH_3C_5), 2.13 (s, 3H, CH_3C_5), 1.85 (s, 3H, CH_3C_5), 1.49 (s, 9H, NC(CH_3)$_3$), 0.86 (s, 3H, Si(CH_3)$_2$), 0.78 (s, 3H, Si(CH_3)$_2$). $^{13}C\{^1H\}$ NMR (THF-d_8): δ 155.8 (Ph), 141.1 (C_5CH_3), 139.8 (C_5CH_3), 132.4 (Ph), 129.3 (Ph), 122.3 (Ph), 112.1 (Ph), 110.2 ($C_5Si(CH_3)_2$), 66.7 (N*C*(CH$_3$)$_3$), 56.9 (O*C*H$_3$), 31.9 (NC(*C*H$_3$)$_3$), 16.3 (C_5CH_3), 11.5 (C_5CH_3), 3.9 (Si*C*H$_3$). The NMR data of the free anion $MeB(C_6F_5)_3^-$ were the same as those described above.

Generation of [[$Me_2Si(Me_4C_5)$(*t*BuN)]Ti(*o*-$MeOC_6H_4S$)(THF-d_8)][$MeB(C_6F_5)_3$] (6-d_8) from [{$Me_2Si(Me_4C_5)$(*t*BuN)}TiMe(*o*-$MeOC_6H_4S$) (3). A solution of **3** (10.0 mg, 0.023 mmol) in THF-d_8 (ca. 0.5 mL) was charged in a Teflon-valved NMR tube, and $B(C_6F_5)_3$ (11.6 mg, 0.023 mmol) was added at room temperature. The tube was sealed, and ^1H NMR spectroscopy was recorded periodically. The conversion of **3** was almost quantitative within 30 min with ca. 95% selectivity for **6-d_8**. The NMR data were the same as those reported above.

Reaction of [Ti{$Me_2Si(Me_4C_5)$(*t*BuN)}(OC(O*i*Pr)═CMe_2)-(THF-d_8)][$MeB(C_6F_5)_3$] (8-d_8) with *t*BuSH in THF-d_8. To a solution of Ti{$Me_2Si(Me_4C_5)$(*t*BuN)}(Me)(OC(O*i*Pr)═CMe_2) (3.6 mg, 0.0082 mmol) in THF-d_8 (ca. 0.5 mL) in a Teflon-valved NMR tube was added at room temperature $B(C_6F_5)_3$ (4.2 mg, 0.0082 mmol). The solution was left for 10 min at 20 °C to ensure the complete formation of **8-d_8**, then *t*BuSH (0.73 mg, 0.0082 mmol) was added via a microsyringe. ^1H NMR spectra were periodically recorded and revealed that the reaction was finished within 3 days, with release of 1 equiv of isopropyl isobutyrate and a mixture of **9** and an unidentified decomposition product. NMR data for isopropyl isobutyrate: ^1H NMR (THF-d_8): δ 4.96 (sept, ^3J = 6.0, 1H,

(15) (a) Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10015−10031. (b) Horton, A. D.; de With, J.; Linden, J. v. d.; Weg, H. v. d. *Organometallics* **1996**, *15*, 2672−2674. (c) Bochmann, M.; Green, M. L. H.; Powell, A. K.; Sassmannshausen, J.; Triller, M. U.; Wocadlo, S. *J. Chem. Soc., Dalton Trans.* **1999**, 43−49. (d) Carpentier, J.-F.; Wu, Z.; Lee, C. W.; Strömberg, S.; Christopher, J. N.; Jordan, R. F. *J. Am. Chem. Soc.* **2000**, *122*, 7750−7767. (e) Klosin, J.; Roof, G. R.; Chen. E. Y.-X.; Abboud, K. A. *Organometallics* **2000**, *19*, 4684−4686.

OC*H*(CH_3)$_2$), 2.43 (sept, ^3J = 7.0, 1H, (CH_3)$_2$C*H*CO), 1.18 (d, ^3J = 6.0, 6H, OCH(C*H*$_3$)$_2$), 1.11 (d, ^3J = 7.0, 6H, (C*H*$_3$)$_2$CHCO). ^{13}C{^{1}H} NMR (THF-d_8): δ 176.7 (*C*OO*i*Pr), 67.2 (O*C*H(CH_3)$_2$), 34.1 (CH_3)$_2$*C*HCO), 21.7 (OCH(*C*H$_3$)$_2$), 19.0 ((*C*H$_3$)$_2$CHCO).

Reaction of [Ti{$Me_2Si(Me_4C_5)$(*t*BuN)}(OC(O*i*Pr)=CMe_2)(THF-d_8)][$MeB(C_6F_5)_3$] (8-d_8) with *o*-$MeOC_6H_4SH$ in THF-d_8. This reaction was conducted as described above starting from Ti{$Me_2Si(Me_4C_5)$(*t*BuN)}(Me)(OC(O*i*Pr)=CMe_2) (3.8 mg, 0.0086 mmol), $B(C_6F_5)_3$ (4.4 mg, 0.0086 mmol), and *o*-$MeOC_6H_4SH$ (1.2 mg, 0.0086 mmol). ^{1}H NMR spectra were periodically recorded and revealed that the reaction was finished within 2 days, with release of 1 equiv of isopropyl isobutyrate and a mixture of **6** and an unidentified decomposition product.

Reaction of [Ti{$Me_2Si(Me_4C_5)$(*t*BuN)}(OC(O*i*Pr)=CMe_2)(THF)][$MeB(C_6F_5)_3$] (8) with *o*-$MeOC_6H_4SH$ in CD_2Cl_2. This reaction was conducted as described above starting from Ti{$Me_2Si(Me_4C_5)$(*t*BuN)}(Me)(OC(O*i*Pr)=CMe_2) (11.5 mg, 0.026 mmol), $B(C_6F_5)_3$·THF (15.2 mg, 0.026 mmol), and *o*-$MeOC_6H_4SH$ (3.65 mg, 0.026 mmol). ^{1}H NMR spectra were periodically recorded and revealed that the reaction was finished within 6 h, with release of 1 equiv of isopropyl isobutyrate and a mixture of **6** and an unidentified decomposition product. NMR data for isopropyl isobutyrate: ^{1}H NMR (CD_2Cl_2): δ 4.97 (sept, ^3J = 6.3, 1H, OC*H*(CH_3)$_2$), 2.53 (sept, ^3J = 7.0, 1H, (CH_3)$_2$C*H*CO), 1.26 (d, ^3J = 6.3, 6H, OCH(C*H*$_3$)$_2$), 1.16 (d, ^3J = 7.0, 6H, (C*H*$_3$)$_2$CHCO).

Solid-State Structure Determination of Complex 3. A suitable single crystal of **3** was mounted onto a glass fiber using the "oil-drop" method. Diffraction data were collected at 100 K using a NONIUS Kappa CCD diffractometer with graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å). A combination of ω- and φ-scans was carried out to obtain at least a unique data set. Crystal structures were solved by means of the Patterson method; remaining atoms were located from difference Fourier synthesis, followed by full-matrix least-squares refinement based on F^2 (programs SHELXS-97 and SHELXL-97).[16] Many hydrogen atoms could be found from the Fourier difference. Carbon-bound hydrogen atoms were placed at calculated positions and forced to ride on the attached carbon atom. The hydrogen atom contributions were calculated but not refined. All non-hydrogen atoms were refined with anisotropic displacement parameters. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities were of no chemical significance. Crystal data and details of data collection and structure refinement are given in Table 1. Crystallographic data for **3** are also available in cif format (see Supporting Information).

Typical Procedure for MMA Polymerization and MMA-BMA Block Copolymerization. To a 10 mL flask equipped with a magnetic stirrer, containing the Ti-{CGC} catalyst (0.05 mmol) in toluene (or THF) solvent, was introduced the activator ($B(C_6F_5)_3$, [$HNMe_2Ph$][$B(C_6F_5)_4$], or [Ph_3C][$B(C_6F_5)_4$]) in toluene (or THF) solvent and kept at the desired polymerization temperature. Then, the proper amount of monomer was rapidly added (within 20 s) by syringe. The polymerization was carried out for a time period, and, in case of block copolymerization, a second or third injection (BMA or MMA) was loaded. The reaction was then quenched by addition of acidified methanol (3% HCl, 200 mL). The precipitated polymer was filtered and dried overnight under vacuum at 60 °C.

Acknowledgment. We thank Total and Arkema Co. (grant to B.L.) and the Centre National de la Recherche Scientifique for financial support of this work. We gratefully thank Dr. M. Glotin and Dr. G. Meunier (Arkema Co.) for valuable discussions.

Supporting Information Available: Crystallographic data for **3** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

OM060838G

(16) (a) Sheldrick, G. M. *SHELXS-97*, Program for the Determination of Crystal Structures; University of Goettingen: Germany, 1997. (b) Sheldrick, G. M. *SHELXL-97*, Program for the Refinement of Crystal Structures; University of Goettingen: Germany, 1997.