Highly Effective Polymerization of Acrylate Catalyzed by a "Constrained Geometry" Titanium Complex/$B(C_6F_5)_3$ System

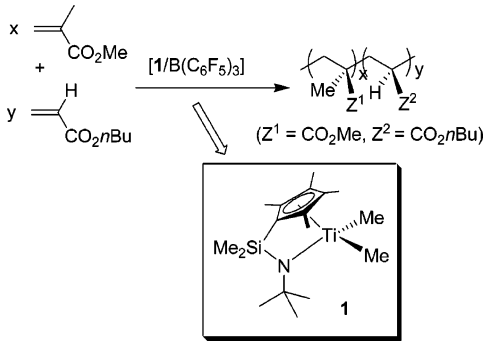
Bing Lian,† Christophe M. Thomas,† Christophe Navarro,‡ and Jean-François Carpentier*,†

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 February 23, 2007

Polymerization of methacrylates mediated by group 4 metal systems has attracted much attention in recent years and met considerable achievements, with significant contributions from the groups of Collins,[1] Chen,[2] and many others.[3] A major interest of these ubiquitous early-transition-metal catalysts/initiators is the high degree of control, i.e., the livingness and stereochemistry of polymerization, they exhibit under suitable conditions. Many efforts have also been paid to realize the controlled polymerization of acrylates (containing active α-H) using group 4 metal systems;[1c,2k,4−6] however, to the best of our knowledge, no real success has been met so far. Thus, Chen et al. reported recently the poor performances of the (*rac*-EBI)ZrMe[OC(O*i*Pr)═CMe_2]/$B(C_6F_5)_3$·THF system for *n*-butyl acrylate (*n*BA) polymerization, which proceeds in an uncontrolled fashion due to several facile catalyst deactivation pathways (backbiting);[2k] in fact, only a 47% monomer conversion can be achieved at room temperature with a high catalyst loading of 1.0 mol % to monomer. In this paper, we present the first example of the effective homopolymerization and block copolymerization of *n*-butyl acrylate (*n*BA) initiated by a group 4 metal system with full monomer conversion to produce syndiotactic-rich, high molecular weight polymers with relatively narrow molecular weight distributions (Scheme 1).

Scheme 1



The group of Chen and ours have previously shown that cationic "constrained geometry" hemi-titanocenes [{CGC}Ti(Z)]$^+$ (CGC = [η^5, η^1-$C_5Me_4SiMe_2N$*t*Bu]; Z = alkyl or enolate)[7] produce syndiotactic-enriched poly(methyl methacrylate) (PMMA) in a living fashion, both at room temperature[2i] and, much more surprisingly, high temperatures up to 100 °C.[3j] The unique robustness of this catalyst/initiator system prompted us to investigate it toward the polymerization of acrylates. Representative results of *n*BA polymerization using the {CGC}$TiMe_2$/$B(C_6F_5)_3$ (1:1) system are reported in Table 1. In fact, full conversion of 200 equiv of monomer was obtained in the temperature range of −20 to 20 °C (entries 1−3). From 40 °C, the polymer yields decreased significantly and, at 80 °C, a low yield (52%) was obtained, indicating that deactivation pathways take place fast at high temperature (entries 4−6). The resulting P(*n*BA)s exhibit unimodal molecular distribution with relatively narrow PDI values (1.49−1.88) over the whole temperature range investigated, as expected for single-site catalysts.[8] The ^{13}C NMR spectra of P(*n*BA) show a syndiotactic-enriched microstructure (76% *rr* at 20 °C; Table 1, entry 3), i.e., a slightly lower stereoselectivity than that achieved for PMMA under the same conditions (ca. 80% *rr*).[2i,3j] The initiation efficiency (*I**) increased monotonously with temperature; considering a monometallic initiating system, *I** increased from ca. 15% at −20 °C to reach a plateau at ca. 53% from 40 °C.[9] The influence of the *n*BA-to-Ti ratio (100:1−800:1) was also investigated at 20 °C (entries 7−9), showing the regular growth of the P(*n*BA) chain (Figure 1a). The kinetics of the polymerization were evaluated at 20 °C with a high loading of 800 equiv of *n*BA (time, conversion: 3 min, 36%; 6 min, 74%; 10 min, 79%; 20 min, 81%), giving a turnover frequency (TOF) value of 5920 mol *n*BA·mol Ti^{-1}·h^{-1} at 70% conversion.

Table 1. *n*BA Polymerization Using the {CGC}$TiMe_2$/$B(C_6F_5)_3$ System[a]

run	*n*BA (equiv)	time[b] (h)	temp (°C)	yield (%)	$M_{n,cal}$[c] (10^4)	$M_{n,exp}$[d] (10^4)	PDI (M_w/M_n)[d]
1	200	18	−20	98	2.51	18.4	1.49
2	200	5	0	98	2.51	11.7	1.65
3	200	1	20	98	2.51	7.16	1.81
4	200	1	40	74	1.89	3.61	1.74
5	200	1	60	65	1.66	3.15	1.70
6	200	1	80	52	1.33	2.53	1.74
7	100	1	20	98	1.25	3.79	1.64
8	400	1	20	98	4.92	11.2	1.88
9	800	1	20	83	8.50	16.3	1.70

[a] Ti = B = 0.05 mmol, solvent = 4 mL of toluene. [b] Time was not necessarily optimized. [c] Calculated M_n values from conv × [*n*BA]/[Ti] × 128 g·mol^{-1}. [d] Determined by GPC in THF vs PS standards.

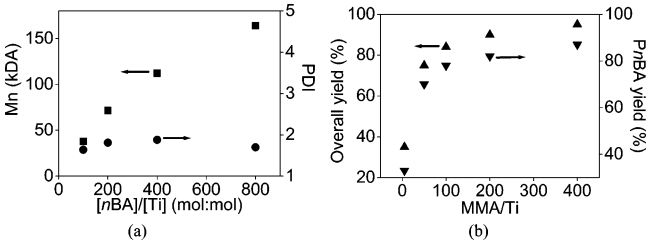


Figure 1. (a) Dependence of M_n and PDI with monomer-to-titanium ratio in the polymerization of *n*BA promoted by **1**/$B(C_6F_5)_3$ (1:1) in toluene at 20 °C: (■) M_n and (●) PDI values determined by GPC. (b) Overall yield and P(*n*BA) yield vs MMA/Ti ratio in the block copolymerization of MMA/*n*BA promoted by **1**/$B(C_6F_5)_3$ in toluene at 80 °C (*n*BA/Ti = 200:1): (▲) overall yield; (▼) P(*n*BA) yield.

Diblock copolymerizations of MMA and *n*BA show also a high degree of control at both 20 and 80 °C. Typical results are summarized in Table 2. Complete conversions of MMA and high conversions of *n*BA were obtained at 20 °C (entries 10 and 11). The diblock copolymers formed had a narrow polydispersity and an average number molecular weight and monomer composition in close agreement with the calculated values. The true diblock nature of these copolymers and the

* Corresponding author: Fax (+33)(0)223-236-939; e-mail jean-francois.carpentier@univ-rennes1.fr.
† Université de Rennes 1.
‡ Arkema.

10.1021/ma070465a CCC: $37.00 © 2007 American Chemical Society
Published on Web 03/03/2007

Table 2. MMA/*n*BA Diblock Copolymerization Using the {CGC}$TiMe_2/B(C_6F_5)_3$ System[a]

run	polymer type	time[b] (h)	temp (°C)	yield (%)	$M_{n,cal}$[c] (10^4)	$M_{n,exp}$[d] (10^4)	PDI (M_w/M_n)[d]
10	A−B 100:200	12 +8	20	93	3.41	4.46	1.20
11	A−B 200:200	12 +8	20	94	4.30	4.72	1.22
12	A−B 200:200	1 +1	80	90	4.10	4.14	1.25
13	A−B 300:100	1 +1	80	96	4.06	4.59	1.16

[a] A = PMMA, B = P(*n*BA), Ti = $B(C_6F_5)_3$ = 0.05 mmol, solvent = 4 mL of toluene. [b] Time was not optimized. [c] Calculated M_n values from {conv(MMA) × [MMA]/[Ti] × 100 + conv(*n*BA) × [*n*BA]/[Ti] × 128} g·mol^{-1}. [d] Determined by GPC in THF vs PS standards.

absence of quantifiable amounts of homo-PMMA and P(*n*BA) were established by liquid adsorption chromatography (LAC) (see Supporting Information). Both the P(*n*BA) and PMMA blocks in these copolymers feature the same degrees of syndiotacticity as those observed in the corresponding homopolymers (e.g., 75% and 80% *rr*, respectively; entry 11). Diblock copolymerizations performed at 80 °C led to results comparable to those observed at 20 °C; only the conversion of *n*BA was somewhat decreased (compare entries 11 and 12). Attempted triblock MMA-*n*BA-MMA (200:100:200) copolymerization at 20 °C led to full conversion of the three loadings of monomers; however, according to GPC, the final product recovered was a mixture of the diblock PMMA-*b*-P(*n*BA) copolymer (60%) and triblock PMMA-*b*-P(*n*BA)-*b*-PMMA copolymer (40%). When the same reaction was run at 80 °C, only formation of the diblock PMMA-*b*-P(*n*BA) copolymer was observed. This confirms that termination processes are fast at this temperature once *n*BA has been introduced in the reaction mixture.

Further experiments were carried out at 80 °C to understand the relationship between the PMMA chain length and the efficiency of subsequent *n*BA polymerization in the diblock copolymerization of MMA and *n*BA. A series of representative results are illustrated in Figure 1b. These results indicate that a preliminary PMMA block of minimal size (50 equiv) allows high conversion of *n*BA.[10] We speculate that such a PMMA chain may enrobe the active Ti species and thus protect it from termination (backbiting) processes.

In conclusion, we have shown that the effective *n*BA homopolymerization and MMA/*n*BA block copolymerization can be achieved for the first time by a thermally robust, simple {CGC}$TiMe_2/B(C_6F_5)_3$ group 4 metal system. The latter shows a good degree of control over the polymerization in view of the M_n and M_w/M_n as well as syndiotacticity of the resulting polymers. Studies on the polymerization mechanism, as well as exploring other discrete metal catalysts for effective acrylate polymerization, are underway in our laboratories.

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: Experimental details for the homopolymerization of *n*-butyl acrylate and its copolymerization with methyl methacrylate, GPC and LAC traces, ^{1}H NMR and ^{13}C NMR spectra of polymers. This material is free of charge via the Internet at http://pubs.acs.org.

References and Notes

(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.; 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) Stuhldreier, T.; Keul, H.; Höcker, H.; Englert, U. *Organometallics* **2000**, *19*, 5231−5234. (d) Frauenrath, H.; Keul, H.; Höcker, H. *Macromolecules* **2001**, *34*, 14−19. (e) Batis, C.; Karanikolopoulos, G.; Pitsikalis, M.; Hadjichristidis, N. *Macromolecules* **2003**, *36*, 9763−9774. (f) Jensen, T. R.; Yoon, S. C.; Dash, A. K.; Luo, L.; Marks, T. J. *J. Am. Chem. Soc.* **2003**, *125*, 14482−14494. (g) 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. (h) Lian, B.; Toupet, L.; Carpentier, J.-F. *Chem.—Eur. J.* **2004**, *10*, 4301−4307. (i) Lian, B.; Lehmann, C. W.; Navarro, C.; Carpentier, J.-F. *Organometallics* **2005**, *24*, 2466−2472. (j) Lian, B.; Thomas, C. M.; Navarro, C.; Carpentier, J.-F. *Organometallics* **2007**, *26*, 187−195.

(4) Deng, H.; Soga. K. *Macromolecules* **1996**, *29*, 1847−1848.

(5) Kostakis, K.; Mourmouris, S.; Pitsikalis, M.; Hadjichristidis, N. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 3337−3348.

(6) For acrylate polymerization catalyzed by discrete organolanthanide and zinc complexes, see: (a) Ihara, E.; Morimoto, M.; Yasuda, H. *Macromolecules* **1995**, *28*, 7886−7892. (b) Garner, L. E.; Zhu, H.; Hlavinka, M. L.; Hagadorn, J. R.; Chen, E. Y.-X. *J. Am. Chem. Soc.* **2006**, *128*, 14822−14823.

(7) 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. *Stud. Surf. Sci. Catal.* **1994**, *89*, 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.

(8) Capacchione, C.; Proto, A.; Ebeling, H.; Mülhaupt, R.; Möller, K.; Spaniol, T. P.; Okuda, J. *J. Am. Chem. Soc.* **2003**, *125*, 4964−4965.

(9) Note that these values may also argue in favor of a fully efficient bimetallic initiating system, though detailed mechanistic issues have not been addressed so far.

(10) It is noteworthy that the produced MMA/*n*-BA block copolymers have lower molecular weight distributions than those of the P(*n*-BA) homopolymers. Such observations, i.e., P(*n*-BA, PDI = 1.26−1.51 vs PMMA-*b*-P(*n*-BA), PDI = 1.18, have been also briefly reported by Chen et al. with a zirconocene initiator; see ref 2k.

MA070465A