

Isobutene–isoprene copolymerization initiated by [Cp*MMe₂][(n-C₁₈H₃₇E)B(C₆F₅)₃] (M = Ti, Hf; E = O, S) and related compounds

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Abstract

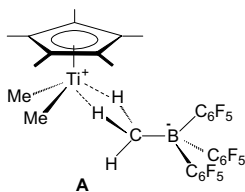
The highly electrophilic borane B(C₆F₅)₃ reacts with e.g., *n*-octadecanol (*n*-C₁₈H₃₇OH) and *n*-octadecanethiol (*n*-C₁₈H₃₇SH) to form equilibrium mixtures of the reactants and their 1:1 adducts (n-C₁₈H₃₇EH)B(C₆F₅)₃ (E = O, S). The latter are acidic, and react with Cp*MMe₃ (M = Ti, Hf) in polar and non-polar solvents to give methane and the unstable complexes [Cp*MMe₂][(n-C₁₈H₃₇E)B(C₆F₅)₃]. The latter are very good initiators for the copolymerization of isobutene with isoprene at relatively high temperatures, giving high conversions to high molecular weight isobutene–isoprene copolymers. The weight average molecular weights are unusually high for the temperatures used, consistent with current theories of the role of weakly coordinating anions. The effects of changing the substituents on the alcohols are also investigated.

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1. Introduction

We have earlier reported the zwitterionic Cp*TiMe₂(μ-Me)B(C₆F₅)₃ (A) as a source of the cationic species [Cp*TiMe₂]⁺, which is an extremely active initiator for not only Ziegler–Natta (ethylene [1–3], propylene [2,3], 1-hexene [4,5]), but also for carbocationic (isobutene [6,7], vinyl ethers [8]) polymerization processes.



We have also presented a detailed description of the utilization of Cp*TiMe₂(μ-Me)B(C₆F₅)₃ as a carbocationic initiator of both the polymerization of isobutene (IB) to polyisobutene (PIB) and the copolymerization of IB and isoprene (IP) [6,7]. In both cases, polymers exhibiting high molecular weights and narrow molecular weight distributions were obtained. It has been suggested that initiation of carbocationic polymerization using metallocene systems stems from either the metal center or from protons generated from adventitious water in the reaction medium, depending on its dryness [9].

Although the chemistry of the propagation and chain transfer steps is extremely complex [10–13], it seems generally agreed [10,11,14] that rates of chain transfer are strongly affected by the nature of the counteranion and can be minimized by utilizing anions which are very weakly nucleophilic. Pi et al. [14] have exploited this fact

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by carrying out proton-induced polymerization of IB in the presence of the weakly nucleophilic anion $[\text{B}(\text{C}_6\text{F}_5)_4]^-$, thereby obtaining PIB of unusually high molecular weight. At a temperature of about -35°C , PIB with $M_n \approx 2 \times 10^5$ was obtained, almost an order of magnitude higher than was achieved under the same conditions with the conventional initiator, AlCl_3 . As commercial manufacture of high molecular weight PIB is carried out at cryogenic temperatures (-100°C), an energy efficient and less expensive higher temperature process is desirable.

The $[\text{Cp}^*\text{TiMe}_2]^+ - [\text{BMe}(\text{C}_6\text{F}_5)_3]^-$ cation–anion combination has also been found to give high molecular weights ($M_w \sim 6 \times 10^5$ at -40°C in toluene) at temperatures significantly above those necessary for conventional initiators [6,7], and it seemed possible that high molecular weight PIB might be formed at even higher temperatures if more weakly coordinating anions than $[\text{BMe}(\text{C}_6\text{F}_5)_3]^-$ were used. Although several very bulky anions have been reported [15–28], only a few of these have been assessed for the carbocationic polymerizations of monomers such as isobutene [29–31]. For instance Bochmann and co-workers [29] used $[\text{Cp}'_4\text{Zr}_2\text{H}_3][\text{CN}\{\text{B}(\text{C}_6\text{F}_5)_3\}_2]$ ($\text{Cp}' = \text{C}_5\text{H}_4\text{SiMe}_3$) as an initiator system and high molecular weight IB–IP copolymers ($M_w \sim 5 \times 10^5$ at -35°C) were obtained.

We have recently reported the utilization of the complexes $[\text{Cp}^*\text{TiMe}_2][\text{B}(\text{C}_6\text{F}_5)_4]$ and $[\text{Cp}^*\text{TiMe}_2][(\text{n-C}_{18}\text{H}_{37}\text{E})\text{B}(\text{C}_6\text{F}_5)_3]$ ($\text{E} = \text{O}, \text{S}$) [32,33], which behave as effective carbocationic initiators of IB homopolymerization at temperatures in the range -40 to -10°C . High conversions to high molecular weight polyisobutene (PIB) in methylene chloride and moderate conversions to high molecular weight PIB in toluene were observed, consistent with the anions $[(\text{n-C}_{18}\text{H}_{37}\text{E})\text{B}(\text{C}_6\text{F}_5)_3]^-$ being very weakly coordinating. Interestingly, Arrhenius-type plots of $\log M_n$ vs T^{-1} could be obtained for polymerization in toluene, and activation energies for degree of polymerization were found to be in the range -11 to -27 kJ/mol, comparable to most conventional IB polymerization initiators. We have now also investigated the copolymerization of IB with IP using this type of initiator system and in a variety of solvents, and the results are reported in this paper.

2. Experimental

All NMR spectra were recorded on Bruker ACF 200 and Bruker AM-300 and -400 spectrometers. Gel permeation chromatography analyses of the polymers were carried out on THF (room temperature) and toluene (70°C) solutions using Waters Associates model GPC-244 and GPC-2690 liquid chromatographs with separation columns consisting of cross-linked polystyrene gel (μ -Styragel) of various pore sizes: 100, 500, 1000,

10,000 Å. The calibration of the instrument was done using polystyrene standards ranging in molecular weights from 2350 to 2,300,000 g/mol. Polymer conversions were determined gravimetrically.

All syntheses and initiator manipulations were carried out under dry nitrogen or argon atmospheres using standard Schlenk line techniques or an MBraun Labmaster glove box. Solvents were dried by refluxing under nitrogen over an appropriate drying agent, and were degassed by freeze thaw procedures prior to use. Toluene, pentane and ether were dried over sodium metal and methylene chloride over calcium hydride. Nitrogen was purified by passage through a heated column of BASF catalyst followed by a column of dry, activated 3A or 4A molecular sieves (Linde). Isobutene (Air Products, purity grade, 99.5%), was purified by passage through columns of 3A molecular sieves and was condensed into a graduated flask which was attached to the reactor. All chemicals, except as noted, were purchased from Aldrich and were purified as appropriate before use. The compounds Cp^*TiMe_3 [34], Cp^*HfMe_3 [35], $\text{B}(\text{C}_6\text{F}_5)_3$ [36,37] were synthesized as in the literature. The compounds *n*-octadecanol (*n*- $\text{C}_{18}\text{H}_{37}\text{OH}$), *n*-octadecanethiol (*n*- $\text{C}_{18}\text{H}_{37}\text{SH}$), heptadecafluorononanol (*n*- $\text{C}_8\text{F}_{17}\text{CH}_2\text{OH}$), hexafluoro-2-propanol and hexafluoro-2-phenyl-2-propanol were purchased from Aldrich and recrystallized before use.

Polymerizations were carried out using a 50 mL glass reactor equipped with a cold finger condenser (dry ice/isopropanol) and an attached 12 mL graduated flask as described previously [32]. In a typical experiment, 12 mL of IB were condensed into the graduated flask which contained ~ 100 mg of isoprene. Solutions of 25 mg of $\text{B}(\text{C}_6\text{F}_5)_3$ (0.048 mmol) and 11 mg (0.048 mmol) Cp^*TiMe_3 in 5 mL each of methylene chloride were made. In many experiments, 0.048 mmol of an alcohol or thiol compound was also added to $\text{B}(\text{C}_6\text{F}_5)_3$ solution. These solutions and 5 mL of pure solvent were put into the reactor and frozen sequentially. The entire system was then evacuated to $\sim 10^{-3}$ torr. The reactor was then positioned in a bath set normally to -30°C , and the reaction mixture was melted and allowed to equilibrate. Following temperature equilibration, which normally took a few minutes, the mixture of IB and IP was added. Polymerizations proceeded at the vapor pressures of the liquid mixtures (IB plus solvents) and in most case the reaction mixtures refluxed vigorously. Most of the experiments were repeated several times to get reproducible results; conversions varied by up to 20%, average molecular weights by about the same amount as temperatures were somewhat difficult to control in some cases. Although some reactions were completed in less time, polymerizations were terminated after one hour by pouring the reaction mixtures into 1 L of methanol. The resulting mixtures, containing solid, white polymers, were stirred overnight, after which the polymers

were collected and dried and then redissolved in 50–100 mL of hexanes. The solvent was removed from the colorless solution to give a white, elastic polymer which was characterized by GPC and by ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy.

3. Results and discussion

The copolymer of isobutene with 1–2 mol% of isoprene is a very important commercial polymer, butyl rubber [10–12]. For useful applications, the material must have high molecular weights (M_w in the range $5\text{--}6 \times 10^5$) and it is normally essential to carry out the polymerization processes at very low temperatures (as low as $-100\text{ }^\circ\text{C}$), where the rates of chain transfer reactions are reduced [10–12]. However cationic polymerizations exhibit high propagation rates even at low temperatures, and the corresponding heat released can be difficult to control unless the viscosity of the reaction mixtures is kept low and the solution is extremely well mixed. To minimize the effects of heating, all of the polymerization experiments reported here were carried out both in a reactor immersed in a cold bath and under reduced pressure such that the accompanying refluxing of the liquid mixtures served both to maximize mixing and to remove much of the heat of reaction [32]. Solvents and IB were dried with care to minimize the moisture content to lowest feasible levels. The copolymers obtained were characterized by ^1H NMR and $^{13}\text{C}\{^1\text{H}\}$ spectroscopy as before [7], but the spectra are unexceptional and will not be discussed further. On the basis of the intensities of the isoprene resonances in the ^1H

NMR spectra [7], the copolymers were found to contain 1–2 mol% isoprene, comparable to the proportion of the isoprene in the reaction mixture.

Initially copolymerizations were conducted using Cp^*TiMe_3 and $\text{B}(\text{C}_6\text{F}_5)_3$, in the absence of co-initiators, in polar (methylene chloride, methyl chloride, trifluorotoluene) and nonpolar (toluene) solvents and the results were compared with homopolymerization of IB. Comparative results are shown in Table 1, experiments 1, 2, 9 and 10. As can be seen, conversions are higher in the more polar solvent, as has been noted previously for this initiator system [7,32], but IB homopolymerizations in toluene give materials with very high weight average molecular weight ($\sim 5 \times 10^5$). Conversions and molecular weights did not change with time, indicating that the polymerizations were normally completed within one hour. The polymers were found to have narrow molecular weight distributions, with M_w/M_n usually < 2 for most of the experiments carried out; again this is as expected [7,32]. Both conversions and M_w are drastically reduced in toluene in the presence of isoprene (experiments 9, 10), but nearly quantitative conversion was obtained in the polar solvent trifluorotoluene (experiment 8).

Similar experiments were carried out using 1:1:1 molar ratios of Cp^*TiMe_3 , $\text{B}(\text{C}_6\text{F}_5)_3$ and $n\text{-C}_{18}\text{H}_{37}\text{SH}$ or $n\text{-C}_8\text{F}_{17}\text{CH}_2\text{OH}$ (experiments 3–7, 11, 12). As has been shown previously, alcohols and thiols coordinate to $\text{B}(\text{C}_6\text{F}_5)_3$ to give adducts in which the Brønsted acidities have been increased [24,32,33]. The resulting acidic adducts react with Cp^*TiMe_3 to generate methane and the cationic species $[\text{Cp}^*\text{TiMe}_2]^+$ which is an excellent carbocationic initiator when paired with a variety of

Table 1

Homopolymerization of IB and Copolymerization of IB with IP using Cp^*MMe_3 (M = Ti, Hf) and $\text{B}(\text{C}_6\text{F}_5)_3$ with alcohols and a thiol as initiators

Experiment number	Initiator system $\text{B}(\text{C}_6\text{F}_5)_3/$	IP added?	Solvent	Conversion (%)	$M_w (\times 10^5)$ (M_w/M_n)
1	$\text{Cp}^*\text{TiMe}_3/\text{B}(\text{C}_6\text{F}_5)_3$	No	CH_2Cl_2	100	3.5 (1.7)
2	$\text{Cp}^*\text{TiMe}_3/\text{B}(\text{C}_6\text{F}_5)_3$	Yes	CH_2Cl_2	100	2.9 (1.8)
3	$\text{Cp}^*\text{TiMe}_3/\text{B}(\text{C}_6\text{F}_5)_3/n\text{-C}_{18}\text{H}_{37}\text{SH}$	No	CH_2Cl_2	100	6.6 (1.8)
4	$\text{Cp}^*\text{TiMe}_3/\text{B}(\text{C}_6\text{F}_5)_3/n\text{-C}_{18}\text{H}_{37}\text{SH}$	Yes	CH_2Cl_2	27	3.8 (1.9)
5	$\text{Cp}^*\text{TiMe}_3/\text{B}(\text{C}_6\text{F}_5)_3/n\text{-C}_{18}\text{H}_{37}\text{SH}$	Yes	CH_3Cl	100	4.4 (1.6)
6	$\text{Cp}^*\text{TiMe}_3/\text{B}(\text{C}_6\text{F}_5)_3/n\text{-C}_8\text{F}_{17}\text{CH}_2\text{OH}$	No	CH_2Cl_2	100	5.2 (1.8)
7	$\text{Cp}^*\text{TiMe}_3/\text{B}(\text{C}_6\text{F}_5)_3/n\text{-C}_8\text{F}_{17}\text{CH}_2\text{OH}$	Yes	CH_2Cl_2	100	5.0 (1.7)
8	$\text{Cp}^*\text{TiMe}_3/\text{B}(\text{C}_6\text{F}_5)_3$	Yes	$\text{CF}_3\text{C}_6\text{H}_5$	90	2.2 (1.6)
9	$\text{Cp}^*\text{TiMe}_3/\text{B}(\text{C}_6\text{F}_5)_3$	No	Toluene	26	5.1 (1.7)
10	$\text{Cp}^*\text{TiMe}_3/\text{B}(\text{C}_6\text{F}_5)_3$	Yes	Toluene	9	1.7 (1.5)
11	$\text{Cp}^*\text{TiMe}_3/\text{B}(\text{C}_6\text{F}_5)_3/n\text{-C}_8\text{F}_{17}\text{CH}_2\text{OH}$	No	Toluene	83	5.3 (2.0)
12	$\text{Cp}^*\text{TiMe}_3/\text{B}(\text{C}_6\text{F}_5)_3/n\text{-C}_8\text{F}_{17}\text{CH}_2\text{OH}$	Yes	Toluene	50	1.0 (1.7)
13	$\text{Cp}^*\text{HfMe}_3/\text{B}(\text{C}_6\text{F}_5)_3$	No	CH_2Cl_2	100	3.4 (4.7)
14	$\text{Cp}^*\text{HfMe}_3/\text{B}(\text{C}_6\text{F}_5)_3$	Yes	CH_2Cl_2	100	1.6 (3.5)
15	$\text{Cp}^*\text{HfMe}_3/\text{B}(\text{C}_6\text{F}_5)_3/n\text{-C}_{18}\text{H}_{37}\text{OH}$	Yes	CH_2Cl_2	27	2.6 (1.7)
16	$\text{Cp}^*\text{HfMe}_3/\text{B}(\text{C}_6\text{F}_5)_3/n\text{-C}_8\text{F}_{17}\text{CH}_2\text{OH}$	No	CH_2Cl_2	100	3.5 (3.0)
17	$\text{Cp}^*\text{HfMe}_3/\text{B}(\text{C}_6\text{F}_5)_3/n\text{-C}_8\text{F}_{17}\text{CH}_2\text{OH}$	Yes	CH_2Cl_2	86	2.9 (2.3)
18	$\text{Cp}^*\text{HfMe}_3/\text{B}(\text{C}_6\text{F}_5)_3/(\text{CF}_3)_2\text{CHOH}$	Yes	CH_2Cl_2	100	2.3 (3.5)
19	$\text{Cp}^*\text{HfMe}_3/\text{B}(\text{C}_6\text{F}_5)_3/\text{C}_6\text{H}_5(\text{CF}_3)_2\text{COH}$	Yes	CH_2Cl_2	81	3.7 (2.6)
20	$\text{Cp}^*\text{HfMe}_3/\text{B}(\text{C}_6\text{F}_5)_3/n\text{-C}_8\text{F}_{17}\text{CH}_2\text{OH}$	Yes	$\text{CF}_3\text{C}_6\text{H}_5$	86	2.5 (1.9)

Table 2

Effect of isoprene concentration in the feed on polymerization using the catalyst system $[\text{Cp}^*\text{TiMe}_3/n\text{-C}_8\text{F}_{17}\text{CH}_2\text{OH}/\text{B}(\text{C}_6\text{F}_5)_3]$ in methylene chloride

Experiment number	IP (mg)	IP (mol%) in feed	Conversion (%)	$M_w \times 10^{-5}$	(M_w/M_n)	IP (%) in polymer
21	115	1.1	100	5.8	2.3	0.8
22	200	2.0	93	3.7	2.6	1.0
23	235	2.3	80	3.9	2.1	1.5
24	300	2.9	82	3.0	2.4	2.6

weakly coordinating counteranions [32]. The fluorinated alcohol $n\text{-C}_8\text{F}_{17}\text{CH}_2\text{OH}$ was investigated because it is expected to be more acidic and therefore result in better charge delocalization in the anion and hence in reduced nucleophilicity for the anion.

Again, polymerizations in dichloromethane were very rapid (experiments 3–7). Interestingly, however, molecular weights were generally higher than was the case without added $n\text{-C}_{18}\text{H}_{37}\text{SH}$ or $n\text{-C}_8\text{F}_{17}\text{CH}_2\text{OH}$ (compare experiment 1 with 3 and 6, experiment 2 with 4 and 7), strongly implying a major role for the species $[(n\text{-C}_{18}\text{H}_{37}\text{S})\text{B}(\text{C}_6\text{F}_5)_3]^-$ and $[(n\text{-C}_8\text{F}_{17}\text{CH}_2\text{O})\text{B}(\text{C}_6\text{F}_5)_3]^-$ as more weakly coordinating anions than is $[\text{BMe}(\text{C}_6\text{F}_5)_3]^-$. Excellent conversion and molecular weight results were also found in methyl chloride (experiment 5).

In dichloromethane, the borane/ $n\text{-C}_8\text{F}_{17}\text{CH}_2\text{OH}$ system gave very high molecular weight PIB, and surprisingly the copolymer molecular weights did not decrease much compared to other systems (experiments 6 and 7). Similar results were reported by Bochmann and co-workers [29] using bulky anions. Table 2 lists a series of complementary experiments in which the effects of increased amounts of isoprene are added to the feed. As shown in Table 2, both conversions and molecular weights were found to decrease when higher amounts of isoprene were used, consistent with earlier findings [7,10,11]. Following incorporation of an isoprene molecule in a growing polymer chain, transfer processes such as $\beta\text{-H}$ eliminations become very facile, resulting in lower molecular weights.

Experiments in toluene included homo- and copolymerizations using $\text{Cp}^*\text{TiMe}_3/\text{B}(\text{C}_6\text{F}_5)_3$ alone (experiments 9, 10) and with $n\text{-C}_8\text{F}_{17}\text{CH}_2\text{OH}$ as co-activator (experiments 11, 12). In these cases use of the co-activator resulted in much higher conversions, although the molecular weights differed little. Again the copolymers exhibited significantly lower molecular weights than did the homopolymers.

The analogous $\text{Cp}^*\text{HfMe}_3/\text{B}(\text{C}_6\text{F}_5)_3$ initiator system was also assessed, with and without co-initiators, and the results (experiments 13–20) show that it is almost as effective as the titanium system. For the most part, conversion are high in polar solvents although molecular weights are relatively low. High conversions and similar molecular weights were obtained for copolymerizations when other fluorinated alcohols were used as

well, and the use of branched alcohols made little difference.

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