Macromolecules

Volume 31, Number 24 December 1, 1998

Polymerization of Isobutylene and the Copolymerization of Isobutylene and Isoprene Initiated by the Metallocene Derivative $Cp^*TiMe_2(\mu\text{-}Me)B(C_6F_5)_3$

Florin Barsan, Arquimedes R. Karam, Michelle A. Parent, and Michael C. Baird*

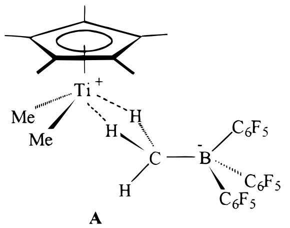
Department of Chemistry, Queen's University, Kingston, ON K7L 3N6, Canada

Received March 2, 1998; Revised Manuscript Received August 10, 1998

ABSTRACT: Isobutylene polymerization is initiated by $Cp^*TiMe_2(\mu\text{-}Me)B(C_6F_5)_3$, formed by combining Cp^*TiMe_3 and $B(C_6F_5)_3$ in a 1:1 ratio. The polymerization process exhibits the signature of a carbocationic mechanism, as molecular weights generally increase with decreasing temperature, polydispersities are ~2, and polymers contain vinylidene end groups. Initiation probably occurs via η^1-coordination of a molecule of monomer to the cationic species $[Cp^*TiMe_2]^+$, while propagation and chain transfer proceed as with conventional Lewis acid initiators. Although addition of the proton trap 2,6-di-*tert*-butylpyridine does have an adverse effect on polymerization, this is not because traces of possible protic initiators are being scavenged but rather because the 2,6-di-*tert*-butylpyridine coordinates to the titanium cation and inhibits activation of monomer. Further evidence that $[Cp^*TiMe_2]^+$ behaves as a carbocationic initiator is that the system induces dimerization of 1,1-diphenylethylene to 1,3,3-triphenyl-3-methylindan and also the formation of isobutylene−isoprene copolymers (butyl rubber) in which the isoprene is incorporated via trans-1,4-addition, again typical of conventional initiators. This initiator system is the first metallocene-based carbocationic initiator system to be discovered, and it also appears to be one of the more active.

There has in recent years been extensive research into the use of group 4 metallocene compounds as homogeneous catalysts for olefin polymerization. The most successful catalysts are the formally 14-electron, cationic complexes $[Cp'_2MR]^+$ (Cp' = functionalized cyclopentadienyl; M = Ti, Zr, Hf; R = alkyl, H),[1] which contain a vacant coordination site and an alkyl ligand and which can therefore readily take part in coordination polymerization (Ziegler−Natta) processes with a variety of olefins. Of great relevance here, crystallographically characterized compounds of the type $Cp'_2MMe(\mu\text{-}Me)B(C_6F_5)_3$ have been studied intensively as precursors for the above-mentioned cationic species $[Cp'_2MR]^+$ and have provided valuable information concerning the optimal requirements of noncoordinating counteranions.[2]

Another family of compounds which satisfy the apparent requirements for Ziegler−Natta catalysis are 10-electron, monocyclopentadienyl complexes of the type $[Cp'MR_2]^+$. Such electronically less saturated and sterically less hindered complexes might be expected to exhibit even higher reactivities than their metallocene counterparts, and we[3] and others[4] have investigated several such systems in detail. Previous work has shown that reaction of Cp^*TiMe_3 with the highly electrophilic borane $B(C_6F_5)_3$ results in attack on the methyl ligand by the borane to give the methyl-bridged compound $Cp^*TiMe_2(\mu\text{-}Me)B(C_6F_5)_3$ (**A**). Although this compound is too unstable to be characterized crystallographically, there are several precedents in the metallocene literature for the proposed mode of bonding,[2] and the spectroscopic properties of $Cp^*TiMe_2(\mu\text{-}Me)B(C_6F_5)_3$ are fully in accord with the structure proposed.



A

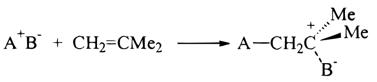
We have found that $Cp^*TiMe_2(\mu\text{-}Me)B(C_6F_5)_3$ reacts with aromatic solvents to form arene complexes of the

10.1021/ma980324w CCC: $15.00

type $[Cp^*TiMe_2(\eta^6\text{-arene})][BMe(C_6F_5)_3]$ (arene = benzene, toluene, etc.)[3b] and with a variety of amines and phosphines L to form complexes of the type $[Cp^*TiMe_2L][BMe(C_6F_5)_3]$.[3h] While the latter are very stable with respect to substitution of L by olefins, $Cp^*TiMe_2(\mu\text{-}Me)B(C_6F_5)_3$ and the arene complexes do behave as sources of the cationic species $[Cp^*TiMe_2]^+$, which has been shown to be an extremely active initiator for both carbocationic (isobutylene,[3e] vinyl ethers,[3g] styrene (below 0 °C)[3h]) and Ziegler–Natta (ethylene,[3h,k] propylene,[3k] 1-hexene,[3l] and styrene[3h]) polymerization processes.

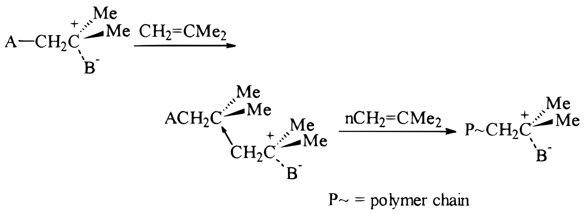
We have previously presented a brief description of the utilization of $Cp^*TiMe_2(\mu\text{-}Me)B(C_6F_5)_3$ as a carbocationic initiator of both the polymerization of isobutylene to polyisobutylene (PIB) and the copolymerization of isobutylene and isoprene.[3e] The polymers formed were shown to be identical to commercial polymers obtained utilizing conventional Lewis acid initiators, and inasmuch as the commercial copolymer is normally manufactured at ~ −90 °C utilizing methyl chloride as solvent, the discovery of an initiator which was active in hydrocarbon solvents at somewhat higher temperatures seemed noteworthy.

As has been well established,[5] carbocationic initiation of isobutylene polymerization by Lewis acid sources of the general formula A^+B^- (AB = e.g. metal halide) proceeds as in eq 1. Here the cationic center A^+



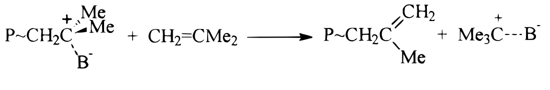
$$A^+B^- + CH_2{=}CMe_2 \longrightarrow A{-}CH_2\overset{+}{C}Me_2\cdots B^- \qquad (1)$$

interacts with the isobutylene π system, forming a σ bond at C-1 and generating a C-2 a carbocationic center which is stabilized via interaction with the counteranion B^-. The carbocationic center formed may also be stabilized by weak Lewis bases. Propagation involves attack at the stabilized carbocationic center by a second molecule of monomer, as in eq 2, polymerization generally involving head-to-tail addition because of the greater stability of the tertiary carbocation. Chain transfer generally involves deprotonation of the carbocationic end group by an isobutylene molecule (eq 3)



$$A{-}CH_2\overset{+}{C}Me_2\cdots B^- \xrightarrow{CH_2=CMe_2} ACH_2CMe_2{-}CH_2\overset{+}{C}Me_2\cdots B^- \xrightarrow{nCH_2=CMe_2} P{\sim}CH_2\overset{+}{C}Me_2\cdots B^- \qquad (2)$$

P~ = polymer chain



$$P{\sim}CH_2\overset{+}{C}Me_2\cdots B^- + CH_2{=}CMe_2 \longrightarrow P{\sim}CH_2C({=}CH_2)Me + Me_3\overset{+}{C}\cdots B^- \qquad (3)$$

or by the anion B^-, the result in either case being a vinylidene end group. The resulting carbocation of eq 3 may then initiate new chain growth.

As mentioned above, we have earlier presented evidence that the excellent Ziegler–Natta catalyst $Cp^*TiMe_2(\mu\text{-}Me)B(C_6F_5)_3$ also behaves as a very efficient carbocationic initiator for the polymerization of isobutylene.[3e] The mechanism suggested, based on well-established precedents (eq 1–3) was as shown in Figure 1. Here the monomer coordinates to the titanium cation in η^1 fashion rather than the more common η^2 fashion, the unusual mode of bonding being stabilized by a postulated interaction between the carbocationic center generated and the borate anion. We now present in full the results of our investigation into this interesting and novel polymerization system.

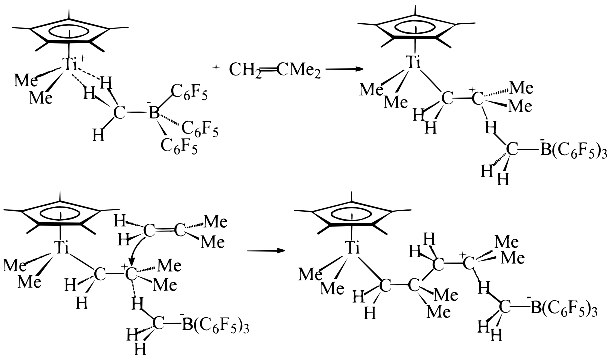


Figure 1. Initiation and propagation of isobutylene polymerization by $Cp^*TiMe_2(\mu\text{-}Me)B(C_6F_5)_3$.

Experimental Section

All spectra, except for those of the polymer samples and ^{19}F NMR and low-temperature NMR studies, were recorded on a Bruker ACF 200 spectrometer (200.132 MHz for ^1H, 50.323 MHz for $^{13}C\{^1H\}$). Polymer samples were recorded on a Bruker AM-400 spectrometer (400.13 MHz for ^1H, 100.6 MHz for $^{13}C\{^1H\}$), as were the ^{19}F NMR spectra (376.5 MHz). Since most of the titanium compounds studied are sensitive to oxygen and water, all NMR samples were prepared under a dry nitrogen atmosphere in a glovebox using predried and degassed solvents. Low-temperature and variable-temperature experiments were performed with a Bruker model B–VT1000 temperature controller. All $^{13}C\{^1H\}$ spectra were broad band proton-decoupled using the JMODXH or POWGATE automated sequences. Exchange spectroscopy by saturation transfer used the standard NOE difference pulse sequence and methodology.

Gel permeation chromatography analyses of the polymers were carried out at room temperature on THF solutions using Waters Associates model GPC-244 and −2690 liquid chromatographs with separation columns consisting of cross-linked polystyrene gel (μ-Styragel) with various pore sizes: 100, 500, 1000, and 10 000 Å. Calibration of the instrument was done using polystyrene standards ranging in molecular weights from 2350 to 2 300 000 g/mol. Weight average (M_w) and number average (M_n) molecular weights of several polymer samples were also calculated using the universal calibration principle which was demonstrated to be valid for PIB and butyl rubber (using $K_{PS} = 1.12 \times 10^{-4}$ dL/g, $\alpha_{PS} = 0.725$; $K_{PIB} = 2 \times 10^{-4}$ dL/g, $\alpha_{PIB} = 0.67$).[6] Polymer conversions were determined gravimetrically.

Glass transition temperatures were determined for isobutylene copolymers on a Mettler TA3000 differential scanning calorimeter equipped with measuring cells DSC20 and DSC30. Since these measuring cells are designed for optimal operation within the temperature range −20−200 °C and the glass transition temperatures for rubbery materials are usually below this temperature range, the values obtained in the T_g measurements (as low as −80 °C) are approximate within ±10 °C. Mass spectral analyses were performed with a Fisons VG QUATRO triple quadrupole mass spectrometer operating in EI- and CI-MS modes.

All syntheses were carried out under dry nitrogen or argon atmospheres using standard Schlenk line techniques. Solvents were dried by refluxing under nitrogen over an appropriate drying agent and were degassed by freeze–thaw procedures prior to use. Benzene, toluene, pentane, ether, hexanes, and THF (predried over calcium hydride) were dried over sodium metal, methylene chloride over calcium hydride, and tri-*iso*-butylaluminum. 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). Isobutylene (Matheson, purity grade, 99.5%), was purified by passage through columns of 3A molecular sieves and barium oxide and was condensed into a graduated flask and transferred to the reactor. Isoprene (Aldrich) was purified by passage through a column for inhibitor removal, stirred over CaH$_2$ for about 2 h, and then filtered, degassed, and distilled under reduced pressure. All chemicals, except as noted below, were purchased from Aldrich and were dried by stirring over calcium hydride and then distillation. Celite (Aldrich) was dried at 180 °C for 24 h prior to use for all the filtering procedures performed under nitrogen. Deuterated solvents were purchased from Aldrich, MSD Isotopes, and Cambridge Isotopes Limited.

Cp*TiMe$_3$,[7a] B(C$_6$F$_5$)$_3$,[7b] and Cp*TiMe$_2$(μ-Me)B(C$_6$F$_5$)$_3$[3h] were synthesized as in the literature, the latter by combining equimolar amounts of Cp*TiMe$_3$ and B(C$_6$F$_5$)$_3$ in solution immediately prior to being used in situ. Typically, for NMR experiments, a solution of Cp*TiMe$_3$ (0.029 g, 0.12 mmol) in 0.3 mL of CD$_2$Cl$_2$ in an NMR tube was placed in the spectrometer probe cooled to −78 °C and a ^{1}H NMR spectrum was recorded. A solution of B(C$_6$F$_5$)$_3$ (0.064 g, 0.12 mmol) in 0.5 mL of CD$_2$Cl$_2$ (−78 °C) was added, and the orange reaction mixture containing Cp*TiMe$_2$(μ-Me)B(C$_6$F$_5$)$_3$ was shaken for a few minutes at −78 °C and then placed in the spectrometer probe cooled to −50 °C. ^{1}H NMR (CD$_2$Cl$_2$, −50 °C): δ 1.97 (s, 15H, Cp* Me), 1.55 (s, 6H, Ti−Me), 1.2 (broad s, 3H, μ-Me). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, −50 °C): δ 131.0 (Cp* ring C), 80 (Ti−Me), 12.5 (Cp* Me).[3a,h]

Synthesis of [Cp*TiMe$_2$(2,6-dimethylpyridine)][MeB(C$_6$F$_5$)$_3$]. On the addition of slightly more than 1 equiv of 2,6-dimethylpyridine (DMP) to a solution of Cp*TiMe$_2$(μ-Me)B(C$_6$F$_5$)$_3$ in CD$_2$Cl$_2$ at −30 °C, the resonances of Cp*TiMe$_2$(μ-Me)B(C$_6$F$_5$)$_3$ were replaced by a set of resonances attributable to [Cp*TiMe$_2$(DMP)][MeB(C$_6$F$_5$)$_3$]. ^{1}H NMR (CD$_2$Cl$_2$, −30 °C): δ 0.39 (s, 3H, B−Me), 1.65 (s, 6H, Ti−Me), 1.89 (s, 15H Cp*), 2.25 (s, 6H, Me of bound DMP), 8.0 (t, 1H, H-4 of bound DMP), 7.38 (d, 2H, H-3,5 of bound DMP), 2.41 (s, 6H, Me of free DMP), 7.45 (t, 1H, H-4 of free DMP), 6.94 (d, 2H, H-3,5 of free DMP). ^{1}H NMR spectra of [Cp*TiMe$_2$(DMP)][MeB(C$_6$F$_5$)$_3$] were recorded at −50, −40, −30, −20, and 0 °C, but little chemical shift variation with temperature was observed. Attempts to isolate the compound failed, as only complex mixtures of solids could be obtained.

Synthesis of [Cp*TiMe$_2$(2,6-di-*tert*-butylpyridine)][MeB(C$_6$F$_5$)$_3$]. On the addition of 1 equiv of 2,6-di-*tert*-butylpyridine (DTBP) to a solution of Cp*TiMe$_2$(μ-Me)B(C$_6$F$_5$)$_3$ in CD$_2$Cl$_2$ at −50 °C, the solution turned red. A ^{1}H NMR spectrum recorded at −50 °C exhibited relatively intense resonances attributable to Cp*TiMe$_2$(μ-Me)B(C$_6$F$_5$)$_3$ (see above) and free DTBP (δ 1.28 (s, *t*-Bu), 7.08 (d, 3,5-H), and 7.52 (t, 4-H)) in addition to weak resonances attributable to [Cp*TiMe$_2$(DTBP)][MeB(C$_6$F$_5$)$_3$] at δ 0.39 (s, B-Me), 1.50 (s, *t*-Bu), 7.49 (br d, 3,5-H), and 7.85 (br t, 4-H). The Ti−Me and Cp* resonances could not be identified unambiguously. Consistent with these assignments, addition of excess DTBP (∼4 equiv) resulted in increases in the intensities of the resonances attributed to [Cp*TiMe$_2$(DTBP)][MeB(C$_6$F$_5$)$_3$] relative to those of Cp*TiMe$_2$(μ-Me)B(C$_6$F$_5$)$_3$.

The ^{1}H NMR spectra of a similar sample of [Cp*TiMe$_2$(DTBP)][MeB(C$_6$F$_5$)$_3$] were recorded at −50, −40, and −8 °C, the latter temperature producing broadening of the resonances assigned to coordinated DTBP. Exchange spectroscopy by saturation transfer was also carried out at −50 °C on a sample containing DTBP and Cp*TiMe$_2$(μ-Me)B(C$_6$F$_5$)$_3$ in a 1:1 ratio, and it was observed that irradiation of the frequency corresponding to the 3,5-H resonance of free DTBP resulted in a positive NOE effect for the 4-H of free DTBP and spin transfer to the 3,5-H resonance of the DTBP of the adduct.

Isobutylene Polymerization Initiated by Cp*TiMe$_2$(μ-Me)B(C$_6$F$_5$)$_3$. The following general procedure was followed for all polymerizations of isobutylene and copolymerizations of isobutylene with isoprene in methylene chloride and toluene. The initiator Cp*TiMe$_2$(μ-Me)B(C$_6$F$_5$)$_3$ was formed by adding Cp*TiMe$_3$ (14 mg, 0.06 mmol, in 1 mL of solvent) and B(C$_6$F$_5$)$_3$ (32 mg, 0.06 mmol, in 1 mL of solvent) to a solution of isobutylene at various temperatures. The initiator concentrations used were ∼0.004 M, the total volumes of solvent used generally being 15 mL. The polymerization experiments were carried out using monomer to initiator ratios of ∼500:1, and in all cases the solutions were found briefly to warm 2−3 °C. After ∼5 min, the reaction mixtures became heterogeneous as the polymer formed a sticky precipitate. Rapid stirring of the reaction mixtures was maintained for another 30 min, after which polymerizations were terminated by addition of acidified methanol (1% HCl). The supernatant liquids were removed, and the polymers were washed with methanol and dried in the oven at 50 °C overnight. All polymerizations were carried out twice.

The resulting samples of polyisobutylene (PIB) were white, rubbery materials, soluble in hexanes, CH$_2$Cl$_2$, toluene, and THF but insoluble in acetone, methyl ethyl ketone, and alcohols. Purification was normally achieved by dissolution in hexanes or methylene chloride followed by precipitation with methanol. Some of the PIB samples, especially those used for the NMR analyses, were also purified by dissolving the polymer in hexanes and passing the hexane solution through a silica column.

All the polymers formed were characterized using gel permeation chromatography, the GPC chromatograms being obtained at room temperature in THF and calibrated using polystyrene standards. The polymers were also characterized by ^{1}H NMR and ^{13}C{^{1}H} NMR spectroscopy.[8] ^{1}H NMR (C$_2$D$_2$Cl$_4$): δ 1.14 (s, 6H, Me), 1.45 (s, 2H, CH$_2$). ^{1}H NMR (CDCl$_3$): δ 1.05 (s, 6H, Me), 1.40 (s, 2H, CH$_2$). Literature: 1.09 (s, 6H, Me), 1.41 (s, 2H, CH$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 31.4 (Me), 38.2 (*tert*-C), 59.7 (CH$_2$). Literature: 31.3 (Me), 38.2 (*tert*-C), 59.6 (CH$_2$). ^{1}H NMR (C$_6$D$_6$): δ 1.26 (s, 6H, Me), 1.59 (s, 2H, CH$_2$). Literature:1.22 (s, 6H, Me), 1.55 (s, 2H, CH$_2$).^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 31.45 (Me), 38.2 (*tert*-C), 59.7 (CH$_2$). Literature: 31.3 (Me), 38.2 (*tert*-C), 59.7 (CH$_2$).

Low-molecular-weight polymers prepared for end-group analyses by NMR spectroscopy were synthesized as above but at higher temperatures. Isobutylene polymerization was initiated by addition of B(C$_6$F$_5$)$_3$ (in CH$_2$Cl$_2$) to reaction mixtures containing Cp*TiMe$_3$ (0.006 and 0.012 M) and isobutylene cooled to −34 °C. The ratios of monomer to initiator were ∼350:1, 700:1, and 900:1, and the polymerizations were terminated by addition of methanol (10 mL) after 1−4 min.

Isobutylene Polymerization Initiated by B(C$_6$F$_5$)$_3$. Solutions of isobutylene in toluene and methylene chloride were cooled to −40 or −60 °C, and polymerizations were initiated by the addition of B(C$_6$F$_5$)$_3$ (0.06 mmol dissolved in 2 mL of solvent). In all cases, the resulting polymer was obtained in only 1−3% conversion and was not characterized.

Copolymerization of Isobutylene and Isoprene Initiated by Cp*TiMe$_2$(μ-Me)B(C$_6$F$_5$)$_3$. The same procedure (in toluene at −60 and −78 °C) was followed for copolymerizations of isobutylene with isoprene, an initiator concentration of ∼0.004 M and isobutylene to initiator molar ratios of 500:1 and 2000:1 being used. Copolymerizations of isobutylene and isoprene were carried out at volume ratios of isobutylene to isoprene of 30:70, 75:25, 90:10, 98:2, 92:1, 98:1, 99:1.

The resulting copolymers were obtained in 20−30% yields and were purified of catalyst residue by dissolution in CH$_2$Cl$_2$ or in 1:1 mixtures of CH$_2$Cl$_2$/hexanes followed by precipitation by addition of acidified methanol. The isobutylene−isoprene copolymer was generally pale yellow because of traces of trapped initiator residues and was soluble in CH$_2$Cl$_2$ and THF but insoluble in methanol and methyl ethyl ketone. The crude copolymer was therefore purified by extraction with methyl ethyl ketone in a Soxhlet apparatus, and the methyl ethyl ketone insoluble fraction was purified further by dissolution in hexanes and elution through a silica column. It was characterized by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy.[9]

Reaction of Cp*TiMe$_2$(μ-Me)B(C$_6$F$_5$)$_3$ with 1,1-Diphenylethylene. A solution of 39 mg of Cp*TiMe$_3$ (0.18 mmol) and 40 mL of 1,1-diphenylethylene (0.37 mmol) in 0.3 mL of CD$_2$Cl$_2$ was cooled to −78 °C and then treated with 90 mg of

$B(C_6F_5)_3$ in 0.5 mL of CD_2Cl_2. Although the solution turned red on warming from to −78 to −10 °C, no changes in the ^1H NMR spectrum were observed until the solution was shaken at 0 °C, when, in addition to the resonances of Cp*$TiMe_2(\mu$-Me)$B(C_6F_5)_3$ and 1,1-diphenylethylene, there were also observed several new resonances. The now brown solution was warmed to room temperature and eluted through an alumina column with toluene to give a yellow product which was identified by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy and mass spectrometry as 1,3,3-triphenyl-3-methylindan.[10] ^1H NMR (CD_2Cl_2): δ 1.58 (s, 3H, Me), 3.42, 3.16 (AB quartet, 2H, CH_2), 7.28−7.19 (m, 19H, aromatic). Literature ($CDCl_3$): δ 1.6 (s, 3H, Me), 3.45, 3.10 (AB quartet, 2H, CH_2), 7.4−7.9 (m, 19H, aromatic). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 147.9−150.2 (m, aromatic C), 125.3−128.9 (m, aromatic C), 61.4, 61.5, 51.3 (five-membered ring C), 28.9 (Me). Literature ($CDCl_3$): δ 147.5−150.5 (m, aromatic C), 125.0−128.8 (m, aromatic C), 61.4, 60.9, 51.2 (five-membered ring C), 28.9 (Me). Assignments were verified using a $^{13}C-^1H$ HETCOR experiment. Mass spectrum (EI) (*m/e*): 77 (C_6H_5), 283 ($M^+ - C_6H_5$), 345 ($M^+ - CH_3$). Mass spectrum (CI) (*m/e*): 375 ($M^+ + CH_3$), 360 (M^+), 298 ($M^+ + CH_3 - C_6H_5$), 283 ($M^+ - C_6H_5$).

Results and Discussion

Polymerization of Isobutylene. As discussed above, reaction of Cp*$TiMe_3$ with the highly electrophilic borane $B(C_6F_5)_3$ results in effect in abstraction of the methyl ligand by the borane to give the methyl-bridged compound Cp*$TiMe_2(\mu$-Me)$B(C_6F_5)_3$ (**A**). The latter readily dissociates the borate anion to form the electronically unsaturated, cationic species $[Cp^*TiMe_2]^+$, which behaves as an excellent initiator for both Ziegler−Natta and carbocationic polymerization processes.[3,4]

Isobutylene is generally polymerized via carbocationic polymerization processes to form products with very broad molecular weight distributions and exhibiting consistencies which vary from liquids, for oligomers, to solids, for high-molecular-weight polymers.[5] The latter are tough elastomers which resemble unvulcanized natural rubber in tensile strength and elasticity and which also exhibit excellent barrier properties for gases.[5b] Cationic copolymerization of isobutylene and isoprene also has a major commercial application in the production of butyl rubber,[5a] a copolymer containing up to 2.5% isoprene which is normally produced in halogenated solvents at cryogenic temperatures (−100 °C) using as initiator aluminum trichloride ($AlCl_3$).[5,11]

To obtain polymers of high molecular weights, it is essential to carry out cationic polymerization processes at low temperatures (−30 to −100 °C), where the rates of chain-transfer reactions are reduced. However cationic polymerizations exhibit high propagation rates even at low temperatures, and the corresponding heat released is difficult to control by refrigerants unless the viscosity of the reaction mixtures is kept low. Commercially, isobutylene polymerization is carried out in a polar solvent which does not dissolve the polymer and results in slurry formation. The solvent preferred for isobutylene polymerization is methyl chloride (bp −24 °C).

Much of the experimental work described here was carried out at temperatures (−40, −60, −75 °C) significantly higher than that normally used commercially for manufacture of high-molecular-weight PIB. Isobutylene polymerization was initiated by the successive additions of Cp*$TiMe_3$ and $B(C_6F_5)_3$ to cooled solutions of isobutylene in methylene chloride or toluene, with initiator concentrations normally $\sim 4 \times 10^{-3}$ M and overall volumes of solvent used 15 mL. Attempts to initiate isobutylene polymerization using very low concentrations of catalyst (0.5 to 1×10^{-4} M) were generally unsuccessfully, probably because concentrations of trace impurities in the reaction mixtures were comparable with the concentration of initiator. Even at the concentrations used, however, some variations in polymer yields and molecular weights were observed.

Table 1. Effects of Solvent and Temperature on the Molecular Weight of the Polyisobutylene Formed by Cp*$TiMe_2(\mu$-Me)$B(C_6F_5)_3$ in Methylene Chloride and Toluene

solvent	T (°C)	conversion[a] (%)	M_w[a]	M_n[a]	M_w/M_n
CH_2Cl_2	−40	78	2.1×10^5	6.6×10^4	3.2
CH_2Cl_2	−60	68	7.4×10^5	2.7×10^5	2.7
CH_2Cl_2	−75	34	8.2×10^5	2.7×10^5	3.0
toluene	−40	62	6.2×10^5	3.0×10^5	2.1
toluene	−60	78	10.7×10^5	5.7×10^5	1.9
toluene	−75	49	9.1×10^5	4.7×10^5	1.9

[a] Averages of two runs.

The results of representative polymerization runs, carried out in duplicate, are presented in Table 1, where it is seen that lower temperatures generally result in higher molecular weights in both methylene chloride and toluene, consistent with a carbocationic mechanism. Polydispersities in these solvents are usually ∼2, also consistent with carbocationic polymerizations by other initiators.[5] While changing the initiator concentration has little effect on the molecular weight distribution, lowering the polarity of the solvent mixture does; the molecular weights are generally lower in methylene chloride than in toluene. A possible explanation for these correlations comes from the fact that solvent polarity and temperature both affect significantly the outcome of the polymerization events. In polar solvents, initiation is enhanced since it is easier to form the ion pair. Also, the more polar the solvent, the easier it is to have chain-transfer events and consequently lower molecular weights.[5] A decrease of the reaction temperature reduces the relative rates of chain transfer and termination processes. While the apparent rates of polymerization, as reflected in part by the conversions, varied somewhat, in general, the experiments with higher initiator concentrations proceeded relatively rapidly, with an initial, temporary temperature increase of 2−3 °C and polymer precipitation within 2 min of addition of the $B(C_6F_5)_3$. The temporary increases in temperature resulted in most cases in low-molecular-weight "tails" in the GPC plots, which in turn artificially lowered the calculated values of M_n.

The neutral compound Cp*$TiMe_3$ by itself did not initiate polymerization of isobutylene, and control experiments were carried out using $B(C_6F_5)_3$ alone in order to verify that Cp*$TiMe_2(\mu$-Me)$B(C_6F_5)_3$ was involved in initiating the polymerization. The borane alone does indeed initiate polymerization of isobutylene, albeit with very low conversions (1−3%). Polymerization by $B(C_6F_5)_3$ occurs possibly because of proton formation from the reaction between $B(C_6F_5)_3$ and the adventitious traces of water (eq 4). The interaction of $B(C_6F_5)_3$ with water has been previously reported even though it has not been studied in detail.[12]

$$2H_2O + B(C_6F_5)_3 \rightarrow H_3O^+ + [HOB(C_6F_5)_3]^- \quad (4)$$

Better yields of PIB are therefore formed in methylene

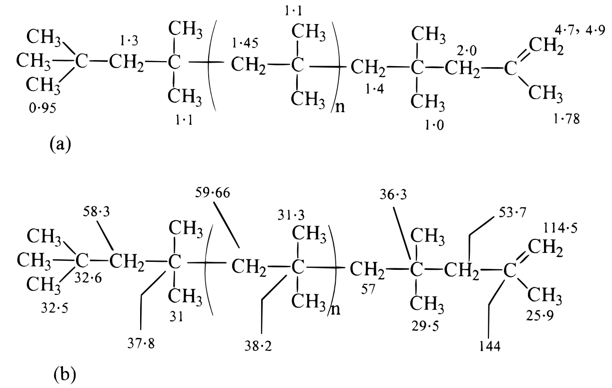


Figure 2. ^1H (a) and $^{13}C\{^1H\}$ (b) NMR chemical shifts (δ in $C_2D_2Cl_4$) assigned to the "head", main chain, and "tail" end groups of PIB.[8]

Table 2. ^1H and $^{13}C\{^1H\}$ NMR Data for Polyisobutylene Obtained in This Work ($C_2D_2Cl_4$)

structural unit	chemical shifts (δ) ^1H	chemical shifts (δ) $^{13}C\{^1H\}$
$CH_2{-}\mathit{C(CH_3)_2}$ (main chain)	1.14	31.46, 38.2
$\mathit{CH_2}{-}C(CH_3)_2$ (main chain)	1.45	59.66
$PIB{-}CH_2{-}\mathit{C}(CH_3){=}\mathit{CH_2}$	4.66, 4.8	114.5, 143.0
$PIB{-}\mathit{CH_2}{-}C(CH_3){=}CH_2$	1.98	53.75
$PIB{-}\mathit{CH_2}{-}C(CH_3)_2{-}CH_2{-}C(CH_3){=}CH_2$	1.33	57.04
$(CH_3)_3C{-}\mathit{CH_2}{-}C(CH_3)_2{-}\mathit{CH_2}{-}PIB$	1.29	58.8, 58.3
$PIB{-}C(CH_3)_2{-}CH_2{-}C(\mathit{CH_3}){=}CH_2$	1.78	25.9
$PIB{-}C(\mathit{CH_3})_2{-}CH_2{-}C(CH_3){=}CH_2$	0.98	29.5
$PIB{-}\mathit{C}(CH_3)_2{-}CH_2{-}C(CH_3){=}CH_2$		36.3
$(CH_3)_3C{-}CH_2{-}\mathit{C}(CH_3)_2{-}CH_2{-}PIB$		37.8−37.92
$\mathit{(CH_3)_3C}{-}CH_2{-}C(CH_3)_2{-}CH_2{-}PIB$	0.95	32.58

chloride when the solvent is incompletely dried, as has been shown elsewhere.[13]

NMR Spectra of the PIB Obtained with $Cp^*TiMe_2(\mu\text{-}Me)B(C_6F_5)_3$. Polyisobutylene (PIB) is generally formed as a head-to-tail polymer $(CH_2CMe_2)_n$ and ignoring end groups, ^1H NMR spectra exhibit two resonances, at δ ~1.1 (s, 6H, Me) and ~1.4 (s, 2H, CH_2), while $^{13}C\{^1H\}$ NMR spectra exhibit three resonances, at δ ~31 (Me), ~38 (*tert*-C), and ~60 (CH_2), depending on the solvent.[8] As indicated in the Experimental Section, the samples of PIB obtained were readily characterized by these criteria.

In an effort, however, to obtain mechanistic information about the mode(s) of initiation and chain transfer, we required low-molecular-weight material, for which the otherwise very weak end-group resonances might be observed. Low-molecular-weight samples of PIB (M_n 960−3400) were therefore obtained in CH_2Cl_2 at −50 °C by initiation with $Cp^*TiMe_2(\mu\text{-}Me)B(C_6F_5)_3$ followed by immediate termination with methanol. We show in Figure 2 the structural features anticipated for PIB formed via carbocationic processes and the approximate ^1H and ^{13}C chemical shifts reported previously in the literature,[8,9] and in Table 2 the chemical shifts and assignments of all resonances observed here.

According to the mechanism for polymerization discussed below, a *tert*-butyl group is expected to be formed at the "head" end of the polymer (the titanium initiator end) after hydrolysis and a terminal olefinic group is expected to be formed at the "tail" end due to proton transfer to monomer. A ^1H NMR spectrum of low-molecular-weight PIB exhibited, in addition to the two strong resonances attributable to the PIB main chain at δ 1.14 and 1.45, weak singlet resonances assigned to the "head" end group and "tail" end group at δ 0.95 (*tert*-butyl end group) and δ 4.66, 4.8 (vinylidene end group)[8] and resonances at δ 1.98 and 1.78, corresponding to the CH_3 and CH_2 groups vicinal to the vinylidene tail end group ($PIB{-}CH_2{-}C(CH_3)_2{-}\mathit{CH_2}{-}C(\mathit{CH_3}){=}CH_2$).

A $^{13}C\{^1H\}$ spectrum of low-molecular-weight polymer exhibited the anticipated strong main chain butyl resonances at δ 31.46, 38.2, and 59.66 and also resonances corresponding to the *tert*-butyl groups at δ 32.58 (br, *tert*-butyl Me group) and the "tail" olefinic end group at δ 114.5 and 143.0 (CH_2 and quaternary C in $PIB{-}(CH_3)\mathit{C}{=}CH_2$). The resonances at δ 25.94 and 29.5 were assigned to methyl groups next to the "tail" end group in $PIB{-}C(\mathit{CH_3})_2{-}CH_2{-}C(\mathit{CH_3}){=}CH_2$, while resonances at δ 58.8, 58.3 (CH_2) and δ 57.04, 53.75 (CH_2) are attributed to secondary carbon atoms situated one and two isobutyl units distance from the "head" and "tail" end groups, respectively.[8] A quaternary ^{13}C resonance at δ 36.3 is attributable to carbon atoms vicinal to the olefin end group while resonances at δ 37.8−37.92 are attributable to carbon atoms situated in the proximity of both types of end groups.[8b]

The ^1H and $^{13}C\{^1H\}$ NMR assignments for the low-molecular-weight polymer obtained here were confirmed by a heteronuclear multiple quantum correlation experiment (HMQC), which resulted in a clear assignment for two pairs of cross-peaks, assigned to the head *tert*-butyl group at δ 32.58 (^{13}C NMR) and δ 0.95 (^1H NMR), and for the first two CH_3 groups vicinal to the tail olefin end group at δ 29.5 (^{13}C NMR) with δ 0.99 (^1H NMR). Two pairs of weak cross-peaks at δ 25.9 (^{13}C NMR) and δ 1.78 (^1H NMR) and at δ 53.75 (^{13}C NMR) and δ 1.98 (^1H NMR) are assigned as the resonances corresponding to the CH_3 and CH_2 groups in the proximity of the vinylidene tail group.

Mechanism of the Formation of PIB Utilizing $Cp^*TiMe_2(\mu\text{-}Me)B(C_6F_5)_3$. The polymerization results are consistent with a carbocationic polymerization mechanism which proceeds as illustrated in Figure 1, the isobutylene coordinating in an η^1 fashion to the $[Cp^*TiMe_2]^+$ and the metal−olefin interaction being stabilized by a complementary interaction between the borate anion $[MeB(C_6F_5)_3]^-$ and the olefin. A carbocationic center is thus generated at C-2 of the isobutylene molecule, and this is attacked by a second isobutylene molecule acting as a nucleophile in a manner typical for conventional carbocationic polymerization processes (eq 1−3). Propagation occurs as shown in Figure 1 and is terminated by alcoholysis of the propagating species to yield a terminal *tert*-butyl group, as indicated in eq 5.

$$Cp^*TiMe_2{-}CH_2CMe_2{\sim}P + 3MeOH \rightarrow Cp^*Ti(OH)_3 + 2CH_4 + CH_3CMe_2{\sim}P \quad (5)$$

The fact that a cationic, highly electrophilic transition metal complex such as $[Cp^*TiMe_2]^+$ can behave as a carbocationic polymerization initiator as well as a Ziegler−Natta catalyst is not surprising, although there are few precedents for the hypothesized η^1 mode of coordination postulated in Figure 1. Much more common, of course, is the η^2 mode of coordination which is normally involved in ethylene and α-olefin polymerization catalyzed by metallocene compounds.[1] However, as we have previously summarized,[3h] η^1 structures of the type postulated in Figure 1 undoubtedly occur during nucleophilic attack on olefins coordinated to electrophilic metals, while nearly η^1 structures have

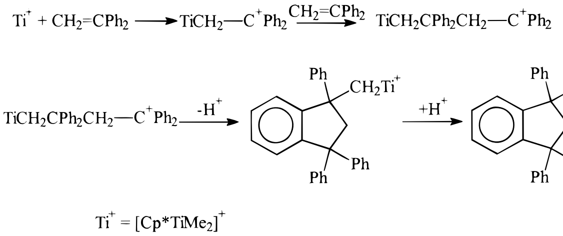
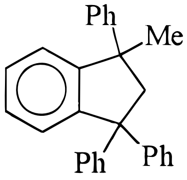


Figure 3. Reaction scheme showing formation of 1,3,3-triphenyl-3-methylindan from 1,1-diphenylethylene.

been found in complexes of olefins containing good π donor substituents.[3h]

Isobutylene is both a bulky, sterically demanding ligand and an asymmetric substituted olefin in which the two donor methyl groups polarize the double bond. The specific conformation of the metal−olefin bonding (η^1 rather than η^2) in the case of isobutylene can thus be rationalized as a result of the effect of the methyl substituents on both the steric and the electronic factors involved in the equilibrium orientation of the olefin in the complex. In other words, the complexed isobutylene ligand in the putative $[Cp^*TiMe_2(\eta^1\text{-}CH_2{=}CMe_2)]-[BMe(C_6F_5)_3]$ may exhibit quite different metal−carbon bond distances for both steric and electronic reasons.

The reaction of $Cp^*TiMe_2(\mu\text{-}Me)B(C_6F_5)_3$ with 1,1-diphenylethylene was carried out in an attempt to obtain evidence for η^1 coordination in a complex of the type $[Cp^*TiMe_2(\eta^1\text{-olefin})][BMe(C_6F_5)_3]$; it is known that, for steric reasons, this olefin is not readily polymerized but instead that interaction with a strong Lewis acid results in dimerization to 1,3,3-triphenyl-3-methylindan (**B**).[10] Attempts to identify a monoolefin complex failed, as the reaction of $Cp^*TiMe_2(\mu\text{-}Me)B(C_6F_5)_3$ with 1,1-diphenylethylene readily yielded a product which was identified as being 1,3,3-triphenyl-3-methylindan. Thus treatment of $Cp^*TiMe_2(\mu\text{-}Me)B(C_6F_5)_3$ with a CD_2Cl_2 solution of 1,1-diphenylethylene at −50 °C did not result in any change of the ^1H NMR spectrum of the reaction mixture until the solution was warmed up to 0 °C. The reaction mixture then changed color to red and then dark brown, and a ^1H NMR spectrum recorded at 0 °C exhibited resonances of unreacted $Cp^*TiMe_2(\mu\text{-}Me)B(C_6F_5)_3$ and 1,1-diphenylethylene in addition to resonances attributable to 1,3,3-triphenyl-3-methylindan. The product was isolated and characterized both by mass spectrometry and by comparisons of the ^1H and $^{13}C\{^1H\}$ NMR spectra with literature data.[10]



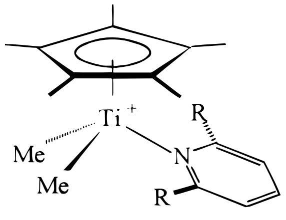
B

Isolation of this indan derivative is indeed evidence for carbocationic initiation as in Figure 1, as it is probably formed by cyclization of the dimer carbocation produced by a cationic mechanism, as in Figure 3. The same product was obtained by Sen et al.[10] from the reaction of 1,1-diphenylethylene at low temperature with electrophilic transition metal cations such as $[Pd(MeCN)_4][BF_4]_2$.

The role of carbocationic initiation of isobutylene polymerization by a number of initiators, including Cp^*TiMe_3 activated by $B(C_6F_5)_3$, has also very recently been considered by Shaffer and Ashborough.[13] In the case of initiation of isobutylene polymerization by $Cp^*TiMe_2(\mu\text{-}Me)B(C_6F_5)_3$, they considered the possibilities that polymerization is initiated by $B(C_6F_5)_3$ alone or by protons arising from the hydrolysis of $B(C_6F_5)_3$ by adventitious water as in eq 4. They demonstrated that $B(C_6F_5)_3$ alone is a poor initiator, confirming our findings, and they also found that addition of the strong, supposedly nonnucleophilic base 2,6-di-*tert*-butylpyridine (DTBP), much utilized as a proton trap,[5b] effectively deactivates partially hydrolyzed $B(C_6F_5)_3$ as a polymerization initiator. The latter result suggests that protons generated as in eq 4 are the actual initiator in polymerizations induced by $B(C_6F_5)_3$.

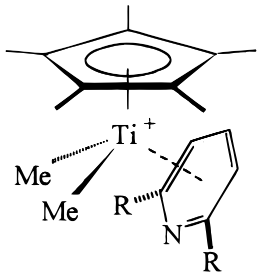
Experiments involving addition of the proton trap DTBP to $Cp^*TiMe_2(\mu\text{-}Me)B(C_6F_5)_3$ prior to initiation of polymerization were therefore carried out in order to assess the possibility that protons resulting from partial hydrolysis play a role in polymer initiation by this system also.[13] It was found that addition of DTBP does reduce somewhat the yield of product formed by the titanium initiator, leading to the suggestion that the number of initiating sites is decreased in the presence of DTPB and that water does contribute to the polymerization. Implicit in this interpretation is the assumption that DTBP is indeed "nonnucleophilic" and does not coordinate to the titanium. Since we have earlier shown that coordinated ligands generally reduce that catalytic activity of $Cp^*TiMe_2(\mu\text{-}Me)B(C_6F_5)_3$ by successfully competing for coordination sites on the titanium,[3h] we have therefore utilized low-temperature ^1H NMR studies to investigate the possible coordinating abilities both of DTBP and of a less sterically demanding but electronically similar ligand, 2,6-dimethylpyridine (DMP).

A number of Lewis base adducts of the type $[Cp^*TiMe_2(base)][MeB(C_6F_5)_3]$ have previously been identified,[3h] and we find that addition of 1 equiv of DMP to a CD_2Cl_2 solution of $Cp^*TiMe_2(\mu\text{-}Me)B(C_6F_5)_3$ at −30 °C yielded quantitatively the new complex $[Cp^*TiMe_2-(DMP)][MeB(C_6F_5)_3]$. The latter exhibits a simple ^1H NMR spectrum (CD_2Cl_2, −30 °C), with resonances for the Cp* (δ 1.89), Ti−Me (δ 1.65), DMP Me (δ 2.25), DMP H-4 (δ 8.0), DMP H-3,5 (δ 7.38), and B−Me (δ 0.39) groups all readily assigned, and thus the compound clearly assumes structure **C** (R = Me), similar to the better characterized Lewis base adducts reported previously.[3h] Addition of excess DMP to the CD_2Cl_2 solution of $[Cp^*TiMe_2(DMP)][MeB(C_6F_5)_3]$ resulted in the appearance of the resonances of free DMP, and thus exchange between free and coordinated ligand is slow on the NMR time scale.



C

In contrast, the addition of 1 equiv of the sterically more hindered DTBP to a CD_2Cl_2 solution of $Cp^*TiMe_2(\mu\text{-}Me)B(C_6F_5)_3$ at −50 °C resulted in the formation of a mixture of $Cp^*TiMe_2(\mu\text{-}Me)B(C_6F_5)_3$ and a small but significant amount of the new complex $[Cp^*TiMe_2(DTBP)][MeB(C_6F_5)_3]$, identified by ^1H NMR spectroscopy. Thus the ^1H NMR spectrum of the reaction mixture exhibited relatively strong resonances of $Cp^*TiMe_2(\mu\text{-}Me)B(C_6F_5)_3$ and free DTBP and weak resonances attributable to $[Cp^*TiMe_2(DTBP)]-[MeB(C_6F_5)_3]$ at δ 0.39 (s, B-Me), 1.50 (s, *t*-Bu), 7.49 (H-3,5), and 7.85 (H-4). The Ti−Me and Cp* resonances were apparently obscured and could not be identified unambiguously, but the similar downfield shifts of the aromatic resonances of both DMP and DTBP suggest that the two complexes are very similar, presumably as in **C** although an arene complex[3b] as in **D** is also possible. On addition of excess DTBP (∼5 equiv) to a CD_2Cl_2 solution of $Cp^*TiMe_2(\mu\text{-}Me)B(C_6F_5)_3$, the ^1H NMR spectrum exhibited significant enhancement of the resonances of $[Cp^*TiMe_2(DTBP)][MeB(C_6F_5)_3]$, although the lability of the system prohibited isolation of the compound. To further characterize the compound, exchange spectroscopy by saturation transfer was carried out at ∼ −55 °C. It was found that irradiation at the frequency of the 3,5-H resonance of free DTBP resulted in a positive NOE effect for the 4-H of free DTBP and in spin transfer to the 3,5-H resonance of the coordinated DTBP, indicating slow exchange between free and coordinated DTBP although variation of the temperature in the range −50 to −8 °C resulted in little change in the chemical shifts.



D

Although one might consider attributing the new resonances at δ 1.50, 7.49, and 7.85 to protonated DTBP, derived from adventitious water in the solvent, this cannot be so. The $Cp^*TiMe_2(\mu\text{-}Me)B(C_6F_5)_3$ present in the solution is itself a very effective scavenger of proton sources, and hydrolysis products would be very obvious in the NMR study done. In addition, we have shown in separate NMR experiments that DTBP in wet CD_2Cl_2 does not form the pyridinium ion, and thus the new compound in solution almost certainly assumes a structure as in **C** (R = *t*-Bu).

As indicated in ref 13, there has recently been considerable interest in the use of DTBP and other Lewis bases to influence carbocationic polymerization processes; there has also been much debate on the nature of the interactions with polymerization systems. For instance, DTBP seems generally thought to be a strong, sterically hindered, nonnucleophilic base and hence to behave as a very effective and specific proton trap.[14] In fact DTBP is an unusually weak base in a variety of solvents[15] and, as is shown here, DTPB does coordinate to the $[Cp^*TiMe_2]^+$ cation and should be capable of interfering weakly, at least, with olefin coordination. It may also, as do other Lewis bases,[5] be capable of interacting with and thus stabilizing the carbocationic centers formed during polymerization (Figure 1 and eqs 1 and 2), but we have not yet assessed this possibility via low-temperature NMR studies.

Table 3. Copolymerization Reactions of Isobutylene (C_4) and Isoprene (C_5) (Initiator Conc 0.004 M)

C-4/C-5 ratio (% vol)	C-4/C-5 ratio (molar)	solvent	*T* (°C)	M_w	M_n	M_w/M_n	T_g* (°C)
30:70	0.5:1	toluene	−78	6.90×10^3	1.6×10^3	4.2	
75:25	3.3:1	toluene	−55	5.40×10^3	2.9×10^3	1.9	−82
90:10	10:1	toluene	−55	2.80×10^4	0.9×10^3	3.0	−50
98:2	54:1	toluene	−60	1.25×10^5	5.7×10^4	2.2	−51
99:1	109:1	toluene	−78	1.90×10^5	8.7×10^4	2.2	−52

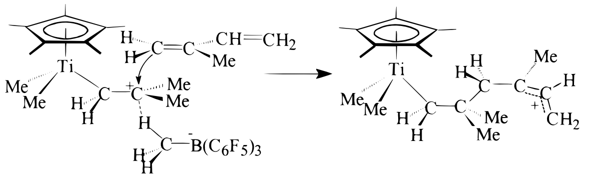


Figure 4. Mode of incorporation of isoprene into a PIB polymer chain.

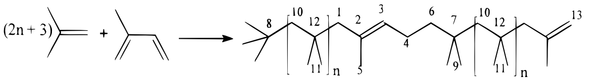


Figure 5. Structure of random copolymer of isobutylene and isoprene.

Copolymerization of Isobutylene and Isoprene. A series of copolymerization experiments were carried out in toluene at temperatures between −60 and −78 °C and with different isobutylene−isoprene ratios in order to evaluate the potential of the titanium initiator system for the synthesis of isobutylene−isoprene copolymer. The results of representative polymerization runs are presented in Table 3, where it is seen that lower temperatures result in higher molecular weights in toluene while the polydispersities in these solvents are ∼2, consistent with a carbocationic mechanism.[5] The ratio of isobutylene to isoprene also has an important effect on the molecular weights, as materials with high M_w values and low polydispersity indexes could be obtained only at very low contents of isoprene. Again these results are consistent with previous work utilizing conventional Lewis acid initiators.[5,9,11]

Mechanism of the Formation of the Isobutylene−Isoprene Copolymer. Formation of a random copolymer via incorporation of small amounts of isoprene in PIB is believed to occur as indicated in Figure 4. Here a molecule of isoprene adds to the isobutyl carbocationic center to form a stabilized allylic cation. Although attack by a molecule of isobutylene could in principle occur at C-2 or C-4 of the allylic cation, to give the products of 1,2- or 1,4-addition, respectively, in fact NMR spectroscopic analysis of the resulting product shows quite clearly that only 1,4-addition occurs (see below), as in Figure 5.

Chain transfer processes resemble that of PIB (eq 3) but now may occur at isobutyl or isoprenyl termini and may involve isobutene or isoprene, as shown in Figure 6.

NMR Spectra of the Isobutylene−Isoprene Copolymers. The ^1H chemical shifts (Table 4) of the major isobutyl resonances in the copolymer ($C_2D_2Cl_4$) were observed at δ 1.14 (s, Me) and 1.45 (s, CH_2), as in the PIB homopolymer, but the presence of isoprenyl units adjacent to isobutyl units induced upfield shifts of the resonances of the latter, that is δ 0.99−1.05 (br

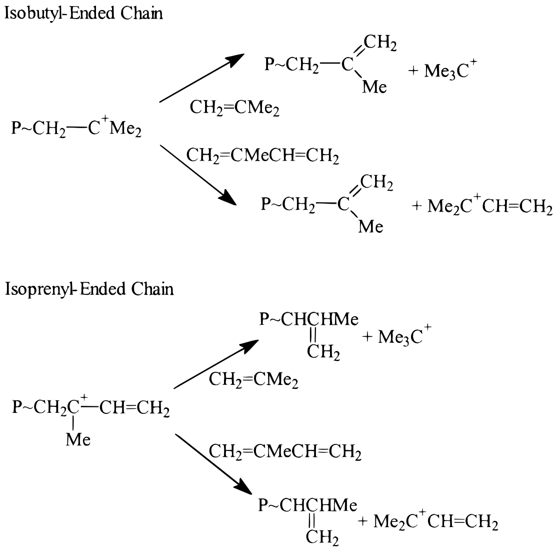


Figure 6. Chain transfer processes during isobutylene–isoprene copolymer formation.

Table 4. ^{1}H Chemical Shifts for the Isoprenyl and Isobutyl Units ($C_2D_2Cl_4$)

C atom in Figure 5	δ	assignment
1	1.95–2.05	CH_2
3	5.12	methine H in CMe=C*H*
4	1.95–2.05	allylic CH_2 in IPR–IPR, IPR–IB
5	1.61–1.65	allylic CH_3 in IPR–IPR, IPR–IB
6	1.30, 1.35	CH_2 isobutyl unit in IB–IB–IPR and IB–IPR–IB triads
9	0.85–0.96	CH_3 isobutyl unit in IB–IB–IPR and IB–IPR–IB triads
10	1.45	CH_2 isobutyl unit, main chain
11	1.14	CH_3 isobutyl unit, main chain
13	4.65, 4.85	C=C*H*$_2$

s, Me in IB–IB–IB triads), 0.95 (br s, Me in IB–IB–IPR triads), 0.85 (br s, Me in IB–IPR–IB triads), 1.30, 1.35 (s, CH_2 in IB–IB–IPR and IB–IPR–IB triads). Similar changes have been noted elsewhere.[9] The ^{1}H NMR olefinic resonances of the isoprenyl units were readily detected (CD_2Cl_4) at δ 5.12 (t, methine H in CMe=C*H*), 4.98 (br d, methine H in ~HC=CH–C*H*(CH_2R)), 4.65, 4.85 (C=C*H*$_2$ end groups), 1.61–1.65 (s, allylic Me in IPR–IPR, IPR–IB diads), and 1.95–2.05 (s, allylic CH_2 in IPR–IPR, IPR–IB diads), and again similar changes have been noted elsewhere.[9] The degree of incorporation of isoprenyl groups in the polymers was determined from the ratio of the methine peak to the methylene or methyl peaks of the isobutyl groups.

The ^{13}C resonances of the isobutyl carbon atoms of the main chain of the copolymer were observed (C_6D_6) at δ 31.45 (Me), 38.2 (*tert*-C), and 59.7 (CH_2), much as for the PIB homopolymer. The $^{13}C\{^1H\}$ NMR resonances of isobutyl groups adjacent to the isoprenyl units were slightly shifted upfield (δ 29.73–31.25 (Me), 35.11–38.21 (*tert*-C), 55.9–59.1 (CH_2)), while the $^{13}C\{^1H\}$ NMR resonances assigned to the isoprenyl carbon atoms were observed at δ ~132 (m, >C=), 128 (s, =CH) ~24 (s, CH_2), ~34 (CH_2), and 19.5 (s, Me).[9] These chemical shifts are consistent with trans-1,4-addition to the isoprene (Figure 5), as reported in the literature for copolymer made utilizing conventional initiators.[9] The ^{1}H and $^{13}C\{^1H\}$ NMR spectra are consistent with the results of Chu et al., who elucidated the structure of the isoprenyl unit incorporated in isobutylene–isoprene copolymers using ^{1}H and $^{13}C\{^1H\}$ NMR spectroscopy complemented by chemical shift calculations (Table 5).[9b]

Table 5. Comparison between the Isoprenyl $^{13}C\{^1H\}$ Chemical Shifts by $^{13}C\{^1H\}$ NMR and the Literature Values

C atom in Figure 5	δ	assignment	δ (lit.)[9b]
1	55.9	CH_2	55.81
2	132.0–133.0	>C=	132.4
3	128.0–129.0	=CH	129.98
4	24.4	CH_2	23.37
5	19.5	CH_3	19.21
6	45.9	CH_2	45.63
7	36.6	CH_2	36.64
8	35.1	>C<	35.19
9	29.7	CH_3	29.46
10	59.9	CH_2	59.6
11	31.4	CH_3	31.28
12	38.0	>C<	38.26

Comparison of the $^{13}C\{^1H\}$ NMR spectra of the copolymers obtained at different temperatures and with different isoprene contents in the reaction medium shows that the copolymers obtained at lower temperature and with low isoprene content exhibit simpler spectra and thus have more regular structures. The presence of an isoprenyl end group generates more possible ways for chain termination than an isobutyl end group even though termination by chain transfer in an isoprenyl end group is analogous to that of polyisobutylene (Figure 6). By comparing experiments carried out at the same temperature (Table 3), it appears that chain transfer to the monomer is more favored at higher content of isoprene, again consistent with the results reported using conventional carbocationic polymerization initiators.[9]

Interestingly, the experiment involving the isobutylene–isoprene molar ratio 109:1 at −78 °C resulted in a copolymer containing approximately 1% isoprene (by ^{1}H NMR) and exhibiting a molecular weight, molecular weight distribution, and NMR spectrum identical with those of a commercial sample of butyl rubber obtained from Bayer Rubber Ltd. Another experiment, using a high feed concentration of isoprene (70 vol %), resulted in a low-molecular-weight copolymer which exhibited quite different ^{1}H and ^{13}C NMR spectra because of the presence of isoprene–isoprene diads (IPR–IPR). Polymerization experiments carried out in mixtures of toluene and hexanes (volume ratio 1:2) produced copolymer with a similar molecular weight.

Summary

The compound $Cp^*TiMe_2(\mu\text{-}Me)B(C_6F_5)_3$ is a source of the electronically unsaturated, cationic species $[Cp^*TiMe_2]^+$, which is an excellent initiator for both the homopolymerization of isobutylene and the copolymerization of isobutylene and isoprene. A number of factors, including the inverse dependence of molecular weights on temperature, the polymer microstructures, the identities of the end groups of both types of polymer, and observations that the system induces dimerization of 1,1-diphenylethylene to 1,3,3-triphenyl-3-methylindan, strongly suggest that both polymerization processes involve conventional carbocationic initiation and propagation steps. While this is the first metallocene system to be identified as a carbocationic initiator for isobutylene polymerization, Shaffer and Ashborough[13] and

Bochmann *et al.*[16a] have since our initial publication[3e] reported similar behavior by metallocenes Cp'_2MMe_2 (Cp' = substituted cyclopentadienyl; M = Zr, Hf) activated with $[Ph_3C][B(C_6F_5)]_4$ and $B(C_6F_5)_3$. The cationic species $[Zr(N\{SiMe_3\}_2)_3]^+$ is also a good initiator.[16b]

Acknowledgment. We thank Queen's University and the Natural Sciences and Engineering Research Council for financial support and Drs. Ron Commander and Judit Puskas for helpful discussions and advice.

References and Notes

(1) For recent reviews see: (a) Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143. (b) Bochmann, M. *J. Chem. Soc., Dalton Trans.* **1996**, 255. (c) Kaminsky, W.; Arndt, M. *Adv. Polym. Sci.* **1997**, *127*, 143. (d) Möhring, P. C.; Coville N. J. *J. Organomet. Chem.* **1994**, *479*, 1.

(2) (a) Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1991**, *113*, 3623. (b) Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10015. (c) Bochmann, M.; Lancaster, S. J.; Hursthouse, M. B.; Malik, K. M. A. *Organometallics* **1994**, *13*, 2235.

(3) (a) Gillis, D. J.; Tudoret, M.-J.; Baird, M. C. *J. Am. Chem. Soc.* **1993**, *115*, 2543. (b) Gillis, D. J.; Quyoum, R.; Tudoret, M.-J.; Wang, Q.; Jeremic, D.; Roszak, A. W.; Baird, M. C. *Organometallics* **1996**, *15*, 3600. (c) Wang, Q.; Quyoum, R.; Gillis, D. J.; Jeremic, D.; Tudoret, M.-J.; Baird, M. C. *J. Organomet. Chem.* **1997**, *527*, 7. (d) Quyoum, R.; Wang, Q.; Tudoret, M.-J.; Gillis, D. J.; Baird, M. C. *J. Am. Chem. Soc.* **1994**, *116*, 6435. (e) Barsan, F.; Baird, M. C. *J. Chem. Soc., Chem. Commun.* **1995**, 1065. (f) Jeremic, D.; Wang, Q.; Quyoum, R.; Baird, M. C. *J. Organomet. Chem.* **1995**, *497*, 143. (g) Wang, Q.; Baird, M. C. *Macromolecules* **1995**, *28*, 8021. (h) Wang, Q.; Quyoum, R.; Gillis, D. J.; Tudoret, M.-J.; Jeremic, D.; Hunter, B. K.; Baird, M. C. *Organometallics* **1996**, *15*, 693. (i) Sarsfield, M. J.; Ewart, S. W.; Tremblay, T. L.; Roszak, A. W.; Baird, M. C., *J. Chem. Soc., Dalton Trans.*, **1997**, 3097. (j) Tremblay, T. L.; Ewart, S. W.; Sarsfield, M. J.; Baird, M. C. *J. Chem. Soc., Chem. Commun.* **1997**, 831. (k) Ewart, S. W.; Sarsfield, M. J.; Jeremic, D.; Tremblay, T. L.; Williams, E. F.; Baird, M. C. *Organometallics*, submitted. (l) Murray, M. C.; Baird, M. C. *J. Mol. Catal.*, in press.

(4) (a) Skupinski, W.; Cieslowska-Glinska, I.; Wasilewski, A. *J. Mol. Catal.* **1985**, *33*, 129. (b) Ishihara, N.; Kuramoto, M.; Uoi, M. *Macromolecules* **1988**, *21*, 3356. (c) Zambelli, A.; Oliva, L.; Pellecchia, C. *Macromolecules* **1989**, *22*, 2129. (d) Chien, J. C. W.; Wang, B. P. *J. Polym. Sci., Part A* **1989**, *27*, 1539. (e) Chien, J. C. W.; Wang, B. P. *J. Polym. Sci., Part A* **1990**, *28*, 15. (f) Rieger, B. *J. Organomet. Chem.* **1991**, *420*, C17. (g) Soga, K.; Park, J. R.; Shiono, T. *Polym. Commun.* **1991**, *32*, 310. (h) Park J. R.; Shiono, T.; Soga, K. *Macromolecules* **1992**, *25*, 521. (i) Pellecchia, C.; Longo, P.; Proto, A.; Zambelli, A. *Makromol. Chem. Rapid Commun.* **1992**, *13*, 265. (j) Pellecchia, C.; Longo, P.; Proto, A.; Zambelli, A. *Makromol. Chem. Rapid Commun.* **1992**, *13*, 277. (k) Chien, J. C. W.; Salajka, Z.; Dong, S. *Macromolecules* **1992**, *25*, 3199. (l) Kucht, A.; Kucht, H.; Barry, S.; Chien, J. C. W.; Rausch, M. D. *Organometallics* **1993**, *12*, 3075. (m) Soga, K.; Koide, R.; Uozumi, T. *Makromol. Chem. Rapid Commun.* **1993**, *14*, 511. (n) Ready, T. E.; Day, R. O.; Chien, J. C. W.; Rausch, M. D. *Macromolecules* **1993**, *26*, 5822. (o) Longo, P.; Proto, A.; Oliva, L. *Makromol. Chem. Rapid Commun.* **1994**, *15*, 151. (p) Zambelli, A.; Pellecchia, C.; Oliva, L.; Longo, P.; Grassi, A. *Makromol. Chem.* **1991**, *192*, 223. (q) Kucht, H.; Kucht, A.; Chien, J. C. W.; Rausch, M. D. *Appl. Organomet. Chem.* **1994**, *8*, 393. (r) Pellecchia, C.; Immirzi, A.; Grassi, A.; Zambelli, A. *Organometallics* **1993**, *12*, 4473. (s) Flores, J. C.; Chien, J. C. W.; Rausch, M. D. *Organometallics* **1994**, *13*, 4140. (t) Flores, J. C.; Wood, J. S.; Chien, J. C. W.; Rausch, M. D. *Organometallics* **1996**, *15*, 4944. (u) Grassi, A.; Zambelli, A.; Laschi, F. *Organometallics* **1996**, *15*, 480. (v) Flores, J. C.; Chien, J. C. W.; Rausch, M. D. *Macromolecules* **1996**, *29*, 8030 and references therein. (w) Soga, K.; Lee, D. H. *Macromol. Chem.* **1992**, *193*, 1687. (x) Grassi, A.; Pellecchia, C.; Oliva, L. *Makromol. Chem. Phys.* **1995**, *196*, 1093.

(5) (a) Kennedy, J. P.; Maréchal, E. *Carbocationic Polymerization*; John Wiley and Sons: New York, 1982. (b) Kennedy, J. P.; Iván, B. *Designed Polymers by Carbocationic Macromolecular Engineering: Theory and Practice*; Hanser Publishers: Munich, 1991. (c) Sawamoto, M. *Prog. Polym. Sci.* **1991**, *16*, 111. (d) Higashimura, T.; Sawamoto, M. In *Comprehensive Polymer Science*; Eastmond, G. C., Ledwith, A., Russo, S., Sigwalt, P., Eds.; Pergamon Press: New York, 1989; Vol. 3, p 673. (e) Rooney, J. M. In *Comprehensive Polymer Science*; Eastmond, G. C., Ledwith, A., Russo, S., Sigwalt, P., Eds.; Pergamon Press: New York, 1989; Vol. 3, p 697. (f) Padwa, A. R. *Prog. Polym. Sci.* **1989**, *14*, 811. (g) Rempp, P.; Merrill, I. *Polymer Synthesis*, 2nd ed.; Hüthig & Wepfzzzzzz; New York, 1991; p 145.

(6) Puskas, J.; Wilds, C. *Rubber Chem. Technol.* **1993**, *66*, 742.

(7) (a) Mena, M.; Royo, P.; Serrano, R.; Pellinghelli, M. A.; Tiripicchio, A. *Organometallics* **1989**, *8*, 476. (b) Massey, A. G.; Park, A. J. *J. Organomet. Chemistry* **1964**, *2*, 245.

(8) (a) Pham, Q.-T.; Petiaud, R. *Spectres RMN des Polymeres $^1H-^{13}C$, Vol. 1, Editions SCM, Paris* **1980**, 164. (b) Lubnin, A. V.; Kennedy, J. P. *J. Macromol. Sci., Pure Appl. Chem.* **1995**, *A32*, 191. (c) Si, J.; Kennedy, J. P. *J. Polym. Sci.: Polym. Chem.* **1994**, *32*, 2011. (d) Lubnin, A. V.; Kennedy, J. P. *J. Macromol. Sci., Pure Appl. Chem.* **1994**, *A31*, 655.

(9) (a) Corno, C.; Proni, A.; Priola, A.; Cesca, S. *Macromolecules* **1980**, *13*, 1092. (b) Chu, C. Y.; Vukov, R. *Macromolecules* **1985**, *18*, 1423. (c) Kuntz, I.; Rose, K. D. *J. Polym. Sci., Part A: Polym. Chem.* **1989**, *27*, 107. (d) Corno, C.; Priola, A.; Spallanzani, G.; Cesca, S. *Macromolecules* **1984**, *17*, 37. (e) White, J. L.; Shaffer, T. D.; Ruff, C. J.; Cross, J. P. *Macromolecules* **1995**, *28*, 3290.

(10) Sen, A.; Lai, T.-W.; Thomas, R. R. *J. Organomet. Chem.* **1988**, *358*, 567.

(11) Senyek, M. *Encycl. Polym. Sci. Technol.* **1987**, *8*, 487.

(12) Massey, A. G.; Park, A. J. *J. Organomet. Chem.* **1966**, *5*, 218.

(13) Shaffer, T. D.; Ashborough, J. R. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 329.

(14) (a) Gyor, M.; Wang, H.-C.; Faust, R. *J. Macromol. Sci.—Pure Appl. Chem.* **1992**, *A29*, 639. (b) Bae, Y. C.; Faust, R. *Macromolecules* **1997**, *30*, 7341.

(15) (a) Katritzky, A. R.; Leahy, D. E.; Maquestiau, A.; Flammang, R. *J. Chem. Soc., Perkin Trans. 2* **1983**, 45. (b) Hopkins, H. P.; Jahagirdar, D. V.; Moulik, P. S.; Aue, D. H.; Webb, H. M.; Davidson, W. R.; Pedley, M. D. *J. Am. Chem. Soc.* **1984**, *106*, 4341. (c) Emsley, J.; Gold, V.; Lee, R. A.. *J. Chem. Soc., Perkin Trans. 2* **1986**, 1861. (d) Benoit, R. L.; Frechette, M.; Lefebvre, D. *Can. J. Chem.* **1988**, *66*, 1159.

(16) (a) Carr, A. G.; Dawson, D. M.; Bochmann, M. *Macromolecules* **1998**, *31*, 2035. (b) Carr, A. G.; Dawson, D. M.; Bochmann, M. *Macromol. Rapid Commun.* **1998**, *19*, 205.

MA980324W