

The First Example of Polymerization of Isobutylene induced by a Metallocene-like Initiator, $[(\eta^5\text{-C}_5\text{Me}_5)\text{TiMe}_2(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3]$

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Addition of equimolar amounts of $(\eta^5\text{-C}_5\text{Me}_5)\text{TiMe}_3$ and $\text{B}(\text{C}_6\text{F}_5)_3$ to solutions of isobutylene or isobutylene and isoprene (99 : 1 molar ratio) in toluene at -78°C results in polymerization to give, respectively, isobutylene homopolymer with a high weight average molecular mass of $\sim 5 \times 10^5$ and a narrow polydispersity (2.1), or an isobutylene-isoprene copolymer exhibiting a composition, a molecular mass distribution and ^1H and ^{13}C NMR spectra identical to those of a sample of commercial butyl rubber.

There has in recent years been extensive research into the utilization of titanocene, zirconocene and hafnocene derivatives as homogeneous catalysts for olefin polymerization¹ and, as made clear in a recent overview,² the new catalytic systems are in some instances becoming economically competitive with current (heterogeneous) olefin polymerization technology. It is widely accepted that metallocene systems function generally as coordination (Ziegler–Natta) polymerization catalysts, and incorporate the following structural features: the presence of a coordinated alkyl ligand, of a vacant site and of a positive charge, as in 16-electron complexes of the type $[\text{Cp}'_2\text{MR}(\text{L})]^+$ ($\text{M} = \text{Ti, Zr, Hf}$; $\text{Cp}' =$ substituted η^5 -cyclopentadienyl group; $\text{R} =$ alkyl group; $\text{L} =$ labile ligand).¹

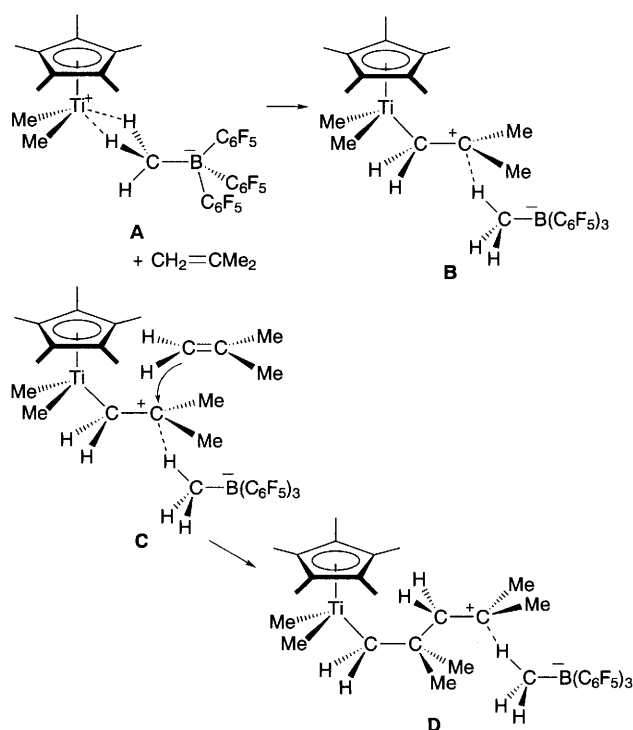
Complementing research on metallocene systems, it has been shown that electronically less saturated and sterically less hindered monocyclopentadienyl complexes of the type $[\text{Cp}'\text{MR}_2\text{L}]^+$ also behave as useful catalysts or initiators for olefin polymerization,^{3,4} and many recent publications describe the utilization of such compounds of titanium and zirconium as olefin polymerization catalysts or initiators for ethylene,^{3b,c,4c,d,f,k,m} α -olefins,^{4d,f,l} conjugated and non-conjugated dienes,^{3d,4j} norbornene,^{3d} aromatic olefins,^{3b,c,4a,b,e,g-i} vinyl ethers^{3b} and *N*-vinylcarbazole.^{3b} The latter two types of olefins are missing from listings of olefins polymerized by metallocene systems,² and also are not normally susceptible to polymerization *via* heterogeneous Ziegler–Natta systems because they coordinate *via* the heteroatoms to the active sites of most types of most catalysts and thus act as catalyst poisons. However, vinyl ethers and *N*-vinylcarbazole are readily polymerized *via* carbocationic processes,⁵ and the recently recognized ability of the system $[(\eta^5\text{-C}_5\text{Me}_5)\text{TiMe}_3/\text{B}(\text{C}_6\text{F}_5)_3]$ **A**^{3b,c} to function as a carbocationic initiator for polymerization of these monomers and for aromatic olefins has greatly broadened the scope of olefin polymerization by metallocene-like systems.

Initiator **A** is formed by methyl abstraction from the compound $[(\eta^5\text{-C}_5\text{Me}_5)\text{TiMe}_3]$ by the excellent Lewis acid $\text{B}(\text{C}_6\text{F}_5)_3$;^{3a,c} it appears to assume the methyl-bridged structure $[(\eta^5\text{-C}_5\text{Me}_5)\text{TiMe}_2(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3]$, shown in Scheme 1, and exists in methylene chloride in equilibrium with the solvent-separated, ionic complex $[(\eta^5\text{-C}_5\text{Me}_5)\text{TiMe}_2(\text{CH}_2\text{Cl}_2)]^+[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$.^{3a,c} In aromatic solvents, arene complexes of the type $[(\eta^5\text{-C}_5\text{Me}_5)\text{TiMe}_2(\eta^6\text{-arene})][\text{MeB}(\text{C}_6\text{F}_5)_3]$ are formed.^{3a} Since the $\text{MeB}(\text{C}_6\text{F}_5)_3^-$, CH_2Cl_2 and arene ligands are all readily displaced, these complexes behave in solution as sources of the cationic, ten-electron species $[(\eta^5\text{-C}_5\text{Me}_5)\text{TiMe}_2]^+$, which is an effective initiator or initiator precursor for the olefin polymerization reactions described above.

An important monomer which seems not to have been previously polymerized by metallocene systems² is isobutylene. However, since isobutylene is readily polymerized by a number of traditional carbocationic initiators,^{5,6} it seemed reasonable that $[(\eta^5\text{-C}_5\text{Me}_5)\text{TiMe}_2]^+$ might also behave as a carbocationic polymerization initiator towards this monomer, as it does for vinyl ethers and *N*-vinylcarbazole. We find that the cationic titanium system does indeed initiate the polymerization of isobutylene to isobutylene homopolymer, and we describe herein our preliminary results.

Isobutylene polymerization may be initiated by adding $[(\eta^5\text{-C}_5\text{Me}_5)\text{TiMe}_3]$ and $\text{B}(\text{C}_6\text{F}_5)_3$ (1:1) to cooled solutions of isobutylene in toluene and methylene chloride. The polymer formed separates rapidly as a sticky precipitate, unoptimized yields after purification being $\leq 50\%$.† The effects of changing the temperature on the weight average molecular masses (M_w) and polydispersities (M_w/M_n) of the polyisobutylene were investigated, and it was found that M_w increases from *ca.* 3×10^4 at -20°C ($M_w/M_n \sim 3$) to *ca.* 2×10^5 at -78°C ($M_w/M_n \sim 2$). These results are consistent with the presumed carbocationic mechanism of the polymerization reaction, which would proceed as shown in Scheme 1.^{5,6} Thus, the isobutylene coordinates in **B** in a non-classical η^1 -fashion, the metal–olefin interaction being stabilized by a complementary borate–olefin interaction. The structure of **B** resembles the structures of several vinyl alcohol, vinyl ethyl ether, vinyl amine and methyleneimidazole complexes of electrophilic metals,⁷ and also the probable transition state involved in nucleophilic attack on olefins activated by coordination to electrophilic metals.⁸ The next step would involve the carbocationic centre of the metal ion-activated isobutylene molecule being attacked by a second isobutylene monomer **C**, in a manner normally postulated for carbocationic polymerization processes,^{5,6} followed by chain growth as in **D**.

The polyisobutylene formed was characterized by ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy, the chemical shifts and coupling constants agreeing very well with literature values^{9a} [C_6H_6 : ^1H



NMR: δ 1.26 (CH₃), δ 1.59 (CH₂); ¹³C{¹H} NMR: δ 31.45 (CH₃), δ 38.2 (tertiary C), δ 59.7 (CH₂). Also present were very weak proton resonances at $\sim \delta$ 4.64 and 4.82, which have been attributed to the vinylidene resonances of the $-\text{CH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{C}(\text{=CH}_2)\text{CH}_3$ end group,^{9b} and a broad, weak resonance at $\sim \delta$ 5.1, which has been attributed to the olefinic resonance of the $-\text{CH}_2\text{C}(\text{CH}_3)_2\text{CH}=\text{C}(\text{CH}_3)_2$ end group.^{9b} A terminal *tert*-butyl group should result from alcoholysis of species such as **D** of Scheme 1, and a weak *tert*-butyl resonance at $\sim \delta$ 0.99^{9c} was indeed observed in ¹H NMR spectra of all polymers formed.

Somewhat lower values of M_w/M_n and somewhat higher M_w/M_n ratios were found in CH₂Cl₂, while polymerizations (in toluene) initiated at -78°C solely by B(C₆F₅)₃, a good carbocationic initiator for other monomers,¹⁰ yielded polymers exhibiting significantly lower values of M_w ($\sim 10^4$) and much higher values of M_w/M_n (4–7).

Also, of potentially great interest are isobutylene–isoprene copolymers (butyl rubber), commercially important materials which normally contain 0.5 to 2.5% by mass isoprene.⁶ Copolymerization reactions of isobutylene and isoprene were carried out in toluene at -60 and -78°C , using varying initiator concentrations (0.005–0.007 mol dm⁻³) and isobutylene to initiator molar ratios (500:1–1700:1). As with isobutylene homopolymerization, M_w increases and M_w/M_n decreases on going to the lower reaction temperature, but the isobutylene:isoprene ratio also has a major effect. Only for very low isoprene contents were materials having high values of M_w and low values of M_w/M_n obtained, results consistent with behaviour reported for conventional carbocationic polymerization initiators.^{5,6} Using an isobutylene:isoprene ratio of *ca.* 99:1 at -78°C , we obtained a copolymer containing *ca.* 1% isoprene (by NMR) and exhibiting a molecular mass distribution ($M_w \sim 2 \times 10^5$; M_w/M_n *ca.* 2.2) and NMR spectra^{9a} essentially identical to those of a commercial sample of butyl rubber.[‡] [¹H NMR in C₆D₆: isobutylene resonances as above, isoprene resonances at δ 5.28 (=CH), δ 1.58 (CH₂), δ 1.26 (CH₃); ¹³C{¹H} NMR in C₆D₆: isobutylene resonances as above, isoprene resonances at $\sim \delta$ 132 (=C), $\sim \delta$ 24, $\sim \delta$ 34 (CH₂), $\sim \delta$ 128 (=CH), δ 19.5 (CH₃).] Furthermore, isoprene incorporation into the isobutylene polymer chain occurs primarily *via* the desired⁶ *trans*-1,4-addition.^{9a,11} The material obtained was certainly not a mixture of homopolymers, since attempted polymerization of isoprene yielded only very low molecular mass oligomers.

While we have not yet carried out a mechanistic investigation of isobutylene polymerization, the results reported here certainly suggest that the cationic species $[(\eta^5\text{-C}_5\text{Me}_5)\text{TiMe}_2]^+$ does behave as a carbocationic initiator for the process (Scheme 1). However, whatever the mechanism of polymerization, this is both the first report of isobutylene polymerization by a metallocene derivative and a preliminary description of a potential commercial process for the manufacture of butyl rubber which involves conditions which are much less extreme and environmentally much more benign than is the case with current technology.⁶ Halogenated butyl rubber is used extensively as liners for tubeless tires, annual world production of this material being in excess of 6×10^5 tonnes.⁶ Commercial butyl rubber of the requisite M_w is made in methyl chloride solution using aluminium trichloride containing small amounts of water as polymerization initiator at temperatures sufficiently low, -90 to -100°C , that chain transfer is reduced. Thus, there are many problems associated with the process, including the necessity to remove the aqueous initiator prior to halogenation and to recover the halogenated solvent, as well as the economic problems associated with utilizing acidic media and operating at cryogenic temperatures.⁶ The advent of potential technology which can avoid the use of a chlorinated solvent is clearly of special significance.

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Footnotes

† All operations were carried out under a dry N₂ atmosphere using thoroughly dried, distilled and degassed solvents and monomers. Reactions typically involved consecutive additions of 0.06×10^{-3} mol each of initiator [15 mg ($\eta^5\text{-C}_5\text{Me}_5$)TiMe₃ in 1 ml of solvent] and coinitiator (32 mg B(C₆F₅)₃ in 2 ml of solvent) to *ca.* 2.5 ml monomer dissolved in 10 ml solvent. Polymerizations were terminated by addition of 1% HCl in methanol, and the solid polymers were reprecipitated from hexane or CH₂Cl₂ solutions with methanol, washed and dried at 60°C for *ca.* 24 h. All polymers were characterized using GPC at room temperature in THF on a Waters chromatograph equipped with RI and UV detectors, the data being analysed using polystyrene standards.

‡ Obtained from Polysar Ltd.

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