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Zirconocenes as Initiators for Carbocationic Isobutene Homo- and Copolymerizations

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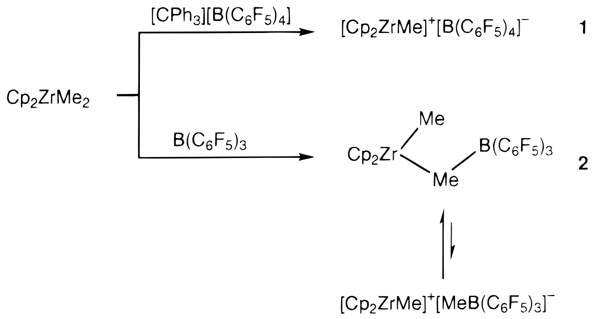
ABSTRACT: The zirconocene complexes Cp_2ZrMe_2 and $Cp^*_2ZrMe_2$ activated with $B(C_6F_5)_3$ initiate the carbocationic polymerization of isobutene and isobutene−isoprene copolymerizations to IIR rubbers at temperatures as high as −30 °C. Unlike conventional metal halide initiators, these metallocene-based initiator systems produce both homo- and copolymers of broadly similar molecular weights. Copolymers prepared in the presence of ca. 2 mol % isoprene show a diene incorporation rate of 1.4−1.7%, with the typical 1,4-trans structure. Comparison of the effectiveness of zirconocene dialkyls with that of the metallocene hydrolysis products $Cp^*_2Zr(OH)_2$ and $(Cp_2ZrMe)_2(\mu\text{-O})$ in the presence of $B(C_6F_5)_3$ suggests that initiation by traces of protons is less efficient than initiation by cationic metallocene alkyl species, while oxo-bridged complexes $(Cp'_2ZrMe)_2(\mu\text{-O})/B(C_6F_5)_3$ ($Cp' = C_5H_5$ or $C_5H_4SiMe_3$) are inactive.

Introduction

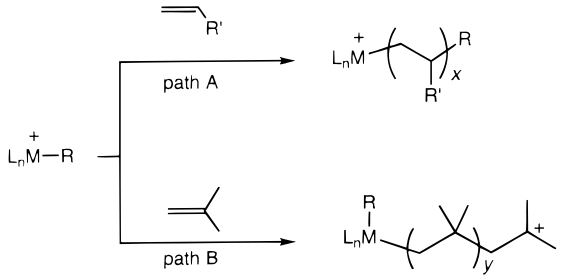
The role of cationic group 4 metallocene alkyl complexes of the type $[Cp_2MR]^+$ (M = Ti, Zr, Hf) as catalysts for the polymerization of 1-alkenes is well-established.[1] Complexes of this type can be generated by treatment of metallocene dialkyls with electrophilic activators such as $B(C_6F_5)_3$ or $[CPh_3][B(C_6F_5)_4]$ (Scheme 1) to give compounds of types **1** and **2**, respectively; the resulting coordinatively and electronically unsaturated species are able to catalyze the polymerization of 1-alkenes by an insertion mechanism (Scheme 2, path A).

However, the highly electrophilic character of cationic metallocenes $[Cp_2MR]^+$ and their behavior as extremely strong Lewis acids suggests that they may also be able to mediate polymerization reactions in a different way, by acting as initiators for carbocationic polymerizations. This reaction mode can become favorable with olefins where the insertion mechanism is disfavored for steric reasons, as is the case with isoalkenes, notably isobutene (Scheme 2, path B). Following this line of reasoning, Baird et al.[2] have recently demonstrated the ability of $Cp^*TiMe_3/B(C_6F_5)_3$ mixtures to initiate the polymerization of isobutene and the copolymerization of isobutene with isoprene ($Cp^* = C_5Me_5$), to give homopolymers with M_w values ranging from 2×10^5 at −78 °C to ca. 3×10^4 at −20 °C, while we have described similar homo- and copolymerizations initiated by $[AlCp_2]^+[MeB(C_6F_5)_3]^-$ to give polymers with high molecular weights more closely comparable to commercial polymers.[3] Conceptually, these new cationic organometallic initiators are related to cationic metal halide species such as BCl_2^+ or $AlBr_2^+$ which are thought to arise by self-ionization in classical metal halide-initiated isobutene polymerizations.[4] We report here on the role of $[Cp_2ZrMe]^+$ as a highly effective initiator in isobutene homo- and copolymerizations. While this work was in progress, we became aware of the related work by Shaffer et al. on the homopolymerization of isobutene in chlorobenzene solutions using $Cp_2MMe_2/[CPh_3][B(C_6F_5)_4]$ and $H_2O/Cp_2MMe_2/[CPh_3][B(C_6F_5)_4]$ mixtures as initiators (M = Zr, Hf).[5]

Scheme 1



Scheme 2



Results and Discussion

The copolymerization of isobutene with isoprene is a large-scale industrial process for the production of isobutene−isoprene rubber (IIR) and employs an $AlCl_3/H_2O$ initiator system as a slurry in chloromethane. Polymerization is initiated by protonation of the monomer to generate *tert*-butyl cations. Under these conditions proton transfer from the carbocationic propagating species of the growing chain to monomer is very facile, a reaction that must be suppressed in order to obtain products of adequately high molecular weights ($M_n \approx (1-2) \times 10^5$); the commercial process is therefore operated at approximately −100 °C.[6] The presence of bases such as Cl^- and H_2O, etc., in this system is most probably instrumental in facilitating chain termination and proton transfer. We reasoned therefore that the absence of such basic components might enable the

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Table 1. Isobutene Homopolymerization and Isobutene−Isoprene Copolymerizations Initiated with $Cp_2ZrMe_2/B(C_6F_5)_3$[a]

run	temp (°C)	isobutene (mL)	isoprene (mL)	polymer yield (g)	$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	M_w/M_n	isoprene incorporation (mol %)
1	−78	10		1.2	144.5	37	3.9	
2	−50	10		0.4	102.5	35.6	2.9	
3	−30	10		0.2	115	50.8	2.3	
4	−78	10	0.15	1.3	137	38	3.6	1.7
5	−50	10	0.15	0.9	177.5	33	3.6	1.4
6	−30	10	0.15	0.9	107	39	2.7	1.5

[a] Conditions: 50 μmol of Cp_2ZrMe_2 in 1 mL of CH_2Cl_2; 50 μmol of $B(C_6F_5)_3$ in 0.5 mL of CH_2Cl_2; stirring rate, 1000 rpm. The reactions were terminated after 5 min by injection of 2 mL of methanol.

Table 2. Isobutene Homo- and Copolymerizations in the Presence of $B(C_6F_5)_3$[a]

run	temp (°C)	isobutene (mL)	isoprene (mL)	polymer yield (g)	$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	M_w/M_n	isoprene incorporation (mol %)
7	−78	10		0.1	1800	714	2.5	
8	−78	10	0.15	0.02	87	18	5.0	1.3

[a] Conditions: 50 μmol of $B(C_6F_5)_3$ in 0.5 mL of CH_2Cl_2; no Cp_2ZrMe_2. Reaction time, 5 min.

synthesis of polymers of similar molecular weights at substantially higher temperatures. Halide-free initiators involving the "noncoordinating" very weakly basic anions[7] $[B(C_6F_5)_4]^-$ and $[MeB(C_6F_5)_3]^-$ therefore offer themselves as possible alternatives. It is noteworthy in this context that salts of CMe_3^+ with the weakly coordinating anion $[Sb_2F_{11}]^-$ are thermally sufficiently stable and resistant to deprotonation to allow crystallization and X-ray structure determination.[8]

Injecting dichloromethane solutions of Cp_2ZrMe_2 and $B(C_6F_5)_3$ in a 1:1 molar ratio into isobutene at −78 °C in a flame-dried all-glass reactor under rigorously anhydrous conditions leads to rapid polymerization. A survey of the ability of zirconocenes to act as initiators was initially carried out on a scale of 10 mL isobutene (cf. Table 1, runs 1−3). The polymerizations were terminated after 5−10 min by the injection of methanol. The polymer separates as a white precipitate which is isolated after washing with methanol. Comparatively high molecular weight polymers were produced in the temperature range from −78 to −30 °C; as is typical for cationic polymerizations, both yields and polymer molecular weights decreased with increasing temperature. All polymers produced with this system are nonsticky elastomers with little or no tendency to show cold flow properties. The polymerizations described here were carried out in neat isobutene containing only minor amounts (1.5 mL) of dichloromethane used as solvent for the metallocene stock solutions, unlike the $Cp_2MMe_2/[CPh_3][B(C_6F_5)_4]$ initiated polymerizations referred to above[5] which were conducted in chlorobenzene as the solvent.

The $Cp_2ZrMe_2/B(C_6F_5)_3$ system is similarly active for isobutene copolymerizations in the presence of ca. 2 mol % of isoprene to give high molecular weight materials (Table 1, entries 4−6). NMR analysis of the copolymers showed the expected structure,[9] with the diene being incorporated predominantly 1,4-trans, at incorporation levels of 1.4−1.7%.

In conventional metal halide-initiated systems isoprene tends to act as both a retardant and a molecular weight regulator,[10] resulting in copolymers of substantially lower molecular weight than homopolymers obtained under identical conditions. This is also borne out drastically in the polymerizations initiated by $B(C_6F_5)_3$ alone (Table 2). Surprisingly, with the present $Cp_2ZrMe_2/B(C_6F_5)_3$ initiator system the molecular weights of the copolymers were remarkably similar to those of the homopolymers (compare for example Table 1, entries 1−3 versus entries 4−6; see also Table 4), and under these conditions a retarding effect of the diene component on either the rate of polymerization or the molecular weight was hardly noticeable. Since after a few propagation steps the course of the polymerizations should be unaffected by the nature of the initiating species, one might suspect the reason for this unusual effect to be related to the particular nature of the anion. However, neither the $[AlCp_2]^+[MeB(C_6F_5)_3]^-$ system nor copolymerizations with the recently developed cationic amido complex $[Zr\{N(SiMe_3)_2\}_3]^+[MeB(C_6F_5)_3]^-$ [11] show this behavior, and we must therefore defer detailed discussion of this phenomenon.

The unusual behavior of the metallocene initiators encouraged us to explore this system in more detail. Three parameters were addressed: (i) the possible initiation by traces of water, (ii) the influence of the initiator concentration, and (iii) counteranion effects.

(i) Influence of Water. Isobutene polymerizations are highly sensitive to traces of water, and indeed Shaffer et al. had found the addition of substoichiometric quantities of water to their $Cp^*_2MMe_2/[CPh_3][B(C_6F_5)_4]$ system (M = Zr, Hf) to be beneficial.[5] While Cp_2ZrMe_2 alone does not initiate polymerization, the addition of $B(C_6F_5)_3$ to isobutene at −70 °C in the *absence* of Cp_2ZrMe_2 results in the formation of rather small amounts of very high molecular weight polyisobutene, as might be expected in the case of very low initiator concentrations. The findings are understandable in view of the strong Lewis acidity and hygroscopic character of $B(C_6F_5)_3$ which is rarely obtained completely free of traces of the acidic hydrate $H_2O{\cdot}B(C_6F_5)_3$ (despite the preparation of $B(C_6F_5)_3$ from LiC_6F_5 and BBr_3 in dry hexane under anaerobic conditions). Characteristically, though, if isoprene is present, $B(C_6F_5)_3$ alone produces only trace amounts of polymer of substantially reduced molecular weight (Table 2), quite unlike the results obtained when combined with zirconocenes. Subsequent NMR studies on CH_2Cl_2 solutions of $B(C_6F_5)_3$ treated with the proton trap 2,6-di-*tert*-butylpyridine (DTBP) showed various batches of $B(C_6F_5)_3$ to contain 5−15 mol % of water, as illustrated in Figure 1 for a representative example, while no traces of moisture were detectable by this method in any of the solvents used or in solutions of Cp_2ZrMe_2.[12]

Water is known to react readily with Cp_2ZrMe_2 to give a number of hydrolysis products. The reaction of Cp_2-

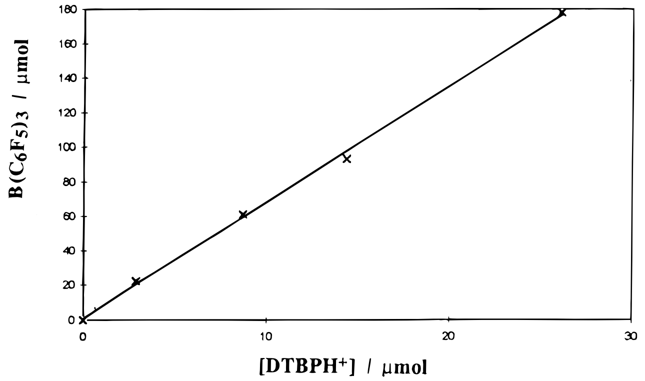
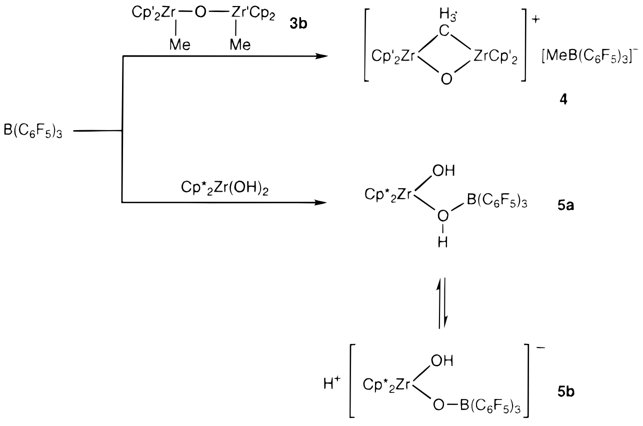


Figure 1. Dependence of H^+ concentration, measured as [$DTBPH^+$], on $B(C_6F_5)_3$ concentration in dichloromethane solution.

Scheme 3



ZrMe₂ with 1 equiv of water gives the oxo-bridged complex $(Cp_2ZrMe)_2(\mu\text{-}O)$ (**3a**).[13] Similarly, the hydrolysis of Cp'_2ZrMe_2 affords $(Cp'_2ZrMe)_2(\mu\text{-}O)$ (**3b**; Cp′ = $C_5H_4SiMe_3$). The hydrolysis of the sterically hindered pentamethylcyclopentadienyl complex $Cp^*_2ZrMe_2$ allows the isolation of $Cp^*_2ZrMe(OH)$ and $Cp^*_2Zr(OH)_2$.[14] The reaction of $B(C_6F_5)_3$ with **3b**, which was preferred for catalytic applications over the poorly soluble derivative **3a**, and with $Cp^*_2Zr(OH)_2$ was followed by variable temperature NMR and shown to proceed as indicated in Scheme 3.

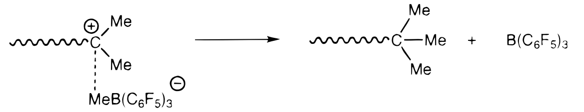
A rapid reaction occurs between **3b** and $B(C_6F_5)_3$ producing $[Cp'_2Zr(\mu\text{-}Me)(\mu\text{-}O)]^+[MeB(C_6F_5)_3]$ (**4b**). The reaction is very clean when performed on an NMR scale, and no further reaction occurs in the presence of an excess of $B(C_6F_5)_3$. The NMR data, especially the detection of eight signals for the eight nonidentical cyclopentadienyl hydrogen atoms, confirm the structure of the cation in **4b**, with a transoid conformation of the two $C_5H_4SiMe_3$ ligands on each Zr atom.

Combining $Cp^*_2Zr(OH)_2$ with $B(C_6F_5)_3$ leads immediately to the formation of the zwitterionic complex $Cp^*_2Zr(OH)(\mu\text{-}OH)B(C_6F_5)_3$ (**5**). The electron deficient borane coordinates to one of the oxygen lone pairs, producing two distinct chemical environments for the hydroxy hydrogens. Compound **5** appears to be thermally unstable, and on attempted isolation there was evidence for decomposition and water abstraction, with the formation of some $H_2O{\cdot}B(C_6F_5)_3$.

The formation of an adduct between a hydroxo complex such as $Cp^*_2Zr(OH)_2$ and $B(C_6F_5)_3$ to give **5** results in a significant increase in the acidity of the bridging OH group, as indicated by the equilibrium between **5a** and **5b** (Scheme 3).[15] If proton initiation was a significant factor in the observed polymerizations, the increased concentration of protons in $Cp^*_2Zr(OH)_2/B(C_6F_5)_3$ mixtures should result in increased polymer yields. The effect of these zirconocene hydrolysis products was therefore compared with the data of Table 1 and the performance of $Cp^*_2ZrMe_2/B(C_6F_5)_3$ (Table 3).

The best results were obtained with $Cp^*_2ZrMe_2/B(C_6F_5)_3$ (Table 3, runs 9−11) which produces higher molecular weights and yields than $Cp_2ZrMe_2/B(C_6F_5)_3$. "Proton enriched" $Cp^*_2Zr(OH)_2/B(C_6F_5)_3$ mixtures do produce homopolymers with even higher molecular weights, but at substantially reduced yields; i.e., the initiator concentration in this system is apparently significantly lower than in the case of metallocene dialkyls. No polymer at all was isolated from **3a** or **3b** activated by $B(C_6F_5)_3$. This lack of reactivity may be understood considering that for the cation in **4** to act as a polymerization initiator the methyl bridge would have to open, an unfavorable process. These results support the assumption that under the present conditions the cationic metallocene alkyl species of the type $[Cp_2ZrMe]^+$ do indeed act as initiators.

(ii) Influence of the Initiator Concentration. Increasing the volume of isobutene to 100 mL while keeping all other conditions constant except for extending the reaction time from 10 to 30 min generally leads to higher molecular weight polymers. The effect is particularly pronounced for homopolymerizations at −70 °C where the reduction of [Zr] (from 4.3×10^{-3} M in Table 1 to 0.5×10^{-3} M in Table 4) increased the M_w value 17-fold and the yield by a factor of 4.7 compared to 10 mL reactions (Table 4). The nature of growth terminating reactions in these systems is as yet unknown. One contributing factor is likely to be the irreversible recombination of the carbocationic chain terminus with the $[MeB(C_6F_5)_3]^-$ anion (eq 1) which can be expected to be reduced at high dilution, where dissociated and solvent separated ion pairs are expected to predominate over tight ion pairing.



(1)

The dilution effect on polymer molecular weights in isobutene−isoprene copolymerizations at −78 °C is less pronounced than for homopolymerizations; the molecular weight increases only about 6-fold. For both homo- and copolymerizations polymer molecular weights as well as yields decrease rapidly as temperatures are increased, to values similar to those observed at higher initiator concentrations (Tables 1 and 4).

The yields in these reactions were very sensitive to the efficiency of mixing of the two initiator components with isobutene, with rapid mixing producing little or no polymer. Under rapid mixing conditions and high dilution in isobutene the generation of the cationic species is possibly very inefficient. Reproducible yields are however achieved when Cp_2ZrMe_2 and $B(C_6F_5)_3$ are premixed in chilled (<−20 °C) dichloromethane solution prior to injection into the monomer, i.e., under conditions which favor the formation of ion pairs.

(iii) Counteranion Effects. The chain termination event described in eq 1 is not possible with $[B(C_6F_5)_4]^-$ as counteranion in place of $[MeB(C_6F_5)_3]^-$, and consequently the former anion could be expected to lead to

Table 3. Protic versus Nonprotic Zirconocene Initiators in Isobutene Homopolymerizations[a]

run	zirconium complex	temp (°C)	isobutene (mL)	polymer yield (g)	$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	M_w/M_n
9	$Cp^*_2ZrMe_2$	−70	10	3.5	1285	472	2.7
10	$Cp^*_2ZrMe_2$	−50	10	1.2	652	306	2.1
11	$Cp^*_2ZrMe_2$	−30	10	0.8	289	157	1.9
12	$Cp^*_2Zr(OH)_2$	−70	10	0.1	2500	740	4.0
13	$Cp^*_2Zr(OH)_2$	−50	10	0.1	1770	810	2.2
14	$Cp^*_2Zr(OH)_2$	−30	10	0.1	330	170	2.1
15	$(Cp'_2ZrMe)_2(\mu\text{-}O)$	−70	10	0			

[a] Conditions: 50 μmol of $Cp^*_2ZrX_2$ in 1 mL of CH_2Cl_2; 50 μmol of $B(C_6F_5)_3$ in 0.5 mL of CH_2Cl_2; stirring rate, 1000 rpm. The reactions were terminated after 5 min by injection of 2 mL of methanol.

Table 4. Isobutene Homo- and Copolymerizations at Low Initiator Concentrations[a]

run	temp (°C)	isobutene (mL)	isoprene (mL)	polymer yield (g)	$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	M_w/M_n	isoprene incorporation (mol %)
16	−78	100		5.7	2500	647	3.8	
17	−50	100		0.6	346	120	2.9	
18	−30	100		0.1	178	72	2.5	
19	−78	100	1.5	0.6	815	228	3.6	1.5
20	−50	100	1.5	0.5	291	100	2.9	1.7
21	−30	100	1.5	0.1	131	58	2.5	1.5

[a] Conditions: 50 μmol of Cp_2ZrMe_2 in 1 mL of CH_2Cl_2; 50 μmol of $B(C_6F_5)_3$ in 0.5 mL of CH_2Cl_2; stirring rate, 1000 rpm. The reactions were terminated after 30 min by injection of 2 mL of methanol.

Table 5. Isobutene Homo- and Copolymerizations with $Cp_2ZrMe_2/[CPh_3][B(C_6F_5)_4]$[a]

run	temp (°C)	isobutene (mL)	isoprene (mL)	polymer yield (g)	$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	M_w/M_n	isoprene incorporation (mol %)
22	−78	100		7.3	2260	500	1.7	
23	−30	100		0.3	554	160	3.5	
24	−78	100	1.5	1.4	458	218	2.1	1.6

[a] Conditions: 50 μmol of Cp_2ZrMe_2 in 1 mL of CH_2Cl_2; 50 μmol of $[CPh_3][B(C_6F_5)_4]$ in 0.5 mL of CH_2Cl_2; stirring rate, 1000 rpm. The reactions were terminated after 30 min by injection of 2 mL of methanol.

higher yields and/or molecular weights. The perfluorotetraphenylborate $[B(C_6F_5)_4]^-$ is known to be one of the least coordinating and least basic anions available,[16] and while $[MeB(C_6F_5)_3]^-$ may be able to stabilize a carbocation by interaction with the $CH_3{-}B$ substituent, an interaction between a $-CMe_2^+$ cation and a fluorine atom of $[B(C_6F_5)_4]^-$ is unlikely to be of significance in solution under the prevailing high-dilution conditions.

A comparison of the $Cp_2ZrMe_2/B(C_6F_5)_3$ and $Cp_2ZrMe_2/[CPh_3][B(C_6F_5)_4]$ initiator systems was therefore carried out (Table 5). As was the case with the $Cp_2ZrMe_2/B(C_6F_5)_3$ system, we found that, in order to initiate homo- and copolymerizations reproducibly, it is essential to premix the CPh_3^+ salt and the zirconocene dimethyl in chilled dichloromethane prior to injection into the isobutene. Over the temperature range of −70 to −30 °C yields are somewhat higher than those obtained with $[MeB(C_6F_5)_3]^-$, though not dramatically so, while at −78 °C the molecular weights are lower for both homo- and copolymerizations by factors of 1.1 and 1.8, respectively (though probably within the limits of reproducibility for reactions of this type). At −30 °C both the yield and the molecular weight of the isobutene homopolymer produced with $Cp_2ZrMe_2/[CPh_3][B(C_6F_5)_4]$ are significantly increased, and it appears that at higher temperatures the less coordinating anion is the more effective counteranion.

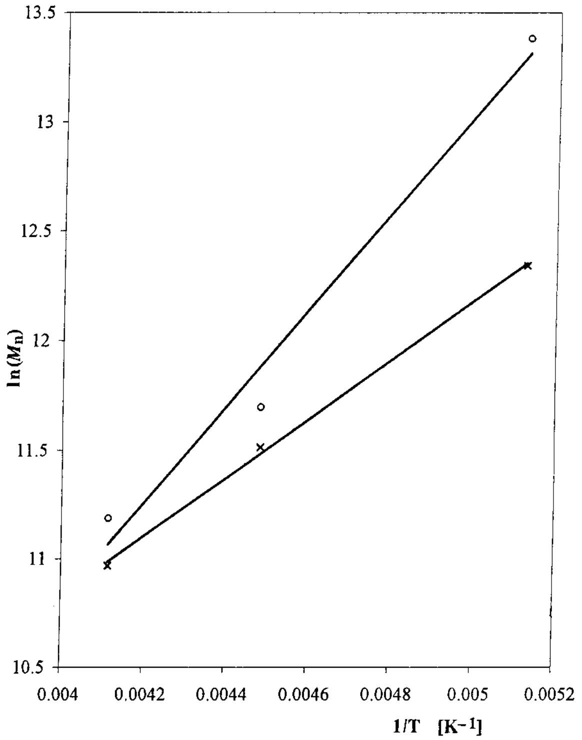


Figure 2. Arrhenius plot of ln(M_n) versus 1/T for isobutene homopolymerizations (○) and isobutene−isoprene copolymerizations (×) initiated by $Cp_2ZrMe_2/B(C_6F_5)_3$ (100 mL scale reactions; cf. Table 4).

The question arises whether the behavior of the metallocene initiated system is conceivably mechanistically different from conventional metal halide-based initiators. The polymerization activation energies were therefore determined from Arrhenius plots of log M_w against $1/T$.[10] There is a linear temperature dependence over the temperature range of 203−243 K; representative plots for homo- and copolymerizations are shown in Figure 2. The approximate E_{DP} values with the $Cp_2ZrMe_2/B(C_6F_5)_3$ initiator system (cf. Table 4) are −18.4 and −11.2 kJ mol^{-1} for the homo- and the copolymerizations, respectively. For the $ZrCp^*_2Me_2/B(C_6F_5)_3$ system the E_{DP} value for the copolymerization is -11.2 kJ mol^{-1}, the same as for Cp_2ZrMe_2, but the value for the homopolymerization has increased to -14.5 kJ mol^{-1}.

Kennedy and Squires[10] obtained an approximate E_{DP} of -23.42 kJ mol^{-1} for isobutene polymerization in methyl chloride using BF_3, $AlCl_3$, and $EtAlCl_2$ as initiators and for the copolymerization with the same systems observed a value which was “somewhat less”. Toman and Marek,[17] using VCl_4 as the initiator under similar conditions, obtained an activation energy of -28.7 kJ mol^{-1} for the homopolymerization and -28.0 kJ mol^{-1} for the copolymerization. Evidently, although the values obtained with metallocene initiators indicate a reduced temperature dependence of molecular weight compared to halide initiators over the same temperature range, they fall within a similar region and give no indication for a qualitatively different propagation and termination mechanism.

Conclusion

Mixtures of zirconocene dimethyl complexes and either $B(C_6F_5)_3$ or $[CPh_3][B(C_6F_5)_4]$ function as initiators for the carbocationic polymerization of isobutene and its copolymerization with isoprene to nonsticky elastomeric high molecular weight polymers at temperatures as high as -30 °C. The active initiator species is most likely to be the 14-electron cation $[Cp_2ZrMe]^+$, while initiation by potential proton sources such as the hydrolysis products of zirconocene dialkyls is significantly less effective. The polymer molecular weights are sensitive to the initiator concentration and the nature of the counteranion. Remarkably, unlike conventional isobutene−isoprene copolymerizations, the zirconocene initiators are only slightly influenced by the retarding effect of isoprene.

Experimental Section

General Procedures. All manipulations are performed under dried nitrogen using Schlenk techniques. Solvents were dried over sodium−potassium alloy (light petroleum, bp 40−60 °C), sodium (toluene), or CaH_2 (dichloromethane) and distilled under nitrogen prior to use. Deuterated solvents were stored over activated 4A molecular sieves and degassed by several freeze−thaw cycles. Isoprene was distilled from sodium prior to use. Isobutene was dried by passing through 4A molecular sieves and stored over $Et_2AlOC_6H_{13}$ at -78 °C. The compounds Cp_2ZrMe_2,[18] $Cp^*_2ZrMe_2$,[19] $B(C_6F_5)_3$,[20] and $[CPh_3][B(C_6F_5)_4]$[21] were prepared following literature procedures. NMR spectra were recorded on a Bruker DPX300 instrument and referenced to the residual solvent protons. Molecular weight analyses were recorded by RAPRA Technology Ltd. using gel permeation chromatography with tetrahydrofuran solvent and PL gel 2 × mixed bed-B, 30 cm, 10 μm columns.

Synthesis of $Cp^*_2Zr(OH)_2$. $ZrCp^*_2Me_2$ (0.78 g, 2.0 mmol) was dissolved in light petroleum (20 mL), and 2 equiv of deoxygenated water (0.07 g, 4.1 mmol) was added. After 5 h the solvent was removed in vacuo. Extraction with toluene yielded $Cp^*_2Zr(OH)_2$ (0.62 g, 78%) as a white microcrystalline solid. The NMR spectroscopic data were in agreement with the literature.[14]

Synthesis of $[(Cp'_2ZrMe)_2(\mu\text{-}O)]$ (3b). Cp'_2ZrMe_2 (0.55 g, 1.4 mmol) was dissolved in petroleum ether (20 mL) and a slight excess of deoxygenated water (0.03 g, 1.6 mmol) added. The solution was stirred for 12 h, the solvent removed in vacuo. and the product extracted with toluene. Recrystallization gave a white microcrystalline compound; yield, 0.69 g (63%). ^1H NMR (C_6D_6, 20 °C): δ 0.29 (s, 36 H, $SiMe_3$), 0.45 (s, 6 H, Zr−Me), 6.10, (m, 4 H, Cp′), 6.13 (m, 4 H, Cp′), 6.18 (t, $J = 2.07$ Hz, 2 H, Cp′) 6.19 (t, $J = 2.04$ Hz, 2 H, Cp′), 6.27 (t, $J = 2.07$ Hz, 2 H, Cp′), 6.28 (t, $J = 2.04$ Hz, 2 H, Cp′). ^{13}C NMR (C_6D_6, 20 °C): δ 0.52 ($SiMe_3$), 21.85 (Zr−Me), 112.24, 116.75, 119.10, 119.96, 115.04 (all Cp′). Anal. Calcd for $C_{34}H_{58}OSi_4Zr_2$: C, 52.52; H, 7.52. Found: C, 52.50; H, 7.15.

Preparation of $[(Cp'_2Zr)_2(\mu\text{-}Me)(\mu\text{-}O)]^+[MeB(C_6F_5)_3]^-$ (4b). Compound **3b** (20 mg, 25.7 μmol) was placed in an NMR tube, and a toluene-d_8 solution of $B(C_6F_5)_3$ (14 mg, 27.3 μmol) was added. The reaction proceeds cleanly to give a single product **4b**. ^1H NMR (C_7D_8, 20 °C): δ 0.11 (s, 36 H, $SiMe_3$), 0.26 (s, 3 H, Zr−Me), 1.22 (br, 3 H, B−Me), 6.11 (t, $J = 2.94$ Hz, 2 H, Cp′), 6.12 (t, $J = 2.79$ Hz, 2 H, Cp′), 6.22 (t, $J = 2.94$ Hz, 2 H, Cp′), 6.23 (t, $J = 2.79$ Hz, 2 H, Cp′), 6.53 (t, $J = 2.50$ Hz, 2 H, Cp′), 6.54 (t, $J = 1.82$ Hz, 2 H, Cp′), 6.67 (t, $J = 2.50$ Hz, 2 H, Cp′), 6.68 (t, $J = 1.82$ Hz, 2 H, Cp′). ^{11}B NMR (C_7D_8): δ −13.76. ^{13}C NMR (C_7D_8): δ −0.3 (Zr−Me−Zr), 11.1 (br, Me−B), 118.2, 119.1, 124.3, 126.6, 129.2 (all Cp′), 137.2 (d, $J_{CF} = 248.2$ Hz, *m* −C_6F_5), 138.8 (d, $J_{CF} = 241.4$ Hz, *p*-C_6F_5), 148.7 (d, $J_{CF} = 238.3$ Hz, *o*-C_6F_5).^{19}F NMR (C_7D_8): δ −132.2 (d, $J_{FF} = 20.69$ Hz, *o*-C_6F_5), −164.9 (t, $J_{FF} = 20.69$, *p*-C_6F_5), −167.2 (t, $J_{FF} = 19.4$ Hz, *m*-C_6F_5).

Preparation of $Cp^*_2Zr(OH)(\mu\text{-}OH)B(C_6F_5)_3$ (5). $Cp^*_2Zr(OH)_2$ (16 mg, 40.4 μmol) was placed in an NMR tube, and a toluene-d_8 solution of $B(C_6F_5)_3$ (21 mg, 41.0 μmol) was added. A bright yellow solution formed immediately. ^1H NMR (C_7D_8, 20 °C): δ 1.53 (s, 30 H, C_5Me_5), 3.22 (s, 1 H, $Zr{-}OH_{term}$), 6.27 [s, vbr, 1 H, Zr(μ-OH)B]. ^{11}B NMR (C_7D_8): δ −0.10. ^{13}C NMR (C_7D_8): δ 10.16 ($C_5\mathit{Me}_5$), 123.4 (C_5Me_5), 137.2 (d, $J_{CF} = 249.1$ Hz, *m*-C_6F_5), 140.0 (d, $J_{CF} = 248.1$ Hz, *p*-C_6F_5), 148.3 (d, $J_{CF} = 244.4$ Hz, *o*-C_6F_5). ^{19}F NMR (C_7D_8): δ −131.8 (d, J_{FF} 20.7 Hz, *o*-C_6F_5), −158.3 (t, $J_{FF} = 20.7$ Hz, *p*-C_6F_5), −164.6 (t, $J_{FF} = 20.7$ Hz, *m*-C_6F_5).

Analysis of Water Content of $B(C_6F_5)_3$. To a mixture of 2,6-di-*tert*-butylpyridine (DTBP) (0.1 mL, 0.44 mmol) in CH_2Cl_2 (0.4 mL) containing CD_2Cl_2 (0.1 mL) was added solid $B(C_6F_5)_3$ in small portions. After each addition the amount of water is estimated by ^1H NMR from the change in relative intensities of the CMe_3 signals for DTBP and $DTBPH^+$. Representative data are indicated in Figure 1.

Polymerization Reactions. Polymerizations were carried out in all-glass reactors of either 20 or 150 mL capacity. The apparatus was flame-dried in vacuo prior to use. The appropriate amount of dry isobutene was condensed into the reactor and equilibrated at the given temperature. For copolymerizations isoprene was added via syringe. The mixture was stirred magnetically at 1000 rpm. For 10 mL reactions, $B(C_6F_5)_3$ in 0.5 mL of dichloromethane was then injected, followed by Cp_2ZrMe_2, in 1.0 mL of dichloromethane. Alternatively, 1.5 mL of a cold stock solution of a 1:1 mixture of Cp_2ZrMe_2 and $B(C_6F_5)_3$, corresponding to 50 μmol of zirconium complex, was injected. The reactions were terminated typically after 10 min (30 min for copolymerizations at 100 mL scale) by injecting 2 mL of methanol. After venting the excess monomer, the polymer was washed with methanol and dried at 60 °C for 24 h to constant weight.

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