ACCOUNTS
of chemical research

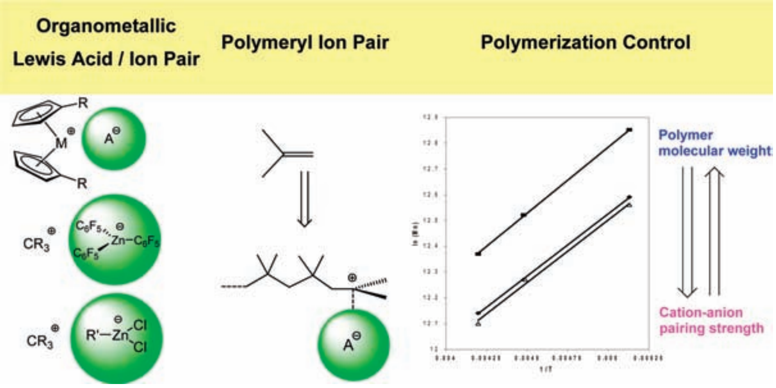
Highly Electrophilic Organometallics for Carbocationic Polymerizations: From Anion Engineering to New Polymer Materials

MANFRED BOCHMANN*

Wolfson Materials and Catalysis Centre, School of Chemistry, University of East Anglia, Norwich NR4 7TJ, U.K.

RECEIVED ON MARCH 9, 2010

CONSPECTUS



Ion–ion interactions are a crucial but often overlooked aspect of many polymerization reactions. The precise nature of cation–anion binding is as yet poorly understood, and little is known of the extent of ionic interactions in the typically nonaqueous, low-polarity reaction media of most polymerizations. Nevertheless, adequate control of cation–anion interactions can greatly enhance the productivity and efficiency of chemical processes and can provide low-energy alternatives to current methods. This is illustrated here with the carbocationic polymerization of isoalkenes.

Carbocationic polymerizations involve, as the name implies, carbocations as propagating species. Of the various types of substrates that can be polymerized cationically, the copolymerization of isobutene to isobutene–isoprene rubber stands out as the only large-scale, industrially important implementation of this reaction type. The products, elastomers with controlled degrees of unsaturation for subsequent cross-linking, have excellent gas barrier and mechanical dampening properties that make them indispensable components in polymer composites. For such applications, the polymer molecular weight has to be high, $\sim 5 \times 10^5$ g/mol, with 1–2 mol % isoprene. Cationic polymerizations are however notoriously difficult to control. As a means of suppressing chain transfer, the process is carried out at temperatures as low as -100 °C, with aluminum chloride initiators in chloromethane. Current industrial production of isobutene–isoprene butyl rubber is thus highly energy intensive and produces aluminum and chloride effluent.

This Account summarizes how highly electrophilic organometallics coupled with new types of very weakly coordinating counteranions can provide the basis for a more environmentally friendly, lower energy alternative. Because any copolymerization of two monomers, here primarily isobutene and isoprene, leads to two different propagating species, each of which is characterized by different chain growth and chain termination kinetics, variation of the associated counteranions can give rather unexpected results. With judicious choice of the initiator and the counteranion, new chemistry can be injected into such processes and can open avenues to new families of polymer materials.

Mechanistic investigations of the initiation process with zirconocene hydrides illustrate the complexity of this first step. Replacing aluminum with zinc initiators not only provides a nontoxic alternative but also generates a system in which the polymer molecular weight is much less affected by temperature and comonomer concentration, which can lead to a range of products, from oligomeric lubricant precursors to C═C-rich high-molecular-weight elastomers. The key in all these cases is the construction of either preformed or in situ-generated complex anions that are resistant

10.1021/ar100044s

to electrophilic or redox degradation and are capable of stabilizing tightly associated carbocations. Such initiator systems allow much more benign operating temperatures, reduce the need for chlorocarbon solvents, and can operate at concentrations as low as 5×10^{-5} M. Along the way are provided the first examples of structurally characterized *sec*-alkyl carbocations and carbocation salts of organometallic zincates.

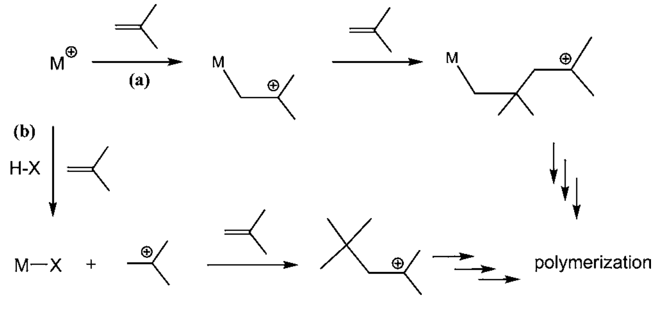
1. Introduction

The polymerization of 1-alkenes mediated by Lewis acidic metal complexes can follow two distinct pathways: (i) by migratory insertion of the 1-alkene into a metal−alkyl bond or (ii) via the formation of a carbocation as propagating species.[1] Polymerization by migratory insertion is the principle of chain growth in Ziegler−Natta catalysis. Here, the monomer binds to a Lewis acidic metal center prior to the migratory chain growth step.[2] Polymerization by a carbocationic mechanism, on the other hand, involves attack of a cationic species M^+ or H^+ on the C=C bond of the monomer, thus creating a carbocation, which acts as propagating species. The major industrially relevant process that uses this principle is the production of isobutene−isoprene butyl rubber ("IIR"). Because of its excellent gas barrier properties, this material is predominantly used as inner tubes or liners of car tires but also as cable insulation and vibration dampers and in sealants and gaskets.[3]

Which polymerization pathway is favored depends on the substitution of the alkene (Scheme 1). Olefin coordination in Ziegler-type catalysts is dissymmetric;[4] the polarity this induces is the basis for the migratory chain growth process. The metal here acts as the catalyst and is involved in every chain growth step.[5]

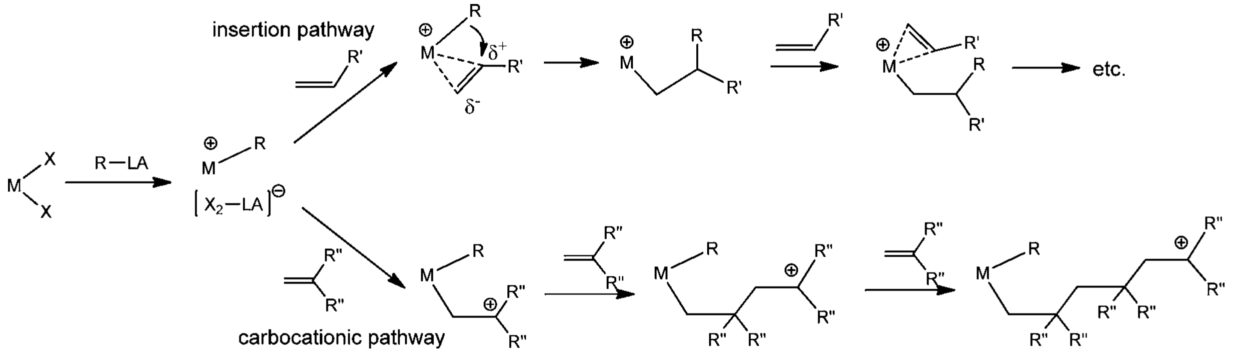
In 1,1-disubstituted alkenes, on the other hand, steric as well as electronic factors favor an even greater polarization of the coordinated monomer, leading to carbocations as propagating species (Scheme 2). Such carbocations may be the result of η^1-coordination of the isoalkene to M^+ or be formed indirectly by the reaction of M^+ with traces of moisture, to give highly reactive protons capable of attacking the monomer and thus initiating the same reaction sequence. In the absence of direct evidence for metal-bound initiating species, it is not easy to distinguish between the two modes of initiation; in any case, the resulting polymers are identical.

SCHEME 2. Proposed Isobutene Polymerization Mechanisms by (a) Direct or (b) Indirect Initiation by a Lewis Acidic Metal Center, M^+



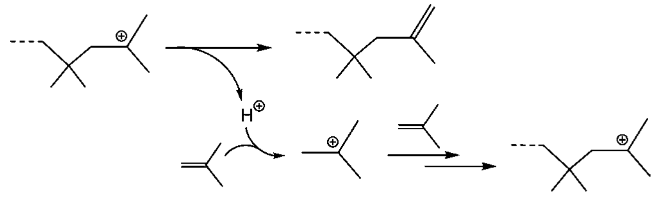
Cationic isobutene (IB) polymerizations differ from catalyzed olefin polymerizations in several important respects. First, chain growth proceeds essentially without an activation barrier and is therefore facile even at very low temperatures. Second, since the propagating species is a *tert*-carbocation $[-CH_2CMe_2]^+$, deprotonation and H^+ transfer to monomer is a major competing reaction pathway (Scheme 3). For most applications, high molecular weight polymers ($\bar{M}_w \approx 5 \times 10^5$ g/mol) are required, and this facile chain transfer has to be suppressed. This means operating large-scale processes at very low temperatures, which is costly and energy intensive. Third, IIR, the most important material, is a copolymer with isoprene (IP); this however is a potent retardant and reduces

SCHEME 1. General Polymerization Mechanisms for (A) Migratory Insertion of 1-Alkenes and (B) Carbocationic Polymerization by Isoalkenes[a]



[a] LA = Lewis acid, X = halide; R, R′, R″ = alkyl substituents.

SCHEME 3. Thermally Induced Chain Transfer in Isobutene Polymerizations



both yield and polymer molecular weight; the isoprene content in commercial polymers is therefore limited to 2−2.5 mol %. Overcoming this limitation remains an important research target.

Various Lewis acids have been employed as initiators for IB/IP copolymerizations. The prominent commercial process for the production of IIR uses an initiating system based on $AlCl_3$ in chloromethane in the presence of water at low temperatures (ca. −100 °C).[3] This is a proton-initiated system. Other systems generate carbocations directly; for example, mixtures of alkyl aluminum halides and alkyl halides, R−X, lead to carbocations R^+ by halide abstraction (eq 1).[6]

$$R'AlCl_2 + R{-}Cl \rightleftharpoons [R]^+[R'AlCl_3]^- \qquad (1)$$

For Et_2AlCl, self-ionization to $[AlEt_2]^+[Et_2AlCl_2]^-$ has been proposed,[7] although from what is now known[8] about the instability of $[AlEt_2]^+$, the formation of aluminum alkyl cations in meaningful concentrations seems highly unlikely. Carbocationic polymerizations using metal halide initiators have recently been reviewed.[9]

Any carbocationic propagating species is of course paired with a counteranion derived from whatever Lewis acid initiator had been used. Since metal halide anions such as BCl_4^- and $AlCl_4^-$ have comparatively high proton affinities, they facilitate deprotonation unless cooled to very low operating temperatures; this presents a major limitation. This Account summarizes the role of organometallic Lewis acids in developing systems designed to overcome the limitations of temperature, molecular weight, and composition that have the potential of providing more environmentally friendly cationic polymerization processes.[10]

Extremely weakly coordinating anions such as $[B(C_6F_5)_4]^-$ are now common in polymerization catalysis.[11] It was realized that the same anions can play an important role in cationic polymerizations: their extremely low proton affinities might enable cationic polymerization processes to be conducted at significantly higher operating temperatures, with concomitant improvements in energy efficiency and environmental benefits, without loss in polymer molecular weight.

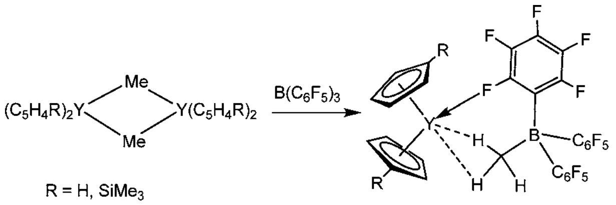
2. Metallocene Complexes as Initiators for Isobutene Polymerizations

The first example of a well-defined cationic aluminum complex capable of inducing cationic isobutene polymerizations was reported in 1996 (eq 2).[12]

$$Cp_2AlMe + B(C_6F_5)_3 \rightarrow [Al(\eta^5\text{-}Cp_2)]^+[MeB(C_6F_5)_3]^- \qquad (2)$$

The $[AlCp_2]^+$ cation shows a sharp ^{27}Al NMR signal at δ −126.4. It initiates IB polymerizations and IB/IP copolymerizations at −25 to −78 °C to give high-molecular weight products with up to 2.7 mol % isoprene content.[13] By contrast, the more stable analogues $[Al(C_5Me_5)_2]^+$ and $[Al(C_5HMe_4)_2]^+$ have no or moderate polymerization activity.[14]

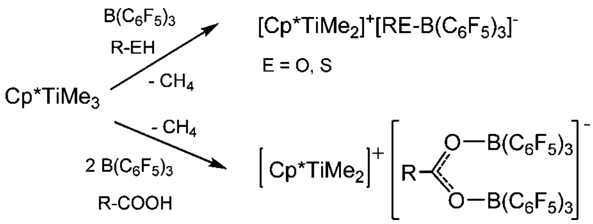
Whereas $[AlCp_2]^+$ adopts a symmetrical sandwich structure, trivalent metals with larger ionic radii form complexes with coordinated anions, as in $(C_5H_4R)_2Y(\mu\text{-}Me)B(C_6F_5)_3$ (R = H, $SiMe_3$) (eq 3). These isolated complexes, as well as mixtures of $[(C_5H_4R)_2YMe]_2$ with $[CPh_3]^+[B(C_6F_5)_4]^-$, polymerize isobutene at −50 to −78 °C to high molecular weight polymers. There is a pronounced anion effect, with $[B(C_6F_5)_4]^-$ giving higher $\bar{M}_w$ values, >10^6 g/mol.[15]



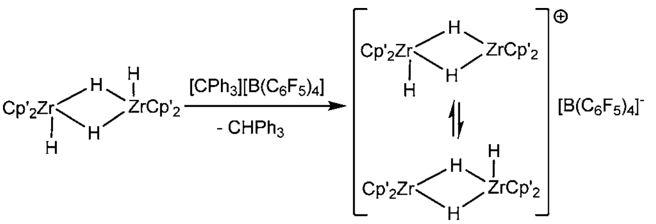
(3)

Initiator systems based on group 4 metallocenes have proven to be particularly successful in terms of initiator efficiency and molecular weight control by the anion. The first example was $Cp^*TiMe_2(\mu\text{-}Me)B(C_6F_5)_3$ ($Cp^* = C_5Me_5$) which was reported by Baird[16−21] as well as Shaffer[22,23] who also investigated a series of zirconocene and hafnocene dimethyl complexes activated with $[CPh_3][B(C_6F_5)_4]$. These systems homopolymerize isobutene in chlorobenzene or dichloromethane at temperatures of −75 to −20 °C. At −60 °C in toluene, $Cp^*TiMe_2(\mu\text{-}Me)B(C_6F_5)_3$ gave IB−IP copolymers with $\bar{M}_w \approx 125\,000$ (2 mol % IP).[18] Replacing $B(C_6F_5)_3$ with $[CPh_3][B(C_6F_5)_4]$ improved polymer yields but not the molecular weight, while surprisingly $Cp^*TiMe_3/Al(C_6F_5)_3$ showed only very low activity.[19] The system can be improved by adding long-chain alcohols, thiols, or carboxylic acids, which react with $B(C_6F_5)_3$ to give even less coordinating anions (Scheme 4). High conversions were achieved, particularly in polar solvents like CH_2Cl_2, with $\bar{M}_w \approx (3{-}5) \times 10^5$ g/mol at −30 °C (IP content 1−1.7 mol %), while in toluene, yields and molecular weights were much reduced.[20,21]

SCHEME 4. Titanium-Based Initiators with Modified Borate Anions



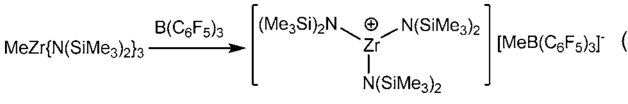
SCHEME 5. Formation of Cationic Zirconocene Hydride Initiators



The performance of initiators for cationic polymerizations depends strongly on the reaction conditions, in particular, the solvent, and the way the initiator is introduced. While studies with $Cp^*TiMe_3/B(C_6F_5)_3$ were best conducted in dichloromethane or methyl chloride (i.e., solvents that assist ionization), $Cp_2ZrMe_2/B(C_6F_5)_3$ and $Cp_2ZrMe_2/[CPh_3][B(C_6F_5)_4]$ gave best results in our hands if the metallocene and activator were allowed to prereact in a small amount of dichloromethane and then injected into neat IB or IB/IP mixtures. This also reduces the use of chlorocarbons. Injecting Cp_2ZrMe_2 and $B(C_6F_5)_3$ separately proved ineffective.

Initial IB homo- and copolymerizations with the "parent" zirconocene system, $Cp_2ZrMe_2/B(C_6F_5)_3$, at IB/Zr ratios of 2000:1 at −78 to −30 °C produced polymers of reasonably high but not outstanding molecular weight ($\bar{M}_w \approx (1-1.5) \times 10^5$).[24] It was shown that these reactions are not proton initiated. Increasing the IB/Zr ratio 10-fold led to a significant increase in both polymer yield and $\bar{M}_w$. In contrast to $H^+/AlCl_3$ initiated systems, the molecular weights of IB—IP copolymers produced with metallocenes were found to be essentially the same as the homopolymers, a very unusual feature in cationic polymerizations. IB/IP copolymerizations with zirconocenes are also much less temperature dependent than those with conventional aluminum-based systems; this fact could be exploited for the production of high molecular weight materials at higher temperatures.

As an alternative to zirconocene dimethyls, the methylamido complex $MeZr\{N(SiMe_3)_2\}_3$ has some attractions since it is insensitive to water. Activation with $B(C_6F_5)_3$ gives $[Zr\{N(SiMe_3)_2\}_3]^+[MeB(C_6F_5)_3]^-$; the anion is not coordinated to Zr for steric reasons (eq 4). At IB/Zr ratios of 2100:1, the homo- and copolymer molecular weights were significantly higher than those obtained with $Cp_2ZrMe_2/B(C_6F_5)_3$ under comparable conditions, while the temperature dependence of the molecular weight resembled that of the zirconocene system.[25]



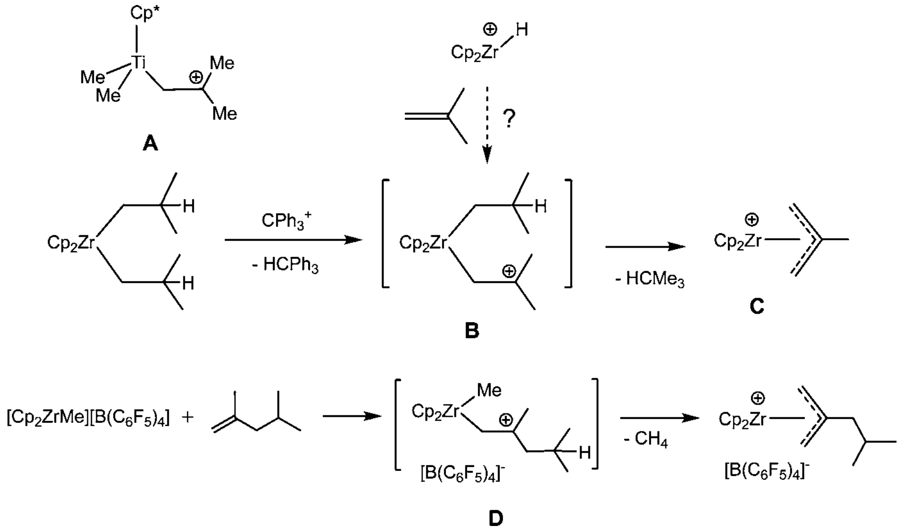
$$MeZr\{N(SiMe_3)_2\}_3 \xrightarrow{B(C_6F_5)_3} \left[(Me_3Si)_2N\overset{\oplus}{Zr}(N(SiMe_3)_2)N(SiMe_3)_2\right][MeB(C_6F_5)_3]^- \quad (4)$$

To be effective and to avoid local exotherms and hence loss of molecular weight control, an initiator system must be dispersed quickly in the reaction medium. This is particularly important for initiators generated from ionogenic precursors like $Cp_2ZrMe_2/[CPh_3][B(C_6F_5)_4]$ in hydrocarbons since the ionic products tend to form oily phases, particularly at low temperatures, which represent high local initiator concentrations. While this may produce fast polymerization in the immediate vicinity of initiator droplets, encapsulation by the polymer can lead to rapid cessation of chain growth and to low polymer yields. It is therefore advantageous to improve the solubility of the initiator by modifying the ligand. For most of our metallocene studies this was achieved using $C_5H_4SiMe_3$ (Cp′) instead of C_5H_5. Careful monitoring of the internal reaction temperature proved necessary to ensure comparability of results in systematic studies.

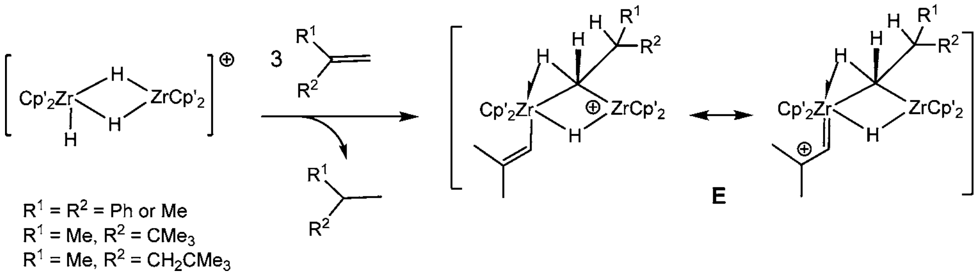
3. Zirconocene Hydride Initiators

Given the polarity of the M—H bonds in early transition metal hydrides, it might be expected that carbocationic propagating species are rapidly quenched by hydrides. We were therefore surprised to find that activating $[Cp'_2ZrH(\mu\text{-}H)]_2$ with $[CPh_3][B(C_6F_5)_4]$ generated particularly effective initiators; in fact, they gave such rapid polymerizations that adequate temperature control was a major problem. The reaction produces the fluxional zirconocene hydride $[Cp'_4Zr_2H_3][B(C_6F_5)_4]$ (Scheme 5).[26] By comparison, polymerizations with $Cp_2ZrMe_2/B(C_6F_5)_3$ or $[CPh_3][B(C_6F_5)_4]$ are typically isothermal or lead only to small temperature increases. Conversion rates and yields were dramatically higher than with $Cp'_2ZrMe_2/[CPh_3][B(C_6F_5)_4]$, while polymer molecular weights were comparable. Since the formation of the $[Cp'_4Zr_2H_3][B(C_6F_5)_4]$ is quantitative and irreversible, very low initiator concentrations can be employed, down to $[Zr] = 5 \times 10^{-5}$ mol/L and IB/Zr ratios of ca. 200 000:1 (limited only by the level of poisoning background impurities and the difficulties of handling very small amounts of liquids).[27] This system suffered much less from the commonly observed retarding effect of isoprene, and comonomer conversion rates and molecular weights obtained with the zirconocene hydride initiators were remarkably similar to IB homopolymers, especially at temperatures of −50 °C and above. Even at −30 °C IB/IP copolymerizations gave good

SCHEME 6. Zirconium η^1-Isoalkene Adducts As Possible Intermediates



SCHEME 7. Reaction of $[Cp'_4Zr_2H_3]^+$ with Isoalkenes and Possible Structure of the Initiating Species



conversions, under conditions where the Cp_2ZrMe_2 produced only trace amounts of product. The system also operates in the complete absence of chlorocarbon cosolvents; replacing CH_2Cl_2 in the premixing stage by a mixture of toluene and 1,2-difluorobenzene resulted in even higher molecular weights at −30 °C.[26]

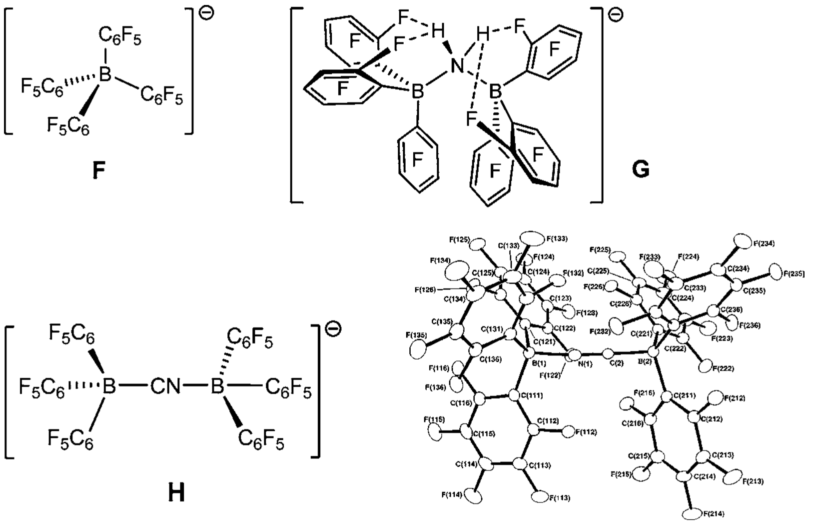
In view of the remarkable activity and apparent simplicity of this system, it was chosen for more detailed investigations into the nature of the initiating species and its reactions with isobutene.

Early in the investigation of cationic polymerizations with metallocene systems, Baird had proposed the η^1-isobutene adduct **A** as initiating species (Scheme 6).[17] It seemed reasonable to assume that a cationic zirconocene hydride might react with isobutene to give **B**. However, it was found that preformed $Cp_2Zr(i\text{Bu})_2$ reacts with $[CPh_3][B(C_6F_5)_4]$ even at −78 °C instantaneously to give the methallyl cation **C**, which is itself a powerful initiator for IB polymerizations. An intermediate of type **B** could not be detected. This, of course, does not prove that such a species does not play a kinetically important role, as the very recent detection of the related η^1-alkene adduct **D** shows.[28]

The reaction of $[Cp'_4Zr_2H_3][B(C_6F_5)_4]$ with isobutene is rather more complex. Using 1,1-diphenylethene as IB surrogate, it could be shown that the $[Cp'_4Zr_2H_3]^+$ cation was converted to another species before a carbocationic reaction ensues. This transformation was accompanied by two successive hydrogenation steps of 1,1-diphenylethene; since $[Cp'_4Zr_2H_3]^+$ contains only three hydrogens, a C−H activation process was suggested to generate the fourth. Spectroscopic studies provided support the formation of a binuclear species, **E** (Scheme 7), although an unequivocal characterization did not prove possible. Analogous products were found in reactions of $[Cp'_4Zr_2H_3]^+$ with 2,3,3-trimethylbut-1-ene, 2,4,4-trimethylpent-1-ene and isobutene itself. These species also contained ^{13}C NMR signals around δ 196, which were in agreement with the proposed formation of a cationic zirconium vinyl complex, although similar chemical shifts would also be expected for the carbocationic resonance structure of an η^1-coordinated isoalkene.[27] Whatever species turns out to be ultimately responsible for the initiation step, the reaction reveals the unexpected complexity of this process.

Whereas the organometallic species is responsible for the formation of the first carbocation, it is the associated counter-

SCHEME 8. Structures of Counteranions Used for Quantifying Anion Effects



anion that dominates the chain growth kinetics, depending on the strength of its interaction with the propagating carbocation. Very bulky nonbasic anions minimize such interactions and compete least with an incoming monomer. Anions **F**−**H**[29,30] (Scheme 8) were used in combination with $[Cp'_4Zr_2H_3]^+$ in IB/IP copolymerizations.

The temperature dependence of $\bar{M}_n$ turns out to be a very sensitive probe for quantifying the strength of the cation−anion association in liquid IB (Figure 1). While **F** and **G** give copolymers of nearly identical molecular weights, the linear anion **H** forms evidently the least associated ion pair and produces IB/IP copolymers with $\bar{M}_w \approx 5 \times 10^5$ even at −35 °C, the only system to reach such high values at these comparatively high temperatures.[31] Interestingly, the anion sequence **F** ≈ **G** < **H** mirrors that found in the zirconocene-catalyzed Ziegler-type polymerization of propene:[32] although the polymerization mechanisms are very different, clearly anion displacement by monomer is important in the rate-determining steps of either system.

Similarly important is the water content of the reaction mixture. The industrial $AlCl_3$-based system contains water in a chloromethane medium, although in this case its action is moderated by the very low reaction temperature. In polymerizations at higher temperatures water is a powerful chain transfer agent; for example, Figure 2 shows the decrease of $\bar{M}_w$ with increasing $[H_2O]$ at −35 °C. At this temperature, industry-standard molecular weights are only obtained under scrupulously dry conditions.

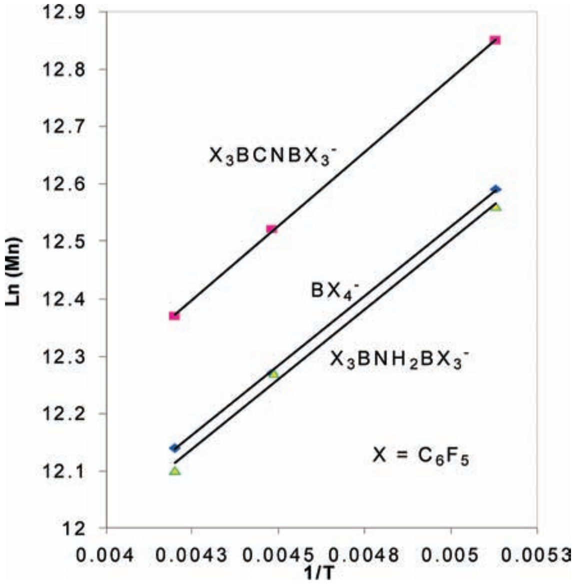


FIGURE 1. Counteranion control of $\bar{M}_n$ in IB/IP copolymerizations as a function of the reaction temperature.[27]

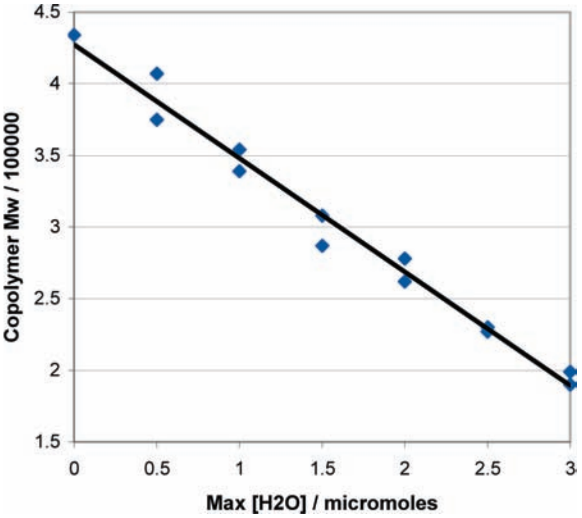


FIGURE 2. Dependence of $\bar{M}_w$ on $[H_2O]$ in IB/IP copolymerizations initiated with $[Cp'_4Zr_2H_3]^+[CN\{B(C_6F_5)_3\}_2]^-$ at −35 °C.

4. Zinc-Based Polymerization Initiators

Although zirconocene complexes activated with trityl perfluoroarylborates had demonstrated excellent initiator efficiencies and the ability to generate very high molecular weight IB/IP copolymers at temperatures as high as −30 °C and at initiator concentrations as low as 5×10^{-4} mol/L, the cost of the anions is not inconsiderable. The search for alternative systems with fewer costly C_6F_5 groups per initiating center led us to the hydrocarbon-soluble Lewis acid $Zn(C_6F_5)_2$(toluene), which is readily made from commercially available $ZnMe_2$ and $B(C_6F_5)_3$.[33] It was anticipated that $Zn(C_6F_5)_2$ would be a strong enough Lewis acid to react with *tert*-alkyl halides to generate reactive carbocations (eq 5). However, unlike the reactions of zirconocenes with trityl borates, eq 5 is an equilibrium, and therefore higher metal concentrations are required to generate adequate concentrations of initiating species.

$$Zn(C_6F_5)_2 + RCMe_2Cl \rightleftharpoons [RCMe_2]^+[ClZn(C_6F_5)_2]^- \qquad (5)$$

Zinc dichloride itself, unlike other simple metal halides, has so far not found use in IB polymerizations, most probably because of its insolubility in low-polarity solvents. Indeed we found mixtures of $RCMe_2Cl$ (R = Me, Ph) and $ZnCl_2$, whether as freshly made precipitate or finely ground solid, to be completely inactive under a variety of conditions. There have been only sporadic reports on the use of zinc compounds in IB polymerizations; for example, a 1971 patent claims a combination of BF_3 with metal dialkylamides including zinc[34] and mixtures of *t*-BuI, ZnI_2, and zinc powder under UV light reportedly give low yields of polyisobutene.[35]

By contrast, $Zn(C_6F_5)_2$ mixed with *t*-butyl chloride or cumyl chloride was highly effective for IB homo- and copolymerizations. The system is readily soluble in IB, CH_2Cl_2, and IB/CH_3Cl mixtures and gave high molecular weight copolymers over the tested temperature range of −78 to −35 °C. The ionization according to eq 5 and the formation of aryl zincate counteranions could be demonstrated by reacting $Zn(C_6F_5)_2$ with Ph_3CCl, which led to the isolation of $[CPh_3]^+[Zn(C_6F_5)_3]^-$ (Figure 3).[36] Clearly C_6F_5-substituted zincate anions are sufficiently resistant to electron or aryl transfer to stabilize carbocations in the solid state and in solution.

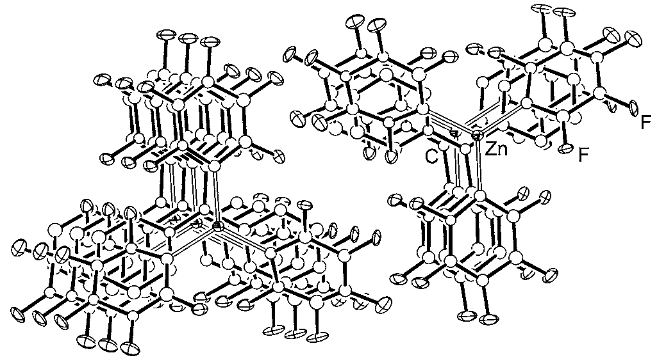


FIGURE 3. Crystal packing diagram of $[CPh_3][Zn(C_6F_5)_3]$.

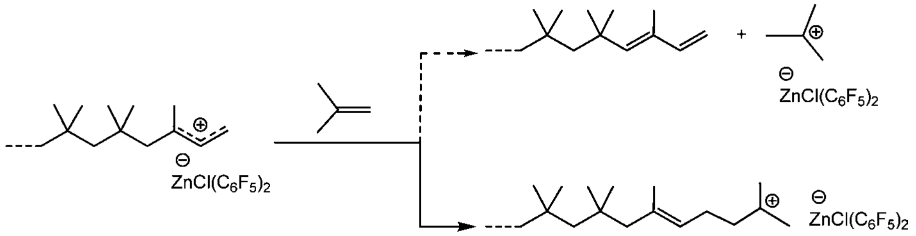
These zinc initiators allowed the incorporation of unexpectedly high amounts of isoprene. Up to about 10 mol % IP could be incorporated without significant reduction in yield or molecular weight. Equally important is the low gel content of these copolymers: high-IP copolymers can be prone to gel formation, which can make them unprocessable. With the zinc system, the gel content was found to be very low even at high IP incorporation.[37]

The ability of the growing polymer chain to produce isoprene-rich high molecular weight polymers, as opposed to chain termination after IP incorporation, depends on the relative reactivity of the terminal allylic cation−anion ion pair that is formed after isoprene addition to the chain. It appears that unlike ion pairs formed from aluminum chlorides, with zincate counteranions addition of IB to an allylic end group is more likely than chain termination (Scheme 9), and the energy difference between the $[-CH_2CMe_2^+ \cdots X^-]$ and the $[-CH_2C(Me)CH{=}CH_2^+ \cdots X^-]$ ion pairs seems to be less for X^- = perfluoroarylzincate than for chloroaluminates.

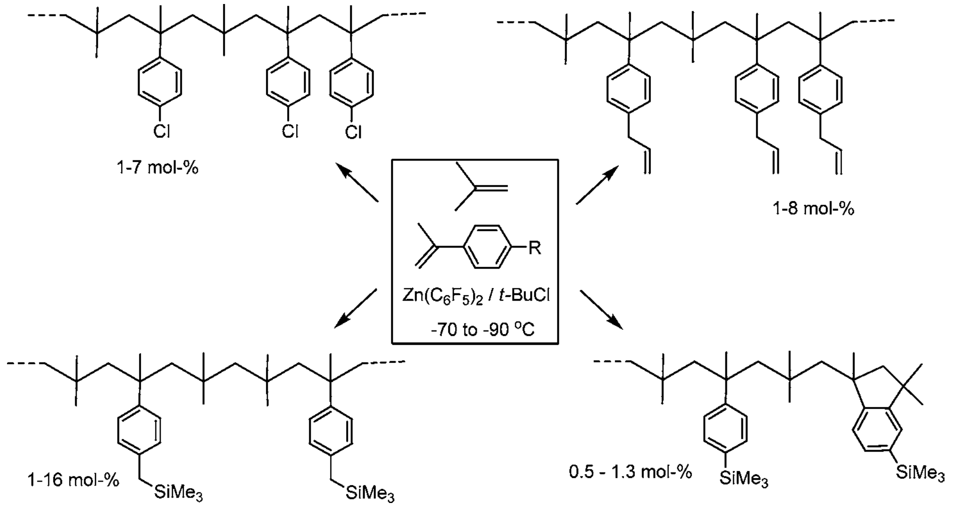
An IP content of around 6 mol % gave the optimum copolymer molecular weight. As Figure 4 shows, this means that this zinc initiator is able to produce new isoprene-rich copolymers with molecular weights well above the threshold level of 500 000 Da, a type of material that would be difficult to generate by conventional initiator systems. Such highly unsaturated copolymers can be expected to facilitate cross-linking to other unsaturated bulk polymers to generate polymer composites with improved bonding characteristics.

The incorporation of dienes into poly(isobutylene) is dependent on the rate of reaction of carbocations with isobutene on the one hand and the diene on the other. As Mayr has shown, these rates are very sensitive to steric as well as electronic parameters and explain why isobutene is well matched to isoprene but not to butadiene.[38] Styrene derivatives show similar variable rates; therefore the level of incorporation and nonblocky distribution of the comonomer is substituent dependent. The $Zn(C_6F_5)_2$/*t*-BuCl system proved capable of producing copolymers with a series of substituted α-methylstyrenes. Copolymers with 4-allyl and 4-chloro-α-methylstyrene showed some tendency toward blockiness. 4-Trimethylsilyl-α-methylstyrene incorporates only at low levels and terminates by ready indane formation, while the

SCHEME 9. Propagation versus Termination from Allylic Ion Pair Chain Ends Following Isoprene Incorporation



SCHEME 10. Copolymers of Isobutene with Substituted α-Methylstyrenes



CH_2SiMe_3 analogue gives random copolymers with good incorporation rates (Scheme 10).[39]

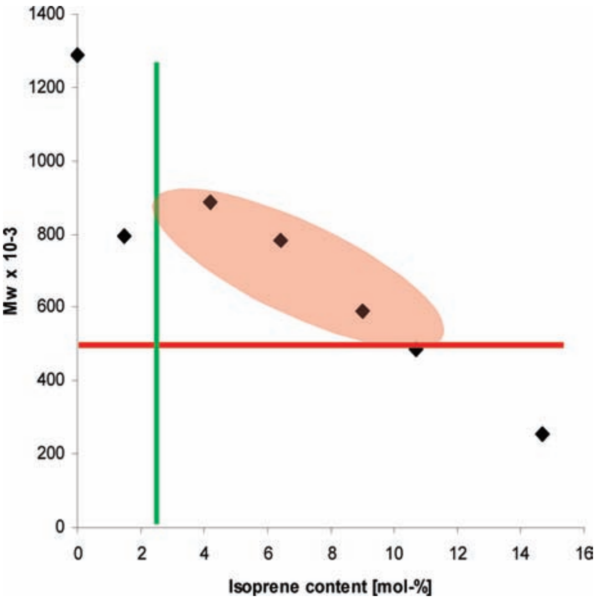


FIGURE 4. Dependence of copolymer molecular weight on IP content ($Zn(C_6F_5)_2$/*t*-BuCl, −78 °C). The shaded area indicates the region of new high-isoprene materials. The red and green lines indicate the $\bar{M}_w$ and the IP content limits, respectively, of standard industrial IIR.

5. Chloro Complexes of Zinc and Zirconium

EtZnCl is a coordination polymer with an infinite lattice consisting of Zn_3Cl_3 six-membered rings[40] and shows very limited solubility in neat isobutene. Unlike the previous reactions, polymerizations with EtZnCl/$RCMe_2Cl$ mixtures (R = Me, Ph) need to be conducted in dichloromethane/IB mixtures and work best at higher temperatures. The system $ZnEt_2$/*t*BuCl is soluble but inactive.

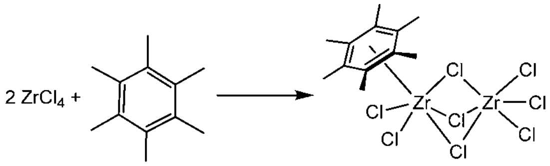
The method of introducing the zinc component into the mixture proved crucial for the success of the polymerization. Thus, premixing EtZnCl and *t*BuCl in CH_2Cl_2 either at low temperature or at 20 °C immediately gave a white precipitate (bulk $ZnCl_2$), which when injected into IB/CH_2Cl_2/*t*BuCl mixtures produced only traces of polymer. There was no polymerization with EtZnCl in the absence of *t*BuCl. The reactions are best carried out by adding EtZnCl into IB/CH_2Cl_2/*t*BuCl mixtures, with *t*BuCl being employed as the limiting reagent. In IB homopolymerizations at 20 °C, high concentrations of *t*BuCl gave rise to nearly quantitative conversions after 30 min reaction time to medium-molecular weight PIB ($\bar{M}_n$ = 10 000−29 000 g/mol).

The molecular weight could be controlled by adjusting the *t*BuCl concentration; it is reduced with rising [*t*BuCl], while the conversion is increased. The polymers showed up to 90% terminal C=C bonds.[41] Low molecular weight polyisobutenes containing more than 60% terminal double bonds are of interest as intermediates in the preparation of additives to lubricants since they can be chemically modified by epoxidation or reaction with maleic anhydride. A high content of vinylidene end groups is desired since only terminal double bonds react at a sufficiently high rate; these materials are therefore referred to as "high reactivity" PIBs. The EtZnCl/*t*BuCl system also gives IB/IP copolymers at room temperature, with up to 4 mol % IP incorporation, with no significant decrease in polymer yield. The molecular weights of these copolymers were remarkably similar to the homopolymers.

While EtZnCl/*t*BuCl initiators polymerize isobutene in the temperature range of +35 to −35 °C, poor solubility renders the system inactive at lower temperatures. However, *n*-octylzinc chloride activated with cumyl chloride shows good activity at temperatures as low as −90 °C to give medium-to-high molecular weight polymers. Both the EtZnCl and the OctZnCl/cumyl chloride systems showed an unexpectedly low activation energy of polymerization, $E_{DP} = -3.3$ kJ mol^{-1}. The polymer molecular weights obtained with these zinc systems are therefore much less temperature dependent than is the case in classical initiator systems ($E_{DP} \approx -23$ kJ mol^{-1} for BF_3, $AlCl_3$ and $EtAlCl_2$)[3a,b] and is also less than for zirconocene systems involving $[B(C_6F_5)_4]^-$ anions.[27] Although both Zn systems showed essentially identical temperature dependence, the octylzinc initiator produced higher molecular weights, consistent with the involvement of more bulky, less coordinating anions such as $[OctZnCl_2]^-$ or $[(OctZnCl)_nCl]^-$.

The alkylzinc systems are equally effective in IB/IP copolymerizations. Like the $Zn(C_6F_5)_2$ initiators, RZnCl proved remarkably insensitive to isoprene; in fact, unusually for a chloride-containing system, the copolymers had rather higher molecular weights than the homopolymers, with $\bar{M}_w = (2-3) \times 10^5$ and 2−6 mol % IP incorporation.[42,43]

Zirconium tetrachloride is another metal halide that at first glance appears to be an attractive, nontoxic alternative to the classical aluminum-based initiators. Bayer AG patented the use of $ZrCl_4$ in the presence of organic nitro compounds.[44] However, one drawback is the aging effect of $ZrCl_4$: whereas freshly sublimed material shows good activity and gives high molecular weight products, the performance rapidly deteriorates on storage. One way to overcome this problem is to use the hexamethylbenzene complex, $Zr_2Cl_8(C_6Me_6)$ (eq 6).[45]



(6)

The complex can be applied in two ways, as a dichloromethane solution or as a solid. In neither case did it prove to be necessary to add an organic halide co-initiator. Remarkably, the homogeneous and the heterogeneous application of $Zr_2Cl_8(C_6Me_6)$ gave very different types of temperature dependence; in particular, the addition of solid $Zr_2Cl_8(C_6Me_6)$ to IB/IP mixtures in dichloromethane at −78 °C allowed reactions to be conducted with good temperature control to give copolymers with narrow polydispersities and high molecular weights (~(4−6) × 10^5, 1−3 mol % IP content).[46] The presence of isoprene proved helpful in controlling the reaction. The results indicate that chlorozirconate anions, which must be involved here, show sufficiently low nucleophilicity to give attractive and comparatively inexpensive isobutene polymerization systems.

The suitability of zirconium and hafnium chloro anions is also evident in polymerizations initiated with the *sec*-carbocation salt $[HC(CHRR')_2]^+[M_2Cl_9]^-$ (R = $SiMe_3$, R′ = $SnMe_3$) (Figure 5 and Scheme 11). Isolable carbocations are of course ideal initiators for carbocationic polymerizations but most are thermally very labile. A number of *tert*-carbocation salts could be structurally characterized at low temperatures.[47] The Zr and Hf salts shown in Scheme 11 are so far the only examples of isolable and room-temperature-stable *sec*-carbocations. They show good activity for

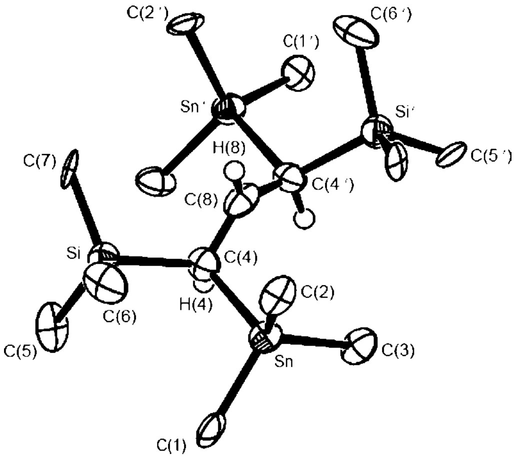
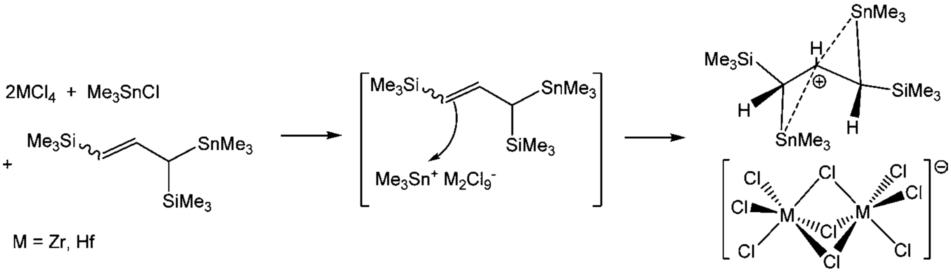


FIGURE 5. Solid state structure of the $[HC(CHRR')_2]^+$ cation (R = $SiMe_3$, R′ = $SnMe_3$) in its $[Hf_2Cl_9]^-$ salt.

SCHEME 11. Formation of Stable Carbocation Salts of Weakly Coordinating $M_2Cl_9^-$ Anions



the formation of high molecular weight IB/IP copolymers at −40 to −78 °C, with 1−4 mol % IP incorporation.[48,49]

6. Concluding Remarks

The production of isobutene−isoprene butyl rubber is a large-scale industrial process that is however based on highly energy intensive low-temperature technology. We have shown how principles of coordination chemistry and ion−ion interactions can be tailored to provide cleaner, more environmentally friendly processes. In particular, a variety of highly electrophilic organometallic species, coupled with weakly coordinating counteranions with low proton affinities, have been shown to provide alternatives that not only match the industrial products in terms of molecular weights but also provide access to new types of highly unsaturated elastomer materials. Such organometallic initiators are able to give high control over reaction temperature, polymer molecular weight, polydispersity, the degree of branching, and main-chain unsaturation. Homogeneous as well as highly active heterogeneous cationic initiator systems now exist. Naturally, the extent to which such new chemistry will be implemented in actual manufacturing processes depends largely on the balance between energy savings, environmental demands, and catalyst costs, and further improvements will no doubt be needed.

The results so far provide several avenues for optimizing polymerization processes, mainly based on anion engineering. Polymer chain growth depends critically on the relative stabilities of various ion pairs, and while the general principles are established, it is clear that the subtleties of cation−anion interactions in low-polarity solvents are far from well understood. The reaction dynamics of ionic systems under such conditions offer a potential that is yet to be fully explored; in fact, ion pair dynamics have implications here as well as in other important catalysts, such as Ziegler−Natta polymerizations, that have only just begun to be realized.[50] We believe the exploration of such ionic interactions and the control of the weak interactions that modulate transition state energies will be important avenues for the future development of much more productive and energy-efficient low-waste processes.

This work was supported by the Engineering and Physical Sciences Research Council, by Bayer AG, Leverkusen (Germany), and by Lanxess Inc., Sarnia (Canada).

BIOGRAPHICAL INFORMATION

Manfred Bochmann is Professor of Inorganic Chemistry and Head of the School of Chemistry at the University of East Anglia, Norwich, U.K. He received his Dipl. Chem. from the University of Marburg and a Ph.D. from Imperial College London. After a spell in industry at ICI's Corporate Laboratory, he moved to the University of East Anglia. From 1995 to 2000, he held the Chair of Inorganic and Structural Chemistry at the University of Leeds before returning to UEA. He is a Fellow of the Royal Society of Chemistry and recipient of the RSC Medal for Organometallic Chemistry. His research focuses on the organometallic chemistry of polymerization catalysts and the mechanism of olefin polymerization catalysis. He is the author of two teaching texts in organometallic chemistry and co-author of the inorganic chemistry textbook Cotton, Wilkinson, Murillo and Bochmann, *Advanced Inorganic Chemistry*, 6th ed. He is an Associate Editor of the ACS journal *Organometallics*.

FOOTNOTES

*E-mail: m.bochmann@uea.ac.uk.

REFERENCES

1 Bochmann, M. Highly Electrophilic Metallocenes and Their Role in Alkene Polymerizations. *Top. Catal.* **1999**, *7*, 9–22.

2 Gavens, P. D.; Bottril, M.; Kelland, J. W.; McMeeking, J. Ziegler−Natta Catalysis. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 3, pp 475−547.

3 (a) Kennedy, J. P.; Marechal, E. *Carbocationic Polymerization*; J Wiley & Sons: New York, 1982. (b) Kennedy, J. P.; Ivan, B. *Designed Polymers by Carbocationic Macromolecular Engineering: Theory and Practice*; Hanser: Munich, Germany, 1991. (c) Nuyken, O.; Pask, S. D. Carbocationic Polymerizations: Alkenes and Dienes. In *Comprehensive Polymer Science*; Allen, G., Bevington, J. C., Eds.; Pergamon: New York, 1989; Vol. 3, pp 619−637. (d) Kenndy, J. P. Carbocationic Polymerization: Copolymerization. In *Comprehensive Polymer Science*; Allen, G., Bevington, J. C., Eds.; Pergamon: New York, 1989; Vol. 3, pp 705−710.

4 Galakhov, M. V.; Heinz, G.; Royo, R. Intramolecular Coordination of an Alkene to a Mixed Dicyclopentadienyl Benzyl Zirconium Cation Studied by NMR Spectroscopy. *Chem. Commun.* **1998**, 17–18. (b) Casey, C. P.; Carpenetti, D. W., III; Sakurai, H. Models for Intermediates in Metallocene-Catalyzed Alkene Polymerization: Alkene

Dissociation from $Cp_2Zr[\eta^1,\eta^2\text{-}CH_2Si(CH_3)_2CH_2CH{=}CH_2][B(C_6F_5)_4]$. *Organometallics* **2001**, *20*, 4262–4265. (c) Stoebenau, E. J., III; Jordan, R. F. Coordination of Alkenes and Alkynes to a Cationic d^0 Zirconocene Alkoxide Complex. *J. Am. Chem. Soc.* **2003**, *125*, 3222–3223.

5 (a) Bochmann, M. Kinetic and Mechanistic Aspects of Metallocene Polymerization Catalysts. *J. Organomet. Chem.* **2004**, *689*, 3982. (b) Bochmann, M. The Use of Spectroscopy in Metallocene-Based Polymerization Catalysis. In *Catalytic Mechanisms from Spectroscopic Measurements*; Heaton, B. T., Ed.; Wiley-VCH: Weinheim, Germany, 2005; pp 311−357.

6 Kennedy, J. P.; Trivedi, P. D. Cationic Olefin Polymerization Using Alkyl Halide Alkylaluminum Initiator Systems. *Adv. Polym. Sci.* **1978**, *28*, 83–151.

7 Magagnini, P. L.; Cesca, S.; Giusti, P.; Priola, A.; Di Maina, M. Studies on Polymerizations Initiated by Syncatalytic Systems Based on Aluminum Organic Compounds 7. Reaction Mechanisms. *Makromol. Chem.* **1977**, *178*, 2235–2248.

8 Bochmann, M.; Sarsfield, M. J. The Reaction of AlR_3 with $[CPh_3][B(C_6F_5)_4]$: Facile Degradation of $[B(C_6F_5)_4]^-$ by Transient "$[AlR_2]^+$". *Organometallics* **1998**, *17*, 5908–5912.

9 (a) Goethals, E. J.; Du Prez, F. Carbocationic Polymerizations. *Prog. Polym. Sci.* **2007**, *32*, 220–246. (b) Aoshima, S.; Kanaoka, S. A Renaissance in Living Cationic Polymerization. *Chem. Rev.* **2009**, *109*, 5245–5287.

10 There are a number of metal-free systems based on borate anions similar to the ones described here but which rely on proton initiation. These are beyond the scope of this Account.

11 Reviews:(a) Bochmann, M. Cationic Group IV Metallocene Complexes and Their Role in Polymerization Catalysis: The Chemistry of Well-Defined Ziegler Catalysts. *J. Chem. Soc., Dalton Trans.* **1996**, 255–270. (b) Chen, E. Y. X.; Marks, T. J. Cocatalysts for Metal-Catalyzed Olefin Polymerization: Activators, Activation Processes, and Structure−Activity Relationships. *Chem. Rev.* **2000**, *100*, 1391–1434.

12 Bochmann, M.; Dawson, D. W. Synthesis and Reactivity of $[Al(C_5H_5)_2]^+$: A Highly Efficient Initiator for the Cationic Polymerisation of Isobutene. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2226–2228.

13 Langstein, G.; Bochmann, M.; Dawson, D. W. (Bayer AG) Process for the Preparation of Polyisoolefins via New Initiator Systems of the Metallocene-Type. US Pat. Appl. 5,703,182, 1996.

14 Lee, S. J.; Shapiro, P. J.; Twamley, B. Synthesis and Characterization of $[(C_5Me_4H)_2Al]^+$, an Initiator for the Polymerization of Isobutene. *Organometallics* **2006**, *25*, 5582–5586.

15 Song, X.; Thornton-Pett, M.; Bochmann, M. Synthesis, Structure and Reactivity of $(C_5H_4SiMe_3)_2Y\{(\mu\text{-}FC_6F_4)(\mu\text{-}Me)B(C_6F_5)_2$: Tight Ion Pairing in a Cationic Lanthanide Complex. *Organometallics* **1998**, *17*, 1004–1006.

16 Barson, F.; Baird, M. C. The First Example of Polymerization of Isobutylene induced by a Metallocene-like Initiator, $(C_5Me_5)TiMe_2(\mu\text{-}Me)B(C_6F_5)_3$. *J. Chem. Soc., Chem. Commun.* **1995**, 1065–1096.

17 Baird, M. C. Carbocationic Alkene Polymerizations Initiated by Organotransition Metal Complexes: An Alternative, Unusual Role for Soluble Ziegler-Natta Catalysts. *Chem. Rev.* **2000**, *100*, 1471–1478.

18 Barsan, F.; Karam, A. R.; Parent, M. A.; Baird, M. C. Polymerization of Isobutylene and the Copolymerization of Isobutylene and Isoprene Initiated by the Metallocene Derivative $Cp^*TiMe_2(\mu\text{-}Me)B(C_6F_5)_3$. *Macromolecules* **1998**, *31*, 8439–8447.

19 Kumar, K. R.; Hall, C.; Penciu, A.; Drewitt, M. J.; McInenly, P. J.; Baird, M. C. Isobutene Polymerization Initiated by $[Cp^*TiMe_2]^+$ in the Presence of a Series of Novel, Weakly Coordinating Counteranions. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 3302–3311.

20 Kumar, K. R.; Penciu, A.; Drewitt, M. J.; Baird, M. C. Isobutene-Isoprene Copolymerization Initiated by $[Cp^*MMe_2][n\text{-}C_{18}H_{37}E)B(C_6F_5)_3]$ (M = Ti, Hf; E = O, S) and Related Compounds. *J. Organomet. Chem.* **2004**, *689*, 2900–2904.

21 Tse, C. K. W.; Kumar, K. R.; Drewitt, M. J.; Baird, M. C. Isobutene Polymerization and Copolymerization with Isoprene Initiated by $[Cp^*TiMe_2]^+$ in the Presence of a Novel Type of Weakly Coordinating Counteranion. *Macromol. Chem. Phys.* **2004**, *205*, 1439–1444.

22 Shaffer, T. D. (Exxon) Cationic Catalysts and Process for Using Said Catalysts. PCT Int. Pat. Appl. WO 95/29940, 1994.

23 Shaffer, T. D.; Ashbaugh, J. R. Noncoordinating Anions in Carbocationic Polymerization. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 329–344.

24 Carr, A. G.; Dawson, D. M.; Bochmann, M. Zirconocenes as Initiators for Carbocationic Isobutene Homo- and Co-Polymerizations. *Macromolecules* **1998**, *31*, 2035–2040.

25 Carr, A. G.; Dawson, D. M.; Bochmann, M. The $[Zr\{N(SiMe_3)_2\}_3]^+$ Cation as a Novel Initiator for Carbocationic Isobutene Homo- and Isobutene/Isoprene Co-Polymerizations. *Macromol. Rapid Commun.* **1998**, *19*, 205–207.

26 Carr, A. G.; Dawson, D. M.; Thornton-Pett, M.; Bochmann, M. Cationic Zirconocene Hydrides: A New Type of Highly Effective Initiators for Carbocationic Polymerizations. *Organometallics* **1999**, *18*, 2933–2935.

27 (a) Garratt, S.; Carr, A. G.; Langstein, G.; Bochmann, M. Isobutene Polymerization and Isobutene-Isoprene Copolymerization Catalyzed by Cationic Zirconocene Hydride Complexes. *Macromolecules* **2003**, *36*, 4276–4287. (b) Langstein, G.; Bochmann, M.; Dawson, D. M.; Carr, A. G. ; Commander, R. (Bayer AG) Process for the Preparation of Polyisoolefins via New Initiator Systems of the Metallocene Type. German Pat. Appl. DE 19836663, 2000.

28 Sauriol, F.; Wong, E.; Leung, A. M. H.; Donaghue, I. E.; Baird, M. C.; Wondimagegn, T.; Ziegler, T. Structure and Properties of Non-chelated d^0 Alkene Complexes: Elusive Intermediates during Ziegler-Natta Polymerizations of Alkenes. *Angew. Chem., Int. Ed.* **2009**, *48*, 3342–3345.

29 Lancaster, S. J.; Rodriguez, A.; Lara-Sanchez, A.; Hannant, M. D.; Walker, D. A.; Hughes, D. L.; Bochmann, M. $[H_2N\{B(C_6F_5)_3\}_2]^-$: A New, Remarkably Stable Diborate Anion for Metallocene Polymerization Catalysts. *Organometallics* **2002**, *21*, 451–453.

30 Lancaster, S. J.; Walker, D. A.; Thornton-Pett, M.; Bochmann, M. New Weakly Coordinating Counteranions for High Activity Polymerisation Catalysts: $[(C_6F_5)_3B\text{-}CN\text{-}B(C_6F_5)_3]$ and $[Ni\{CNB(C_6F_5)_3\}_4]^{2-}$. *Chem. Commun.* **1999**, 1533–1534.

31 Similar anions have more recently also been used in combination with cationic transition metal acetonitrile complexes to generate low molecular weight polyisobutene at 30 °C: (a) Nuyken, O.; Vierle, M.; Kühn, F. E.; Zhang, Y. Solvent-Ligated Transition Metal Complexes as Initiators for the Polymerization of Isobutene. *Macromol. Symp.* **2006**, *236*, 69. (b) Hijazi, A. K.; Yeong, H. Y.; Zhang, Y.; Herdtweck, E.; Nuyken, O.; Kühn, F. E. Isobutene Polymerization Using $[Cu^{II}(NCMe)_6]^{2+}$ with Non-Coordinating Anions as Catalysts. *Macromol. Rapid Commun.* **2007**, *28*, 670–675. (c) Li, Y.; Voon, L. T.; Leong, H. Y.; Hijazi, A. K.; Radhakrishnan; Köhler, K.; Voit, B.; Nuyken, O.; Kühn, F. E. Solvent-Ligated Copper(II) Complexes for the Homopolymerization of 2-Methylpropene. *Chem.—Eur. J.* **2008**, *14*, 7997–8003.

32 Zhou, J.; Lancaster, S. J.; Walker, D. A.; Beck, S.; Thornton-Pett, M.; Bochmann, M. Synthesis, Structures and Reactivity of Weakly Coordinating Anions with Delocalized Borate Structure: The Assessment of Anion Effects in Metallocene Polymerization Catalysts. *J. Am. Chem. Soc.* **2001**, *123*, 223–237.

33 (a) Walker, D. A.; Woodman, T. J.; Hughes, D. L.; Bochmann, M. The Reactions of Zinc Dialkyls with (Perfluorophenyl)boron Compounds: Alkylzinc Cation Formation versus C_6F_5 Transfer. *Organometallics* **2001**, *20*, 3772–3776. (b) Guerrero, A.; Martin, E.; Hughes, D. L.; Kaltsoyannis, N.; Bochmann, M. Zinc(II) η^1- and η^2-Toluene Complexes: Structure and Bonding in $Zn(C_6F_5)_2\cdot$toluene and $Zn(\text{perfluorobiphenyl})_2\cdot$toluene. *Organometallics* **2006**, *25*, 3311–3113.

34 (Sumitomo Chem. Co.) Method for the Preparation of Isobutene Polymers and Catalysts for Use therein. Brit. Pat. Appl. 1,343,670, 1971.

35 Diem, T.; Kennedy, J. P.; Chou, R. T. Isobutylene Polymerization in the Presence of UV Light, Organic Iodides and Zinc Iodide. *Polym. Bull.* **1979**, *1*, 281–285.

36 Garratt, S.; Guerrero, A.; Hughes, D. L.; Bochmann, M. Arylzinc Complexes as New Initiator Systems for the Production of Isobutene Copolymers with High Isoprene Content. *Angew. Chem., Int. Ed.* **2004**, *43*, 2166–2169.

37 Bochmann, M.; Garratt, S. (Bayer Inc.) Process for the Production of Butyl Rubber. Eur. Pat. Appl. 1,516,883, 2005.

38 Mayr, H.; Patz, M. Scales of Nucleophilicity and Electrophilicity: A System for Ordering Polar Organic and Organometallic Reactions. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 938–957.

39 Guerrero, A. Ph.D. Thesis, University of East Anglia, 2007.

40 Guerrero, A.; Hughes, D. L.; Bochmann, M. Synthesis and Crystal Structure of Ethyl Zinc Chloride. *Organometallics* **2006**, *25*, 1525–1527.

41 Guerrero, A.; Kulbaba, K.; Bochmann, M. "Highly Reactive" Poly(isobutene)s via Room-Temperature Polymerization with a New Zinc-Based Initiator System. *Macromolecules* **2007**, *40*, 4124–4126.

42 Guerrero, A.; Kulbaba, K.; Bochmann, M. Alkylzink Chlorides as New Initiators for the Polymerization and Copolymerization of Isobutene. *Macromol. Chem. Phys.* **2008**, *209*, 1714–1720.

43 Bochmann, M.; Guerrero, A.; Kulbaba, K. (Lanxess Inc., Canada) Polymerization process using zinc halide initiators. Eur. Pat. Appl. 1,834,964, 2007.

44 Langstein, G.; Bohnenpoll, M.; Sumner, A.; Verhelst, M. (Bayer AG) Process for the Preparation of Isoolefin Copolymers. Eur. Pat. Appl. E.P. 1,215,220, 2002.

45 Calderazzo, F.; Ferri, I.; Pampaloni, G.; Troyanov, S. η^6-Arene Derivatives of Titanium(IV), Zirconium(IV) and Hafnium(IV). *J. Organomet. Chem.* **1996**, *518*, 189–196.

46 Harding, D. A. J.; Bochmann, M. results to be published.

47 Laube, T. Interactions between Carbocations and Anions in Crystals. *Chem. Rev.* **1998**, *98*, 1277–1312.

48 (a) Schormann, M.; Garratt, S.; Hughes, D. L.; Green, J. C.; Bochmann, M. Isolation and Structure of $[HC\{CH(SiMe_3)(SnMe_3)\}_2]^+$: A Remarkably Stable *sec*-Alkyl Cation. *J. Am. Chem. Soc.* **2002**, *124*, 11266–11267. (b) Schormann, M.; Garratt, S.; Bochmann, M. The Reactivity of Silyl-Substituted Allyl Compounds with Group 4, 5, 9 and 10 Metals: Routes to η^3-Allyls, Alkylidenes and *sec*-Alkyl Carbocations. *Organometallics* **2005**, *24*, 1718–1724.

49 Bochmann, M.; Schormann, M.; Garratt, S. (Lanxess Inc. Canada) Process for Preparing Isobutylene-based Polymers. PCT Appl. WO 03,062,284 2003.

50 (a) Alonso-Moreno, C.; Lancaster, S. J.; Zuccaccia, C.; Macchioni, A.; Bochmann, M. Evidence for Mixed-Ion Clusters in Metallocene Catalysts: Influence on Ligand Exchange Dynamics and Catalyst Activity. *J. Am. Chem. Soc.* **2007**, *127*, 9282–9283. (b) Alonso-Moreno, C.; Lancaster, S. J.; Wright, J. A.; Hughes, D. L.; Zuccaccia, C.; Correa, A.; Macchioni, A.; Cavallo, L.; Bochmann, M. Ligand Mobility and Solution Structures of the Metallocenium Ion Pairs $[Me_2C(Cp)(fluorenyl)MCH_2SiMe_3{}^+\cdots X^-]$ [M = Zr, Hf; X = $MeB(C_6F_5)_3$, $B(C_6F_5)_4$]. *Organometallics* **2008**, *27*, 5474–5487.