Solvent-Ligated Transition Metal Complexes as Initiators for the Polymerization of Isobutene

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Summary: After a brief introduction of the history of polyisobutene and the description of an interesting commercial process, this article is focused on the mechanism of the isobutene initiation and propagation. Furthermore, the INIFER technique will be briefly discussed. Finally, it will be shown that polyisobutene with a high content of terminal olefinic groups can be synthesized by using transition metal complexes in homogeneous solution at room temperature. Mechanisms of the isobutene polymerization initiated by this new class of initiators will be suggested.

Introduction

It was as early as 1873 that it was observed that the reaction of "weak" sulfuric acid with isobutene yields beside trimethylcarbinol triisobutene (b.p. 173 °C).[1] About fifty years later Lebedev et al. discovered that heated silicate can function as initiator for the polymerization of isobutene.[2,3] A breakthrough in the field of cationic polymerization of isobutene was the patent of Otto and Müller-Cunradi, which was commercialized by IG Farben Ludwigshafen 1938.[4] This process is running since that time almost unchanged. Polymerization is carried out in chlorinated solvents or in ethene using Lewis acids such as BF_3, $AlCl_3$, $TiCl_4$ and others as initiator. Molecular weights are basically controlled via temperature:

$$\log M_n = k\, T^{-1}$$

From this equation it can be concluded that high molecular weights (up to many millions $g \cdot mol^{-1}$) need low temperatures (down to -100 °C).

Another milestone is the discovery of the copolymerization of isobutene with isoprene yielding *butyl rubber*. The technology of this process, introduced 1943 was changed only slightly during the last 60 years.[5]

Polyisobutene has a perfectly saturated carbon chain forming a helix with 8 monomer units per turn, it is chemically resistant and non-toxic. It has high dumping properties and it is one of best known carbon-based barrier for gases.

Commercial polyisobutenes can be divided according to their molecular weights into three large groups, which have different properties and uses. High-molecular weight polyisobutenes with a molecular weight higher than 300 $kg \cdot mol^{-1}$ are rubber-like and used in non-crosslinked rubber goods and as chewing gum base. Medium-molecular weight polyisobutenes with molecular weights between 40 and 120 $kg \cdot mol^{-1}$ are highly viscous liquids, mainly applied as glues and for sealants. Low molecular polyisobutenes have molecular weights of 0.3 to 3 $kg \cdot mol^{-1}$. These polymers are colourless, honey like liquids. Usually, they are prepared with Lewis acids as initiators and contain less than 10% terminal C=C bonds.[6] Of great commercial interest are so-called highly reactive polyisobutenes with molecular weights in the range between 0.3 and 3 $kg \cdot mol^{-1}$, which contain up to 60%

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Table 1.
Poly(isobutene) properties.

Molar Mass [g/mol]	Name	Properties	Application
300–3000	Oily poly(isobutene)s	Oily, transparent, honey-linke, sticky	Oil additives additives for adhesives
40000–120000	High-viscosity poly(isobutene)s	High viscosity, very sticky	Sealants Adhesives Chewing-gum
300000–3 Mio	IR, Isobutene-rubber	Elastic, hard	Non-crosslinked rubbers Insulations
300000–3 Mio	IIR, Butyl-rubber	Elastic, crosslinkable	Tire-inliners Tubes

terminal olefins. After functionalization of those olefins they are applied as lubricants or oil additives.[7,8]

Recently, we have published a new class of initiators, transition metal complexes with bulky counterions, for the polymerization of isobutene.[9] The great advantage of this route is that polymerization at ambient temperature becomes possible.[9,10] The potential of these initiators and the mechanism of initiation, propagation and termination will be discussed in some detail.
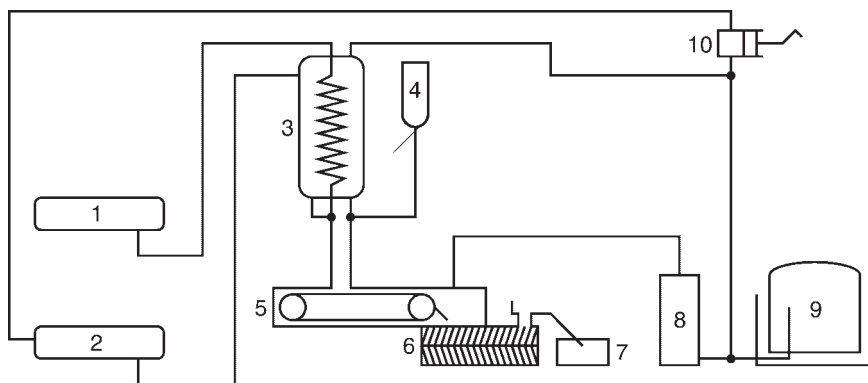
Industrial Isobutene Polymerization

It is well established that isobutene can be polymerized by means of cationic initiators such as protonic or Lewis acids. Typical initiators are $AlCl_3$, BCl_3, BF_3 and water as coinitiator. Typical solvents are methylchloride, dichloromethane and ethene at temperature of $-80\,^{\circ}C$ or below ($-100\,^{\circ}C$ in case of ethene as solvent). Polymerization is extremely fast and exothermic. Temperature is commonly controlled by the boiling solvent. BF_3 combined with aliphatic alcohols as deactivators is applied for the production of highly reactive polyisobutene. Temperatures of $-30\,^{\circ}C$ up to $0\,^{\circ}C$ are commonly used for this process. As already stated before the molecular weights are controlled via temperatures – at higher temperatures one gets low molecular weights and vice versa. In any case, since temperatures below room temperature are applied, all these processes need much energy for cooling the solvents.

An interesting process, the manufacture of Oppanol B®, running at BASF AG Ludwigshafen since 1938 almost unchanged, is depicted in Figure 1.

Liquid isobutene (1) and liquid ethene (2) are pumped into the reactor (5) together

Figure 1.
Process for the manufacture of Oppanol B®: 1: liquid isobutene, 2: liquid ethylene, 3: cooler-mixer, 4: BF_3-ethylene reservoir, 5: continous belt, 6: compacting rolls, 7: product, 8: CaO to purify ethylene recycle, 9: gasometer, 10: compressor.

with the initiator (4) after pathing a cooler mixer (3). Isobutene polymerizes immediately and is transported to the end of the tube-like reactor via a continuous belt and then the polymer is separated from residual monomer, solvent and initiator via compacting rolls. The polymer does not need further purification and is filled into container ready for transportation (7). Solvent and monomer are purified over CaO (8) and stored in a gasometer(9). Compressors are used for the cooling of the solvent (10). Indeed, these compressors are running since 1938.

Mechanism

As already mentioned isobutene is polymerized cationically via carbenium ions. The mechanism shown in Scheme 1 is generally accepted:[11–16]

The initiating proton is formed by reaction of the Lewis acid (e.g. BF_3) with traces of water. The proton adds to the olefin yielding a carbenium ion, growing by further monomer addition. With decreasing temperature the tendency of transfer reactions, e.g. with monomers is decreasing and therefore undisturbed chain growing allows the formation of very high molecular weights up to many millions $g \cdot mol^{-1}$. Polymerization is terminated either by

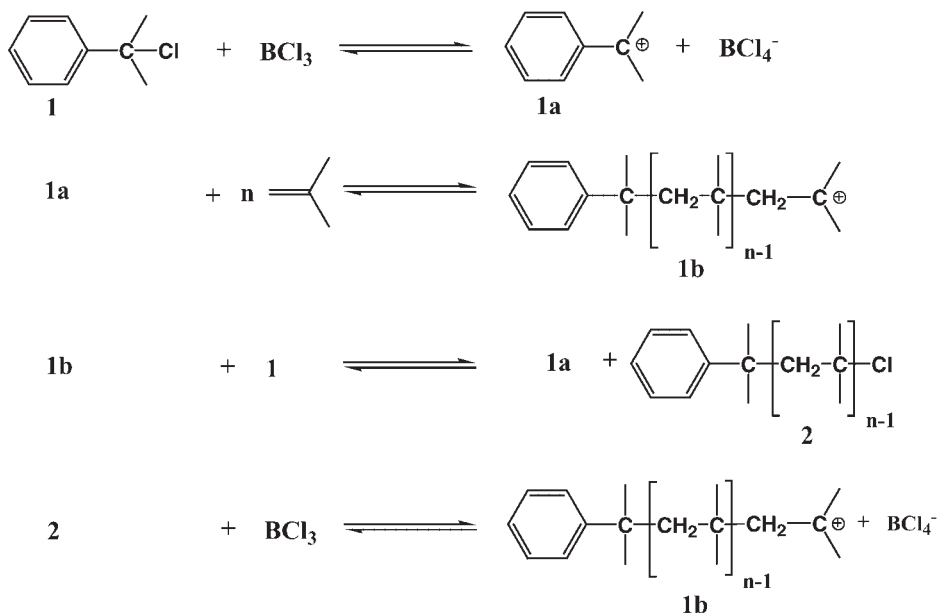impurities (water) or by addition of additives (e.g. water, methanol).

A revolutionary contribution to the isobutene polymerization was the discovery of the INIFERs (initiator transfer agents) by Kennnedy et al.,[17,18] allowing not only control over the molecular weight but also over the functional end groups. It opened avenues for the synthesis of telechelics (polymers with well defined functional groups at each end of the chain). The basic steps of the INIFER mechanism are depicted in Scheme 2.

Compounds such as (2-chloro isopropyl) benzene (1) are reacted with an excess of BCl_3 yielding the corresponding carbenium ion (1a). 1a reacts with monomer yielding 1b. 1b can either react with the counterion BCl_4^- (reversible termination) or with 1 (transfer) yielding a Cl-terminated chain. The reaction cycles are repeated as long 1 and monomer are available. The polymerization finishes with a polymer 2, having a aromatic unit and Cl-functions on its ends. The experimental observations of complete consumption of 1 and monomer can only be explained by assuming that aliphatic Cl-end groups can be activated again (reversible termination). This was proven by using α,ω-dichlor aliphates and Cl-terminated telechelic polyisobutene as initiators.[19–21] If 1,4-di(2-chloroisopropyl)benzene is applied instead of 1 telechelics
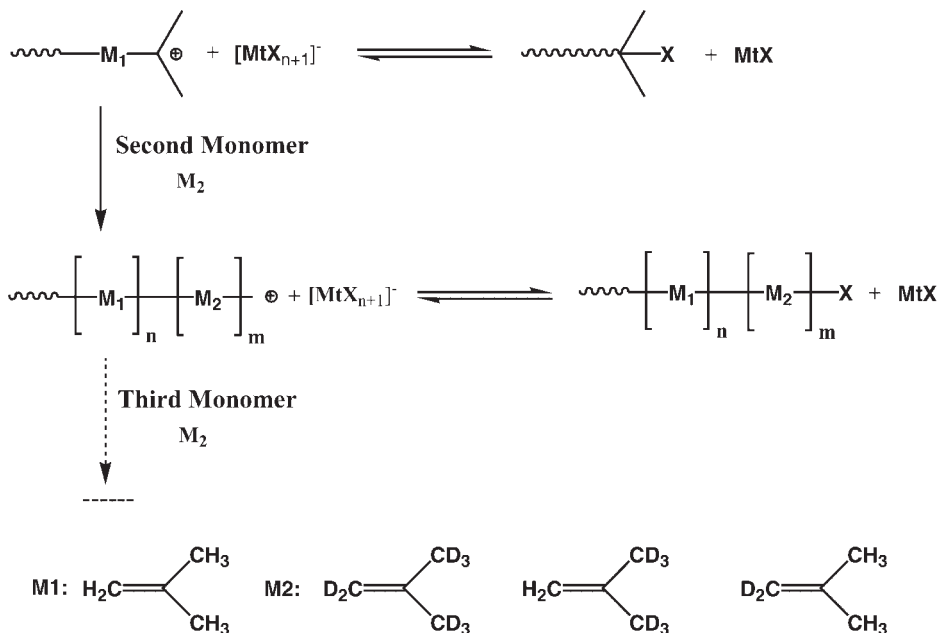
Scheme 1.
Basic steps of the polymerization of isobutene.

Scheme 2.
Basic steps of the INIFER mechanism.

having a central aromat and Cl-functions on both ends of the linear polymer become available. Finally, we were able to synthesize blockcopolymers via a living polymerization mechanism, with reversible termination being the heart of this mechanism.[22]
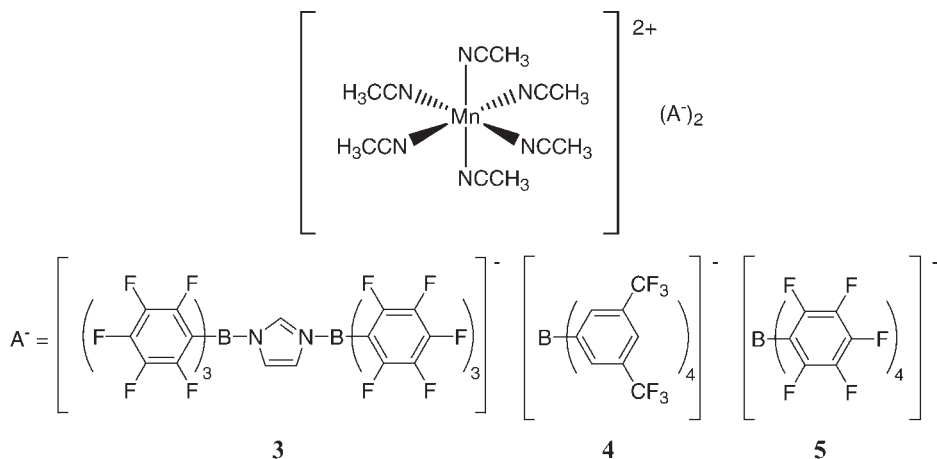

Scheme 3.
Blockcopolymers.

Figure 2.
Typical Solvent ligated complexes, applied for the polymerization of isobutene.

New developments in the field of the polymerization of isobutene are transition metals complexes consisting of metal cations complexed with acetonitrile and bulky counterions.[23] In the following chapter some of our newer results will be presented and discussed in some detail.

Solvent-ligated Transition Metal Complexes for the Polymerization of Isobutene

Typical complexes are depicted in Fig. 2. These compounds are surprisingly temperature-stable (decomposition temperatures, determined by thermogravimetry: 271 °C (**3**); 249 °C (**4**) and 258 °C (**5**)). Their synthesis was already described.[23] These complexes are moderately stable at air and moisture and can be handled in the laboratory atmosphere without problems. Since we were unable to obtain high-quality crystals from **3**, **4** and **5** an X–ray was taken from a well crystallized analogue of **5**, in which acetonitrile is replaced by propionitrile (**5a**). No interactions between cations and anions can be detected in the crystals of **5a** (Fig. 3).

The tube technique was applied for the polymerization experiments. For each experimental series 12 tubes with identical content (monomer, solvent, initiator) were prepared and kept at −40 °C. All tubes were warmed up to the desired polymerization temperature (e.g.: 20 °C, 30 °C or 40 °C) at the same time. At these temperatures the initiators are perfectly soluble in dichloromethane. Solubilities of the com-
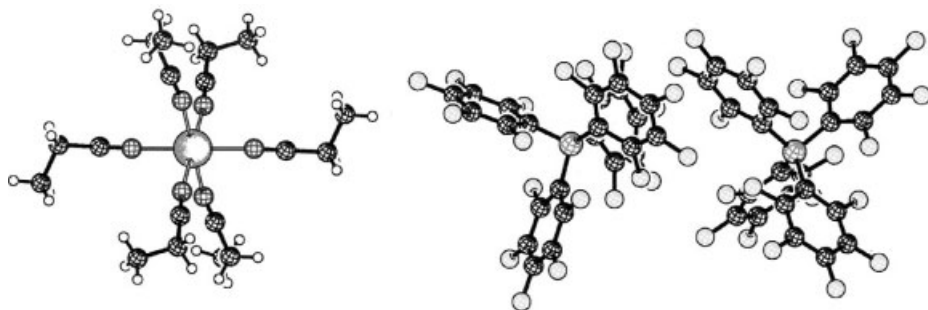

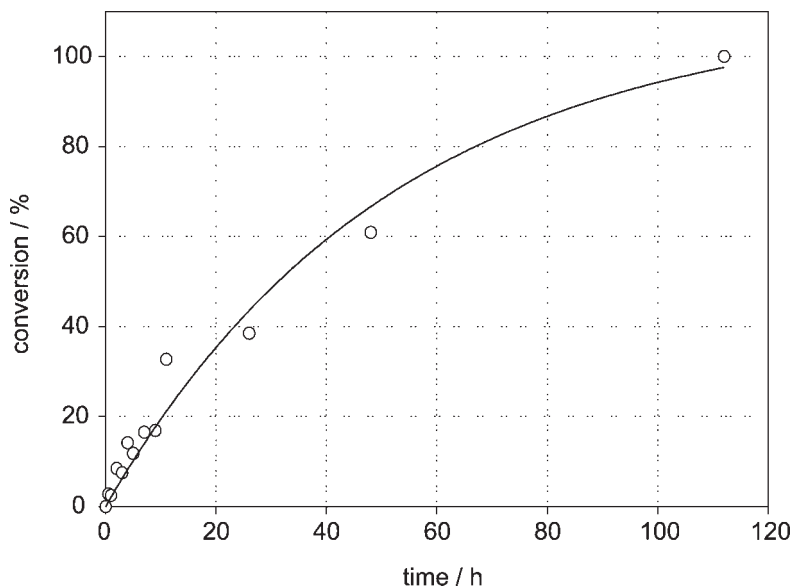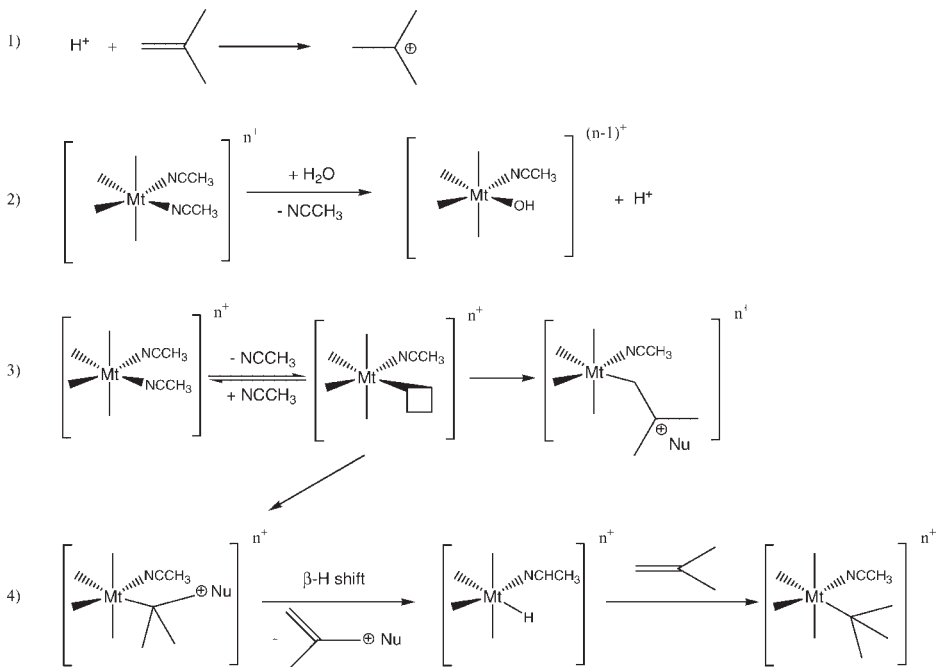**Figure 3.**
Crystal structure of **5a**.

Figure 4.
Homopolymerisation of isobutene, conversion = f(t); Reaction conditions: T = 30 °C, [**4**] = 2,5 · 10^{-4} mol · L^{-1}, [isobutene] = 1,38 mol · L^{-1}.
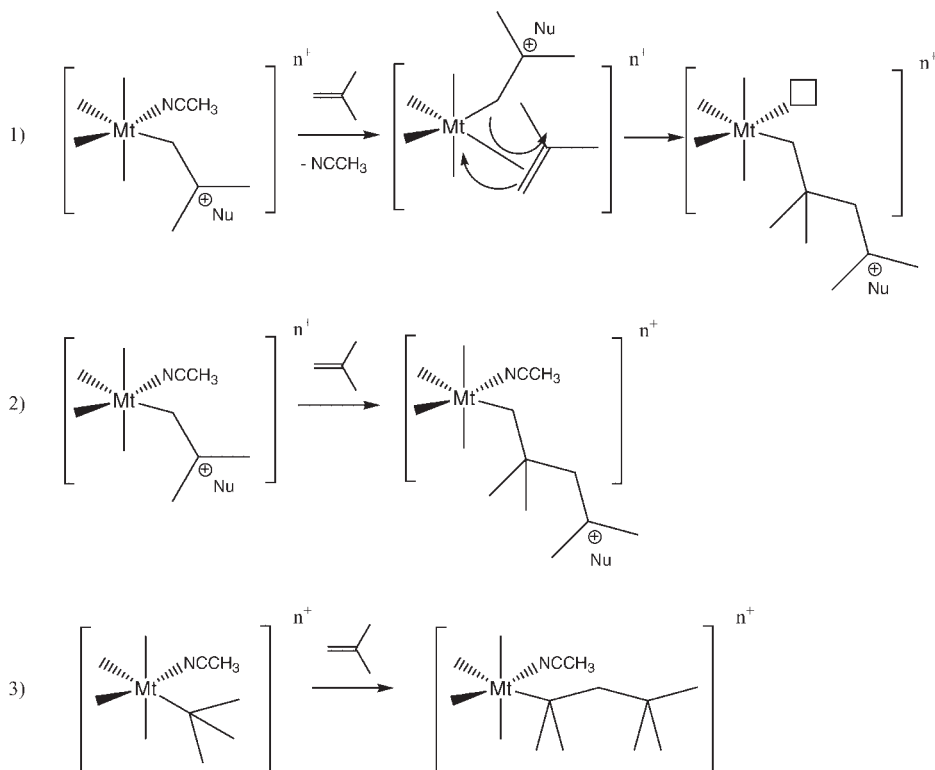
plexes **3**, **4** and **5** become a problem below room temperature. For kinetics polymerizations were stopped at different times and the monomer conversion was determined gravimetrically (via the amount of polymer), see Fig. 4. Amount and structure of

Scheme 4.
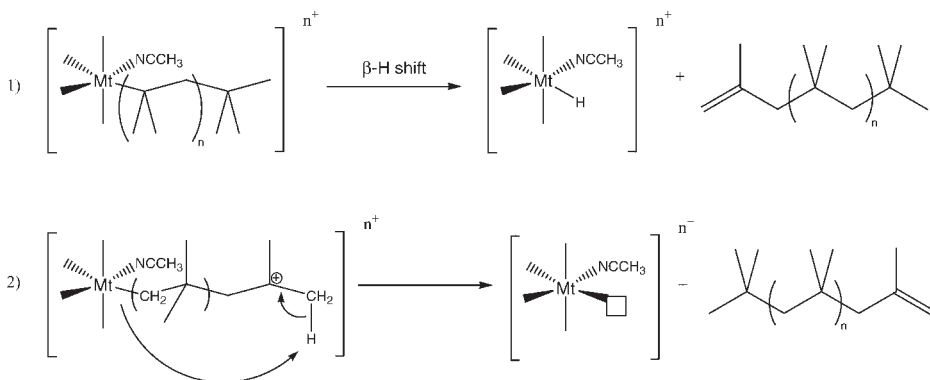Possible initiation mechanism.

Scheme 5.
Propagation mechanism: 1. cationic insertion, 2. common cationic, 3. insertion, $Mt = Mn$.

the polymers were analyzed. Molecular weights between 0.6 and 13 $kg \cdot mol^{-1}$ were available. The polymers are colourless and have an extremely high degree of terminal $C=C$ bonds, up to 100%.

Due to the low polymerization rates and the relative insensitivity of the systems against water it is rather unlikely that protons, available from the reaction of traces of water with impurities, are responsible for the initiation (scheme 4, route 1). It is also unlikely that solvent ligands are replaced by water yielding an OH-ligand and H^+ (scheme 4, route 2). Nevertheless, we were able to show that replacement of solvent ligands by water yields well-defined complexes of the general structure $Mn(H_2O)_2(CH_3CN)_4{}^{2+}$. However, those complexes are inactive for the polymerization of isobutene.

Alternatively, we assume that in the first step one of the ligands is replaced by isobutene yielding a $(CH_3CN)_5Mn–CH_2-C(CH_3)^{2+}$, where one molecule of CH_3CN could possibly function as Nu. This species could grow via a common cationic mechanism (scheme 4, route 3). However, this would also mean that the concentration of those species must either be very low or these species must be much less active than free ions. Instead of chain growing β–H shift could take place yielding Mn-H. Further monomer could now add to Mn-H yielding $Mn-C(CH_3)_3$ (scheme 4, route 4). Insertion of monomer into the Mn-C-bond would yield $Mn-[C(CH_3)_2CH_2]_nC(CH_3)_3$. This would not only explain the $C(CH_3)_3$ end group but also the high degree of terminal olefins resulting from a β-H shift of the methyl groups of the monomer unit next to the metal, regenerating the active Mn-H species. Alternatively one could discuss a combined insertion cationic mechanism as depicted in scheme 5, route 1.

1)

2)

Scheme 6.
Formation of the olefin endgroup.

If chain growing takes place via Mn-$[CH_2\text{-}C(CH_3)_2]_n\text{-}C(CH_3)^{2+}$ Nu (scheme 5, route 2) the olefinic end group could become available by a deprotonation of the positively charged end, furthermore the proton had to move to the Mn-C bond forming a methyl group and leaving behind a "naked" metal for the coordination of the next monomer (scheme 6, route 2).

In Scheme 6, route 1 we suggest, that the olefinic end group is the result of a β-H shift, regenerating a Mt-H as active species for further polymerization (Scheme 5, route 3). Although, at present we do not have any experimental evidence for one or the other intermediate; our results are best explained assuming Mt-H intermediates. This hypothesis explains the formation of almost 100 % $CH_2{=}C(CH_3)$-functions on one of the polymers and of $(CH_3)_3C$-groups on the other end. Furthermore, it explains the extremely interesting observation, that polymerization continues after complete conversion of monomer if a new portion of monomer is added and that always the same molecular weight was reached. Nevertheless, further investigations are necessary and we will keep our eyes open for alternative explanations.[24,25]

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