# The Role of Solvent Ligated Metal Complexes Associated with Weakly Coordinating Counteranions (WCAs) in Isobutylene Polymerization

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**Summary:** Polyisobutylene is an industrially important polymer which is conventionally prepared by polymerization at temperatures below 0 °C. The application of solvent ligated metal complexes associated with weakly coordinating counteranions (WCAs), however, allows the room temperature (30 °C) polymerization of isobutylene resulting in highly reactive polyisobutylene (HR-PIB) containing a high content of terminal double bonds. Recently described complexes include manganese (II), copper(II), molybdenum(III) and zink(II) complexes which were coordinated octahedrally with the boron and alumina based WCAs, each with its own advantages and traits.

**Keywords:** isobutylene; polymerization; transition metal complexes

## Introduction

Isobutylene is of one the most investigated monomers which readily polymerizes to high molar masses in the presence of cationic initiators.[1] The synthesis of polyisobutylene (PIB) is mainly dominated by the usage of Lewis acids as coinitiator and traces of alcohol or water as initiator[3,4] such as $H_20/BF_3$.[2] In a typical cationic polymerization of isobutylene, the proton adds to the monomer to produce a carbenium ion which propagates by the addition of further monomers. The proton abstraction from the growing polyisobutylene chain - by transfer to monomer or solvent - will result in two main types of terminal unsaturated end groups which are exo double bonds (α terminated) and endo double bonds (β terminated) as shown in Scheme 1. Additionally, internal double bonds are found in PIB arising probably from 1,3-methide shift, concerted 1,2-hydride-1,2 methide shift and tail to tail addition of isobutylene.[5] Exo terminal double bonds are highly reactive and less-stable while the endo and other internal end groups are more stable and thermodynamically favoured.

Commercial polyisobutylenes are categorized according to the molecular weight. The applications of polyisobutylene cover a wide range, from sealants and roofing (high molecular weight PIB above of 300000 g/mol) to sealants, adhesives, extenders, and chewing gum base (medium molecular weight PIB between 4000 to 120000 g/mol) and finally to glues, lubricants and modifiers and oil additives (low molecular weight PIB between 500 and 5000). In order to maintain control over the molecular weight and to achieve high molar mass products, the cationic polymerization of isobutylene is typically carried out at cryogenic temperature which minimizes the unfavorable transfer reactions but leads to a costly process. The effect of temperature on the molecular weight can be expressed by the Arrhenius plots ($M_n$ dependence on 1/T).[2]

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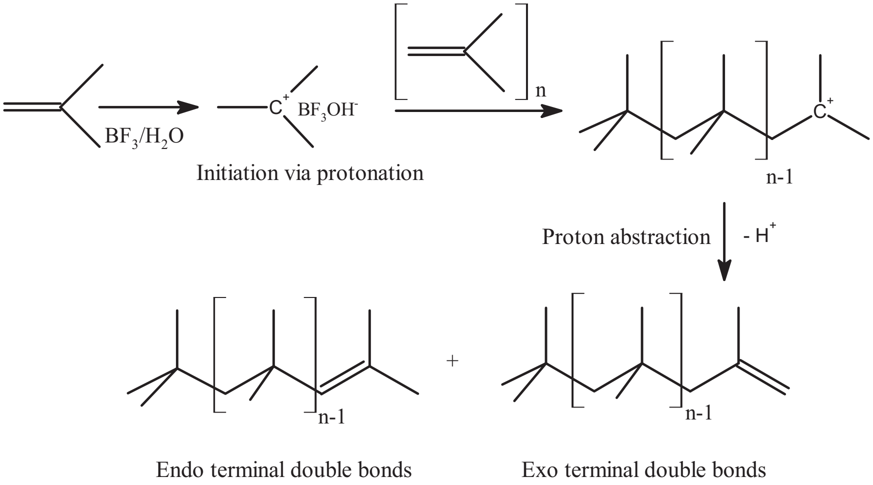


**Scheme 1.**
The typical initiation reaction of isobutylene via protonation and the two main types of terminal unsaturated end groups formed.

Highly reactive polyisobutylenes (HR-PIBs) with molecular weight between 500 to 5000 g/mol and a high content of exo terminal double groups (70%-80%) are of high commercial interest. The terminal unsaturated groups play an important role in the post functionalization or modification of the PIB for applications such as lubricants and fuel additives.[6] Various routes for the synthesis of HR-PIBs have been described and patented, which mainly focus on the usage of Lewis acid based initiators such as $BF_3$ at reaction temperature significantly below 0 °C.[7]

First row transition metal complexes of the general formula $[M(NCCH_3)_6](A)_2$ ($M^{II}$ = Cr, Mn, Fe, Co, Ni, Cu, Zn; A = anion) and some of their dimeric second and third row congeners of formula $[M_2(NCCH_3)_{8-10}](A)_2$ ($M^{II}$ = Mo, Tc, Re, Rh; A = counterion such as $BF_4^-$) have already been described and were applied as catalysts for cationic polymerization of cyclopentadiene and methylcyclopentadiene in both homogeneous and heterogeneous phases.[8] The previous work on the polymerization of cyclopentadiene showed that the counteranions influence the effectiveness of the initiator. The replacement of $[BF_4]^-$ with bulky WCAs such as $[B(C_6F_5)_4]^-$, $[B(C_6H_3(CF_3)_2)_4]^-$, and $[(C_6F_5)_3BC_3H_3N_2\text{-}B(C_6F_5)_3]^-$ has significantly increased the TOFs (Turn Over Frequency) of the complexes and further enables the polymerization of industrially interesting monomers such as isobutylene at room temperature (30 °C) resulting in polyisobutylene which exhibits a high content of exo double bonds.[9]

The application of WCAs in the polymerization of isobutylene is well described and published, including earlier work by Shaffer et al.[10] and Baird et al.[11] Shaffer et al. showed that traditional organometallic insertion polymerization catalysts can be used to initiate isobutylene polymerizations when they are activated with non-coordinating anion based activators such as $[B(C_6F_5)_3]$ and $[B(C_6F_5)_4]^-$.[10] Kennedy et al. noted that unusually high molecular weight products can be obtained by utilizing $[B(C_6F_5)_4]^-$.[12] Baird et al. showed that metallocene-like initiators such as $(\eta^5\text{-}C_5Me_5)TiMe_2\{\mu\text{-}Me)B(C_6F_5)_3$ can be applied in the polymerization of isobutylene and certain similar compounds can be used to polymerize isobutylene with high isoprene content (15 wt%) even at relatively high temperatures (-30°C) with good conversions.[11,13] Bochmann et al.

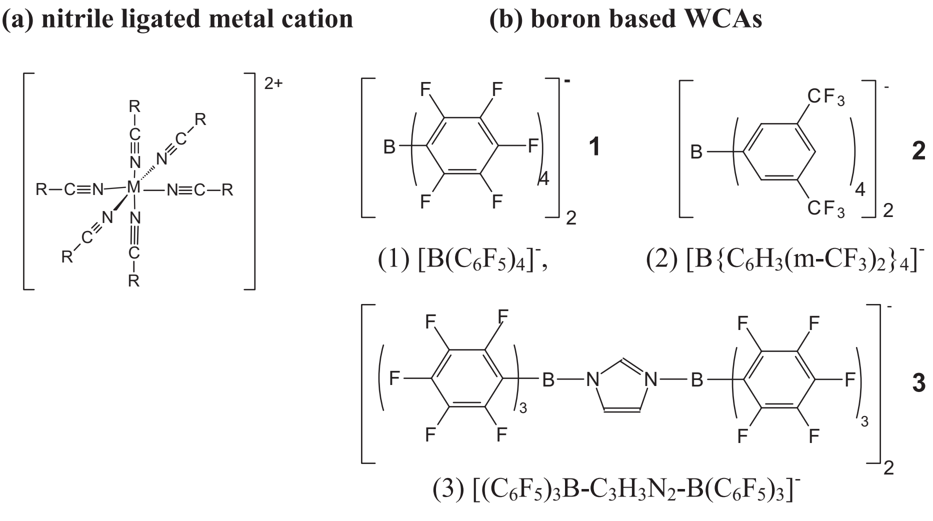
demonstrated that zirconocene based WCAs are excellent initiators for the isobutylene polymerization and its copolymerization with isoprene to very high molecular weight products at relatively high temperatures of –35 °C. He also described that the adventitious water acts as chain transfer agent and reduces the catalyst activity for polymerization.[14] Piers and Collins et al. recently described the polymerization of isobutylene in hydrocarbons as well as in aqueous suspension by using chelating diboranes as coinitiators.[15]

Most of the above described work was conducted at temperatures below 0 °C. Recently, Bochmann et al. described the successful room temperature polymerization of isobutylene when EtZnCl was added to a mixture of t-BuCl and isobutylene in methylene chloride at 20 °C, yielding products with medium molecular weight with high content of exo double bonds.[16]

## Results and Discussion

The nitrile ligated transition metal complexes with weakly coordinating counteranions and their catalytic applications have been reviewed recently by Kühn et al.[17] It has been shown that this particular category of nitrile ligated metal complexes associated with the boron based WCAs, mainly (1) $[B(C_6F_5)_4]^-$, (2) $[B\{C_6H_3(m\text{-}CF_3)_2\}_4]^-$, and (3) $[(C_6F_5)_3B\text{-}C_3H_3N_2\text{-}B(C_6F_5)_3]^-$ as shown in Scheme 2, are effective initiators – or better catalysts - for the polymerization of isobutylene at room temperature (30 °C) yielding low molecular weight HR-PIB.[9,18–22]

In early work, the isobutylene polymerization and copolymerization with isoprene were successfully performed at 30 °C using the manganese (II) complexes which were octahedrally ligated with six acetonitrile ligands and associated with the boron based WCAs.[9,18] The manganese (II) complexes applied are surprisingly temperature stable and moderately stable to air and can be easily handled in laboratory atmosphere. The reaction of the manganese (II) complex with an excess amount of water results in the slow formation of an aqua complex $[Mn(H_2O)_2(NCCH_3)_4](A)_2$, in which excess water molecules replaces two of the axial ligands and which was


(a) nitrile ligated metal cation

(b) boron based WCAs

(1) $[B(C_6F_5)_4]^-$,

(2) $[B\{C_6H_3(m\text{-}CF_3)_2\}_4]^-$

(3) $[(C_6F_5)_3B\text{-}C_3H_3N_2\text{-}B(C_6F_5)_3]^-$

***Scheme 2.***
Typical nitrile ligated metal cations and boron WCAs applied for the polymerization of isobutylene. ($R = CH_3$ (AN), $C_6H_5$ (BN) and M = metal centre; Mn(II),[11,21,22] Mo(III),[22] Cu(II)[20,21]) [Please note the typical abbreviations for the catalytic systems such as MnAN1 or MoAN3 with the corresponding metal (Mn(II), Mo(III) or Cu(II)); ligands (AN or BN) and the corresponding WCAs (1,2 or 3)].

found to be inactive. Kinetic studies revealed that the polymerization was completed only after 55 to 110 hours depending on the complexes used, which is much slower than the conventional cationic polymerization of isobutylene. The HR-PIBs obtained were in the molecular weight range of 500 g/mol to 13000 g/mol with an exo double bond content of more than 90%. The ideal reaction medium reported was methylene chloride owing to its aprotic and polar character whereas the addition of hexane reduces the isobutylene conversion. The influence of the water has also been explored with the manganese (II) complexes. Only a slight decrease in monomer conversion was observed when up to a tenfold excess of water to the amount of initiator were added. Increasing water content above the tenfold excess, however, causes the conversion to decrease dramatically.[19(b)]

In order to increase the efficiency of the manganese (II) complexes the ligands were changed from acetonitrile to benzonitrile, both being similar effective catalysts (Figure 1, Table 1).[19] It was found that in general low catalyst and high monomer concentration are favourable to attain high conversion and high content of exo double bonds whereas molar mass is rather independent of those parameters (Table 1). Online $^1$H NMR studies of the polymerization process indicated that no fragments of the metal complex of the WCAs have been incorporated into the polymer chain as head or end groups. Also high and constant content of exo double bonds can be observed until significant high monomer conversions. Nonetheless, the content of the exo double bonds decreased when the reaction time was prolonged, an effect that might be caused by isomerization to endo and internal double bonds.

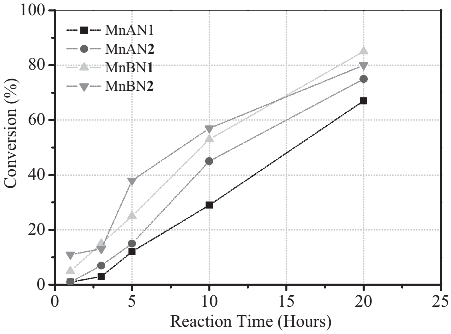


***Figure 1.***
The conversion obtained for the homopolymerization of isobutylene conversion (%) versus reaction time (hours) plot; $[IB]_0 = 1.78$ mol/l, $[initiator] = 0.5 \times 10^{-4}$ mol/l, solvent = $CH_2Cl_2$, reaction temperature = 30 °C.

The successful application of the manganese (II) complexes in the polymerization of isobutylene at room temperature (30 °C) led to the exploration of different metal complexes. [20–22] Copper (II) complexes were found to be superior to the previously described manganese (II) complexes with regard to considerable faster reaction time and the possibility to use

***Table 1.***
Comparison between MnAN1 and MnBN2 for the homopolymerization of isobutylene; $[IB]_0 = 1.78$ mol/l, solvent = $CH_2Cl_2$, reaction temperature = 30 °C. [Data compiled from reference. [19]

| Complex | Concentration ($10^{-4}$) (mol/L) | Reaction Time (Hours) | Conversion (%) | Molecular Weight (Mn) (g/mol) | PDI | Exo Double Bond (%) |
|---|---|---|---|---|---|---|
| **MnAN2** | 5.00 | 20 | 70 | 3700 | 2.5 | 61 |
| | 3.75 | 20 | 70 | 3900 | 2.5 | 58 |
| | 2.50 | 20 | 70 | 2600 | 3.0 | 43 |
| | 1.25 | 20 | 88 | 2200 | 3.0 | 56 |
| | 0.50 | 20 | 89 | 2500 | 2.9 | 64 |
| **MnBN2** | 0.5 | 1 | 11 | 5200 | 1.7 | - |
| | 0.5 | 3 | 13 | 900 | 1.7 | - |
| | 0.5 | 5 | 38 | 1100 | 1.9 | 80 |
| | 0.5 | 10 | 57 | 1000 | 1.8 | 79 |
| | 0.5 | 20 | 80 | 700 | 1.6 | 78 |

non-halogenated solvents such as toluene. Optimal results could be obtained with CuAN1 and CuAN2 complexes which were able to initiate the polymerization of isobutylene to high monomer conversion (up to 90%) in pure toluene yielding products with high exo double bonds content up to 85%. Usually, no polymerization was observed in pure non-polar solvents but the copper catalysts allowed polymerization even in hexane rich systems (Figure 2). The effect of the ligands and the metal cations can be seen most impressively by comparing the needed polymerization time: CuBN1 reduces the polymerization time for a reasonable monomer conversion to 15 minutes as compared to up to 20 hours for the manganese (II) complexes.[21]

Recently, a series of acetonitrile ligated molybdenum (III) complexes associated with the boron based WCAs were described for the polymerization of isobutylene at 30 °C which showed also significant advantages over the previously described manganese (II) complexes.[22] These molybdenum (III) complexes MoAN1 ($[Mo(NCCH_3)_5Cl][B(C_6F_5)_4]_2$), MoAN2 ($[Mo(NCCH_3)_5Cl][B\{C_6H_3(m\text{-}CF_3)_2\}_4]_2$) and MoAN3 ($[Mo(NCCH_3)_5Cl][(C_6F_5)_3B\text{-}C_3H_3N_2\text{-}B(C_6F_5)_3]_2$), have been proven to be effective initiators for the polymerization of isobutylene with a substantial high reaction rate and the polyisobutylene obtained fulfilled the characteristic of HR-PIB. For example, the homopolymerization of isobutylene with the MoAN3 complex at a very low initiator concentration ($0.5 \times 10^{-4}$ mol/l) reached a monomer conversion of 67% (Mn = 600 g/mol and PDI = 1.5) within two hours in toluene leading to products with an exo double bond content of 90%.

Microstructures of polyisobutylenes obtained from copper (II) and molybdenum (III) complexes were similar to those from manganese complexes. However, the most active complexes also led to the strongest and fastest reduction of exo double bonds and the formation of internal unsaturated units with increasing reaction time. In a typical cationic polymerization, the proton abstraction from the tertiary cations of the propagating chain will mainly lead to exo or endo terminal double bonds. But transfer or isomerization reactions might also lead to the formation of varieties of internal double bonds as shown in Scheme 3.[19] As mentioned earlier, the decrease of the exo terminal double bond content with reaction time might be attributed to the double bond isomerization which might be catalyzed by the metal complexes.[21]

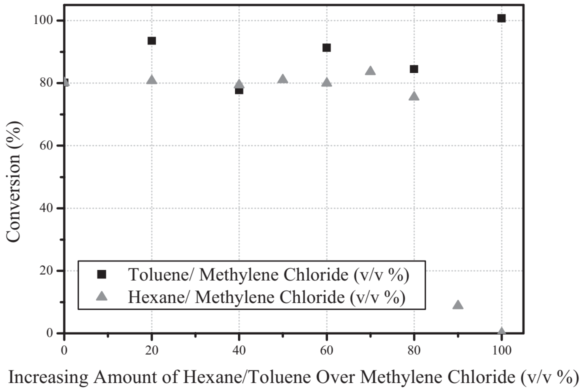


***Figure 2.***
The effect of the increasing percentage of hexane or toluene over methylene chloride (% v/v) on the conversion for the homopolymerization of isobutylene with the complex CuAN1; $[IB]_0 = 1.78$ mol/l, [initiator] $= 1.0 \times 10^{-4}$ mol/l, reaction temperature = 30 °C, reaction time = 28 hours.[21]

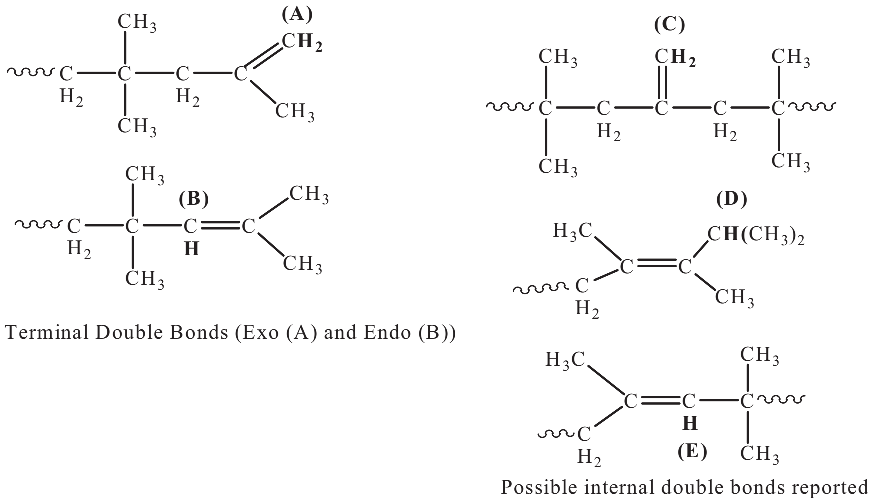
*Table 2.*
Comparison between the copper(II) and the molybdenum(III) complexes for the homopolymerization of isobutylene; $[IB]_0 = 1.78$ mol/l, reaction temperature = 30 °C (DCM = Methylene Chloride, Tol = Toluene). [Data compiled from reference [19 –22].

| Complex Used | Concentration Used ($10^{-4}$) (mol/L) | Reaction Time (Hours) | Conversion (%) | Molecular Weight (Mn) (g/mol) | PDI | Solvent |
|---|---|---|---|---|---|---|
| CuAN1 | 1.0 | 0.5 | 40 | 1700 | 1.4 | DCM |
| CuAN2 | 1.0 | 0.5 | 78 | 1400 | 1.4 | DCM |
| CuAN3 | 6.0 | 0.5 | 3 | 1400 | 1.4 | DCM |
| CuBN1 | 0.5 | 0.5 | 80 | 600 | 1.4 | Tol |
| MoAN1 | 0.5 | 10 | 90 | 1300 | 3.2 | DCM |
| MoAN2 | 0.5 | 10 | 94 | 1400 | 3.1 | DCM |
| MoAN3 | 0.5 | 2 | 67 | 600 | 1.5 | Tol |

Recently, we developed a new series of alumina based WCAs, mainly (4) $[Al\{OC(CF_3)_3\}_4]^-$, (5) $[Al\{OC(C_6H_5)(CF_3)_2\}_4]^-$ and (6) $[Al\{OC(C_6H_4CH_3)(CF_3)_2\}_4]^-$ which were also associated with the nitrile ligated metal cations as shown in Scheme 4.

Preliminary results on that tailored series of nitrile ligated metal complexes associated with the alumina WCAs also indicate a high potential for the room temperature polymerization of isobutylene. Presently, this system is under investigation in order to determine the influence of these newly tailored complexes on their catalytic potential and to elucidate mechanistic aspects. Reaction parameters have been varied to identify their influence on the polymerization process and the structure of the resulting products, particularly the content of the double bonds.

So far all the studied WCA complexes associated with nitrile ligated metal cations proved to be effective in the room temperature polymerization of isobutylene. The products show the characteristics of the typical HR-PIB prepared by conventional low temperature cationic polymerization. Whereas the reaction time and the content of exo double bonds could be optimized significantly by varying WCA and ligand structure, the effect of the complex structure and the applied initiator concentration on molar mass is rather low. So far, no conclusive model for the

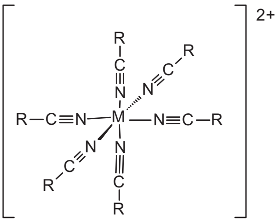


Terminal Double Bonds (Exo (A) and Endo (B))

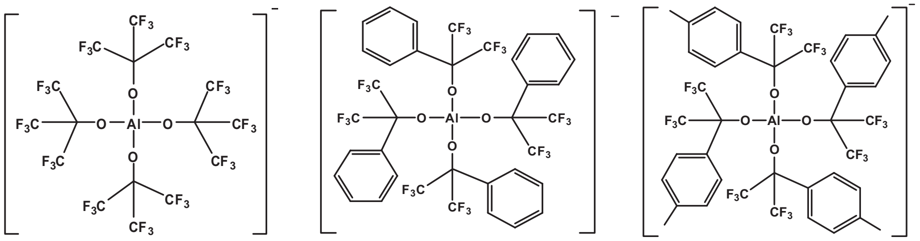
Possible internal double bonds reported

*Scheme 3.*
Unsaturated structural units proven in the $^1H$ NMR spectra of PIB synthesized with the manganese (II) complexes.[19]

**(a) nitrile ligated metal cation**



**(b) alumina based WCAs**



(4) $[Al\{OC(CF_3)_3\}_4]^-$ (5) $[Al\{OC(C_6H_5)(CF_3)_2\}_4]^-$ (6) $[Al\{OC(C_6H_4CH_3)(CF_3)_2\}_4]^-$

***Scheme 4.***
Typical nitrile ligated metal cations and the alumina based WCAs applied for the polymerization of isobutylene. ($R = CH_3$, $C_6H_5$ and M = metal centre such as Cu(II) Zn(II)).

initiation process and the polymerization mechanism can be proposed. Efforts are currently underway to elucidate the mechanism of this room temperature polymerization process.

## Conclusion

Nitrile ligated metal cations associated with boron based WCAs, in particular $[Mn(NCR)_6][A]_2$, $[Cu(NCR)_6][A]_2$ and $[Mo(NCR)_5Cl][A]_2$ ($R = CH_3$, $C_6H_5$ and A = the corresponding boron based WCAs) were shown to be excellent initiators for the polymerization of isobutylene at room temperature (30 °C) and the preparation of the industrially interesting low molar mass highly reactive HR-PIB with high exo double bond content. Such complexes offer significant advantages over conventional polymerization initiators of isobutylene as they allow the polymerization to be carried out at room temperature compared to the usually needed cryogenic temperatures. The new initiator systems could be fine-tuned to allow even the use of non-chlorinated solvents and very short reaction times of only 15 min.

Mechanisms for the polymerization reactions initiated by this category of catalysts have been proposed and discussed.[18(c)] Further work is now in progress to fully elucidate the mechanisms in order to understand the role of the nitrile ligated metal complexes and the WCAs. Efforts are also undertaken to tap into the diversity of the WCAs described in the literature to fully explore the possibilities in view of designing and synthesizing more tailor-made initiator systems. In line with this effort, alumina based WCAs associated with nitrile ligated metal complexes have also been synthesized and applied successfully in the polymerization of isobutylene at room temperature.

[1] P. H. Plesch, *The Chemistry of Cationic Polymerization*, Pergamon Press, Oxford **1963**.

[2] J. P. Kennedy, E. Marechal, *Carbocationic Polymerization*, Wiley, New York **1982**.

[3] A. G. Evans, G. W. Meadows, *Trans Faraday Soc*, **1950**, *46*, 327.

[4] A. G. Evans, G. W. Meadows, *J Polym Sci*, **1949**, *3*, 359.

[5] I. Puskas, S. J. Meyerson, *Org Chem*, **1984**, *49*, 258.

[6] P. Börzel, K. Bronstert, F. Hovermann, DE 2702604, (**1978**), to BASF AG.

[7] (a) H. P. Rath, (to BASF AG). WO Patent 99/64482, **1999**, *Chem Abstr*, **1999**, *13*, 23299; (b) J. T. Nolan, Jr. H. Chafetz, (to Texaco Inc.). U.S. Patent 3,166,546 1965. *Chem Abstr* **1965**, *62*, 44376.

[8] (a) R. T. Henriques, E. Herdtweck, F. E. Kühn, A. D. Lopes, J. Mink, C. C. Romao, *J Chem Soc Dalton Trans*, **1998**, 1293; (b) W. E. Buschmann, J. S. Miller, *Chem Eur J*, **1998**, *4*, 1731; (c) S. N. Bernstein, K. R. Dunbar, *Angew Chem Int Ed*, **1992**, *31*, 1360; (d) F. A. Cotton, S. C. Haefner, A. P. Sattelberger, *J Am Chem Soc*, **1996**, *118*, 5486; (e) F. A. Cotton, F. E. Kühn, *J Am Chem Soc*, **1996**, *118*, 5826; (f) F. E. Kühn, J. R. Ismeier, D. Schön, W. M. Xue, G. Zhang, O. Nuyken, *Macromol Rapid Commun*, **1999**, *20*, 555; (g) F. E. Kühn, D. Schön, G. Zhang, O. Nuyken, *J Macromol Sci, Pure Appl Chem*, **2000**, *37*, 971.

[9] M. Vierle, Y. Zhang, E. Herdtweck, M. Bohnenpoll, O. Nuyken, F. E. Kühn, *Angew Chem Int Ed*, **2003**, *42*, 1307.

[10] (a) T. D. Shaffer, J. R. Ashbaugh, *J Polym Sci Part A Polym Chem*, **1997**, *35*, 329–344; (b) T. D. Shaffer, A. J. Dias, I. D. Finkelstein, M. B. Kurtzman, WO 9529940, **1997**, to Exxon Chemical Patents Inc.

[11] (a) F. Barsan, M. C. Baird, *J Chem Soc Chem Comm*, **1995**, *1065*; (b) S. W. Ewart, M. J. Sarsfield, E. F. Williams, M. C. Baird, *J Organomet Chem*, **1999**, *579*, 106; (c) M. Lin, M. C. Baird, *J Organomet Chem*, **2001**, *619*, 62; (d) M. C. Baird, *Chem Rev*, **2000**, *100*, 1471.

[12] Z. Pi, S. Jacob, J. P. Kennedy, In: J. R. Puskas, (Ed.), *Ionic polymerizations and related processes*, Dordrecht, The Netherlands Kluwer, **1999**, p. 1.

[13] (a) P.J. McInenly, J. Mark, M.C. Baird, *Macromol. Chem. Phys.* **2004**, *205*, 1707–1712; (b) C. K. W. Tse, A. Penciu, P. J. McInenly, K. R. Kumar, J. Mark, M. C. Baird, *European Polymer Journal*, **2004**, *40*, 2653–2657.

[14] (a) S. Garratt, A. Guerrero, D. L. Hughes, M. Bochmann, *Angew Chem, Int Ed*, **2004**, *43*, 2166; (b) S. Garratt, A. G. Carr, G. Langstein, M. Bochmann, *Macromolecules*, **2003**, 36.

[15] (a) S. P. Lewis, N. J. Taylor, W. E. Piers, S. Collins, Scott, *J Am Chem Soc*, **2003**, *125*, 14686; (b) S. P. Lewis, L. D. Henderson, B. D. Chandler, M. Parvez, W. E. Piers, S. Collins, *J Am Chem Soc*, **2005**, *127*, 46; (c) S. P. Lewis, J. F. Chai, S. Collins, T. J. J. Sciarone, L. D. Henderson, C. Fan, M. Parvez, W. E. Piers, *Organometallics*, **2009**, *28*, 249–263.

[16] A. Guerrero, K. Kulbaba, M. Bochmann, *Macromolecules*, **2007**, *40*, 4124.

[17] S. F. Rach, F. E. Kühn, *Chem. Rev.*, **2009**, *109*(5), pp 2061–2080.

[18] (a) M. Bohnenpoll, J. Ismeier, O. Nuyken, M. Vierle, D. Schön, F. E. Kühn, EP 1344785, 2003, to Bayer AG; (b) M. Vierle, Y. Zhang, A. N. Santos, K. Köhler, C. Haeßner, E. Herdtweck, M. Bohnenpoll, O. Nuyken, F. E. Kühn, *Chem Eur J*, **2004**, *10*, 1; (c) O. Nuyken, M. Vierle, F. E. Kühn, Y. Zhang, *Macromol Symp*, **2006**, *236*, 69.

[19] R. Narayanan, A. K. Hijazi, H. Komber, B. Voit, S. Zschoche, F. E. Kühn, O. Nuyken, M. Walter, P. Hanefeld, *J. Polym. Sci. Part A: Polym. Chem*, **2007**, *45*, 5636–5648.

[20] A. K. Hijazi, H. Y. Yeong, Y. Zhang, E. Herdtweck, O. Nuyken, F. E. Kühn, *Macromol Rapid Commun.* **2007**, *28*, 670–675.

[21] Y. Li, L. T. Voon, H. Y. Yeong, A. K. Hijazi, R. Narayanan, K. Köhler, B. Voit, O. Nuyken, F. E. Kühn, *Chem. Eur. J.*, **2008**, *14*, 7997–8003.

[22] A. K. Hijazi, R. Narayanan, K. R. Jain, E. Herdtweck, O. Nuyken, H. M. Walter, P. Hanefeld, B. Voit, F. E. Kühn, *Angew. Chem. – Int. Ed.* **2007**, *46*, 7290.