Recent progress in the Lewis acids co-initiated cationic polymerization of isobutylene and 1,3-dienes

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Recent progress in the Lewis acids co-initiated cationic polymerization of isobutylene and 1,3-dienes

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This article reviews recent approaches toward synthesis of *exo*-olefin terminated polyisobutylene (PIB) or so-called highly reactive PIB (HR PIB). The advantages and disadvantages of methods based either on living cationic polymerization or using complexes of Lewis acids with ethers are discussed here from point of view of their industrial relevance. The first method is unique in terms of synthesis well-defined di- or trifunctional *exo*-olefin terminated polyisobutylenes. The second one is the best candidate to replace BF_3-based process, which is currently used for production HR PIB at the industrial scale. Special focus is laid on the recent progress in the cationic polymerization of 1,3-dienes (isoprene, 1,3-pentadiene) allowing to synthesize well-defined low molecular weight poly(1,3-diene)s with high degree of unsaturation of the polymer chain (>85%). This review article shows that the Lewis acid-co-initiated cationic polymerization of isobutylene and 1,3-dienes is still not fully explored, and new innovative initiating systems of high commercial interest can be discovered.

1. Introduction

The discovery of catalytic effect of aluminium chloride in the reactions of alkylation of arenes by Friedel and Crafts[1,2] induced the growing interest to the application of metal halides as catalysts in the cationic polymerization processes.[3,4] It was clearly demonstrated that using of metal halides instead of Brönsted acids allowed to generate for the first time high molecular weight polymers via cationic mechanism.[3] The next breakthrough in the field of cationic polymerization was made by Otto in the late 1930s who synthesized high molecular weight polyisobutylene ($M_n > 10^6$ g mol^{-1}) *via* low temperature BF_3-catalyzed cationic polymerization.[5] Shortly after, Thomas and Sparks discovered the new family of polyisobutylene-based elastomers (butyl rubber and latter chlorobutyl or bromobutyl rubber) synthesized by copolymerization of isobutylene with small amount of isoprene in the presence of $AlCl_3$ as a catalyst.[6] To date, these products are the most important industrial materials produced by cationic polymerization.

The further fundamental investigations in this area revealed the necessity to use cationogens (H_2O, HCl) together with metal halides, since Lewis acid by itself did not catalyze the cationic polymerization in perfectly dried conditions.[3] Based on this finding, it was proposed to term cationogen as initiator and Lewis acid (metal halide) as co-initiator or activator.[3] Finally, the major breakthrough was made by Higashimura and Kennedy teams when they reported independently the living cationic polymerization of vinyl ethers[7] and isobutylene (IB)[8] in 1980s, respectively. The discovery of living cationic polymerization was made possible mainly due to the rational design of appropriate initiator/co-initiator combination.[4,9] Since this discovery, a great variety of metal halides such as widely used ZnX_2 (X=Cl, Br, I), BCl_3, $AlCl_3$, $TiCl_4$, $SnCl_4$, $EtAlCl_2$ and rarely utilized $GaCl_3$, $InCl_3$, $NbCl_5$, $BiCl_3$ etc. were shown to induce the living cationic polymerization.[4,9]

The conventional and living cationic (co)polymerization of isobutylene is still the most studied filed due to both the unique structure of monomer (polymerized only by cationic mechanism) and the commercial importance of the obtained (co)polymers.[9,10] The cationic homopolymerization of 1,3-dienes is considerably less studied in comparison with isobutylene presumably owing to the complicity of the process which accompanied by number of side reactions leading to ill-defined low molecular weight (M_n) products.[11,12,13] Therefore, the commercial application of the cationic polymerization of 1,3-dienes is limited to the $AlCl_3$-co-initiated synthesis of hydrocarbon resins from C_5 mixture (contained predominantly 1,3-penadiene, isoprene and cyclopentadiene) and synthetic caoutchouc oligomer of piperylene (SKOP) via $TiCl_4$-co-initiated polymerization of 1,3-pentadiene.[11]

In recent years, considerable efforts have been made on the application in the cationic polymerization of organometallic catalysts bearing so-called weakly coordinating counteranions (WCAs) such as, for example, metallocenes (Cp^*TiCl_3, Cp_2AlMe, $[Cp_2^*ZrH(\mu\text{-}H)]_2$) activated by $B(C_6F_5)_3$ and its derivatives as well as adducts of $B(C_6F_5)_3$ with long chain carboxylic acids.[14] The main feature of catalysts generating WCA*s* is their low proton affinities that enables to synthesize high molecular weight (co)polymers at elevated temperatures (conventional cationic polymerization is typically required cryogenic temperatures to obtain polymers with high M_n). The use of such type of catalysts for the synthesis of high M_n polyisobutylenes and its copolymers with isoprene (butyl rubber) was recently well reviewed by Baird and Bochmann.[14] Quite recently, nitrile-ligated metal complexes associated with WCA*s* were developed by Kühn and Voit as highly active single-site catalysts for the synthesis of low molecular weight polyisobutylene with high content of vinylidene end groups (so-called highly reactive polyisobutylene, HR PIB),[15,16] a key intermediate for the manufacturing of fuel and oil additives.[17] In addition, univalent gallium salts of WCA*s* was recently shown to be very efficient catalysts for the synthesis of HR PIB.[18] The main advantages of these complexes are that they can be used in the catalytic amounts ($<10^{-4}$ M) at room or even higher temperatures.[14–18]

Despite of the intensive development of the new catalysts associated with WCA*s*, the conventional metal halides are still the most used co-initiators for cationic polymerization both in the fundamental investigations and at the industrial scale. In this review article, the recent developments in the using of conventional metal halides as co-initiators of cationic polymerization are reported with a focus on the synthesis of two type of polymers: (i) low molecular weight polyisobutylene (HR PIB) and (ii) poly(1,3-diene)s such as poly(isoprene) and poly(1,3-pentadiene).

2. Polyisobutylene

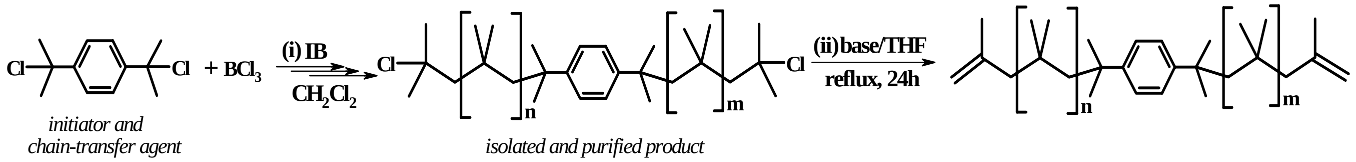
Low molecular weight polyisobutylene (PIB) (M_n=500-5000 g mol^{-1}) is the most important industrial class of IB polymers representing of 75-80% of the total PIB market due to their use for manufacturing of motor oil and fuel additives.[17] Two types of low molecular weight PIB are currently available in the market: (i) highly reactive and (ii) “conventional” polyisobutylenes.

HR PIB contains predominantly *exo*-olefin terminal groups (>75%) and produced commercially by the polymerization of pure isobutylene (IB) or, rarely, C_4 mixture (IB, 1-butene, 2-butenes and hydrocarbons) using complexes of BF_3 with alcohols and/or ethers as co-initiator in hydrocarbons at moderately high temperatures (–20 to –10 °C).[17,19] Another industrial technique to synthesize low molecular weight PIB is based on the $AlCl_3$- or $EtAlCl_2$-co-initiated polymerization of C_4 mixture, but the obtained “conventional” PIB contains predominantly *tri*- and *tetra*-substituted olefinic end groups,[20] which are far less reactive as compared to *exo*-olefin end groups. Therefore, chlorination-dehydrochlorination procedure is required for conventional PIB before its functionalization by maleic anhydride. This leads to large quantities of chlorine-containing waste water. As far as chlorination-dehydrochlorination is not necessary for HR PIB and final product does not contain any chlorine, HR PIB is more preferably than conventional one for the production of ashless dispersants. The main disadvantage of the existing technique of HR PIB synthesis is gaseous state of BF_3 that makes difficulties to handle and is detrimental to equipments. Moreover, due to upcoming changes in the technical standards for lubricating oils/fuel additives, the demand for HR PIB is constantly increased during the last years. This leads to the growing interest towards improvement of the synthesis of HR PIB by various research groups and industrial companies.

Currently, three general approaches for the synthesis of HR PIB are being intensively developed. The first approach is based on the use of living cationic polymerization technique, while the second one consists in the using of conventional modified metal halides as co-initiators of IB cationic polymerization. The third approach, which involves the utilization of solvent-ligated complexes with weakly coordinating borate and aluminate anions ($[M(NCCH_3)_6](A_2)$, where M=Mn, Mo, Zn Fe or Cu), was recently reviewed[15,16] and, therefore, is outside of the scope of this review article.

2.1. HR PIB via living cationic polymerization

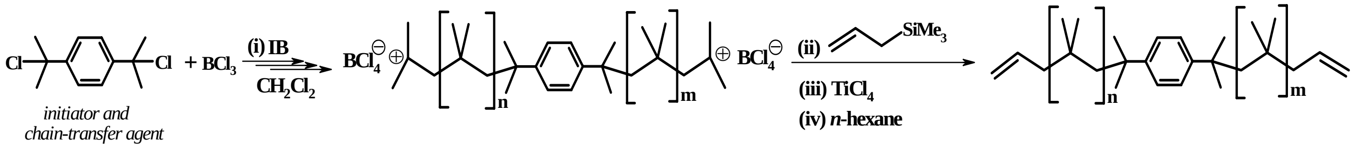
2.1.1. Dehydrochlorination of *tert*-chlorine-terminated PIB. One of the first reports on the synthesis of mono- and difunctional PIB with nearly quantitative *exo*-olefin end group content is dated to 1979.[21] In this report, the desired product was obtained into two stages including synthesis of telechelic PIB carrying *tert*-chlorine end groups with DiCumCl/BCl_3 (DiCumCl represents 1,4-*bis*(1-chloro-1-methylethyl)benzene) initiating system via so-called inifer technique[22] (DiCumCl acts both as initiator and chain-transfer agent), on the first stage. On the second stage, after purification of the polymer, its dehydrochlorination was occurred by refluxing the *tert*-chlorine terminated PIB with corresponding base in THF (or mixture of THF with alcohol) during 24 h[21] (Scheme 1). The different bases such as pyridine, tributylamine, NaOH, NaOMe, NaOEt and ^{t}BuOK were tested in the dehydrochlorination reaction.[21,23] Among them, only ^{t}BuOK in THF and NaOEt in a THF/EtOH mixture allowed to achieve quantitative formation of *exo*-olefin terminated telechelic PIB. The recent re-examination of this approach by Ivan et al.[24] revealed that maximal *exo*-olefin content did not exceed 95% due to the competing thermal HCl elimination leading to the formation of *endo*-olefin end group. Despite of the perfect functionality of PIBs obtained by this approach (*exo*≥95%), the main disadvantage of this method is the necessity of polymer purification as well as quite long time for dehydrochlorination (up to 24 h) and using THF as a solvent.



Scheme 1 Synthesis of difunctional *exo*-olefin terminated PIB via two stages process including (i) cationic polymerization of IB with DiCumCl/BCl_3 initiating system at –50 °C or –70 °C and (ii) dehydrochlorination of *tert*-chlorine-terminated PIB with bases (^{t}BuOK or NaOEt) in THF or THF/ethanol mixture, respectively.

2.1.2. End-quenching by allyl(isobutenyl)trimethylsilane. In order to simplify the cumbersome procedure for obtaining of olefin-terminated PIB via dehydrochlorination of *tert*-chlorine-terminated PIB, the new method was developed by Kennedy’s team. Originally, this method consisted in “one-pot two step” procedure involving synthesis of mono- or multifunctional *tert*-chlorine PIB via inifer technique with BCl_3 as co-initiator followed by (without isolating of product) the reaction with allyltrimethylsilane (ATMS) yielding desired allyl-terminated PIB at –80 °C.[25] It was demonstrated that quantitative allylation could be achieved in less than 1 h by using of 2-3 fold excess of ATMS relative to *tert*-chlorine end groups as well as by addition of excess $TiCl_4$ and diluting the reaction mixture by *n*-hexane[25] (Scheme 2). This procedure was further modified by Ivan and Kennedy[26] by using more stable initiators than DiCumCl such as DiCumOMe (1,4-*bis*(1-methoxy-1-

methylethyl)benzene), TriCumOMe (1,3,5-*tris*(1-methoxy-1-methylethyl)benzene) and conducting the polymerization in the presence of $TiCl_4$ instead of BCl_3 in non-polar reaction media (CH_3Cl: *n*-hexane 40: 60 v/v). This allowed simplifying significantly the procedure by excluding the necessity to change the Lewis acid and adjusting the solvent polarity (steps (iii) and (iv) in Scheme 2).



Scheme 2 One-pot two step procedure towards synthesis of allyl-terminated telechelic PIB via cationic polymerization of IB with DiCumCl/BCl_3 initiating system at –80 °C followed by end-quenching by allyltrimethylsilane.

An attempt to substitute ATMS to isobutenyltrimethylsilane (IBTMS) in this “one-pot two step” procedure (in order to get the same chain end structure as *exo*-olefin terminated PIB has) was unsuccessful. Particularly, it was demonstrated that quite low functionalization (less than 40%) was observed with IBTMS[27] in the same conditions where ATMS showed high efficiency.[26] The increase of both IBTMS concentration and reaction time (up to 6h) resulted in the increase of yield of isobutenylation reaction up to 100%, but the close inspection of GPC curves revealed the appearance of shoulders in high molecular weight region resulting in duplication and tripilication of molecular weight.[27]

Such observation was attributed by authors to chain coupling through the reaction of carbocations with isobutenyl (*exo*-olefin) groups.[27] However, the coupled polymer chains should appear at 4.82 ppm in ^1H NMR spectrum as a shoulder to one of the signals of *exo*-olefin end group at 4.85 ppm[28] that is not observed in ^1H NMR spectra of products obtained via end-quenching of living PIB chains by isobutenyltrimethylsilane.[27] Therefore, the reasons for the appearance of several peaks on GPC curves are not very clear. In addition, it was clearly demonstrated that IBTMS can react with isolated *tert*-chlorine-terminated PIB in the presence of $TiCl_4$ yielding almost exclusively *exo*-olefin-terminated PIB.[27,29]

To summarize, the end-quenching of living PIB chains by ATMS and, in some degree, IBTMS is a simpler, faster and more economic process to prepare olefin-terminated PIB in comparison with dehydrochlorination approach. However, the main disadvantage of this method is the relatively high cost of quenching agents, which are used in excess with respect to the chain ends.

2.1.3. End-quenching with hindered bases. This approach originated from the observations of Ivan[30] and Faust[31] of low stability of living PIB chains in the presence of proton traps (sterically hindered substituted pyridines such as 2,6-di-*tert*-butylpyridine (DTBP), which interacted efficiently with protons but too sterically hindered to react with carbocations or Lewis acids[4]) under monomer starved conditions[30] or when DTBP had insufficient purity.[31] One explanation for the formation of olefin-terminated PIB chains in the presence of DTBP was the direct participation of DTBP in the *β*-H abstraction,[30] while another one was based on the action of cyclic imine base, which presented as impurity in DTBP.[31] In ten years, Storey and co-workers observed the unexpected formation of exclusively *exo*-olefin terminated chains in the course of investigations of alkylation of pyrrole derivatives by the living PIB carbenium ions[32] when 2,5-dimethylpyrrole (2,5DMP) was used.[33]

Motivated by this finding, Storey and co-workers investigated the efficiency of different bases (DTBP, 1,2,2,6,6-pentamethylpiperidine (PMP), 2,2,6,6-tetramethylpiperidine (TMP), 2-*tert*-butylpyridine (2TBP) and 2,6-lutidine (Lut), see Figure 1) on the formation of *exo*-olefin end group through the end-quenching of $TiCl_4$-co-initiated living cationic polymerization of IB.[33,34,35] Among these bases, the highest efficiency showed PMP and TMP which yielded PIB with 100% of *exo*-olefin end groups and can be used at relatively concentrated conditions ([IB]≤1.5 M).[34,35] The low efficiency of DTBP is consistent with its steric hindrance that prevents the efficient *β*-H abstraction, on the one hand. On the other hand, 2TBP and Lut are sufficiently sterically unhindedred to form strong complex with $TiCl_4$ and, therefore, the concentration of free base, which needs for the efficient *β*-H abstraction, is too low (Figure 1).

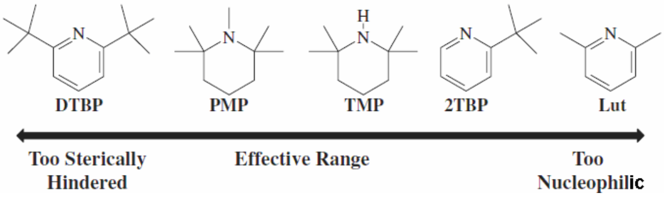
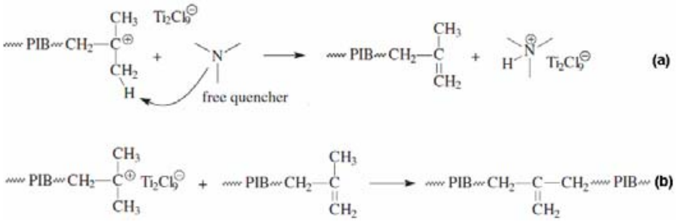


Fig. 1 Effective range of bases as quenching agents in the $TiCl_4$-co-initiated living polymerization of IB in relation to steric hindrance around nitrogen (Reproduced from Ref. 35 with permission from John Wiley and Sons).

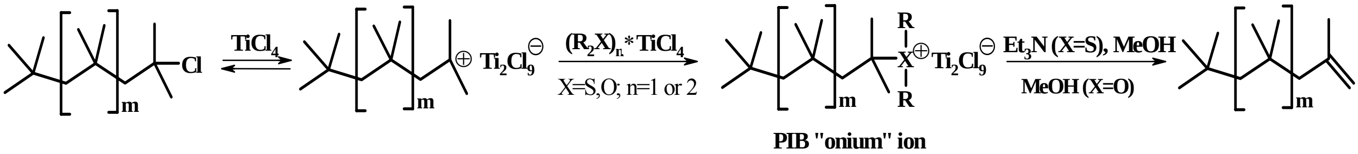
The mechanism of the formation of *exo*-olefin end group via end-quenching of $TiCl_4$-co-initaited living cationic polymerization by hindered bases is shown in Scheme 3.[33–35]



Scheme 3 Mechanism of *exo*-olefin end group formation in the presence of hindered bases (Reproduced from Ref. 35 with permission from John Wiley and Sons).

According to this mechanism, the *free* base (presents in the system due to its incomplete complexation with $TiCl_4$ owing to steric hindrance) regiospecifically abstracts a *β*-proton from the PIB carbenium ion to form *exo*-olefin chain ends ((**a**) in Scheme 3). The main side reaction under these conditions is coupling of two PIB chains ((**b**) in Scheme 3); this reaction becomes significant when the *β*-proton abstraction is relatively slow. Quite different mechanism was proved to operate in the case of *exo*-olefin end group formation in the presence of 2,5DMP as quenching agent.[36] However, although the proposed approach allowed to synthesize *exo*-olefin terminated PIB with quantitative functionality, it still suffers from the high price of quenchers as well as a necessity to use low reaction temperatures (below –40 °C). Another limitation of this process is the formation of coupled polymer chains at high chain ends concentration (corresponds to [IB]<1.5 M).

2.1.4. End-quenching with sulfides and ethers. In order to improve further the synthesis of HR PIB (*exo*-olefin terminated PIB) via quenching of living PIB chains, another type of quenching agents was developed by Storey et al.[34,35,37,38] It was proposed to use sulfides or ethers as quenchers instead of hindered bases. In this case, the quenching proceeded into two steps through the formation of stable at low temperatures sulfonium or oxonium PIB ions (after attaching of sulfide or ether to polyisobutylene macrocations) followed by decomposition of resulting onium ions by addition of excess of nucleophile (Scheme 4).[34,35,38] The addition of strong base (triethylamine, 2,6-lutidine etc.) before deactivation of Lewis acid by methanol is mandatory when sulfides are used as quenchers.



Scheme 4 One-pot two-step synthesis of *exo*-olefin terminated PIB via end-quenching of living polyisobutylene by sulfides and ethers

The steric bulkiness of quencher played the critical role in the regiospecificity of β-H elimination for both types of quenchers i.e. sulfides or ethers.[34,38] For example, the content of *exo*-olefin end groups increased with increasing bulkiness of the substituent on the sulfide in the following series: *n*-alkyl (39–55%)< phenyl (70%)< isopropyl (98%)< *tert*-butyl (100%).[38] The similar dependence of the *exo*-olefin end groups content on the bulkiness of the substituent was observed for the ethers: *n*-alkyl (68–81%)< isopropyl (100%)~ *sec*-butyl (100%).[34] It should be also noted that the synthesis of HR PIB via end quenching with sulfides and ethers can be easily scaled up to 1 kg of polymer without any deleterious effect on the functionality.[34,38] This method was also successfully adapted to the synthesis of difunctional (telechelic) *exo*-olefin terminated PIB with quantitative functionality.[34,38]

2.1.5. Comparison of various methods. As we showed above, a number of methods for the synthesis of HR PIB based on the living cationic polymerization of isobutylene or inifer techniques were developed. The great advantage of this approach is the ability to synthesize polyisobutylenes with nearly quantitative functionality (see Table 1) with precisely controlled molecular weight and very narrow molecular weight distribution ($M_w/M_n<1.2$). In addition, apart from the monofucntional PIB, di- and trifunctional polymers can be easily prepared using methods based on living cationic polymerization.

Table 1 Comparison of various methods towards *exo*-olefin terminated PIB based on living cationic polymerization

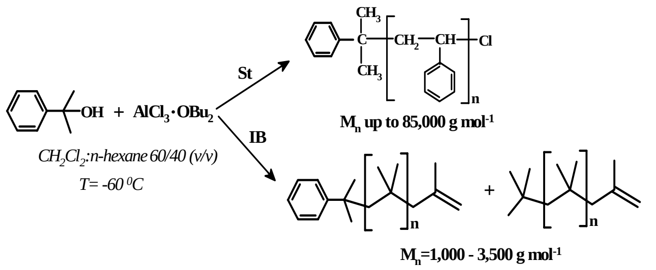
Quencher	[PIB] (mM)	[IB] (M)	[Quencher]/ [PIB]	*exo*-Olefin (mol%)
NaOEt	–[a]	–[a]	1.2	~95[b]
IBTMS	39	1.5	2.8	100
IBTMS	77	3.0	2.8	97
PMP	39	1.5	2.8	100
^{t}Bu$_2$S	100	3.9	2.0	100
^{i}Pr$_2$O	100	3.9	4.0	95
^{i}Pr$_2$O[c]	100	3.9	4.0	100

Polymerization and quenching conditions: *n*-hexane/CH_3Cl 60/40 (v/v); –60 °C. [a] Isolation of polymer before dehydrochlorination. [b] Although extend of dehydrochlorintion was found to be 100% in original publication,[23] it was shown latter[24] than content of *exo*-olefin end group does not exceed 95%. [c] Temperature: –70 °C (Results taken from Refs. 23, 27 and 34).

Among different methods discussed above, one based on the dehydrochlorination of *tert*-chlorine terminated PIB is quite cumbersome and does not lead to quantitative formation of *exo*-olefin end groups (Table 1). The methods based on end-quenching of living PIB by isobutenyltrimethylsilane and strong bases results in 100% of *exo*-olefin content only at quite diluted conditions: the concentration of PIB chains should not exceed 40 mM that corresponds to IB concentration of about 1.5 M (Table 1). From this point of view, bulky sulfides and ethers are the most effective *exo*-olefin producing quenchers: they give 100% of *exo*-olefin end groups even under relatively concentrated conditions ([PIB]=100 mM and [IB]=3.9 M, respectively) (Table 1). The significant advantages of the ether relative to the sulfide are lower cost and absence of odor. However, all methods for the synthesis of *exo*-olefin based on living cationic polymerization suffer from the necessity to work at low temperatures (below –60 °C) and use the toxic chlorinated solvents (CH_3Cl or CH_2Cl_2).

2.2. HR PIB via conventional cationic polymerization

2.2.1. $AlCl_3$×OR_2-based initiating systems. It is well known that conventional Lewis acids such as $AlCl_3$ or $EtAlCl_2$ are used for many years for the industrial production of low molecular weight polyisobutylene (“conventional” PIB) containing mainly *tri*- and *tetra*-substituted olefinic end groups (Exxon process).[3] Such end groups, which are characterized by very low reactivity toward further functionalization, were formed due to the isomerization of growing carbocations via methide or hydride shifts followed by β-H elimination or chain scission.[20,39] Quite surprisingly, we discovered recently that complex of $AlCl_3$ with Bu_2O in conjunction with CumOH as an initiator, in strong contrast to neat $AlCl_3$, allowed to synthesize HR PIB (*exo* =85–95%).[40,41] This initiating system originated from our systematic investigations of the controlled cationic polymerization of styrene using complexes of $TiCl_4$[42] and $AlCl_3$[43] with an excess or equimolar amount of ether to Lewis acid. Particularly, it was clearly demonstrated that CumOH/$AlCl_3$×OBu_2 system initiated the living cationic polymerization of styrene at –60 °C leading to the polymers with very high molecular weight (M_n up to 85,000 g mol^{-1}) (Scheme 5). However, the cationic polymerization of isobutylene with the same initiating system resulted in oil-like product of low molecular weight (M_n<4,000 g mol^{-1}), fortunately, with almost quantitative content of *exo*-olefin end groups (Scheme 5).



Scheme 5 Cationic polymerization of styrene (St) and isobutylene (IB) with CumOH/$AlCl_3$×OBu_2 initiating system.

Motivated by these findings, the polymerization of isobutylene with CumOH/$AlCl_3$×OBu_2 initiating system was investigated in more detail.[41] It was found that monomer conversion and, to a lesser extent, molecular weight depended on the initiator concentration (Table 2). Besides, both molecular weight and polydispersity decreased with increasing temperature from –60 °C to –20 °C, while the content of *exo*-olefin end groups almost did not depend on the temperature[41,44] (Table 2). All synthesized polymers are characterized by relatively narrow and monomodal MWD (Table 2).

Table 2 Cationic polymerization of isobutylene with CumOH/$AlCl_3$×OBu_2 initiating system in CH_2Cl_2/*n*-hexane 80:20 v/v mixture

CumOH (mM)	T (°C)	Conv. (%)	M_n (g mol^{-1})	M_w/M_n	*exo*-Olefin (mol%)	F_n[a] (%)
3[b]	–60	47	3510	1.93	95	37
18	–60	85	2330	1.81	86	91
18	–40	62	1560	1.46	91	75
18[c]	–40	37	1270	1.17	93	48
18[d]	–40	1	1000	–	97	3
36[e]	–40	73	1200	1.20	90	91
18	–20	49	1150	1.16	91	65

Polymerization conditions: [IB]=0.91 M; [$AlCl_3$×OBu_2]=22 mM; time: 3 min. [a] Initiator efficiency. [b] CH_2Cl_2/*n*-hexane 60:40 v/v; time: 30 min; [c]Pyridine (0.25mM) was added; [d] DTBP (6 mM) was added; [$AlCl_3$×OBu_2]=32 mM; [e] [$AlCl_3$×OBu_2]=44 mM (Results taken from Refs. 41 and 46).

The chain end structure analysis by means of ^{1}H NMR spectroscopy revealed the presence of high proportion (86–97%) of *exo*-olefin end groups (two signals at 4.65 ppm and 4.85 ppm, respectively) as well as small fractions of *endo*-olefin terminated (5.15 ppm) and coupled (4.85 ppm) chains at the ω-end[41] (see also Figure 2 for typical ^{1}H NMR spectrum of HR PIB synthesized using $AlCl_3$×OBu_2 as co-initiator). In addition, a very small amount of *tert*-chlorine end groups (<2%) was also typically presented in PIB synthesized with CumOH/$AlCl_3$×OBu_2 initiating system.

It should be also noted that all polymers synthesized using CumOH/$AlCl_3$×OBu_2 initiating system were characterized by high functionality at the α-end: the initiator efficiency was 75–90% under optimal conditions (Table 2). The presence of cumyl group at the chain end was confirmed by both ^{1}H NMR spectroscopy and MALDI-TOF MS.[41] This observation indicates that CumOH, similarly to the case of styrene polymerization,[43] acted as an initiator during IB polymerization with CumOH/$AlCl_3$×OBu_2 initiating system (see Scheme 5). However, it was shown that addition of proton traps (pyridine or DTBP) to the system led to strong decrease of both the monomer conversion and the initiator efficiency[41,46] (Table 2). At the proton trap concentration of 6 mM the polymerization is almost fully terminated[46] (Table 2). The other initiators tested (2-chloro-2,4,4-trimethylpentane (TMPCl), CumCl or *tert*-butyl alchohol) also showed zero activity in the presence of proton trap[46] and even without an addition of proton trap in the case when 1-phenylethyl chloride was used.[47] Thus, it was concluded that CumOH was not an initiator under investigated conditions and the ionization of CumOH was an indirect process which required an initial reaction of $AlCl_3$ with the adventitious H_2O as depicted in Scheme 6.[46]

$$\mathrm{AlCl_3.Bu_2O} \rightleftarrows \mathrm{AlCl_3} + \mathrm{Bu_2O}$$

$$\mathrm{AlCl_3} + \mathrm{CumOH} \xrightarrow{\times} \mathrm{Cum^+, AlCl_3OH^-}$$

$$\mathrm{AlCl_3} + \mathrm{H_2O} \longrightarrow \mathrm{H^+, AlCl_3OH^-}$$

$$\mathrm{H^+} + \mathrm{CumOH} \longrightarrow \mathrm{Cum^+} + \mathrm{H_2O}$$

Scheme 6 Mechanism of initiation during isobutylene polymerization with CumOH/$AlCl_3OBu_2$ initiating system proposed by Faust and co-workers.[46]

It was shown later than adventitious H_2O in the presence of complexes of $AlCl_3$ with ethers is a good initiator for the synthesis of HR PIB.[41,44] This initiating system allowed to synthesize HR PIB with high *exo*-olefin end group content (*exo*>85%) even at room temperature, but the polymerization was relatively slow as compared to one with CumOH as initiator.[41,44]

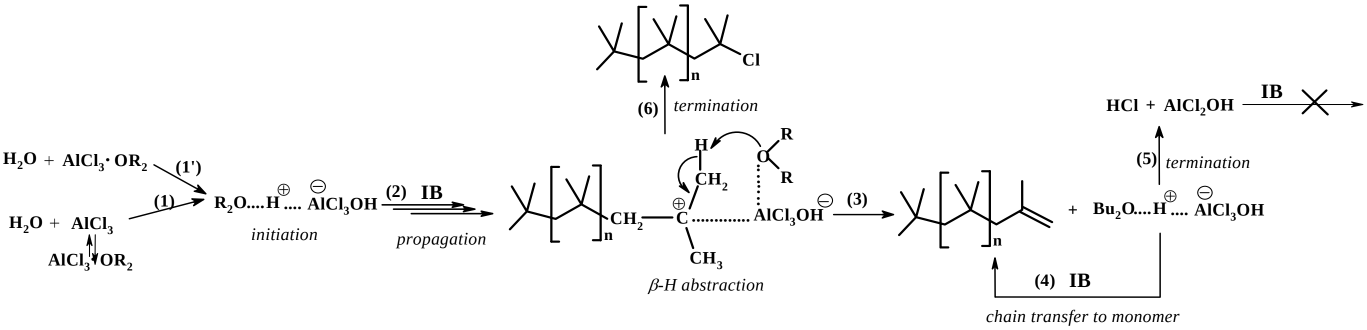
Important feature of $AlCl_3$×OR_2-based initiating systems is that regioselectivity of *β*-H elimination strongly depends on $AlCl_3$/ether ratio: predominantly *exo*-olefin end groups were formed when 1:1 complex was used, while the presence of slight excess of Lewis acid over ether ($AlCl_3$:OBu_2=1:0.8 mol/mol) lead to "conventional" PIB containing mainly *tri*- and *tetra*-substituted end groups.[45] The use of an excess of ether towards Lewis acid resulted in the increase of *exo*-olefin content and the decrease of molecular weight, but at the expense of significant reduction of monomer conversion.[44,46]

The optimal concentration of the catalytic complex is about 20 mM: the increase of its concentration led to the loss of *exo*-olefin double bond, while the decrease of [$AlCl_3$×OR_2] resulted in strong reduction of the reaction rate.[44]

From these intriguing results, an important question arose regarding the difference in the polymerization mechanism in the presence of $AlCl_3$×OR_2 in comparison with neat $AlCl_3$. As it was already mentioned, $AlCl_3$:OR_2 ratio is crucial for achievement of the high functionality. Which other factors can influence the regioselectivity of *β*-H elimination? To answer this question, an effect of different ethers (linear, branched and cyclic) on the $AlCl_3$×OR_2-co-initiated cationic polymerization of IB was investigated.[41,44–48] A number of very important conclusions have been made based on these investigations. (i) Basicity of ether plays a key role in the synthesis of PIBs with high *exo*-content: the highest content of *exo*-olefin end groups was obtained when complexes of $AlCl_3$ with ethers of moderate basicity (pK_a between –3.59 and –5.4) were used as co-initiators, while application of weak electron donors (pK_a< –6.54) for the complex preparation led to the total loss of the control over the selectivity of *β*-H elimination. In addition, the use of strong base such as, for example, pyridine (pK_a=5.25) resulted in the significant decrease of monomer conversion and, in some cases, *exo*-olefin end group content.[41,44–47] (ii) In a series of linear alkyl ethers, the best selectivity towards *β*-H abstraction as well as polymer yield were obtained with Et_2O and Bu_2O, while ethers with longer alkyl chain length (Am_2O,

Hex_2O) led to the decrease of both *exo*-olefin content and polymer yield,[45] probably, due to the decrease of solubility of corresponding complexes with $AlCl_3$.[48] (iii) The complex of $AlCl_3$ with moderately branched ether ($^iPr_2O$, pK_a=–4.3) was superior to those with linear ethers in terms of both *exo*-olefin content and polymer yield.[45,44,46] (iv) Not only steric structure but also electronic properties of ether used for complex preparation strongly influenced the reaction rate, molecular weight and, to a lesser extent, the *exo*-olefin content: ethers containing electron-withdrawing substituents in *β*-position to oxygen (2-chloroethyl ethyl ether or *bis*(2-chloroethyl ether)) lead to faster polymerization due to their decreased nucleophility as well as to PIB*s* with lower M_n*s* in comparison with those obtained when diisopropyl ether was used.[48]

The general mechanism to explain the behaviour of $AlCl_3 \times OR_2$-based initiating systems in the polymerization of IB proposed by Kostjuk[41,47] and Faust[46] is summarized in Scheme 7. Two possible pathways for initiation were postulated, one based on the assumption that free Lewis acid, which is generated by dissociation of $AlCl_3 \times OR_2$ complex, participates in the initiation (dissociative mechanism, 1 in Scheme 7).[41,47] The second one claims the initiation via direct reaction of H_2O with complex to yield $H^+AlCl_3OH^-$ with the simultaneous release of the ether (associative mechanism, 1′ in Scheme 7).[46]



Scheme 7 General mechanism for isobutylene polymerization with $H_2O/AlCl_3OR_2$ initiating systems

After protonation of the monomer propagation occurs up to regioselective *β*-H abstraction by free ether (2 in Scheme 7) to yield PIB with *exo*-olefin end group and regenerate the initial active species ($H^+AlCl_3OH^-$) (3), which can initiate the new chain (4) or ion pair collapse may also occur with the formation of inactive in the polymerization $AlCl_2OH$ (5 in Scheme 7). Another termination pathway is ion pair collapse yielding *tert*-chlorine terminated PIB (6, in Scheme 7). Indeed, the presence of small fraction of PIB-Cl chains (~2%) was detected by ^1H NMR spectroscopy and UV-vis in the polymer synthesized with $H_2O/AlCl_3 \times OBu_2$ initiating system.[46]

To summarize, the complexes of $AlCl_3$ with ethers are very efficient co-initiators for the synthesis of HR PIB with high content of *exo*-olefin terminal groups (*exo* >90%), desired low molecular weight (M_n=1,000 g mol^{-1}–3,500 g mol^{-1}) and relatively narrow MWD (M_w/M_n<2) in CH_2Cl_2 or its mixture with *n*-hexane at elevated temperatures (from –20 °C to 20 °C).[41,44,46] In addition, it was also demonstrated that $AlCl_3$-based initiating systems showed high selectivity toward polymerization of C_4 mixed feed to afford HR PIB with high *exo*-olefin content (80–95%).[49] However, the use of chlorinated solvents is not consistent with the industrial requirements. Moreover, all experiments discussed above were performed at relatively low monomer concentration ([IB]=0.9–1.8 M), while BF_3-based process currently used in industry operated at [IB]~5 M. Therefore, to meet industrial requirements, $AlCl_3 \times OR_2$-based process should be adapted to non-polar solvents and to high monomer concentrations.

The efficiency of $H_2O/AlCl_3 \times OR_2$ initiating systems towards synthesis of HR PIB was then investigated in such non-polar solvents as toluene[47,50] and *n*-hexane.[45,46] It should be noted that ^1H NMR spectra of HR PIB*s* obtained in non-polar solvents are more complicated in comparison with those synthesised in CH_2Cl_2: among the signals of *exo*- (4.65 ppm and 4.85 ppm), *endo*-olefin (5.15 ppm) end groups and coupled polymer chains (4.85 ppm), the new signals corresponding to the *tri*- (5.17 ppm and 5.36 ppm) and *tetra*-substituted double bonds (2.85 ppm) are appeared (Figure 2).

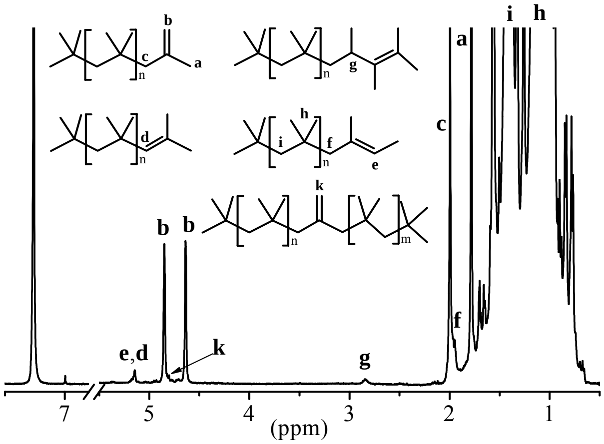


Fig. 2 Typical ^1H NMR spectrum of HR PIB synthesized in *n*-hexane with $H_2O/AlCl_3 \times OBu_2$ initiating system

The results of comparative study of the cationic polymerization of isobutylene co-initiated by $AlCl_3 \times OBu_2$ and $AlCl_3 \times O^iPr_2$ complexes in non-polar toluene (ε=2.38) and *n*-hexane (ε=1.88) at different temperatures and monomer concentrations revealing the similarities as well as key differences in the polymerization behavior are summarized in Table 3.

In both solvents, $AlCl_3 \times O^iPr_2$ showed higher activity in the polymerization of IB as compared to $AlCl_3 \times OBu_2$ affording HR PIB*s* with lower M_n and narrower MWD (compare runs 1, 2 and runs 3, 4 in Table 3). The small excess of diisopropyl ether over Lewis acid (5–10 mol%) allowed to improve the selectivity towards *β*-H abstraction as well as led to decrease of molecular weight and polydispersity (runs 4, 5 and runs 11, 12, Table 3). Particularly, HR PIB with almost quantitative functionality (*exo*=98%) was synthesized using $AlCl_3 \times 1.1O^iPr_2$

as co-initiator in toluene at –20 °C (run 5, Table 3). The polymerization is significantly faster in toluene than in *n*-hexane, whereas the content of *exo*-olefin end groups is considerably higher for PIB*s* synthesized in toluene as compared to polymers obtained in *n*-hexane (Table 3). Moreover, the content of *exo*-olefin end groups is strongly decreased with raising polymerization temperature for PIB*s* synthesized in *n*-hexane, while even increase of functionality with increasing temperature was observed for polymers obtained in toluene (Table 3). Finally, $AlCl_3{\times}OR_2$ based initiating systems can be also used for the synthesis of HR PIB at high monomer concentration ([IB]~5.2 M, i.e. monomer/solvent ~ 50: 50 (v/v)) in both non-polar solvents studied, although the content of *exo*-olefin end groups decreased slightly in toluene and more significantly when *n*-hexane was used as a solvent (Table 3).

Table 3 Cationic polymerization of isobutylene co-initiated by $AlCl_3{\times}O^iPr_2$ or $AlCl_3{\times}OBu_2$ in toluene and *n*-hexane at different temperatures and monomer concentrations

Run	Temp. (°C)	[IB] (M)	Solvent	Co-initiator	Time (min)	Conv. (%)	M_n (g mol^{-1})	M_w/M_n	End groups distribution (mol%)[b]		
									exo	endo+tri	tetra
1	–20	0.9	toluene	$AlCl_3{\times}OBu_2$	30	93	3530	3.9	91	5	4
2	–20	0.9	toluene	$AlCl_3{\times}O^iPr_2$	30	100	2160	2.9	87	10	3
3	–20	0.9	*n*-hexane	$AlCl_3{\times}OBu_2$	30	32	3540	4.1	84	9	7
4	–20	0.9	*n*-hexane	$AlCl_3{\times}O^iPr_2$	30	67	3810	3.1	86	7	7
5	–20	0.9	toluene	$AlCl_3{\times}1.1O^iPr_2$	30	61	910	2.1	98	2	0
6	–20	5.2	toluene	$AlCl_3{\times}OBu_2$	10	88	4540	3.6	81	7	12
7	–20	5.2	toluene	$AlCl_3{\times}1.05O^iPr_2$	10	90	3000	3.8	77	11	12
8	–20	5.2	*n*-hexane	$AlCl_3{\times}OBu_2$	10	70	5950	3.8	71	12	17
9	–20	5.2	*n*-hexane	$AlCl_3{\times}1.05O^iPr_2$	10	35	10960	2.2	83	9	8
10	10	5.2	toluene	$AlCl_3{\times}1.05O^iPr_2$	10	78	1540	3.3	85	8	8
11	10	5.2	*n*-hexane	$AlCl_3{\times}OBu_2$	10	57	2950	2.7	71	12	17
12	10	5.2	*n*-hexane	$AlCl_3{\times}1.1O^iPr$	10	60	3470	2.4	77	8	15

Conditions: $[AlCl_3{\times}O^iPr_2]=[AlCl_3{\times}OBu_2]$=22 mM. [b] The content of coupled polymer chains is less than 1% (Results taken from Refs. 45, 57 and 50).

Thus, $H_2O/AlCl_3{\times}OBu_2$ and, especially, $H_2O/AlCl_3{\times}O^iPr_2$ initiating systems showed great potential towards synthesis of HR PIB with desired low molecular weight (M_n=1,500–2,500 g mol^{-1}) and high *exo*-olefin content (85–90%) at high monomer concentration ([M]~5.2 M) and high reaction temperature (from 0 °C to 20 °C) in toluene.[47,50] The application of these initiating systems in *n*-hexane is limited to low reaction temperature: good functionality (*exo*≥80%) can be obtained only when the polymerizations proceeded at –20 °C, while the increase of temperature resulted in significant decrease of *exo*-olefin content. Another limitation of using $AlCl_3{\times}OR_2$-based initiating systems in *n*-hexane is relatively high molecular weight (M_n=3,500–10,000 g mol^{-1}) of synthesized PIB*s* especially those obtained at high monomer concentrations.[45,46,50]

2.2.2. $FeCl_3{\times}OR_2$- and $GaCl_3{\times}OR_2$-based initiating systems.

In order to further improve the process of synthesis of HR PIB, the new catalytic systems based on $FeCl_3$ and $GaCl_3$ complexes were introduced.[48,51–55] Initially, the complexes of $FeCl_3$ with different ethers (Et_2O, Bu_2O and $^iPr_2O$) were tested in the polymerization of IB in CH_2Cl_2 at 0 °C.[51] The rate of IB polymerization initiated by $H_2O/FeCl_3{\times}OR_2$ systems, similarly to $H_2O/AlCl_3{\times}OR_2$ initiating systems, increased in the following series: $Et_2O<Bu_2O<^iPr_2O$.[45,51] The use of some excess of ether over Lewis acid led to decrease of M_n and narrowing of MWD but did not influence significantly the *exo*-olefin end groups content (exo≥87%).[51] Importantly, $H_2O/FeCl_3{\times}OR_2$ initiating systems afforded HR PIB with high *exo*-olefin content even at room temperature and M_n can be controlled by the reaction temperature in the range of M_n=900 g mol^{-1}– 2,000 g mol^{-1} by decreasing the temperature from 20°C to –20°C. It was demonstrated that the main advantage of $FeCl_3{\times}OR_2$-based initiating systems over $AlCl_3{\times}OR_2$–based is the possibility to use much lower concentrations of catalytic complex in the former case (5 mM vs. 20 mM).[51]

To estimate further the usefulness of $FeCl_3$-based initiating systems for the synthesis of HR PIB in non-polar solvents, the influence of *n*-hexane content in CH_2Cl_2/*n*-hexane mixture on the *exo*-olefin end groups content and molecular weight of synthesized polymers was investigated at different temperatures by Wu and co-workers.[52] In this study, slightly modified initiating system, i.e. $H_2O/FeCl_3/^iPrOH$, was used and the typical concentrations of the reagents were: $[H_2O]$=0.8 mM; $[FeCl_3]$=40 mM; $[^iPrOH]$=56 mM; [IB]=2.9 mM. Under these conditions, the monomer conversion slightly decreased while the molecular weight insignificantly increased with the increase of *n*-hexane fraction in CH_2Cl_2/*n*-hexane mixture from 60% to 100%. Remarkable, the decrease of solvent polarity resulted in significant increase of the content of *exo*-olefin end groups from 60–70% to about 95% in pure *n*-hexane at –15 °C.[52] In addition, this initiating system was also very efficient in the synthesis of HR PIB from C_4 mixed feed. However, the polymerization of IB with $H_2O/FeCl_3/^iPrOH$ is relatively slow (about 70% of monomer conversion in 30 min) and the content of *exo*-olefin end groups is decreased down to 83% with increasing polymerization temperature from –15 to 20°C.[52]

Despite of the fact that clear improvement in the synthesis of HR PIB in non-polar *n*-hexane in terms of *exo*-olefin content was achieved by changing $AlCl_3{\times}OR_2$ to $FeCl_3/^iPrOH$ (especially at high reaction temperature), both of these initiating systems suffer from slow reaction rate and termination of the polymerization at incomplete monomer conversion (*vide supra*). These limitations are consistent with the quite low solubility of water in *n*-hexane: the concentration of adventitious or purposely added H_2O in the system does not exceed 0.8 mM.[46,51] Therefore, the polymerization is stopped at incomplete conversions because of all H_2O is consumed in the course of polymerization due to the irreversible termination (Scheme 7). The attempts to increase the reaction rate and ultimate monomer conversion by using such widely used initiators as TMPCl, CumCl, ^{t}BuCl instead of H_2O in conjunction with $AlCl_3 \times OR_2$ were unsuccessful, most probably, due to the known oxophilic nature of this Lewis acid.[56] In other words, $AlCl_3$ is much more oxophilic than chlorophilic and, therefore, alkyl halides can not displace the ether from the $AlCl_3 \times OR_2$ complex to create the initial cation for initiation of polymerization. On the other hand, $FeCl_3$ and $GaCl_3$ are chlorophilic Lewis acids[56] and, therefore, alkyl chlorides can be used as initiators with the complexes of these Lewis acids.

Indeed, Faust and co-workers[53] showed that TMPCl in conjunction with $FeCl_3 \times O^iPr_2$ or $GaCl_3 \times O^iPr_2$ induced the cationic polymerization of IB to afford desired low molecular weight HR PIB (M_n~1400 g mol^{-1}) with relatively narrow MWD ($M_w/M_n<2.3$) in high yield (up to 90%) and high content of *exo*-olefin end groups (70–80%).[53] The comparative study of the efficiency of $FeCl_3$- and $GaCl_3$-based initiating systems revealed that polymerization was faster and the *exo*-olefin content was higher when complex of $FeCl_3$ with diisopropyl ether was used as co-initiator (Figure 3). Moreover, HR PIB synthesized with TMPCl/$GaCl_3 \times O^iPr_2$ initiating system contained significant fraction of *tert*-chlorine terminated chains, especially at low monomer conversions (up to 34% of PIB-Cl at about 40 % of conversion).[53] Therefore, the use of $FeCl_3$-based initiating systems is more preferably than corresponding $GaCl_3$ complexes due to the faster polymerization and lower content of undesirable PIB-Cl chains in the product. In summary, TMPCl/$FeCl_3 \times O^iPr_2$ and ^tBuCl/$FeCl_3 \times O^iPr_2$ initiating systems under optimized conditions ([IB]=1 M; [TMPCl]=[^tBuCl]=20 mM; [$FeCl_3 \times O^iPr_2$]=20 mM) afforded HR PIB with good functionality (*exo*-olefin content of about 80%) and close to complete monomer conversion (90-98%) in 20 min at 0 °C in hexanes.[53]

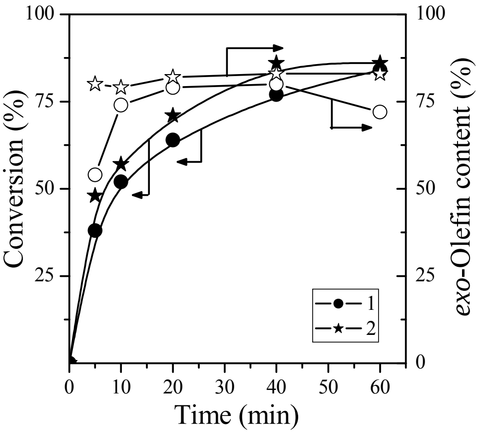
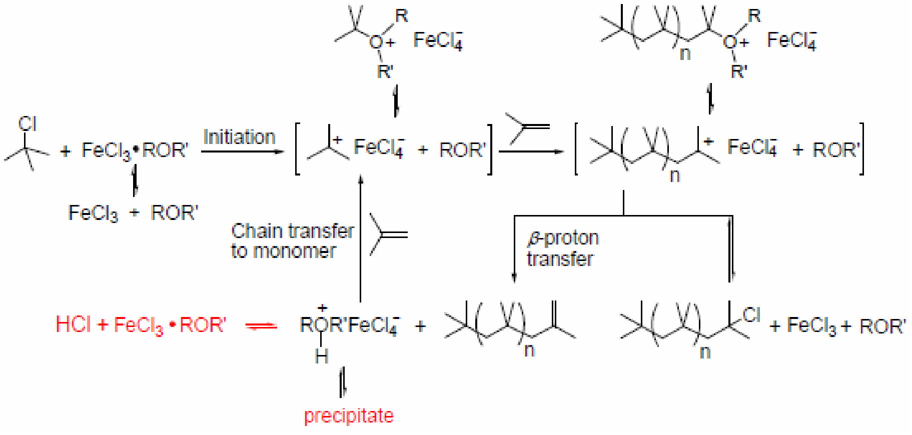


Fig. 3 Conversion and *exo*-olefin content vs. time dependences for IB polymerization with TMPCl/$GaCl_3 \times O^iPr_2$ (1) and TMPCl/$FeCl_3 \times O^iPr_2$ (2) initiating systems at 0 °C in hexanes: [TMPCl]=10 mM; [$GaCl_3 \times O^iPr_2$]=[$FeCl_3 \times O^iPr_2$]=20 mM; [IB]=1 M (Results taken from Ref. 53).

It should be noted that among complexes of MCl_3 (M=Fe or Ga) with different ethers studied, only complexes with moderately branched $^iPr_2O$, *sec*-Bu_2O or $^iBu_2O$ were active toward IB polymerization, while complexes with linear ethers (Et_2O, Bu_2O or BuOMe) were totally inactive.[53] It was shown further that complexes of $FeCl_3$ with ethers containing electron-withdrawing substituents in β-position to oxygen such as 2-chloroethyl ethyl ether (CEEE) or *bis*(2-chloroethyl ether) (CEE) led to faster polymerization due to their decreased nucleophility as well as to polymer with lower M_n in comparison with those obtained with $FeCl_3 \times O^iPr_2$.[48] However, the *exo*-olefin content was also decreased from 80% to 70% when CEEE or CEE were used as a component of catalytic complex instead of $^iPr_2O$.



Scheme 8 Mechanism of isobutylene polymerization using ^tBuCl/ $FeCl_3 \times ROR'$ initiating system (ROR'= $^iPr_2O$, CEEE, CEE) (Reproduced from Ref. 54)

The kinetic investigations of the IB polymerization using ^tBuCl/$FeCl_3 \times ROR'$ initiating systems (ROR'= $^iPr_2O$, CEEE, CEE) revealed that the first-order plots were curved in all cases indicating that the concentration of macrocations decreased in the course of polymerization.[54] This behavior was attributed to the precipitation of protonated complex salt $H^+ROR'FeCl_4^-$, which has a much lower solubility than that of $FeCl_3 \times ROR'$ complex. Based on the obtained results, more accurate mechanism describing the cationic polymerization of IB with ^tBuCl/$FeCl_3 \times ROR'$ initiating system was proposed (Scheme 8).[54] The difference of this mechanism from one presented in Scheme 7 is the regeneration the Lewis acid/ether complex from protonated ether by loss of HCl providing thereby a free Lewis acid for ionization of initiator (^tBuCl). This mechanistic scheme also includes the reversible formation of oxonium ion similarly to one observed by Storey et al. during end-quenching of living PIB chains by $^iPr_2O$[34,35] (*vide supra*). However, the concentration of oxonium ions is typically low at high reaction temperatures[34,57] and, therefore, the polymerization of isobutylene does not terminate under these conditions. The last feature of the mechanism depicted in Scheme 8, as it was already mentioned above, is the precipitation of protonated complex salt $H^+ROR'FeCl_4^-$ leading to the decrease of the concentration of macrocations and, in turn, the reaction rate.[54]

In summary, tertiary alkyl chlorides (^{t}BuCl, TMPCl) in conjunction with the complexes of $FeCl_3$ with ethers (${}^iPr_2O$, CEEE, CEE) represent the efficient initiating systems towards synthesis of HR PIB with desired low molecular weight (M_n=1,000 g mol^{-1} – 1,500 g mol^{-1}) in hexanes at elevated temperatures (0 °C and 10 °C). Moreover, $RCl/FeCl_3\times OR_2$ initiating systems, in contrast to $AlCl_3\times OR_2$-based systems, allow to reach almost complete monomer conversion that is very important from the industrial point of view. However, the polymerization is relatively slow (close to complete monomer conversion in 20–30 min), while the content of *exo*-olefin end groups does not exceed 80% in the best case. These limitations of $FeCl_3\times OR_2$-based initiating systems are consistent with low solubility both the complex of Lewis acid with ether and the protonated complex salt in non-polar hexanes.[54] To overcome these limitations the complexes of alkylaluminum dichlorides ($EtAlCl_2$, ${}^iBuAlCl_2$) with ethers were recently introduced as very efficient co-initiators for the synthesis of HR PIB in hexanes.[58–60]

2.2.3. $RAlCl_2\times OR_2$-based initiating systems. Initially, complexes of isobutylaluminum dichloride (${}^iBuAlCl_2$) and ethylaluminum dichloride ($EtAlCl_2$) with diisopropyl ether (${}^iPr_2O$ gives the best results in conjunction with $AlCl_3$ and, in some cases, with $FeCl_3$) were screened for their potential in the synthesis of HR PIB in *n*-hexane at 10 °C.[58] It was shown that 1:1 complexes of ${}^iBuAlCl_2$ with ${}^iPr_2O$ afforded low molecular weight (M_n=500 g mol^{-1}; M_w/M_n=2.1) PIB with high *exo*-content (95%), but the monomer conversion was very low (~10% in 30 min). The monomer conversion can be increased up to 30% without any deleterious effect on the functionality by changing ${}^iBuAlCl_2$: ${}^iPr_2O$ ratio from 1:1 to 1:0.8 or even to 1:0.6 mol/mol. This behavior of alkylaluminum dichlorides complexes is completely different from that observed for $AlCl_3$, $FeCl_3$ or $GaCl_3$ complexes, where the use of even small excess of Lewis acid over ether reduced the *exo*-olefin end groups content significantly.[45,53] Another interesting feature of alkylaluminum dichlorides-based initiating systems is the increase of conversion with increasing monomer concentration, while the functionality does not depend significantly on the isobutylene concentration: low molecular weight (M_n=1,000 g mol^{-1}–1,400 g mol^{-1}) HR PIB*s* (*exo*-olefin content=82-91%) were obtained in moderate yield (40–60%) at [IB]=5.8 M with ${}^iBuAlCl_2\times 0.9O{}^iPr_2$ and $EtAlCl_2\times 0.8O{}^iPr_2$ as co-initiators (Figure 4).

In all above mentioned experiments the preformed or *in situ* generated Lewis acid-ether complex was used as co-initiator and polymerization was initiated by the addition of monomer to the reaction mixture containing catalytic complex and solvent. It was hypothesized that separate addition of Lewis acid and ether into the system would allow to increase the monomer conversion. The idea here was that *free* Lewis acid would co-initiate the polymerization, while *free* ether would still abstract the protons efficiently enough to generate predominantly *exo*-olefin end group. Under these conditions, HR PIB (*exo* ~83–84%) with M_n~1400 g mol^{-1}– 1600 g mol^{-1} in relatively high yield (up to 70 %) were synthesized (Figure 4).[58] Remarkably, this approach did not work with complexes of $AlCl_3$ and $GaCl_3$ giving predominantly conventional PIB with *tri*- and *tetra*-substituted double bonds.[46,53] This indicates that different mechanisms operated during IB polymerization with $RAlCl_2\times O{}^iPr_2$-based (R=Et, ^{i}Bu) and $MCl_3\times O{}^iPr_2$-based (M=Al, Ga, Fe) initiating systems, respectively (*vide infra*).

The comparison of kinetics of the polymerizations performed under these two approaches, i.e. when Lewis acid-ether complex was used as co-initiator (curve 1, Figure 4) or when Lewis acid and ether added separately (curve 2, Figure 4), revealed that in both cases reaction was quite fast during first 5–10 min; after this period of time the monomer conversion increased slowly with time to reach ultimate value after about 30 min. The evolution of molecular weight with monomer conversion presented in Figure 4b showed that conventional chain transfer-dominated polymerization took place in both cases: experimental M_n*s* were decreased with increasing monomer conversion reaching the values of M_n of ca. 1170 g mol^{-1} and 1550 g mol^{-1} when Lewis acid-ether complex and free Lewis acid were used as co-initiators, respectively. The one difference between these two approaches was the evolution of MWD with conversion: in first case the MWD became progressively broader, while in the second one it passed through the maximum (Figure 4b).

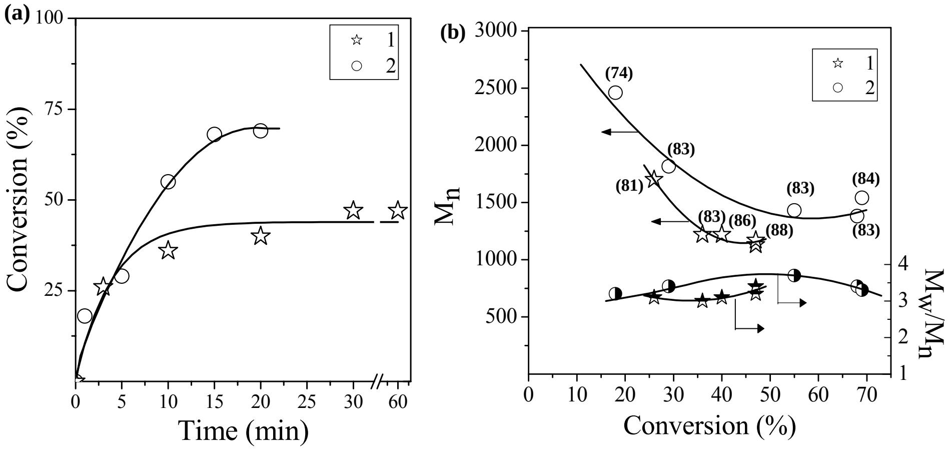
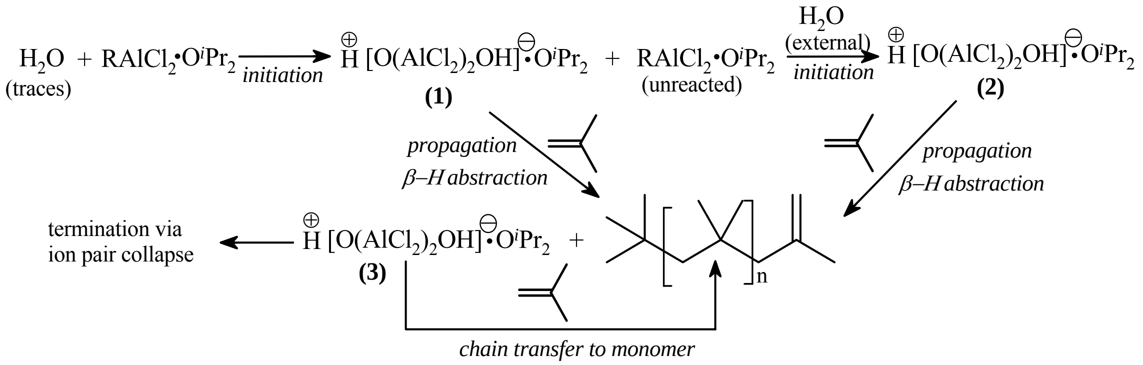


Fig. 4 (a) Conversion vs. time and (b) M_n(NMR), M_w/M_n vs. conversion plots for the isobutylene polymerization co-initiated by $EtAlCl_2\times 0.8O{}^iPr_2$ or $EtAlCl_2$ and separately added diisopropyl ether in *n*-hexane at 10 °C: [$EtAlCl_2$]=22 mM; [${}^iPr_2O$]=18 mM; [IB]=2.8 M. The sequence of components addition: (**1**) complex ($EtAlCl_2\times 0.8O{}^iPr_2$) was formed *in situ* and IB was added to system as the last component; (**2**) $EtAlCl_2$ was added to the system containing ether and monomer as the last component (Adapted from Ref. 58).

In contrast to $MCl_3{\times}O^iPr_2$-based initiating systems (M=Al, Ga, Fe), the alkylaluminum dichlorides-based counterparts afforded HR PIB with high *exo*-olefin end groups content even at high monomer concentrations and high reaction temperatures. In addition, the amount of undesirable *tert*-chloride-terminated PIB chains is very low in comparison with those obtained with metal chlorides. However, the monomer conversion was relatively low (70 % in the best case) for the adoption of this method to industry. As it was already discussed above, the low monomer conversion in *n*-hexane is consistent with quite low solubility of H_2O, an initiator, in such non-polar media. Therefore, the polymerization is terminated after the consumption of H_2O. The problem of low initiator concentration was solved by addition of external H_2O into the system, which was not fully soluble in the reaction mixture but rather formed the suspension.[59]

The sequence of H_2O introduction into the system had the crucial effect on the polymerization rate, saturated monomer conversion and, to a lesser extent, the content of *exo*-olefin end groups, but almost does not influence the molecular weight and molecular weight distribution. The highest polymerization rate (>70% of monomer conversion in 10 min) was observed for the polymerization experiments performed using “preactivation of catalyst” approach where $^iBuAlCl_2{\times}0.8O^iPr_2$ reacted with H_2O before the monomer addition to initiate the polymerization. However, the *exo*-olefin end groups content is slightly decreased in this case in comparison with experiments without addition of H_2O (from ~90% to 83%). Much better functionality was obtained when H_2O was introduced into the system in the course of the polymerization (after 3–10 min since the initiation of reaction). Under these conditions, highly reactive polyisobutylenes (*exo*-olefin content is 86–89%) with desired low molecular weight (M_n=1,000–2,000 g mol^{-1}) in a high yield (up to 95% of monomer conversion in 20 min) were readily synthesized.[59]

Since the behaviour of $RAlCl_2{\times}O^iPr_2$-based initiating systems in the polymerization of IB is quite different from those based on complexes of metal halides (see Scheme 7 and Scheme 8 for details), the following mechanism was proposed to explain the observed differences (Scheme 9). The key difference is the nature of counterion. It was indirectly proved that in the case of using of $RAlCl_2{\times}O^iPr_2$ the formation of aluminoxane-like counterion took place (1 in Scheme 9). If only adventitious H_2O is used as initiator, part of catalytic complex remains unreacted since $[H_2O] \ll [RAlCl_2{\times}O^iPr_2]$ under these conditions and polymerization terminated at incomplete monomer conversion right after consumption of H_2O.



Scheme 9 Proposed mechanism for isobutylene polymerization using externally added $H_2O/^iBuAlCl_2{\times}OiPr_2$ initiating system.[59]

Upon addition of external H_2O remaining catalytic complex converts into active species (2). Then, the polymerization proceeds similarly to that with $H_2O/MCl_3{\times}OR_2$ (M=Al, Fe) initiating system: chains grow up to regioselective β-H abstraction by free ether with the regeneration of initial active species (3), which can initiate new chain or irreversible termination can occur via ion-pair collapse (Scheme 9).[58,59]

Alternative $RAlCl_2$-based initiating systems leading to HR PIB with high yield (up to 100%) in hexanes at 0 °C was proposed by Faust and co-workers.[60] Remarkably, the polymerization was absent when complexes of $EtAlCl_2$ with $^iPr_2O$ or 2-chloroethyl ethyl ether (CEEE) were used as co-initiators (Table 4). On the other hand, ^tBuCl in conjunction with 1:1 complex of $EtAlCl_2$ with *bis*(2-chloroethyl)ether (CEE), a weakest base in comparison with $^iPr_2O$ and CEEE, initiated fast polymerization of IB (complete monomer conversion in 6 min) but the *exo*-olefin content was rather low (see Table 4). It was shown further that functionality can be significantly improved by adjusting $EtAlCl_2$: ether ratio. Indeed, the increase of $EtAlCl_2$: CEE ratio from 1:1 to 1:1.5 resulted in the increase of content of *exo*-olefin end groups from 70% to 85% as well as in the decrease of molecular weight from M_n=1600 g mol^{-1} to M_n=1000 g mol^{-1}.[60] Importantly, the excess of CEE almost did not affect the polymerization rate when $EtAlCl_2{\times}CEE$ was used as co-initiator in contrast to $FeCl_3{\times}CEE$.[60]

The influence of temperature on the isobutylene polymerization with $^tBuCl/EtAlCl_2{\times}CEE$ initiating system was then studied in the range from –20 °C to +10 °C (Table 4). It was shown that reaction rate decreased with decreasing temperature. In addition, the first-order plots are linear (slightly curved upward)[60] in comparison with those for $^tBuCl/FeCl_3{\times}CEE$ initiating system (showed significant downward curvature).[55]

This difference is consistent with different solubility in *n*-hexane both the catalytic complex and protonated complex salt $H^+ROR'R_nMCl_{4-n}^-$ (M=Al or Fe, n=0 or 1). The M_ns were higher at lower temperature as well as at higher monomer concentration (Table 4) indicating that β-H abstraction was slower under these conditions. In addition, ^{t}BuCl/$EtAlCl_2$×CEE initiating system allowed to synthesize HR PIB with high *exo*-content (85–92%) even at high monomer concentration ([IB]=4 M) at temperatures below 0 °C, while at 10 °C the functionality decreased to 70% (Table 4).

The polymerization mechanism proposed for ^{t}BuCl/$FeCl_3$×ROR′ initiating system (Scheme 8) adequately explains all the findings and is also relevant for ^{t}BuCl/$EtAlCl_2$×CEE initiating system. The only major difference is that ion pair collapse yielding PIB-Cl is virtually absent with $EtAlCl_2$×CEE as co-initiator in comparison with $FeCl_3$×ROR′.[60]

Table 4 Cationic polymerization of isobutylene with ^{t}BuCl/$EtAlCl_2$×ether initiating systems at different $EtAlCl_2$: ether ratios and temperatures in hexanes

Run	Ether	[ether]/[$EtAlCl_2$]	Time (min)	Temp. (°C)	Conv. (%)	M_n (g mol^{-1})	M_w/M_n	End groups distribution (mol%)				
								exo	endo +tri	tetra	PIB-Cl	coupled
1^a	^{i}Pr$_2$O	1	20	–20	0	–	–	–	–	–	–	–
2^{a,b}	CEEE	1	20	–20	5	–	–	–	–	–	–	–
3^a	CEE	1	20	–20	100	1000	–	72	18	10	0	0
4	CEE	1.1	5	0	100	1900	2.7	72	16	12	0	0
5	CEE	1.2	10	0	100	1300	2.8	74	16	10	0	0
6	CEE	1.5	60	–10	65	1000	3.2	91	5	4	0	0
7^c	CEE	1.5	60	–10	100	2000	2.8	92	5	3	0	0
8	CEE	1.5	20	0	100	1000	2.8	85	7	4	3	1
9^c	CEE	1.5	20	0	100	1600	3.5	85	9	6	0	0
10	CEE	1.5	20	10	100	600	3.6	79	11	8	0	2
11^c	CEE	1.5	15	10	100	1000	4.4	70	16	13	0	1

Conditions: [$EtAlCl_2$×ether]=[^{t}BuCl]=10 mM; ^{a}[$EtAlCl_2$×ether]= [^{t}BuCl]=20 mM ; [IB]=1 M. ^{b} Without ^{t}BuCl. ^{c} [IB]=4 M (Results taken from Ref. 60).

To summarize, among initiating systems based on complexes of metal halides with ethers, $H_2O/RAlCl_2$×O^{i}Pr$_2$ (R=Et, ^{i}Bu) and ^{t}BuCl/$EtAlCl_2$×CEE initiating systems are the best candidates for the industrial adoption and may in the future replace the BF_3 process. The major advantage of these initiating systems is that complexes of $RAlCl_2$ with ethers are soluble in *n*-hexane allowing to synthesize desired low molecular weight HR PIB with high *exo*-olefin end group content (>85%) even at high monomer concentration ([IB]=4–5 M) and high reaction temperatures (0 °C – +20°C) in non-polar solvents.

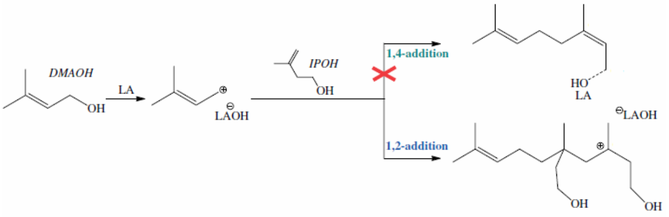
3. 1,3-Dienes

Cationic polymerization of linear conjugated 1,3-diens (mainly isoprene (IP) and 1,3-pentadiene) has been studied for more than 70 years.[11–13] The cationic polymerization of 1,3-dienes was studied in the presence of such Lewis acids as $AlCl_3$, $AlBr_3$, $EtAlCl_2$, $TiCl_4$, $SnCl_4$, BF_3OEt_2 and others as co-initiators, and H_2O, CCl_3COOH, ^{t}BuCl, cumyl methyl ether, cumyl acetate as initiators. It was shown that depending on the initiating system and polymerization conditions fully soluble in organic solvents low molecular weight poly(1,3-diene)s or polymers containing high molecular weight fraction (HMWF) and even insoluble gel fraction (IF) were formed.[11–13] Besides, poly(1,3-diene)s synthesized by cationic mechanism are typically characterized by reduced unsaturation: content of double bonds is between 25–70% that leads to significant alteration in the properties of synthesized polymers in comparison with 100% unsaturated counterpart (i.e. one double bond per 1,3-diene unit in a polymer chain).[11–13] The loss of double bonds is consistent with the operating of such side reactions as chain transfer to polymer (leads to formation of branched and cross-linked chains) as well as intramolecular cyclization (results in the formation of rigid cyclic sequences in a polymer chain). As a result of these side reactions, ill-defined polymers with broad, often multimodal molecular weight distribution were typically obtained.[11–13]

The state of the art in the field of cationic polymerization of 1,3-dienes has been well reviewed until 2010.[11–13] However, during the last 5 years considerable progress in understanding the complex mechanism of 1,3-dienes cationic polymerization has been made allowing to find conditions for the synthesis well-defined poly(1,3-dine)s via cationic mechanism. These new intriguing results will be critically reviewed below.

3.1. Polymerization of isoprene

3.1.1. Polymerization in the presence of conventional Lewis acids. In recent years, the cationic polymerization of isoprene has attracted significant attention mainly due to the assumption that natural rubber (natural rubber represents *cis*-1,4-polyisoprene of high molecular weight) biosynthesis resembles a cationic step-growth/chain growth polycondensation reaction initiated by allylic carbocations, where the monomer (isopentenyl pyrophosphate) can only react with activated allylic carbocation at the polymer chain end.[12,61] In order to proof this concept, the cationic polymerization of 3-methyl-3-buten-1-ol (isoprenyl alcohol, to mimic isopentenyl pyrophosphate) using initiating system based on dimethylallyl alcohol (DMAOH) as initiator and BF_3×$2H_2O$ as co-initiator was initially investigated.[62] However, instead of anticipated 1,4-insertion of isoprenyl alcohol (IPOH), selective 1,2-insertion took place yielding oligomers with pendant hydroxyethyl groups (Scheme 10).[12,62]



Scheme 10 Cationic polymerization of isoprenyl alcohol initiated by DMAOH/LA initiating system (LA=BF_3×$2H_2O$).[12]

The cationic polymerization of isoprene in the presence of dimethylallyl bromide (DMABr) and DMAOH as initiators and $TiCl_4$ or $BF_3{\times}OEt_2$ as co-initiators was then investigated.[63,64] These initiating systems, however, afforded ill-defined oligoisoprenes ($M_n \leq 2{,}000$ g mol^{-1}) with broad MWD ($M_w/M_n \sim 4.5$) and reduced unsaturation (double bond content: 40–60%) having predominantly *trans*-1,4 units (small fraction *cis*-1,4-units was also detected) in a polymer chain irrespectively of solvent nature or reaction temperature.[63,64] Such of behaviour was attributed to numerous side reactions such as chain transfer to monomer and cyclization.[63,64]

3.1.2. Polymerization in the presence of Lewis acids generating WCA*s* and mechanism. It was shown recently that the rate of side reactions is strongly affected by the basicity of the counteranion; these can be minimized using Lewis acid co-initiators generating weakly coordinating anions.[14] For example, $(CH_3)_3Si^+[B(C_6F_5)_4]^-$ initiating system allowed to synthesize copolymers of isobutylene with isoprene with unusually high IP incorporation (up to 8.5 mol%) without formation of gel fraction at elevated temperatures.[65] Another example of efficiency of Lewis acid generating WCA in cationic polymerization can be the synthesis of high molecular weight poly(*p*-methoxystyrene)s ($M_n \sim 50{,}000$ g mol^{-1}) that was made possibly due to the suppression of side reactions.[66] Taking into account the advantages of using $B(C_6F_5)_3$ in cationic polymerization of vinyl monomers,[65,66] the $B(C_6F_5)_3$-co-initiated cationic polymerization of IP in the presence of different initiators (DMAX, X=Cl, Br, OH, OAc; 2-cyclohexylidene ethanol; 1-(4-methoxyphenyl)ethanol), pMOS-OH; 1-(4-methoxyphenyl) ethyl acetate), was also investigated.[67–70]

There are a number of important conclusions have been made based on these investigations. (i) Propagation occurred *only* via primary allylic carbocation form resulting in formation of *trans*-1,4-microstrucutre, while the tertiary carbocation form of allylic cation yields exclusively to proton elimination.[67] (ii) Polymers obtained with DMAX/$B(C_6F_5)_3$ (X=Cl, Br, OH, OAc) and pMOS-OH/$B(C_6F_5)_3$ initiating systems in CH_2Cl_2 at 20 °C contained insoluble part (gel fraction) and were characterized by very broad MWD (M_w/M_n=4–17), low content of intact double bonds (27%–50%) and high T_g values (from 3 °C to 56 °C) indicating that side reactions are significant at such conditions.[68,70] The addition of proton trap (DTBP)[70] or lowering of temperature[69,68] allowed to synthesize polymers with narrower MWD (M_w/M_n=1.8–3.5), higher content of intact double bonds (50%–70%) and lower T_g (from –33 °C to –61°C). This indicates that side reactions are considerably suppressed under such conditions. (iii) MALDI-TOF analysis of polyisoprenes synthesized with 2-cyclohexylidene ethanol/$B(C_6F_5)_3$ initiating system allowed to conclude that initiation (even in the presence of proton trap) occurred both via initiator and protons formed due to the β-H elimination, which is the main termination process.[69] Since no peaks bearing two or more initiator fragments were detected in MALDI-TOF mass spectra, the branching via "grafting from" mechanism is predominant under investigated conditions. In other words, the branching occurred via protonation of double bond of polymer followed by a propagation reaction from resulting macrocation. The middle chain cation can also interact with other double bond of the same polymer chain giving cyclic structures.[69] Based on the above mentioned observations the predominant mechanisms for propagation, chain branching, cyclization and cross-linking at different stage of reaction were proposed by Peruch and co-workers (Figure 5).[70] As it can be seen in Figure 5, at the latter stages of polymerization, the side reactions such as branching and cross-linking are predominant. However, at the early stages of reaction (low monomer conversions) the propagation is predominant and most of the chains are formed from initiator, although the chain transfer is also significant. At this stage of reaction, mainly linear or slightly branched chains are formed (Figure 5). In other words, the synthesis of well-defined polyisoprenes via cationic mechanism can be possible through rational choice of initiating system and reaction conditions (to suppress chain transfer to monomer) and when the reaction will be terminated at incomplete monomer conversions (to minimize chain transfer to polymer).

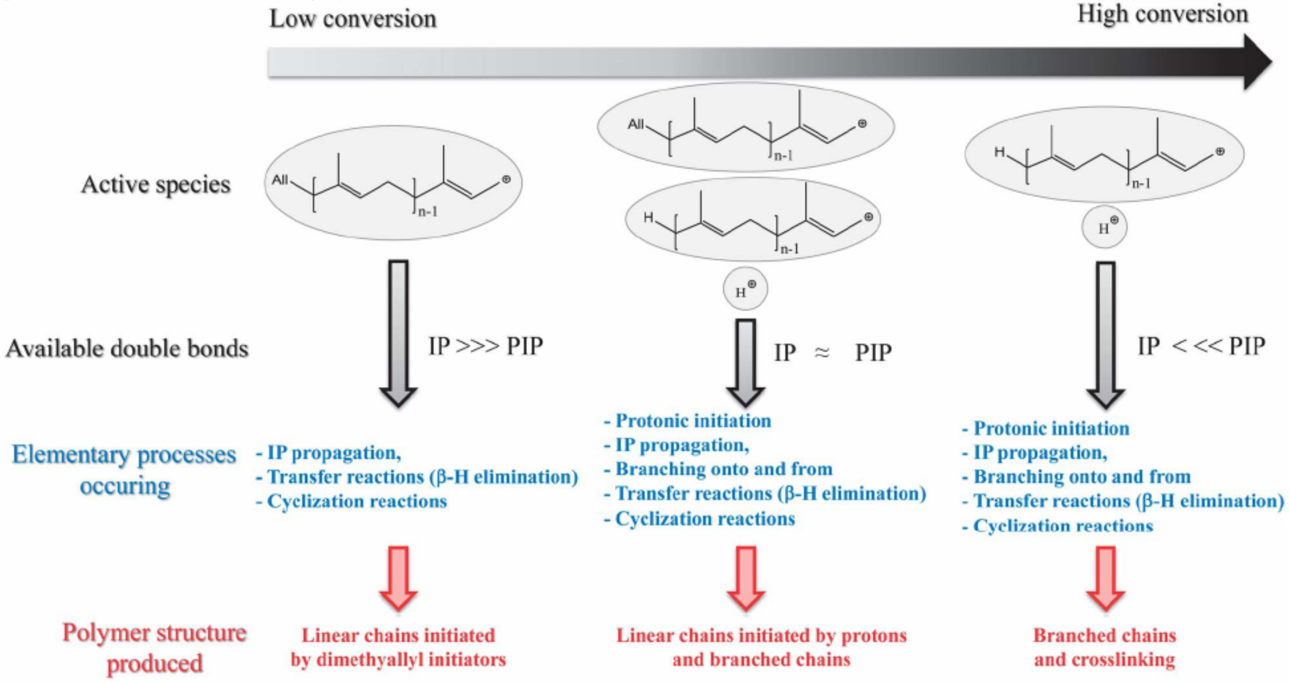


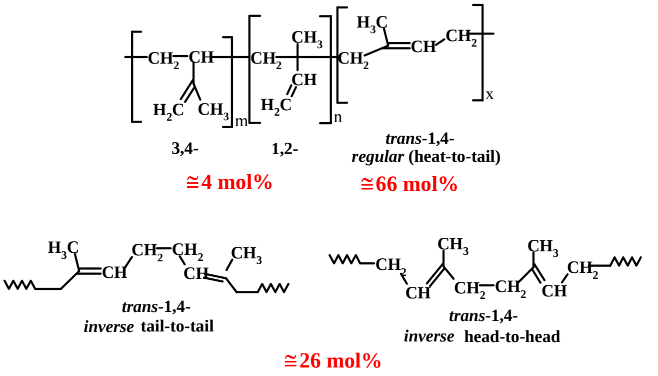
Fig. 5 Predominant processes occurring at different monomer conversions during isoprene cationic polymerization (Reproduced from Ref. 70).

Indeed, it was shown that cationic polymerization of isoprene with pMOS-OH/$B(C_6F_5)_3$ initiating system in CH_2Cl_2 or α,α,α-trifluorotoluene at –30 °C afforded predominantly linear *trans*-1,4-polyisoprenes (content of *trans*-1,4- units: 92-94%) with low molecular weight (M_n=2500 g mol^{-1} – 5500 g mol^{-1}), narrow MWD (M_w/M_n=1.4–2.9) and high content of intact double bonds (80%–90%).[68] Moreover, according to ^1H NMR spectroscopy and MALDI-TOF-MS almost all polyisoprene chains contain the fragment of initiator at the α-end and double bond at the ω-end.[68] In addition, higher molecular weigh well-defined *trans*-1,4-polyisoprenes (M_n=9,000 g mol^{-1} – 18,000 g mol^{-1}; M_w/M_n=1.9–2.4; content of intact double bonds 70%–80%) can be synthesized with adventitious $H_2O/B(C_6F_5)_3$ initiating system at –30 °C in CH_2Cl_2 or α,α,α-trifluorotoluene as solvents.[68]

Remarkably, much better results were obtained when the polymerization of isoprene was performed in aqueous media (dispersion, suspension or emulsion) with the same initiating system (pMOS-OH/$B(C_6F_5)_3$): linear polyisoprenes with low molecular weight (M_n≤1,000 mol^{-1}), narrow MWD (M_w/M_n=1.4–1.7) and very high content of intact double bonds (97%–99%) were synthesized with high regioselectivity (*trans*-1,4- units: 96–97%). This indicates that side reactions are almost totally suppressed when polymerization proceed in aqueous media.[68]

Another approach towards well-defined oligoisoprenes was developed by Rozentsvet and co-workers.[71] This approach consists in the using of high excess of initiator towards Lewis acid (typically initiator/Lewis acid ratio is 100-1000: 1 mol: mol). Under such conditions, $^tBuCl/ZnX_2$ or CCl_3COOH/ZnX_2 initiating systems (X=Cl, Br) induced cationic polymerization of isoprene (70–90 % of monomer conversion in 1 h) in CH_2Cl_2 at different temperatures to afford oligoisoprenes (M_n=600 g mol^{-1}– 800 g mol^{-1}) with relatively narrow MWD (M_w/M_n<2.4) and relatively high content of intact double bonds (60%–70%) without any insoluble fraction.[71]

3.1.3. Microstructure. The same team made a lot of efforts to determine the microstructure of polyisoprenes synthesized via cationic mechanism.[11,71,72] The main difficulty here is that characteristic signals in ^{13}C NMR spectra of cationic polyisoprenes with reduced unsaturation do not separate in baseline in strong contrast to spectra of polymers with unsaturation near 100%.[11,71,72] Nevertheless, it was unambiguously shown using high-resolution ^1H and ^{13}C NMR spectroscopy (including two-dimensional heteronuclear experiments) that polyisoprene chain consists of both regular (head-to-tail) and inverse (head-to-head or tail-to-tail) *trans*-1,4-units, while 1,2- and 3,4-units are present in small amounts (Scheme 11).[11,71,72] Regardless of Lewis acid used, the polyisoprenes obtained by cationic mechanism contain about 66 mol% of regular *trans*-1,4-units, ~26 mol% of inverse *trans*-1,4-units and ~4 mol% of 1,2- and 3,4-units.



Scheme 11 Possible structures of unsaturated part of polyisoprenes obtained by cationic polymerization.

In summary, despite of numerous side reactions accompanied the cationic polymerization of isoprene, considerably progress in this field was achieved during last years by rational selection of initiating systems and polymerization conditions. Particularly, using of initiating systems based on Lewis acids generating WCA*s* or conventional Lewis acids in conjunction with high excess of initiator towards co-initiator allowed to synthesize well-defined predominantly linear polyisoprenes with high content of intact double bonds.

3.2. Polymerization of 1,3-pentadiene

1,3-Pentadiene (piperylene) is a large-scale by-product of process of hydrocarbons cracking or isoprene production via dehydrogentation of isoprene.[11,73] One of the most effective methods of utilization of this monomer is the synthesis of so-called hydrocarbon resins via cationic polymerization of 1,3-pentadiene, which are widely used in the production of sticky tapes, adhesives, and paint and lacquer materials.[11] However, due to the structural similarity of this monomer to isoprene, the similar difficulties arose in the course of cationic polymerization of this monomer: the loss of double bonds and formation of branched and cross-linked insoluble polymers irrespective of Lewis acid nature, solvent or temperature.[11,13,73–79]

3.2.1. Effect of nucleophiles. An attempt to control the polymerization of 1,3-pentadiene was performed by Cheradame and co-workers by addition to the system of different nucleophiles, e.g. alkyl sulfides,[80] esters or amides[81] as well as ethers and bulky amines such as $N(PhBr)_3$, NPh_3.[82] This approach was proved to be very efficient in control of the cationic polymerization of various vinyl monomers such as vinyl ethers, isobutylene and styrene and its derivatives.[4,9] Indeed, the addition of such nucleophiles (at optimal Lewis acid: additive ratio) allowed to decrease the content of insoluble fraction and polydispersity (from M_w/M_n~25–35 to M_w/M_n~3–5) and to increase the unsaturation.[80–82] However, the insoluble fraction was still present in polymer and unsaturation (60-70%) was far from 100%, i.e. the polymerization was not controlled.[80–82] In addition, it was also shown that strong nucleophiles were prone to give polymers with higher content of insoluble fraction and steric structure of nucleophilic additive strongly influenced the reaction rate and polymer properties.[80–82] Interestingly, in the case of using a certain nucleophiles (butylamine[83] or triphenylamine[84]) in conjunction with $AlCl_3$ as co-initiator in non-polar solvents at 20 °C, the increase of number average molecular weight from ca 2,000 g mol^{-1} to 12,000 g mol^{-1} with increasing polymer yield, one of the important features of controlled polymerization,[4,9] was observed. However, polydispersity also increased with polymer yield and the first-order plots were not linear.[83,84] The further investigations showed that this behavior was attributed to continuous grafting of polymer or nucleophile by growing macrocations rather than to living nature of above mentioned polymerizations.[83,84] In other words, the addition of nucleophiles allowed to improve the process of cationic polymerization of 1,3-pentadiene, but it still suffered from side reactions leading to the loss of unsaturation and formation of insoluble fraction.

3.2.2. Polymerization at [I]>>[LA]. As it was already shown for polymerization of isoprene, the simplest approach towards well-defined polyisoprenes was the use of relatively weak Lewis acids such as zinc halides as co-initiators together with initiators (CCl_3COOH, ^{t}BuCl), which were used in high excess towards ZnX_2 (X=Cl, Br) (*vide supra*).[71] The same methodology showed high efficiency in the polymerization of 1,3-pentadiene.[85] ZnX_2-based initiating systems allowed to synthesize fully soluble low molecular weight (M_n=1000–3000 g mol^{-1}) poly(1,3-pentadiene)s with relatively narrow molecular weight distribution ($M_w/M_n<2.0$), which do not contain any high molecular weight and insoluble fractions in the whole range of monomer conversion. In addition, the unsaturation of obtained poly(1,3-pentadiene)s was relatively high (74-84 mol%), does not depend on the monomer conversion and slightly increased with decreasing reaction temperature.[85] It should be noted that above mentioned methodology was also efficient for the polymerization of 1,3-pentadiene in the presence of strong Lewis acid such as $TiCl_4$: ^{t}BuCl/$TiCl_4$ initiating system (^{t}BuCl: $TiCl_4$=340:1 mol/mol) [86] induced fast polymerization of 1,3-pentadiene to afford well-defined poly(1,3-penadiene)s with high unsaturation (content of intact double bonds 84–87 mol%) and relatively narrow and monomodal molecular weight distribution in the whole range of monomer conversions at –78 °C (Figure 6). The one of limitations of this initiating system is the formation of polymer with broad and multimodal MWD (M_w/M_n~60) containing high molecular fraction if the polymerization was conducted at room temperature.[86]

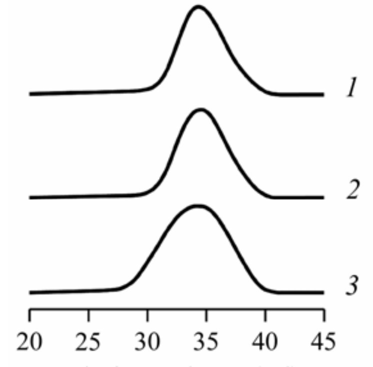
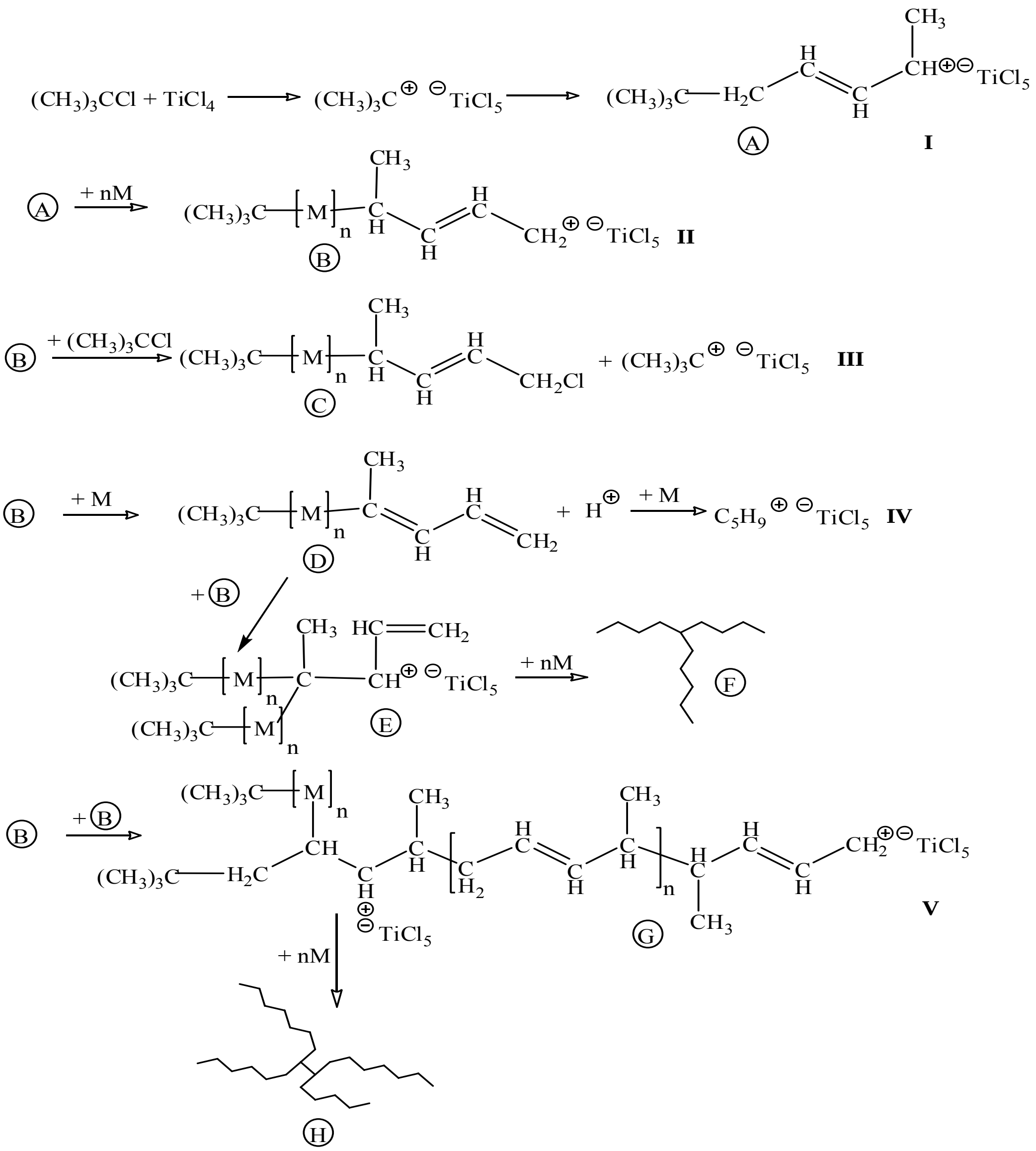


Fig 6 GPC traces of poly(1,3-pentadiene)s synthesized using ^{t}BuCl/$TiCl_4$ initiating system at different monomer conversions in CH_2Cl_2 at –78°C. Monomer conversion (%): (1) 40.3; (2) 59.2; (3) 99.5. [C_5H_8]=4.0 M; [$TiCl_4$]=1.5×10^{-2} M; ^{t}BuCl/$TiCl_4$=340 (Reproduced from Ref. 86 with permission from John Wiley and Sons).

3.2.3. Polymerization mechanism. An exhaustive study of the kinetics and characterization of synthesized polymers allowed to propose the following mechanism for 1,3-pentadiene cationic polymerization using ^{t}BuCl/$TiCl_4$ initiating system (Scheme 12).[86] The steps I and II represent the cationation, initiation and propagation and are similar to those for the cationic polymerization of other vinyl monomers. The chain transfer to initiator (^{t}BuCl acts as inifer[22]) leads to the formation of a polymer chain with chlorine end group and the regeneration of initial active species seems to be predominant chain-breaking process in the conditions when high excess of initiator to Lewis acid is used (see III in Scheme 12).[86] Similarly to the polymerization of isoprene (see Figure 5 and discussion therein),[69,70] the β-H elimination (chain transfer to monomer) is also a significant side reaction during the 1,3-pentadiene cationic polymerization (especially when [^{t}BuCl]~[$TiCl_4$]) leading to the formation of polymer chains containing conjugated double bonds (structure "**D**", Scheme 12). However, due to the high reactivity of terminal conjugated double bonds initially formed macromolecules "**D**" interact/copolymerize with growing chains "**B**" with the formation of branched chains "**E**" with trifunctional branch point and substituted allyl cation as a terminal group (step IV in Scheme 12). Macrocations "**E**" could be quite stable due to the impossibility of β-H abstraction and most probably are responsible for the coloration of reaction mixture often observed during cationic polymerization of 1,3-dienes, which is disappeared only after deactivation of reaction mixture by alchohol.[11] Alternatively, these species "**E**" could also initiate the polymerization of 1,3-pentadiene to generate branched structure "**F**" **(**step IV in Scheme 12**)**. The reduced unsaturation of synthesized poly(1,3-pentadiene)s even at low monomer conversions indicates that chain transfer to polymer via interaction of growing chains "**B**" with a main-chain double bond of another macromolecule (dead or growing) with the formation of branched macro-dications "**G**" occurs. These macrocations "**G**" could initiate the polymerization of 1,3-pentadiene to give branched macromolecule "**H**" with tetrafunctional branch point ("grafting from" mechanism, see Scheme 12). These side-reactions are more pronounced at high reaction temperatures, low ^{t}BuCl/$TiCl_4$ ratios and under monomer starved conditions. The following facts could be considered in favour of conducting branching reactions: (i) polydispersity of synthesized polymers dramatically increased with increasing monomer conversion; (ii) in all cases the functionality at the α-end is higher than unity; (iii) sometimes the formation of insoluble fraction is observed.[86]

The decrease of unsaturation of poly(1,3-diene)s during the cationic polymerization was usually explained by a intramolecular cyclization leading to rigid polymer backbone.[69,70,78–84] However, for the cationic polymerization of 1,3-pentadiene with ^{t}BuCl/$TiCl_4$ initiating system the intramolecular cyclization is unlikely. Indeed, ^{13}C NMR spectra of hydrogenated poly(1,3-pentadiene) samples did not show the characteristic signals of central methine carbon atoms at 60–63 ppm for di- and tricyclic six-membered structures.[86]

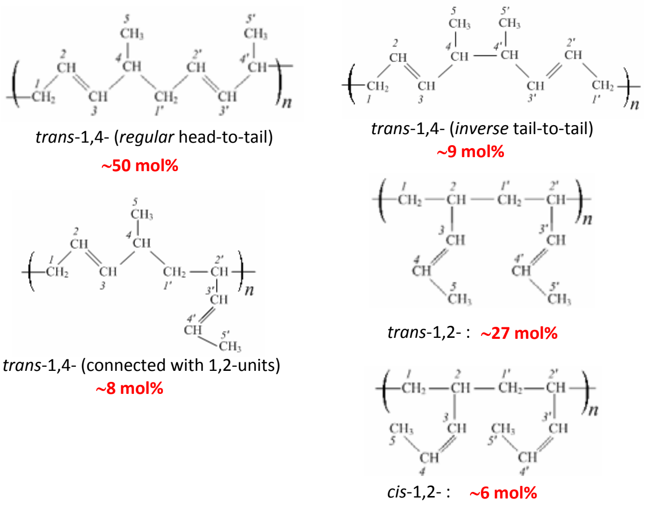


Scheme 12 Proposed mechanism for the cationic polymerization of 1,3-pentadiene using tBuCl/TiCl$_4$ initiating system.[86]

In summary, the main features of the mechanism of polymerization of 1,3-dienes proposed by Rozentsvet and co-workers[68] are (i) the absence of intramolecular cyclization; (ii) the branching occurred via interaction of growing chains with macromonomers possessing terminal conjugated double bonds to give branched chain with trifunctional branch point; (iii) chain branching proceeded via "grafting onto" followed by "grafting from" reactions.

3.2.4. Microstructure. Similar to polyisoprene difficulties arose during the investigation of microstructure of poly(1,3-pentadiene)s synthesized via cationic mechanism, i.e. characteristic signals in ^{13}C NMR spectra do not separate in baseline due to the reduced unsaturation of polymer chain. Therefore, the combination of one-dimensional (1D)-NMR and 2D-NMR spectroscopy was recently used to determine precisely the structure of cationic poly(1,3-pentadiene)s.[87] As an addition tool in the study of microstructure of cationic poly(1,3-pentadiene)s, the ^{13}C NMR investigations of hydrogenated polymer samples was also performed.[87] As a result, an original methodology was developed to determine and quantify different structural units of poly(1,3-pentadiene) chain.[87] Particularly, for poly(1,3-pentadiene) synthesized with ^{t}BuCl/TiCl$_4$ initiating system, almost all signals of carbon atoms in *trans*-1,4- (*regular* head-to-tail, *inverse* tail-to-tail and connected with 1,2-structures), *trans*-1,2- and *cis*-1,2-units were identified, while the total absence of *cis*-1,4- and 3,4-units in a polymer chain was unambiguously demonstrated (see Scheme 13).

Other interesting conclusions concerning the structure of chain end groups have been made based on NMR investigations of poly(1,3-pentadiene) synthesized by cationic polymerization of 1,3-pentadiene with $^{t}BuCl/TiCl_4$ initiating system. Particularly, *tert*-butyl group of initiator is connected predominantly with *trans*-1,4-unit of poly(1,3-pentadiene) chain, while chloromethyl end groups is formed *only* after *inverse trans*-4,1-monomer addition.[87]



Scheme 13 Possible structures of unsaturated part of poly(1,3-pentadiene)s obtained by cationic polymerization.

In addition, it was shown for the first time by Rozentsvet and co-workers[88] that content of 1,2-structures is considerably higher in the first monomer units than in polymer chain as a whole. This interesting result was obtained in the course of investigations the cationic polymerization of 1,3-pentadiene with initiating system consists of CF_3COOD as a deuterated initiator and $TiCl_4$ as co-initiator.[88]

3.3. Polymerization of cyclopentadiene

Cyclopentadiene, a cyclic 1,3-conjugated diene monomer is characterized by high reactivity in the cationic polymerization processes.[89] This monomer is prone to a lesser extent to side reactions such as chain branching and cross-linking in comparison with the linear 1,3-conjugated dienes (isoprene, 1,3-pentadiene).[89] Therefore, the living cationic polymerization of this diene monomer was realized by Sawamoto and co-workers at cryogenic temperatures using initiating systems based on conventional Lewis acids.[90] It was shown latter that living cationic polymerization of cyclopentadiene can be also performed under mild conditions (room temperature, non-purified solvents and monomer) when the initiating systems based on Lewis acids generating WCA*s* were used as co-initiators.[91] This topic was recently well reviewed and, therefore, is outside of this review article.[91] The living cationic polymerization of other cyclic conjugated diene, i.e. tetrahydroindene (bicyclo[4.3.0]-2,9-nonadiene), was recently reported by Kamigaito's groups.[92]

Conclusions

Although Lewis acid-co-initiated cationic polymerization of isobutylene and 1,3-dienes has been known for more than 100 years, this field is still full of surprises. In the area of cationic polymerization of isobutylene, the synthesis of low molecular weight *exo*-olefin terminated polyisobutylene (HR PIB) is currently mainly investigated due to the its growing commercial importance. The two major methods outlined above, i.e. based on (i) living cationic polymerization and (ii) using complexes of Lewis acids with ethers – have a high potential for commercial application. Although methods based on the living cationic polymerization are too expensive to be used for the production of HR PIB, they represent a unique opportunity for the synthesis well-defined di- or trifunctional *exo*-olefin terminated polyisobutylenes. Considerably progress has been achieved in this area via discovery of cheap and quite efficient end-quenching agents such as sulfides or ethers that allowed conducting functionalization at high monomer concentrations. Remarkably, the certain functional end-quenching agents can connect to PIB chain giving a series of multifunctional PIB with hydroxyl-, amino-, azido- and others functional groups.[93] Therefore, this methodology opens new possibilities for the synthesis multifunctional PIB precursors, which can be used as building blocks for the synthesis of more complex polymer architectures.[94]

Among the catalysts investigated with the aim to replace the BF_3 process for the synthesis of HR PIB, the complexes of metal halides with ethers are the most promising in terms of their efficiency, low price and high regioselectivity toward β-H abstraction. These initiating systems were discovered accidentally and currently are the most investigated catalysts in this field. The application of the first generation of these initiating systems (complexes of $AlCl_3$ with dibutyl or diisopropyl ethers) is restricted to polar CH_2Cl_2 and toluene. In these solvents both high activity and regioselectivity are achieved, whereas a number of limitations are observed in non-polar *n*-hexane. The second generation of initiating systems (complexes of $FeCl_3$ and $GaCl_3$ with diisopropyl and *bis*(2-chloroethyl) ethers in conjunction with tertiary alkyl halides) affords HR PIB in close to quantitative yield in *n*-hexane but the *exo*-olefin content does not exceed 80% and the reaction is relatively slow. The third generation of catalysts consists of complexes of alkylaluminum dichlorides ($EtAlCl_2$, $^{i}BuAlCl_2$) with ethers ($^{i}Pr_2O$, CEE) in conjunction with H_2O or $^{t}BuCl$ as initiators. The major advantage of these initiating systems is that complexes of $RAlCl_2$ with ethers are soluble in *n*-hexane and, therefore, allow to synthesize desired low molecular weight HR PIB with high *exo*-olefin end group content (>85%) even at high monomer concentration ([IB]=4–5 M) and high reaction temperatures (0 °C – +20°C) in non-polar solvents. Currently, $RAlCl_2 \times OR_2$-based initiating systems are the best candidates for the industrial adoption and may replace the BF_3 process in the future. One of significant limitations of these catalysts to be solved in the nearest future is the relatively broad MWD of synthesized polymers.

The recent investigations of the cationic polymerization of 1,3-dienes (isoprene, 1,3-pentadiene) allowed to propose the relevant mechanism of the process and define the main side reactions leading to the formation of ill-defined polymers. This enables to design the initiating systems and polymerization conditions in such a way that side reactions are considerably minimized. Particularly, the using of initiating systems based on Lewis acids generating WCA*s* or conventional Lewis acids in conjunction with high excess of initiator towards co-initiator allowed to synthesize well-defined predominantly linear poly(1,3-diene)s with high content of intact double bonds. An interesting example of synthesis of fully unsaturated linear polyisoprene represents the cationic polymerization of isoprene using quite unusual conditions, i.e. water dispersion. However, despite of these recent improvements, poly(1,3-diene)s with relatively low molecular weight have been still obtained. Therefore, further progress in the control of 1,3-dienes cationic polymerization can reasonably be expected.

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Notes and references

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