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Living and Controlled Polymerization of Isobutylene with Alkylaluminum Halides as Coinitiators

Savvas Hadjikyriacou, Metin Acar, and Rudolf Faust*

*Polymer Science Program, Department of Chemistry, University of Massachusetts Lowell,
One University Avenue, Lowell, Massachusetts 01854*

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ABSTRACT: The living polymerization of isobutylene (IB) coinitiated by dimethylaluminum chloride (Me_2AlCl) was reinvestigated in hexanes/CH_3Cl 60/40 (v/v) solvent mixture at −80 °C in the presence and absence of a proton trap, 2,6-di-*tert*-butylpyridine (DTBP). Termination and chain transfer were not detected in either case. The polymerization, however, was much slower in the presence of DTBP. Experiments carried out at varied DTBP concentrations confirmed that DTBP does not interact with the Lewis acid or with carbocations and its role is to scavenge protic impurities. The large difference in the polymerization rate in the presence and absence of proton trap was attributed to the different nature of the true coinitiator, Me_2AlCl, in the presence of DTBP and $MeAlCl_2$ (or more likely methylaluminum sesquichloride), a stronger Lewis acid that could be present as an impurity or may form by the reaction of Me_2AlCl with protic impurities (e.g., HCl), in the absence of DTBP. Polymerizations employing Me_2AlCl or $MeAlCl_2$ separately or the mixture of the two Lewis acids confirmed that $MeAlCl_2$ is at least 200 000 times stronger than Me_2AlCl. Therefore, even in the presence of traces of $MeAlCl_2$ in Me_2AlCl, the polymerization is coinitiated by $MeAlCl_2$. Separate experiments confirmed that the living polymerization of IB can be accomplished with methylaluminum sesquichloride or $MeAlCl_2$ as Lewis acid in hexanes/CH_3Cl 60/40 (v/v) at −80 °C. Controlled polymerization of IB coinitiated by $MeAlCl_2$ or methylaluminum sesquichloride that yields polymers with theoretical molecular weights and narrow molecular weight distributions, however, was possible only at [Lewis acid] $\leq 3 \times 10^{-3}$ M. Under these conditions the M_n was directly proportional to the monomer/initiator ratio up to [monomer]/[initiator] = 1000, and in chain extension experiments the M_ns doubled and tripled upon addition of a second and third monomer increment, respectively. The loss of control at higher Lewis acid concentration was attributed to the extremely rapid nature of the polymerization. The new highly active catalysts are promising candidates to substitute $TiCl_4$, the only Lewis acid presently employed commercially, in the living polymerization of IB.

Introduction

Since the first reports on living cationic polymerization in the mid-1980s,[1,2] most cationically polymerizable monomers have been polymerized in living cationic polymerization. In the design of living polymerization systems the key is to match the reactivity of the monomer to the strength of the Lewis acid coinitiator. Generally, weak Lewis acids are employed for the living polymerization of reactive monomers such as vinyl ethers, *p*-methoxystyrene, and *N*-vinylcarbazole[3] so that the polymerization proceeds in controlled fashion in a desired time scale (minutes to hours). Weak Lewis acids, however, are ineffective for polymerizing less reactive monomers such as isobutylene (IB), commercially the most important monomer that can be homopolymerized only by cationic polymerization. Among strong Lewis acids only a few are known to induce the living polymerization of IB. Titanium tetrachloride ($TiCl_4$) is by far the most commonly used Lewis acid that is also effective in solvents of medium polarity where high molecular weight polyisobutylene (PIB) is soluble. Recently, the living polymerization of IB catalyzed by dimethylaluminum chloride (Me_2AlCl) in hexane/methylene chloride (60/40 v/v) at −80 °C was reported.[4] More recently, we reported on the propagation rate constant for ion pairs ($k_p^{\pm}$) in the living cationic polymerization of IB.[5,6] The $k_p^{\pm}$ values were independent of the nature of Lewis acid as virtually identical $k_p^{\pm}$ values were obtained for $TiCl_4$, $EtAlCl_2$, and Me_2AlCl even though the polymerization rates decreased drastically in the order $EtAlCl_2 \gg TiCl_4 \gg Me_2AlCl$.[6] Comparison of our results with Me_2AlCl and that of Bahadur et al.,[4] however, revealed that our polymerizations were much slower under similar conditions. We therefore investigated the polymerization of IB coinitiated by methylaluminum chlorides in detail, which led to the discovery of new highly effective initiating systems, reported in this article.

Experimental Section

Materials. Hexanes were rendered olefin free by refluxing over concentrated sulfuric acid for 48 h. They were washed with 10% NaOH (Aldrich, 97%) aqueous solution and then with deionized water until neutral and stored over anhydrous $MgSO_4$ (Aldrich) for 24 h. It was refluxed over CaH_2 (Aldrich) overnight and distilled under nitrogen. 2-Chloro-2,4,4-trimethylpentane (TMPCl) was prepared by passing dry HCl through a 30% solution of 2,4,4-trimethyl-1-pentene (Aldrich, 99%) in dried and distilled CH_2Cl_2 (Aldrich) at 0 °C for 3 h. After 3 h the solution was allowed to warm to room temperature and the excess HCl to escape. The solvent and remaining dissolved HCl were removed on the rotavap, and the crude product was purified by distillation from CaH_2. $MeAlCl_2$ (1 M solution in hexanes), Me_2AlCl (1 M solution in hexanes), 2,6-di-*tert*-butylpyridine (DTBP, 97%), and $TiCl_4$ (99.9%) (all Aldrich) were used as received. Methylaluminum sesquichloride in hexanes was obtained by mixing $MeAlCl_2$ and Me_2AlCl solutions in stoichiometric amounts at room temperature.

Polymerization. Polymerizations were carried out under a dry nitrogen atmosphere ([H_2O] < 1 ppm) in an MBraun 150-M glovebox (Innovative Technology Inc., Newburyport, MA). Large (75 mL) culture tubes were used as polymerization

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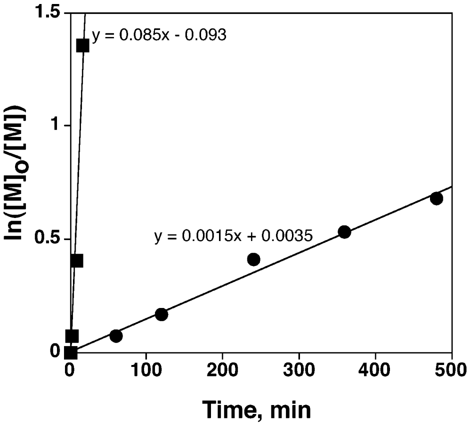

Figure 1. First-order plot for the polymerization of IB coinitiated by Me_2AlCl in hexanes/CH_3Cl 60/40 (v/v) at −80 °C in the absence (■) and presence of DTBP ([DTBP] = 3×10^{-3} M) (●). [TMPCl] = 2×10^{-3} M, [Me_2AlCl] = 1×10^{-2} M, [IB] = 0.64 M.

reactors. The total volume of the reaction mixture was 20 mL. The kinetic study of the polymerization of IB by Me_2AlCl was carried out as follows. Hexane (10.0 mL) was measured at room temperature in each of six culture tubes and cooled to −80 °C. CH_3Cl (6.9 mL) was delivered next at −80 °C followed by the addition of 1.0 mL of DTBP stock solution cooled to −80 °C. Next, Me_2AlCl (1.56 mL, 1.7 mmol) from a stock solution at −80 °C was added and mixed for 5 min. The initiator (0.2 mmol) was delivered by adding 1.0 mL of initiator stock solution, followed by the immediate addition of 1.0 mL (12.8 mmol) of IB. The final concentrations of the components in the reaction mixtures were as follows: [TMPCl] = 1×10^{-2} M, [DTBP] = 6×10^{-3} M, [Me_2AlCl] = 8.4×10^{-2} M, [IB] = 0.64 M.

At predetermined times the polymerizations were quenched using prechilled methanol. The polymers were purified by repeated precipitation into methanol and dried at room temperature under vacuum for 24 h. Monomer conversions were determined gravimetrically.

Characterization. Molecular weights were measured at room temperature using a Waters HPLC system equipped with a model 510 HPLC pump, a model 250 dual refractometer/viscometer detector (Viscotek) equipped with a 670 nm light source, a model 712 sample processor, and five Styragel-HR GPC columns connected in the following series: 500, 10^3, 10^4, 10^5, and 100 Å. The molecular weights and molecular weight distributions (PDI) were determined using the universal calibration curve and Viscotek TriSEC GPC software. THF was used as eluent at a flow rate of 1.0 mL min^{-1}.

Results and Discussion

As mentioned in the Introduction, the polymerization of IB initiated by the TMPCl/Me_2AlCl initiating system in the presence of proton trap DTBP in hexanes/CH_3Cl 60/40 (v/v) at −80 °C were much slower than that reported by Bahadur et al.[4] carried out in the absence of DTBP but otherwise similar conditions. The polar solvent component in our case was also different (CH_3Cl vs CH_2Cl_2). To confirm that the minor change in the solvent polarity cannot be responsible for the large discrepancy in the polymerization rate, we have carried out the polymerization of IB in hexanes/CH_3Cl 60/40 (v/v) at −80 °C in both the absence and presence of DTBP. The first-order ln([M]$_0$/[M]) vs time plots, shown in Figure 1, are linear starting at the origin both in the absence and presence of DTBP. The concentrations of TMPCl and Me_2AlCl in our experiments were similar to those used by Bahadur et al.;[4] however, the concentration of IB was lower (0.64 M vs 2.9 M) in our experiments to minimize temperature increase during polymerization and avoid a large change in solvent polarity with conversion. Because of these differences, the polymerization rate in the absence of DTBP was somewhat higher than that reported in ref 4. While the polymerization in the absence of DTBP proceeded at a reasonable rate and complete monomer conversion was achieved in 1 h, under the same conditions but in the presence of DTBP the polymerization was ~60 times slower and quantitative monomer conversion was not attained even after 8 h. The M_n and M_w/M_n vs conversion plots are shown in Figure 2. The M_n vs conversion plots are linear starting at the origin and run close to the theoretical line in both the presence and absence of DTBP. There is a difference, however, in the M_w/M_n vs conversion plots. The plot for the absence of DTBP shows the general tendency observed in living polymerizations with dynamic exchange between dormant and active center; i.e., the M_w/M_n values gradually decrease with the increase of conversion. The molecular weight distribution of PIBs obtained in the presence of DTBP, however, is very narrow even at low conversion, which suggests a much faster dormant-active exchange relative to propagation. Although the polymers obtained in the absence of DTBP exhibited narrow molecular weight distributions at high conversions, GPC RI traces of samples (Figure 3) showed a small hump in the high molecular weight area. The formation of this hump may be explained by uncontrolled initiation from protic impurities as a similar high molecular weight hump has also been reported and attributed to protic initiation with $TiCl_4$.[7] Protic initiation was verified in separate experiments in the absence of TMPCl as initiator. Complete conversions and very high M_n in the range of 200 000−600 000 were obtained in the absence of DTBP, while polymerization was absent in its presence.

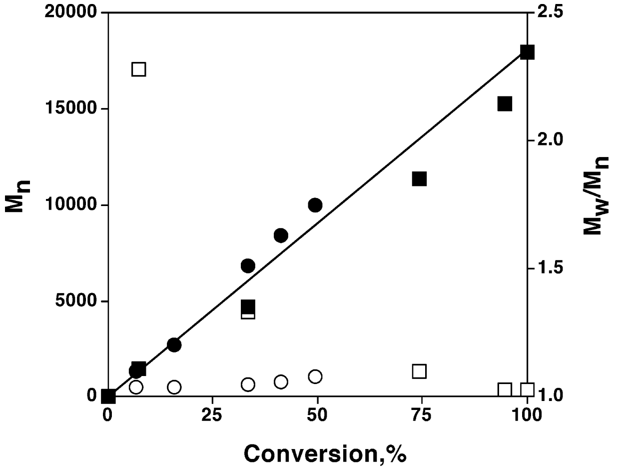

Figure 2. M_n (filled symbols) and M_w/M_n (open symbols) vs conversion plots for the polymerization of IB coinitiated by Me_2AlCl in hexanes/CH_3Cl 60/40 (v/v) at −80 °C in the absence (■, □) and presence of DTBP ([DTBP] = 3×10^{-3} M) (●, ○). [TMPCl] = 2×10^{-3} M, [Me_2AlCl] = 1×10^{-2} M, [IB] = 0.64 M. Drawn line corresponds to theoretical M_ns.

While the polymerization was very slow with [TMPCl] = 2×10^{-3} M, close to 5 times higher rate was observed when the initiator concentration was increased 5-fold to [TMPCl] = 1×10^{-2} M, and close to quantitative conversion was obtained in 5 h. The livingness of the polymerization was confirmed by the diagnostic plots of ln([M]$_0$/[M]) vs time (Figure 4) and M_n vs conversion (Figure 5). Both plots are linear showing that

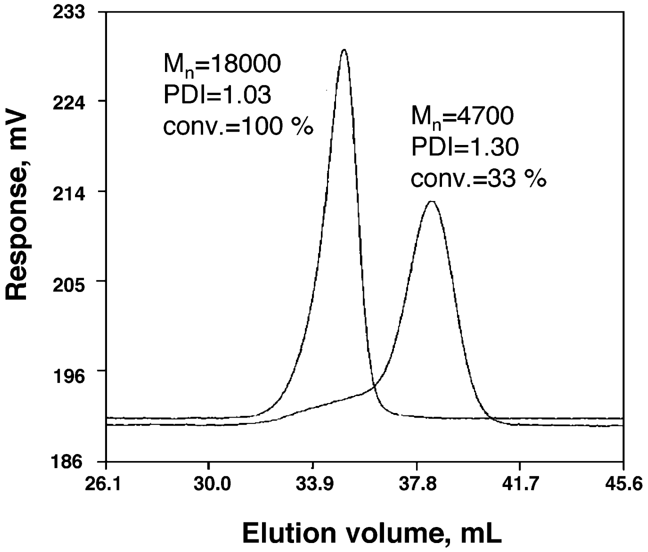

Figure 3. GPC RI traces of representative samples obtained in the polymerization of IB coinitiated by Me_2AlCl in hexanes/CH_3Cl 60/40 (v/v) at −80 °C in the absence of DTBP. [TMPCl] = 2×10^{-3} M, [Me_2AlCl] = 1×10^{-2} M, [IB] = 0.64 M.

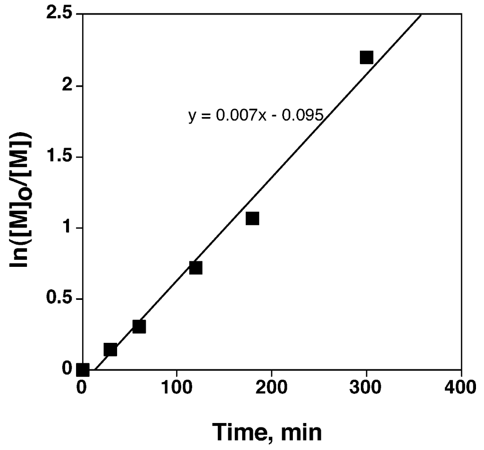

Figure 4. First-order plot for the polymerization of IB coinitiated by Me_2AlCl in hexanes/CH_3Cl 60/40 (v/v) at −80 °C. [TMPCl] = 1×10^{-2} M, [DTBP] = 6×10^{-3} M, [Me_2AlCl] = 8.4×10^{-2} M, [IB] = 0.64 M.

termination and chain transfer are undetectable. The polymers also exhibited narrow molecular weight distribution (Figure 5).

The proton trap DTBP is generally used in living cationic polymerization to prevent protic initiation. In the polymerization of IB catalyzed by $TiCl_4$ for instance, polymerization rates, molecular weights, and polydispersities are unaffected by excess DTBP. To determine the role of DTBP in the polymerization of IB coinitiated by Me_2AlCl, the effect of the DTBP concentration on the rate of the polymerization was studied in the range of [DTBP] = 0−6.0 × 10^{-3} M. In Figure 6 the conversion vs time plots are shown for different DTBP concentration. At [DTBP] = 5.0×10^{-4} M the polymerization is very fast, and quantitative conversion is achieved in 30 min. Although the polymerization is fast, polymers with close to theoretical M_n and narrow molecular weight distributions ($M_w/M_n < 1.1$) were obtained (Figure 7). Under identical conditions but in the absence of DTBP, complete conversion was reached in 5 min, but the M_n of the product was about 10 times higher than the theoretical value. When the DTBP concentration was increased to 1.0×10^{-3} M, the polymerization rate decreased further, and complete polymerization was reached in ~150 min. Further increase in the concentration of DTBP brought about little change in the rate

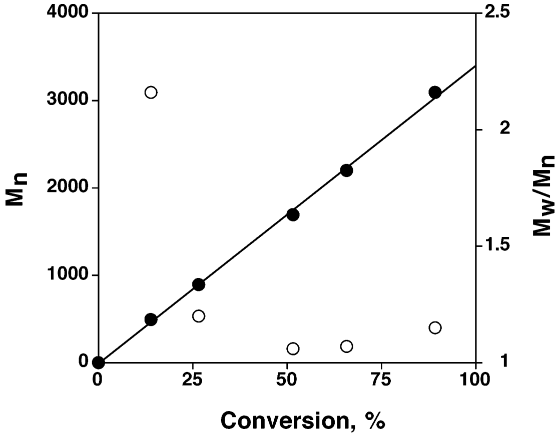

Figure 5. M_n (filled symbols) and M_w/M_n (open symbols) vs conversion plot for the polymerization of IB coinitiated by Me_2AlCl in hexanes/CH_3Cl 60/40 (v/v) at −80 °C. [TMPCl] = 1×10^{-2} M, [DTBP] = 6×10^{-3} M, [Me_2AlCl] = 8.4×10^{-2} M, [IB] = 0.64 M. Drawn line corresponds to theoretical M_ns.

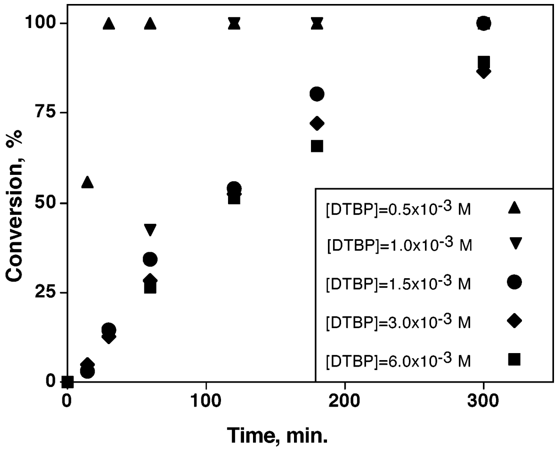

Figure 6. M_n vs conversion plot for the polymerization of IB coinitiated by Me_2AlCl in hexanes/CH_3Cl 60/40 (v/v) at −80 °C at different DTBP concentrations. [TMPCl] = 1×10^{-2} M, [Me_2AlCl] = 8.4×10^{-2} M, [IB] = 0.64 M.

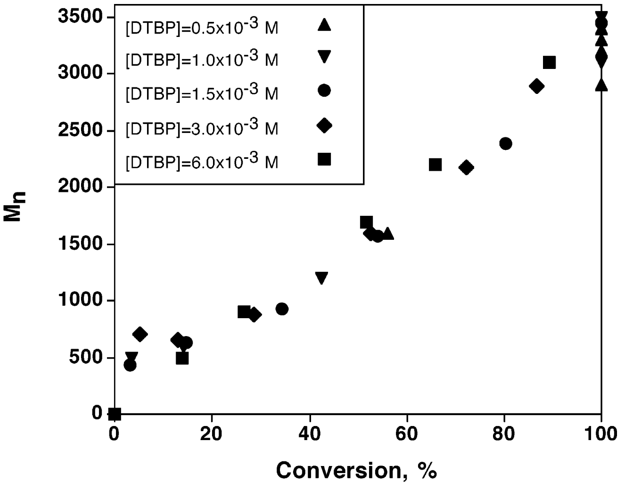

Figure 7. M_n vs conversion plot for the polymerization of IB coinitiated by Me_2AlCl in hexanes/CH_3Cl 60/40 (v/v) at −80 °C at different DTBP concentrations. [TMPCl] = 1×10^{-2} M, [Me_2AlCl] = 8.4×10^{-2} M, [IB] = 0.64 M. Drawn line corresponds to theoretical M_ns.

Table 1. $Me_2AlCl/MeAlCl_2$-Mediated Polymerization of IB in the Presence of DTBP in Hexanes/CH_3Cl (60/40 v/v) at −80 °C

[TMPCl], M	coinitiator	pzn time, min	conversion, %	M_n	M_w/M_n
0.02	$[Me_2AlCl] = 0.1$ M	300	85	3000	1.02
0.02	$[MeAlCl_2] = 0.002$ M	0.5	100	3500	1.4
0.02	$[Me_2AlCl] = 0.1$ M + $[MeAlCl_2] = 0.002$ M	0.5	100	3500	1.4
0.002	$[Me_2AlCl] = 0.1$ M	500	50	10000	1.08
0.002	$[Me_2AlCl] = 0.1$ M + $[MeAlCl_2] = 0.002$ M	0.5	100	21000	1.2

as virtually identical rates were obtained for $[DTBP] = (1.5-6.0) \times 10^{-3}$ M. Thus, we conclude that at $[DTBP] = (1-1.5) \times 10^{-3}$ M all protic impurities are scavenged. All M_n vs conversion plots (Figure 7) are linear and close to the theoretical line. Thus, similarly to the observation with $TiCl_4$, DTBP does not form a complex with Me_2AlCl (or the equilibrium constant of complexation is low), and there is no interaction between the carbocation and DTBP.

The very large difference in the polymerization rate in the presence and absence of DTBP, shown in Figure 1, can be attributed to different concentration or different reactivity of active centers. Since the propagation rate constant for ion pairs is independent of Lewis acid[6] and ion pairs and free ions should have similar reactivity,[8] the concentration of active centers must be different in the presence and absence of DTBP. The concentration of active centers may be different because in the presence of DTBP propagation takes place on ion pairs while in the absence of DTBP the active centers are mainly free ions, and the total active center concentration is higher. However, this cannot explain why the polymerization is so rapid at $[DTBP] = 5.0 \times 10^{-4}$ M since due to the common ion effect even at this low concentration propagation should be mainly by ion pairs.

On the basis of the analysis above, we hypothesized that the counterion and therefore the true coinitiator is different in the presence and absence of DTBP. It is reasonable to assume that the true coinitiator in the presence of DTBP is Me_2AlCl. In its absence, however, the true coinitiator may be a stronger Lewis acid (MeAlClX, where X is Cl or OH) that either forms in a reaction with protic impurities or it may be present as an impurity in Me_2AlCl. In the presence of DTBP, however, this stronger Lewis acid is scavenged via a reaction with protic impurities and DTBP. Me_2AlCl is known to contain traces of $MeAlCl_2$, which is a much stronger Lewis acid compared to Me_2AlCl.[9] Since a quantitative Lewis acidity scale does not exist, we have compared the strength of these Lewis acids in polymerization experiments. Table 1 lists the monomer conversion, M_n, and M_w/M_n values for polymerizations carried out in hexanes/CH_3Cl (60/40 v/v) at −80 °C coinitiated by Me_2AlCl, $MeAlCl_2$, and mixtures of the two Lewis acids in the presence of DTBP. At [TMPCl] = 0.02 M the polymerization time to completion is more than 600 times shorter with $MeAlCl_2$ compared to Me_2AlCl even though the concentration of $MeAlCl_2$ was 60 times lower than that of Me_2AlCl. Results for the polymerization in the presence of mixed Lewis acids were identical to that employing $MeAlCl_2$, suggesting that $MeAlCl_2$ is much stronger Lewis acid. From the last two entries we estimate that $MeAlCl_2$ is at least 200 000 times stronger than Me_2AlCl, and consequently even in the presence of traces of $MeAlCl_2$ in Me_2AlCl the polymerization will be coinitiated by $MeAlCl_2$. In all polymerization experiments the products exhibited M_ns close to the theoretical molecular weight; however, the molecular weight distributions were narrower when Me_2AlCl was employed alone.

Table 2. Polymerization of Isobutylene with TMPCl ([TMPCl] = 0.002 M)/$Me_{1.5}AlCl_{1.5}$ in the Presence of DTBP in Hexanes/CH_3Cl (60/40 v/v) at −80 °C

$[Me_{1.5}AlCl_{1.5}]$, M	conv, %	M_n	M_w/M_n
2×10^{-2}	100	236 000	3.6
1×10^{-2}	100	133 000	2.5
4×10^{-3}	100	42 000	2.1
3×10^{-3}	100	40 000	1.05
2×10^{-3}	100[a]	25 000	1.05
1×10^{-3}	0		
5×10^{-4}	0		

[a] In less than 30 s. Isobutylene added last.

Numerous publications report that alkylaluminum compounds are dimeric in solution or even in the gas phase especially at low temperature or low pressure.[10] Bahadur et al.[4] also found that the polymerization of IB is second order in $[Me_2AlCl]$, suggesting that the true coinitiator is the dimeric species. Meier and co-workers recently studied the structure of organoaluminum (chloride) complexes by experimental far-infrared spectroscopy and by quantum mechanical simulations.[11] Species preferably formed dinuclear aluminum complexes by chloride bridges; alkyl-bridged dimers were much less stable. The dimerization energy for methylaluminum sesquichloride ($Me_3Al_2Cl_3$) was calculated to be 19.4 kcal/mol, lower than average of dimerization energy in the dimerization of Me_2AlCl and $MeAlCl_2$. It is likely therefore that in the presence of traces of $MeAlCl_2$ in Me_2AlCl the actual coinitiator is $Me_3Al_2Cl_3$. Therefore, we also carried out experiments with $Me_3Al_2Cl_3$. Table 2 lists the results obtained at different concentration of Lewis acid. At high Lewis acid concentrations the polymerization is uncontrolled as the polymers have much higher M_ns than the theoretical value, and the molecular weight distributions are broad. By decreasing the Lewis acid concentration the M_n and M_w/M_n values decrease, and at $[Me_{1.5}AlCl_{1.5}]^{12} = 2 \times 10^{-3}$ M close to theoretical M_n and narrow molecular weight distribution is obtained. At this Lewis acid concentration the polymerization is still very rapid and complete in 0.5 min, suggesting that methylaluminum sesquichloride is also at least 200 000 times stronger than Me_2AlCl. The polymerization was absent, however, when the concentration of the Lewis acid was decreased further, presumably because the Lewis acid is completely consumed in reactions with protic impurities followed by salt formation with proton trap. Further control of the M_n was possible even at $[Me_{1.5}AlCl_{1.5}] = 3 \times 10^{-3}$ M by changing the addition order and introducing a mixture of IB and TMPCl to the polymerization system last (see Table 3). It is important to note that the Lewis acid concentrations are nominal values. The effective concentration may be very different when the nominal concentration is close to the concentration of protic impurities, which in our systems is estimated at $(1-1.5) \times 10^{-3}$ M and may vary from experiment to experiment.

Table 3. Polymerization of Isobutylene with TMPCl/ $Me_{1.5}AlCl_{1.5}$ in Hexanes/CH_3Cl (60/40 v/v) at −80 °C[a]

[IB]/[TMPCl]	conv, %	M_n	$M_{n,theo}$	M_w/M_n
All Monomer In (AMI)				
50	100	3 500	2 800	1.1
100	100	7 600	5 600	1.1
200	100	14 000	11 200	1.1
400	100	26 000	22 400	1.01
650	100	39 000	36 400	1.03
1000	90	51 000	50 400	1.06
Incremental Monomer Addition (IMA, 10 min)				
200	100	11 500	11 200	1.03
400	200	22 000	22 000	1.06
600	300	32 500	33 600	1.08

[a] [TMPCl] = 2 × 10^{-3} M, [$Me_{1.5}AlCl_{1.5}$] = 3 × 10^{-3} M, [DTBP] = 3 × 10^{-3} M, [IB] = 0.1−2 M. Addition order: solvent, DTBP, $Me_{1.5}AlCl_{1.5}$, IB +TMPCl. Polymerization time: 2 min.

Table 4. Polymerization of Isobutylene with TMPCl/ $MeAlCl_2$ in Hexanes/CH_3Cl (60/40 v/v) at −80 °C[a]

[IB]/[TMPCl]	conv, %	M_n	$M_{n,theo}$	M_w/M_n
All Monomer In (AMI)				
50	100	4 200	2 800	1.4
100	100	6 300	5 600	1.5
200	100	13 000	11 200	1.3
400	100	22 500	22 400	1.5
650	100	31 000	36 400	1.4
1000	90	42 000	50 400	1.4
Incremental Monomer Addition (IMA, 2 min)				
200	100	9 300	11 200	1.5
400	200	18 000	22 000	2.0
600	300	30 000	33 600	1.7
800	400	40 000	44 000	1.7

[a] [TMPCl] = 2 × 10^{-3} M, [$MeAlCl_2$] = 3 × 10^{-3} M, [DTBP] = 3 × 10^{-3} M, [IB] = 0.1−2 M. Addition order: solvent, DTBP, $MeAlCl_2$, IB + TMPCl. Polymerization time: 2 min.

Since the polymerization was too fast for sampling, the diagnostic first-order and M_n vs conversion plots could not be constructed. To confirm the absence of chain transfer and termination, a series of experiments were carried out by varying the initial monomer to initiator molar ratio from 50 to 1000. As shown in Table 3, the M_ns are proportional to the [IB]/[TMPCl] ratio and the M_n values are in acceptable agreement with the theoretical M_ns calculated with the assumption that chain transfer is absent and one molecule of TMPCl initiates one polymer chain. In separate chain extension experiments the so-called incremental monomer addition (IMA) technique was also applied. Thus, after 10 min under monomer-starved conditions a second and subsequently a third feed of IB were added to a completely polymerized system. The additional IB smoothly polymerized without a noticeable decrease in the polymerization rate, the molecular weight doubled and tripled, and the molecular weight distribution stayed narrow.

Identical AMI and IMA polymerization experiments (with 2 min between increments) were also carried out with $MeAlCl_2$ as Lewis acid. The results shown in Table 4 are similar to those with methylaluminum sesquichloride except that the molecular weight distributions are higher. The observed M_ns are directly proportional to the monomer-to-initiator ratio in the AMI experiments and increased smoothly after the addition of up to three IB increments to close to theoretical values.

Conclusion

The Lewis acid Me_2AlCl catalyzes a very slow living polymerization of IB in the presence of proton trap in hexanes/CH_3Cl 60/40 (v/v) at −80 °C. In the absence of proton trap the living polymerization is much faster, and we propose that this polymerization is induced by traces of a much stronger Lewis acid, e.g., methylaluminum sesquichloride or $MeAlCl_2$. This proposition is supported by results indicating that $MeAlCl_2$ or methylaluminum sesquichloride are at least 200 000 times stronger Lewis acids than Me_2AlCl and by the discovery that the living polymerization of IB can be coinitiated by methylaluminum sesquichloride or $MeAlCl_2$ in hexanes/CH_3Cl 60/40 (v/v) at −80 °C. For controlled polymerization, however, the Lewis acid concentration must be $\leq 3 \times 10^{-3}$ M. At higher concentrations the polymerization is uncontrolled due to the extremely rapid polymerization. Even though the polymerization is very rapid and complete in 0.5 min at [Lewis acid] = 3 × 10^{-3} M, the concentration of Lewis acid cannot be lowered below 2 × 10^{-3} M under our conditions due to the presence of protic impurities estimated at (1−2) × 10^{-3} M. In commercial polymerization systems, however, where the concentration of protic impurities is much lower, further decrease of the Lewis acid concentration may be possible and desirable to gain further control of the polymerization. A clear advantage of the new highly active catalysts is that high polymerization rates are achieved even at low Lewis acid concentrations, and after quenching the aluminum oxide compounds may be left in the polymer without deleterious effects.

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