Dimethylaluminum Chloride Catalyzed Living Isobutylene Polymerization

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ABSTRACT: The first examples of dimethylaluminum chloride catalyzed living isobutylene polymerizations are presented. The polymerizations are carried out with conventional tertiary alkyl chloride initiators and 60/40 v/v nonpolar/polar solvent mixtures, the most common solvent systems used for isobutylene triblock synthesis. Additives like proton traps and electron donors are not required. The “living” nature of these polymerizations is demonstrated at −75 to −80 °C in both 60/40 v/v hexane/methylene chloride and hexane/methyl chloride solvent systems using first-order rate plots, trends in M_n and M_w/M_n versus conversion, and delayed incremental-monomer-addition experiments. Polyisobutylenes are prepared with $M_n = 150$ kDa and $M_w/M_n = 1.2$. Since initiation from adventitious moisture is of minor concern in this system, experiments were also run in the presence of dimethyl phthalate. “Livingness” was preserved though polymerization rates are slower with dimethyl phthalate than in its absence.

Only two Lewis acids, boron trichloride and titanium tetrachloride, are commonly used in the living polymerization of isobutylene.[1] Considerable attention has been focused on the $TiCl_4$ systems because of their ability to prepare triblock copolymers.[1−8] New Lewis acid co-initiators for living isobutylene polymerization are desired in order to expand the range of synthetic possibilities. The first examples of living isobutylene polymerization by Et_2AlCl (diethylaluminum chloride) have been recently disclosed.[9,10] The system introduced by Cheradame et al.[10] hinges on the use of tertiary azide initiators. The azide group participates in reversible termination of propagating chains, a key step in living carbocationic polymerization systems. Additives are not required to achieve living polymerization kinetics in this system. In addition, polyisobutylene is prepared with tertiary alkyl azide chain ends. Initiation from adventitious moisture does not present difficulties in this system due to the unique nature of Et_2AlCl.[11] Living character was observed to M_n values less than 50 kDa but showed slight deviation from linearity beyond 50 kDa. For triblock copolymers with optimal thermoplastic elastomer properties, the polyisobutylene midsegment should have a M_n above 50 kDa.[9] On this basis, this co-initiator/initiator pair is not adequate for triblock preparation.

Another polymerization system based on Et_2AlCl and tertiary alkyl halide initiators has been reported but requires the use of an 80/20 v/v nonpolar/polar solvent mixture.[9] However, styrene−isobutylene triblock copolymers have limited solubility in this solvent mixture.

This paper presents the first aluminum catalyst system capable of preparing living polyisobutylene suitable for triblock copolymer synthesis. The successful Me_2AlCl (dimethylaluminum chloride) catalyst system uses conventional tertiary alkyl chlorides as initiators and solvent systems in which styrene−isobutylene triblocks can be prepared. Results for the comparable Et_2AlCl system are briefly presented as background for our selection of Me_2AlCl as a suitable Lewis acid.

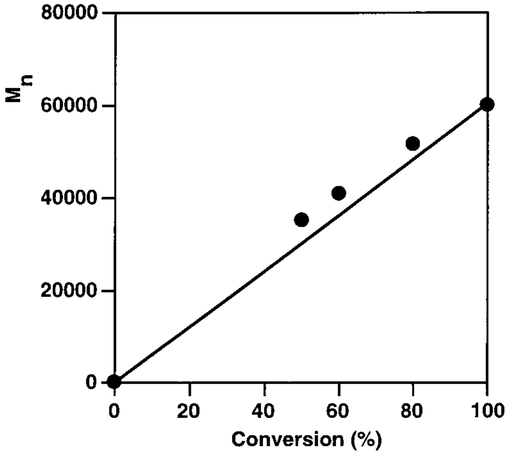

Figure 1. Plot of M_n versus conversion for Et_2AlCl-mediated isobutylene polymerization in 80/20 methylcyclohexane/methylene chloride at −75 °C; [isobutylene] = 1.9 mol/L, [5-*tert*-butyl-1,3-bis(1-chloro-1-methylethyl)benzene] = 1.8×10^{-3} mol/L, [Et_2AlCl] = 3.0×10^{-2} mol/L, [2,6-di-*tert*-butylpyridine] = 2.9×10^{-2} mol/L (solid line is theoretical).

Results and Discussion

We have shown that narrow M_w/M_n polyisobutylene can be prepared with Et_2AlCl at −75 °C in a 80/20 (v/v) methylcyclohexane/methylene chloride solvent system.[9] The use of the more common 60/40 nonpolar/polar solvent mixtures leads to broader M_w/M_n values (≥ 2.0). The need to use a more nonpolar solvent mixture is somewhat surprising, considering that Et_2AlCl is usually considered a weaker Lewis acid than $TiCl_4$.[10] In Figures 1 and 2, previously unpublished M_n vs percent conversion and P_n/I_n[12] vs percent conversion plots are shown for this Et_2AlCl system. The data in each figure loosely follow a living trend through at least 60 kDa, with $M_w/M_n < 1.5$. However, these polymerizations are not living and suffer from side reactions that are particularly noticeable at high conversion. The consequence of these side reactions is quickly discovered through incremental monomer addition experiments. Addition of a second monomer charge, after reaching complete conversion of the first, leads to broadening of the M_w/M_n and the appearance of bimodal GPC traces (not shown) in the final polymer. In Figure 3, this trend

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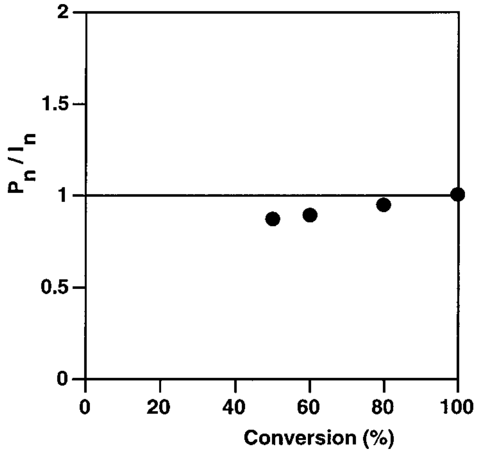

Figure 2. Plot of P_n/I_n (ratio of the number of polymer chains to initiator molecules) versus conversion for Et_2AlCl-mediated isobutylene polymerization in 80/20 methylcyclohexane/methylene chloride at −75 °C; [isobutylene] = 1.9 mol/L, [5-*tert*-butyl-1,3-bis(1-chloro-1-methylethyl)benzene] = 1.8 × 10^{-3} mol/L, [Et_2AlCl] = 3.0 × 10^{-2} mol/L, [2,6-di-*tert*-butylpyridine] = 2.9 × 10^{-2} mol/L (solid line is theoretical).

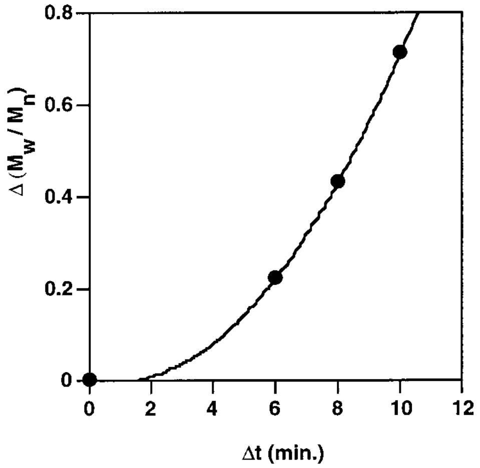

Figure 3. Plot of the change in M_w/M_n versus delay time between complete consumption of the first monomer charge and addition of the second in 80/20 methylcyclohexane/methylene chloride; [isobutylene] = 1.9 mol/L, [5-*tert*-butyl-1,3-bis(1-chloro-1-methylethyl)benzene] = 1.8 × 10^{-3} mol/L, [Et_2AlCl] = 3.0 × 10^{-2} mol/L; [2,6-di-*tert*-butylpyridine] = 2.9 × 10^{-2} mol/L, $T = -75$ °C. M_n before second monomer addition = 60 kDa, M_w/M_n = 1.5 (solid line is trend line).

is shown by plotting the change in M_w/M_n of the polymer before (M_n = 60 kDa; M_w/M_n = 1.5) and after complete consumption of an incremental monomer addition versus the delay time between 100% conversion of the first charge and addition of the second charge.

The broadening and bimodality of the molecular weight distribution indicates the presence of terminated chains that are incapable of reinitiation. Irreversible termination of the polymer chains may result from terminative proton trapping (due to the presence of 2,6-di-*tert*-butylpyridine) or several possible reactions with the counterion including alkylation, hydridation, or elimination. Kennedy identified alkylation and hydridation as main termination pathways with Et_2AlCl in conventional systems.[13] The nature of the termination process(es) active in this Et_2AlCl system was not studied further, as termination precludes the system's utility in triblock copolymer preparation.

Me_2AlCl is a poorer alkylating agent than Et_2AlCl and cannot participate in hydridation because it lacks β-hydrogens.[14] As with Et_2AlCl, adventitious moisture is a poor initiator with Me_2AlCl and other dialkylaluminum chlorides.[13,15] Both of these traits make Me_2AlCl an attractive alternative as an aluminum-based Lewis acid for living isobutylene polymerizations. Me_2AlCl catalyzed polymerizations were run in a 60/40 (v/v) hexane/methylene chloride solvent system at −80 °C. To test for initiation for adventitious moisture, solutions of isobutylene and the solvents were treated with Me_2AlCl. These solutions could be stored for hours without forming polymer. This result suggests that initiation from adventitious moisture is absent. Aging the monomer and solvents with Me_2AlCl before addition of the initiator leads to narrower M_w/M_n polymers (see Experimental Section). However, for the work reported here, Me_2AlCl is added last.

The results of all-monomer-in experiments at three different Me_2AlCl concentrations are shown in Figures 4 and 5. The relationship between M_n and percent conversion is linear for at least the two lowest Me_2AlCl concentrations. The molecular weight distribution quickly drops to around 1.3, where it stays for the remainder of the polymerization. The P_n/I_n ratio closely follows the theoretical prediction at high conversion. At low conversion, the P_n/I_n values are slightly greater than one. We ascribe this inconsistency to the inaccurate determination of the low-M_n polymer because of the broader M_w/M_n and the method of GPC calibration. The trend in M_w/M_n follows the trend observed in $TiCl_4$ living systems.[16−18] A reinitiation or incremental monomer addition experiment was carried out to test the "livingness" of the system. In Figure 6, the broadening in M_w/M_n is plotted as a function of delay time between 100% conversion of the initial monomer charge and the incremental monomer addition. The target M_n is 150 kDa with the first charge reaching 100 kDa. All polymers in this test reached both M_n targets. The final polydispersity values did not vary with increasing delays between complete consumption of the first monomer charge and addition of the second. This result shows that the polymer chain ends are still active for at least 15 min after the initial monomer charge is consumed.

The final test for living polymerization is the shape of the first-order rate plot. First-order plots were constructed for polymerizations initiated with 2-chloro-2,4,4-trimethylpentane and three different concentrations of Me_2AlCl. As expected, increasing the Me_2AlCl concentration increases the rate of polymerization. The first-order rate plots shown in Figure 7 are linear. Polymerizations at the highest Me_2AlCl concentration reach 100% conversion in less than 15 min to provide a polymer with M_n = 80 kDa. From the slopes of the first-order plots, k_{app} values are obtained. A plot of the apparent rate constants, k_{app}, versus ln[Me_2AlCl], shown in Figure 8, gives a slope nearly equal to 2, suggesting a second-order dependence on Me_2AlCl. This finding is consistent with the known structure of most alkyl aluminums.[14]

Since initiation from adventitious moisture is minimal in this system, we investigated the role of an added electron donor, dimethyl phthalate.[19] For these experiments, we used methyl chloride as the polar solvent and 5-*tert*-butyl-1,3-bis(1-chloro-1-methylethyl)benzene as the initiator to better match the conditions desired for triblock copolymer preparation. Polymerizations with

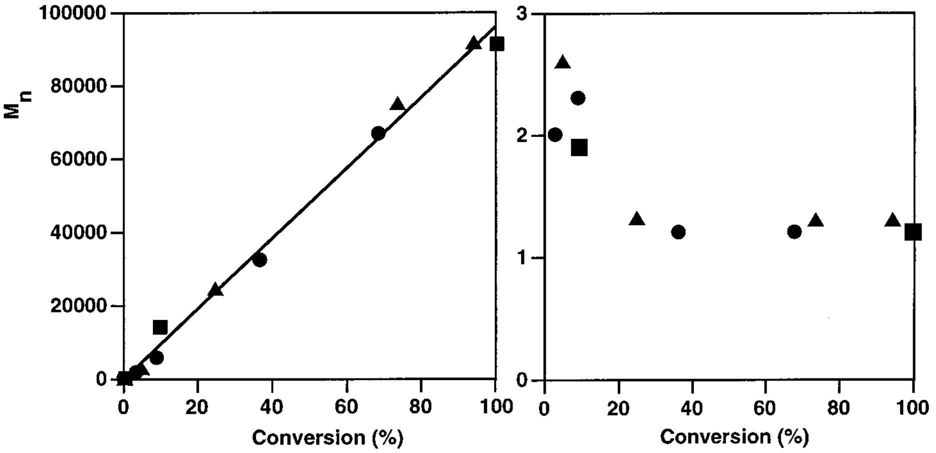

Figure 4. Plots of M_n versus percent conversion and M_w/M_n versus percent conversion for Me_2AlCl-mediated isobutylene polymerization in 60/40 hexane/methylene chloride at −80 °C; [isobutylene] = 2.9 mol/L, [2-chloro-2,4,4-trimethylpentane] = 1.8×10^{-3} mol/L. ●, [Me_2AlCl] = 1.3×10^{-2} mol/L; ▲, 2.6×10^{-2} mol/L; ■, 3.9×10^{-2} mol/L (solid line is theoretical).

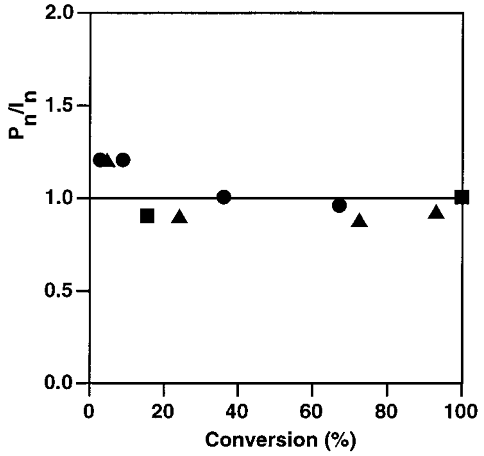

Figure 5. Plot of P_n/I_n versus conversion for Me_2AlCl-mediated isobutylene polymerization as in Figure 4 (solid line is theoretical).

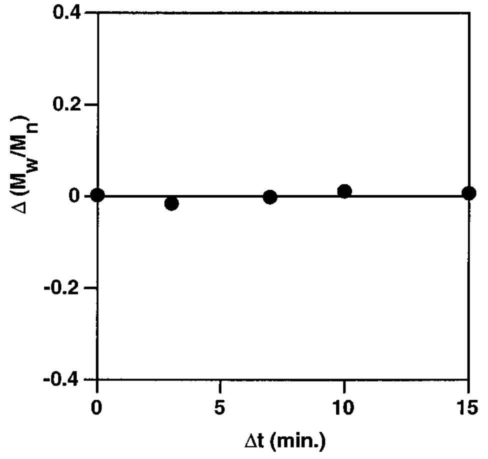

Figure 6. Plot of the change in M_w/M_n versus delay time between complete consumption of the first monomer charge and addition of the second in 60/40 hexane/methylene chloride at −80 °C; [isobutylene] = 1.6 mol/L, [5-*tert*-butyl-1,3-bis(1-chloro-1-methylethyl)benzene] = 9.0×10^{-4} mol/L, [Me_2AlCl] = 7.0×10^{-3} mol/L, $T = -80$ °C. M_n before second monomer addition = 100 kDa, $M_w/M_n = 1.2$ (solid line is trend line).

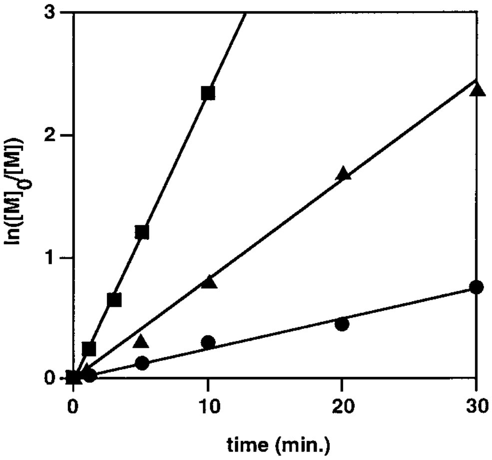

Figure 7. Plot of $\ln([M]_0/[M])$ versus time in the polymerization of isobutylene in 60/40 hexane/methylene chloride at −80 °C; [isobutylene] = 2.9 mol/L, [2-chloro-2,4,4-trimethylpentane] = 1.8×10^{-3} mol/L. ●, [Me_2AlCl] = 1.3×10^{-2} mol/L; ▲, 2.6×10^{-2} mol/L; ■, 3.9×10^{-2} mol/L.

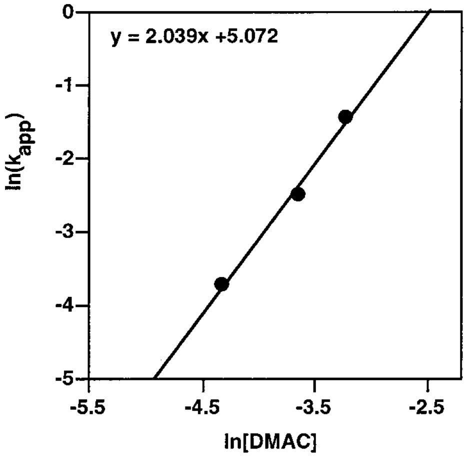

Figure 8. Reaction order of [$MeAlCl_2$] for polymerization of isobutylene in 60/40 v/v hexane/methylene chloride at −80 °C; [isobutylene] = 2.9 mol/L, [2-chloro-2,4,4-trimethylpentane] = 1.8×10^{-3} mol/L.

dimethyl phthalate are slower than in its absence. The polymerizations, however, remain living. Figures 9 and 10 plot M_n and P_n/I_n versus conversion for two different Me_2AlCl concentrations in the presence of dimethyl phthalate. Both plots follow the expected trends for living systems. M_w/M_n values are as low as 1.2 for the high molecular weight polymers. The first-order rate plots, shown in Figure 11, are linear for the two

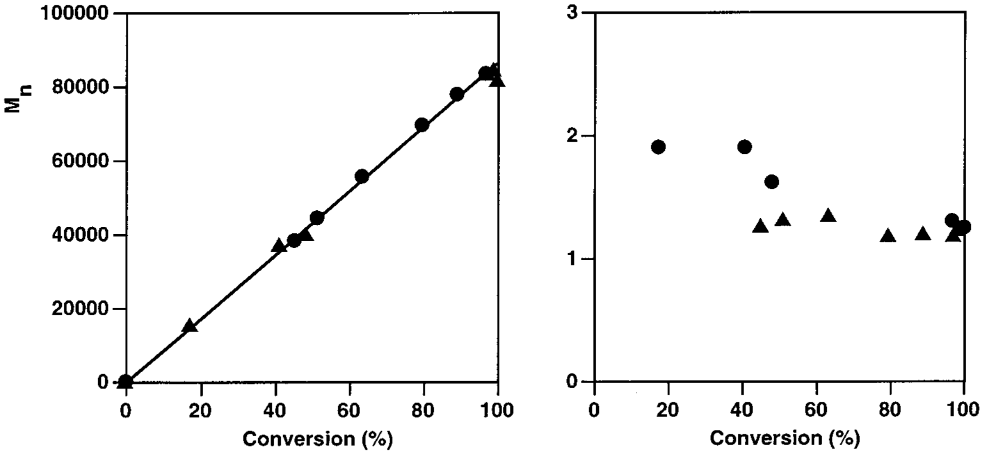

Figure 9. Plot of M_n vs percent conversion and plot of M_w/M_n versus percent conversion for Me_2AlCl-mediated isobutylene polymerization in 60/40 hexane/methyl chloride at −80 °C in the presence of dimethyl phthalate; [isobutylene] = 1.65 mol/L; [5-*tert*-butyl-1,3-bis(1-chloro-1-methylethyl)benzene] = 1.1×10^{-3} mol/L; [dimethyl phthalate] = 10^{-5} mol/L. ●, [Me_2AlCl] = 1.3×10^{-2} mol/L; ▲, [Me_2AlCl] = 2.5×10^{-2} mol/L (solid line is theoretical).

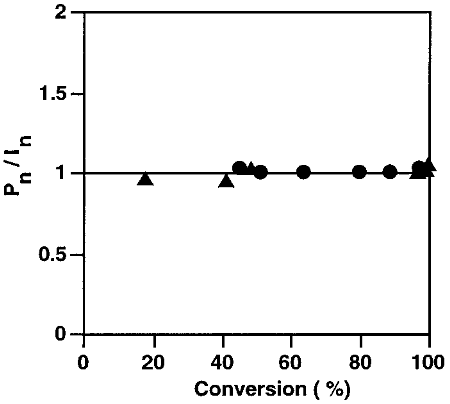

Figure 10. Plot of P_n/I_n versus conversion for Me_2AlCl-mediated isobutylene polymerization as in Figure 9 (solid line is theoretical).

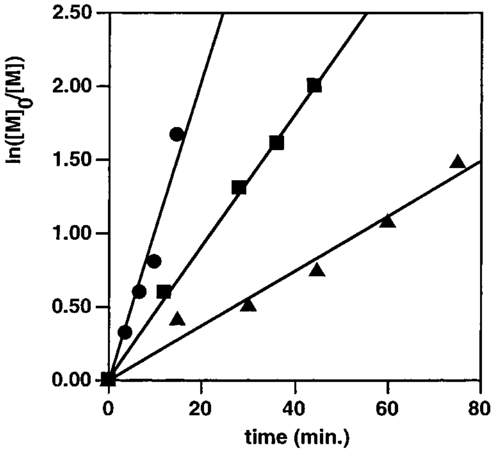

Figure 11. Plot of ln([M]$_0$/[M]) versus time in the polymerization of isobutylene in the presence and absence of dimethyl phthalate in 60/40 hexane/methyl chloride at −80 °C. ●, [dimethyl phthalate] = 0; ■, 2×10^{-5} mol/L; ▲, 1×10^{-4} mol/L. Other polymerization conditions: [isobutylene] = 1.74 mol/L; [5-*tert*-butyl-1,3-bis(1-chloro-1-methylethyl)benzene] = 1.2×10^{-3} mol/L; [Me_2AlCl] = 0.0375 mol/L.

concentrations of dimethyl phthalate used here. Comparison to a run under identical conditions, but without dimethyl phthalate, is also included. The retardation of the apparent polymerization rate is clear from these plots. The magnitude of the rate depression is quite surprising, considering the amount of dimethyl phthalate added to the system. Rate depressions have been observed in other living isobutylene polymerization systems that use electron donors.[2,20−28] Several hypotheses have been forwarded to explain the rate depressions observed in these systems.[2,20−28] A likely reason for the observed rate depression is a decrease in the effective concentration of Me_2AlCl. A similar explanation is used for observed rate depressions in $TiCl_4$-based living isobutylene polymerizations carried out in the presence of Lewis bases.[28]

In conclusion, we have presented a new aluminum-based system for the preparation of living polyisobutylene. The Me_2AlCl system does not require additives to avoid initiation from adventitious moisture or to achieve living kinetics. The addition of dimethyl phthalate to this system slows the polymerization but does not seem to influence the "livingness" of the polymer. This system is an excellent candidate for triblock preparation because it achieves a polyisobutylene molecular weight of at least 100K and remains living for at least 15 min after complete consumption of the monomer. The use of a 60/40 v/v nonpolar/polar solvent mixture is an added bonus since it is compatible with triblock preparation.

Experimental Section

Materials. Isobutylene (Matheson, 99.9+%) was dried by passing the gas through two stainless steel columns containing barium oxide (Aldrich, 97%, 2 kg total) and collecting the condensed liquid inside the drybox. Methyl chloride (Air Products, 99.5%) was purified by double distillation through two stainless steel columns containing barium oxide (approximately 2 kg). Between the distillations, the condensed liquid was stored over triethylaluminum (Aldrich, 93%, approximately 10 mL per 3 L of methyl chloride). Hexane (house supply, 99+%) was purified and dried using sodium benzophenone ketal as drying agent. Distilled hexane was stored over 4 Å molecular sieves and filtered before use. Methylene chloride (Aldrich, 99.9%) was purified and dried from calcium hydride (Aldrich, 95%) and stored over 4 Å molecular sieves. Both solvents are filtered before use. 5-*tert*-Butyl-1,3-bis(1-chloro-1-methylethyl)benzene and 2-chloro-2,4,4-trimethylpentane were prepared according to literature procedures.[5,21] Dimethyl phthalate (99+%), diethylaluminum chloride (97%), 2,6-di-*tert*-butylpyridine (97%) (all from Aldrich), and dimethylaluminum chloride (Albemarle, 98%) were used as received.

Characterization. Molecular weights were measured using a Waters 150C using both RI and UV detection with THF as eluent at 45 °C. Flow rate was 1 mL/min through five Polymer Laboratories columns of 10^6, 10^5, 10^4, 10^3, and 500 Å pore size. Determination of the molecular weights and the polydispersities were made using a universal calibration constructed from polystyrene standards (Polysciences) and Mark−Houwink constants ($K = 0.0368$, $\alpha = 0.601$) for polyisobutylene. The curve was checked against narrow molecular weight ($M_w/M_n \leq 1.1$) polyisobutylene standards prepared in house and characterized by light scattering.

Polymerizations. All polymerizations were carried out in a drybox that nominally contains between 1 and 4 ppm water. Polymerizations were assembled and run in either 75 mL test tubes or 150 mL resin kettles at −80 °C, cooling provided by an internally contained pentane bath. Total reaction volumes of test tube experiments were 25 and 50 mL for resin kettle experiments. The experiments were assembled as follows: solvents, isobutylene, 2,6-di-*tert*-butylpyridine or dimethyl phthalate if used, initiator, and finally the Lewis acid. The Lewis acid was added as a cooled 2.5 mol/L solution in hexane. Control experiments were carried out in the absence of initiator and additive to confirm the absence of uncontrolled initiation. These solutions could be stored for hours with no formation of polymer. However, assembling the experiments by reversing the addition order of the last two components and aging the solution 5 min before addition of the initiator does result in a product with a narrower M_w/M_n. Polymerizations were quenched by methanol addition. Conversions were measured gravimetrically. An example polymerization follows. A solution of 24 mL of hexane, 15 mL of condensed anhydrous methyl chloride, and 6 mL (0.076 mol) of condensed isobutylene was prepared at −80 °C. At this temperature, 0.016 g (5.6×10^{-5} mol) of 5-*tert*-butyl-1,3-bis(1-chloro-1-methylethyl)benzene, dissolved into 1 mL of hexane, was added. This solution was stirred for 5 min to equilibrate. The polymerization was initiated by adding a cooled solution of 0.168 mL (0.0018 mol) of neat Me_2AlCl dissolved into 1.0 mL of anhydrous hexane. The polymerization was continued for 20 min before it was quenched with the addition of a few milliliters of chilled methanol. Weathering off the methyl chloride and precipitating the polymer into methanol isolated the polymer. The polymer was dried at 45 °C under vacuum overnight. The polymer was collected in 100% yield. The polymer was characterized by GPC ($M_n = 76\,000$; $M_w/M_n = 1.2$).

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