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Highly Branched Polypropylene via Li^+-Catalyzed Radical Polymerization

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S *Supporting Information*

While radical polymerization techniques are well suited for polar monomers, they are not used to polymerize simple α-olefins as the allylic hydrogens on the latter are subject to chain transfer in the presence of a reactive propagating radical.[1] Thus, with the exception of ethylene produced commercially at very high pressures and temperatures (and a few reports of propylene under similar intense conditions[2,3]), only short oligomers of simple alkenes such as propylene or 1-hexene can be obtained using conventional radical polymerization techniques. Against this backdrop, our group recently reported that a variety of simple alkenes could, in fact, be polymerized under radical conditions at ambient temperatures and pressures in the presence of a lithium cation in the form of $LiCB_{11}(CH_3)_{12}$.[4] By all indications, including the use of radical and ionic traps, the polymerization proceeds as a radical process. We believe that Li^+ coordination to the alkene in weakly ligating organic media alters the relative rates of propagation and degradative chain transfer in favor of propagation (Scheme 1).

Following these initial reports, we began investigating this system more fully with isobutylene, whose six allylic hydrogens render it a most unlikely candidate for radical polymerization.[5] This system proved quite unique, as it appears that both a radical process and a cationic one can be induced simultaneously. Under nonoxidative conditions, the radical process produced a polyisobutylene (*b*-PIB) with a highly branched architecture, unlike anything previously reported or prepared commercially. Under oxidative conditions, the radical process still occurred and produced *b*-PIB, while a concurrent cationic one generated perfectly linear *l*-PIB that differed from ordinary PIB only in that a carborate anion was covalently attached at the chain end.[6] Under these conditions, $LiCB_{11}(CH_3)_{12}$ acted not only as a catalyst but also as a reagent and could not be recovered from the reaction mixture quantitatively or at all. A concurrent study of $LiCB_{11}(CH_3)_{12}$-catalyzed radical polymerization of 1-hexene and 1-octene has so far only revealed the formation of low molecular weight oligomers.[7] The contrast to the polymerization of propene described below is striking, and other reaction conditions are still being examined.

Here, we report on our investigation of the nature and architecture of polypropylene (PP) that is generated under nonoxidizing conditions in the weakly ligating solvent 1,2-dichloroethane (DCE), using azo-*tert*-butane (ATB) initiator. Figure 1 illustrates the ^{13}C NMR spectrum of a sample of *b*-PP generated at moderate pressures (15 atm) and temperatures (80 °C) in DCE solvent with ATB initiation under $LiCB_{11}(CH_3)_{12}$ catalysis (for precise experimental conditions see Supporting Information). Polymer yield in this reaction was around 40%. The *b*-PP formed is very highly branched, as can be seen by the plethora of resonances observed in the spectrum between 10 and 45 ppm, which is unlike that of any commercially available PP prepared by coordination polymerization. It also contains a fair percentage of olefinic units, as can be seen from the resonances around 130 ppm in the ^{13}C NMR spectrum and 5.5 ppm in the ^1H NMR spectrum (Supporting Information). The olefinic

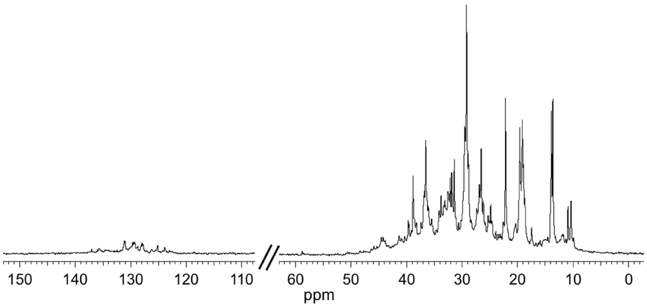
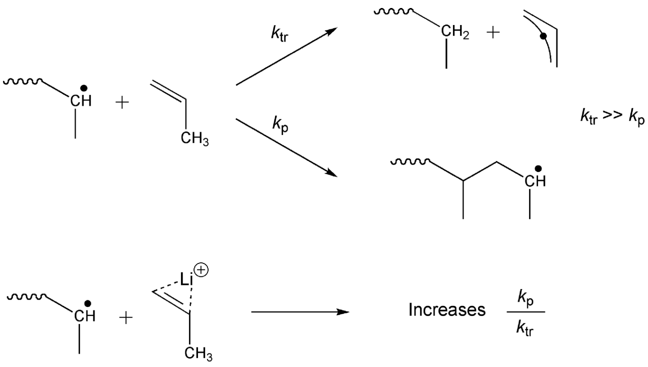


Figure 1. ^{13}C NMR of *b*-PP sample mediated by $LiCB_{11}(CH_3)_{12}$ in DCE at 80 °C, initiated with ATB. Recorded at room temperature in 1,1,2,2-tetrachloroethane-d_2.

Scheme 1



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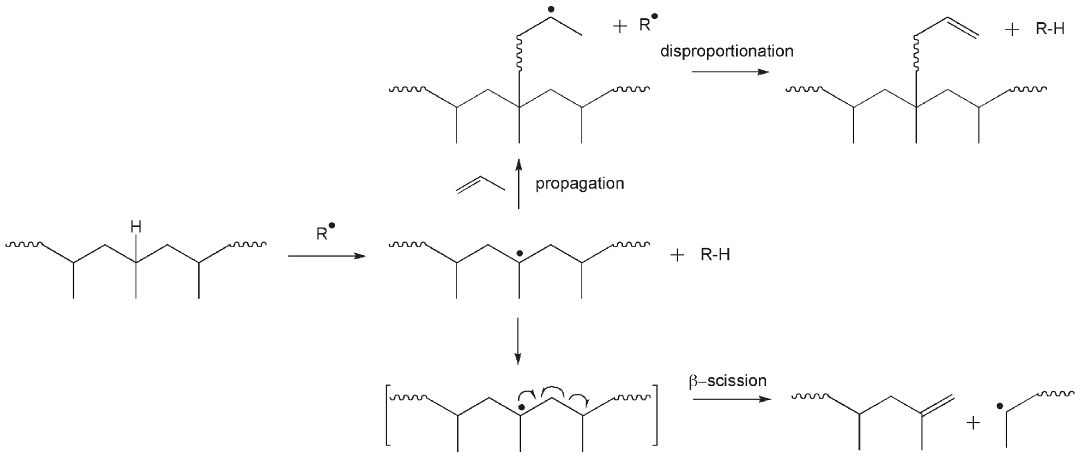
Scheme 2



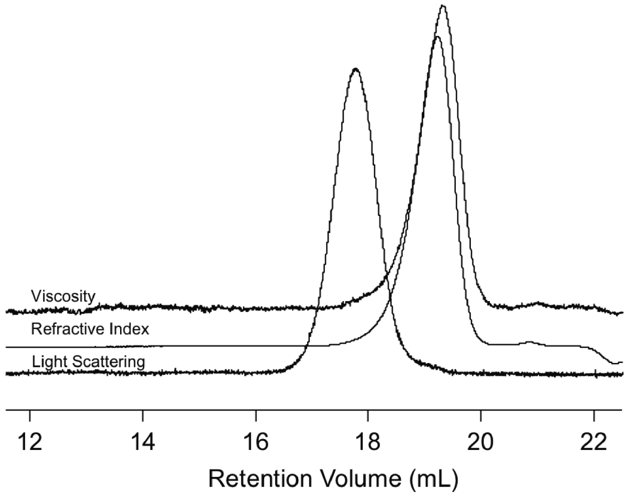


Figure 2. Typical triple detector GPC traces in THF at room temperature for *b*-PP samples with M_n = ~5 kg/mol and M_w = ~30 kg/mol, prepared with $LiCB_{11}(CH_3)_{12}$ catalysis.

protons account for less than 2% of the total protons in the polymer, as determined by ^{1}H NMR integration.

The *b*-PP sample analyzed in Figure 1 was a viscous oil at room temperature. (For every 1 g of this oil, about 20 mg of a white waxy solid completely insoluble in any organic medium was also generated in the polymerization under these conditions; vide infra.) The oil had a glass transition temperature of approximately −22 °C, a value consistent with samples of commercially available atactic PP.[8] Curiously, it also displayed a second thermal transition around 11 °C (Supporting Information), which might be attributable to the different environments of the side vs main polymer chain. By comparison, it has been reported that radical-induced polypropylene generated at 7000 atm was partially in the isotactic configuration,[9] although a more systematic study of our *b*-PP sample would be necessary before anything definite could be said about its tacticity.

The polymer was washed with MeOH to remove the $LiCB_{11}(CH_3)_{12}$ catalyst, which appeared intact by NMR and could subsequently be reused without loss of activity. To the naked eye, the polymer appears to be miscible with THF. Standard GPC analysis was first conducted in this solvent, measured against linear polystyrene standards and employing a refractive index detector. This instrumental setup suggested the material had a number-average molecular weight (M_n) of only ~1 kg/mol. However, because size exclusion chromatography measures hydrodynamic volume, the molecular weights of branched materials are underestimated using this setup. The advantages of measuring polymer weight-average molecular weight (M_w) using a light scattering detector against intrinsic viscosity $[\eta]$ of the polymer with GPC equipment utilizing a triple detection system (index of refraction, viscosimetry, and light scattering) has been well documented for dendrimers and polymers with highly compact structures.[10] Using the latter setup, the molecular weight of this *b*-PP sample was more accurately determined as M_n ~ 5 kg/mol and M_w ~ 30 kg/mol (Figure 2 illustrates a typical GPC trace). However, molecular weights were found to vary widely from sample to sample, from M_n = ~5 to over 40 kg/mol, depending on how the polymers were worked up and stored. We will address this phenomenon, together with the broad molecular weight distribution, after some mechanistic discussion below.

Analysis of the intrinsic viscosity $[\eta]$ of the polymer with its molecular weight M through the Mark−Houwink equation, $[\eta] = KM^a$, allowed the evaluation of the a parameter as ~0.2 in THF at room temperature (where an a value of 0.0 indicates that the polymer is a perfect sphere, a value between 0.65 and 0.75 is typical for a linear random coil in a good solvent, and values greater than 1.0 are characteristic of linear rigid polymers). While a value of ~0.2 is consistent with values observed for many hyperbranched polymers,[11] it will also dramatically depend on the solvation in a particular solvent, and the polymer could potentially uncoil more at higher temperatures.

The olefinic resonances observed in the carbon and proton NMR spectra of these *b*-PP samples are unusually intense, and ^{1}H NMR and GPC analysis for a typical sample suggest there are approximately six olefinic units in *b*-PP with a degree of polymerization of 120. Their presence is likely attributable to processes initiated by abstraction of a methine hydrogen from the polymer chain by the initiating radical or a propagating chain. Each such abstraction produces a potential chain growth center, which may generate an unsaturated chain end by disproportionation. Each such center also provides an opportunity for β-scission of the polymer chain.[12] Scheme 2 shows both processes.

$R^\bullet$ represents a free radical from either an initiator or a propagating chain, and abstraction of a hydrogen atom from the polypropylene backbone results in the generation of a midchain radical. Such hydrogen atom abstraction has been well studied and widely utilized to introduce grafts and other functionalities onto polyolefin backbones.[13] β-Scission is a well-documented side reaction in the grafting process, and PP is known to be particularly susceptible to it. While β-scission generally leads to polymers with lower molecular weights, it should be noted that this process is not always considered a side reaction, as it has been utilized as an integral step in the synthesis of some PP block copolymers.[14]

In the case of our $LiCB_{11}(CH_3)_{12}$-catalyzed propylene polymerizations, β-scission may not be a side reaction either, but rather a route to generating PP macromonomers that could be reincorporated into another growing chain to generate higher molecular weight branched materials. While these olefin-terminated macromonomers contain allylic hydrogens and therefore could not be polymerized under normal free radical conditions, $LiCB_{11}(CH_3)_{12}$ is known to be quite capable of mediating the radical polymerization of isobutylene to a highly branched *b*-PIB polymer.[5,6] A further quite unexpected observation, which helps to validate this hypothesis, was made when PP samples were not immediately purified of the $LiCB_{11}(CH_3)_{12}$ catalyst. After the 80 °C polymerization reaction is conducted for 48 h and the solvent has been completely removed under reduced pressure, if the PP oil is not washed of catalyst but left to sit in a closed vial for several days at ambient temperature, it forms a waxy solid that cannot be dissolved and passed through a 0.2 μm filter. The resulting polymer is not even soluble in hot 1,2,4-trichlorobenzene, a solvent commonly used to analyze linear polypropylene samples. It appears that the polymer spontaneously cross-links.

This observation is reminiscent of those reported for lithium salts of the anions $CH_2{=}CH{-}(CH_2)_n{-}CB_{11}(CH_3)_{11}^-$. After a day on the benchtop, these microcrystalline powders spontaneously turn into an oligomeric gummy material whose NMR no longer shows any vinylic protons.[15] This transformation does not occur in the absence of air, and it was ultimately proposed that oxygen acts as a radical initiator,[16] likely by oxidizing the carborate anion to a radical, which in turn initiates polymerization. Our group has since used oxygen to initiate other alkene radical polymerizations in the presence of $LiCB_{11}(CH_3)_{12}$ under ambient conditions.[4,6] Because of the relatively high concentration of unsaturation remaining in the prepared polymer and the ability of $LiCB_{11}(CH_3)_{12}$ to polymerize these olefins, polymer molecular weights are difficult to reproduce. GPC traces are quite broad, and when polymers are not immediately purified of catalyst, they can even become multimodal.

When prepared as initially reported,[17] $LiCB_{11}(CH_3)_{12}$ contains a small amount of sulfolane solvent (between 2 and 10 mol %). The importance of this "additive" was not fully realized until polymerization results could not be reproduced with highly purified $LiCB_{11}(CH_3)_{12}$.[5] It has been proposed to serve the function of breaking up $LiCB_{11}(CH_3)_{12}$ aggregates.[6] A preparation of sulfolane-free $LiCB_{11}(CH_3)_{12}$ has since been published.[18] In all cases, the production of *b*-PP described in this work was performed with $LiCB_{11}(CH_3)_{12}$ whose sulfolane content was adjusted to ~15 mol %.

We then reexamined whether cheap commercially available Li^+ salts, which had previously been found inactive as catalysts, could be made active with the sulfolane additive. However, no conditions were found for which homopolymers of propylene, butylene, or isobutylene could be generated. Radical initiators ATB, azoisobutyronitrile (AIBN), or di-*tert*-butyl peroxide (DTBP) were used with $LiPF_6$, $LiBPh_4$, Li acetate, Li hexanoate, or Li stearate in benzene, toluene, cyclohexane, or in neat bulk monomer. A variety of temperatures (room temperature to 130 °C), pressures (ambient to 20 atm), and concentrations of sulfolane additive (0.1−2.0 mol equiv) were also tested, but the only successful polymerizations were those conducted in the presence of $LiCB_{11}(CH_3)_{12}$.

However, over the course of this investigation, we discovered that in DCE, at temperatures above 130 °C in a pressurized vessel, very highly branched polymers were generated from propylene, butylene, or isobutylene, even in the absence of any lithium salt. Analysis of the complex NMR spectra (Supporting Information) revealed that the polymer produced in this fashion from propylene was not the same as the *b*-PP obtained using $LiCB_{11}(CH_3)_{12}$ at 80 °C, in that numerous alkyl chloride and olefinic moieties were present in the backbone.

It is widely known that free radicals, in addition to strong Lewis or Bronstead acids or bases, can catalyze the decomposition of DCE into vinyl chloride monomer (VCM) via HCl elimination through a radical or ionic mechanism.[19] VCM is readily polymerizable under radical conditions.[20] While temperatures in excess of 300 °C are typically employed to efficiently convert DCE into VCM for industrial use,[21] it appears that DCE decomposition is sufficiently promoted under our reaction conditions even at 130 °C to generate enough of the monomer to polymerize or copolymerize.

To verify this, we ran a series of experiments to determine whether or not we were incorporating *in situ* generated VCM into our $LiCB_{11}(CH_3)_{12}$-mediated propylene polymerizations described above. In the first control experiment, 0.9 g of DTBP initiator was added to 9 mL of deoxygenated DCE solvent. When the solution was sealed and heated at 130 °C for 48 h, PVC was produced in low but significant yields (500 mg of polymer, NMR in Supporting Information). However, at 80 °C, in the presence of free radicals generated from AIBN or DTBP in the presence of Li hexanoate or $LiCB_{11}(CH_3)_{12}$, decomposition of DCE into VCM is not significant enough to induce any detectable PVC formation.

While simple terminal alkenes cannot be homopolymerized via a radical mechanism in the absence of $LiCB_{11}(CH_3)_{12}$, they have often been reported to copolymerize under certain conditions with a polar monomer to give polymers with molecular weights of several kg/mol, owing to fast rates of cross-propagation relative to chain transfer.[22,23] We find that a PP−PVC copolymer can be produced at 130 °C (with DTBP initiator and no Li^+ catalyst) as a highly branched material (Supporting Information). PVC is generally not stable at high temperatures over prolonged time periods, as it begins to dehydrochlorinate and leave unsaturation in the polymer.[1] However, alkyl chloride resonances are clearly observed in the ^{1}H NMR at ~3.5−4 ppm (these resonances are distinctly absent in the spectra of the *b*-PP samples described earlier), and proton resonance integration suggests that there is only one double bond for every eight alkyl chloride moieties. This suggests that the copolymer is reasonably stable under these conditions. It is generated in ~40% yield, is comprised of ~55% propylene, and is a tacky yellow amorphous material at room temperature, with values of M_n = ~2 kg/mol and M_w = ~3 kg/mol, as determined using the GPC setup in THF described earlier. The Mark−Houwink *a* parameter is ~0.2, consistent with the branched structure apparent from the NMR spectrum. Virtually identical results were obtained with microwave heating at 100 °C, although accurately measuring the temperature in such an apparatus (even with a fiber-optic probe) is not necessarily straightforward.[24]

In summary, it has been demonstrated that $LiCB_{11}(CH_3)_{12}$ catalysis permits the synthesis of high molecular weight homopolymers of PP at moderate temperatures and pressures in DCE. The resulting *b*-PP material has a highly branched architecture unlike any commercially available PP and contains a significant fraction of olefinic units. This renders it susceptible to cross-linking in the presence of $LiCB_{11}(CH_3)_{12}$ and air. Its detailed structure and properties appear to be a sensitive function of reaction conditions.

■ ASSOCIATED CONTENT

S Supporting Information. Detailed experimental procedures and ^1H and ^{13}C NMR spectra of all polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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