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One-pot Synthesis of Long Chain Branch PP (LCBPP) Using Ziegler-Natta Catalyst and Branching Reagents

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Summary: A new class of long chain branched isotactic polypropylene (LCBPP) polymers with high molecular weights and well-controlled structures are prepared via a combination of *rac*-$Me_2Si(2\text{-}Me\text{-}4\text{-}Ph\text{-}Ind)ZrCl_2$/MAO catalyst and a T-reagent, such as p-(3-butenyl)styrene. The T-reagent can simultaneously serve two functions (comonomer and chain transfer agent) during metallocene-mediated propylene polymerization in the presence of a small amount of hydrogen. ^1H NMR and SEC equipped with triple detectors revealed most of polymer chain containing LCB structure. LCBPPs displayed a systematic increase in zero-shear viscosity and Arrhenius flow activation energy as branch density increased. LCBPPs with high branch point density displayed thermorheologically complex behavior, and strain hardening was observed in extensional flow.

Keywords: LCB; polypropylene; T-reagent; Ziegler-Natta catalyst

Introduction

Long chain branched (LCB) polymers have value in processing techniques which demand high melt strength, including thermoforming, film blowing, extrusion coating, and blow molding processes.[1] Within the polyolefin family, polyethylenes have received much attention in respect to the many types of branching, while polypropylenes have gained much less attention due to the difficulties in preparing branched polypropylenes. Several post-polymerization processes have been developed, including reactive extrusion[2,3] and electron beam irradiation,[4–6] which prepare branched polymers with increased zero-shear viscosities, broadened relaxation spectra, and strain hardening behavior,[7–9] but the structures have only been partially characterized. This lack of structure characterization is in part due to the complicated nature of the materials.

Direct synthesis of long chain branched isotactic polypropylenes (LCBPP) has been limited. In situ formation of polypropylene macromonomers has been studied by the use of a single metallocene catalyst[10] and the use of tandem catalysis.[11] Additionally, previously prepared polypropylene macromonomers have been added to the polymerization of propylene with a metallocene catalyst.[12–14] These methods require careful selection of an isospecific catalyst which can successfully incorporate the polypropylene macromonomers while producing high molecular weight isotactic polypropylene. Some reports[15–18] showed the incorporation of diene units that creates the branch points with tetrafunctional structure. Polymers created by this process exhibited broadened molecular weight distributions to values of M_w/M_n greater than 5. It has also been shown these branched polymers display strain hardening behavior under elongational flows.[19] At higher concentrations of diene, the storage and loss modulus indicated the formation of a lightly crosslinked network.

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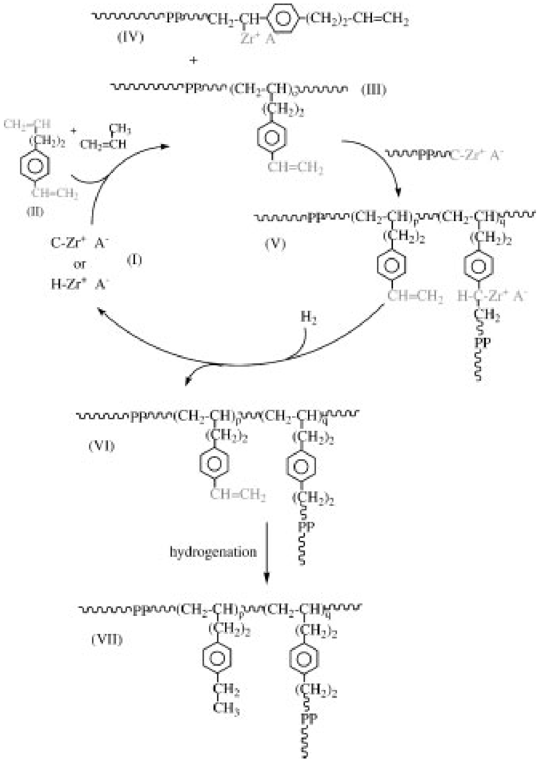
Previously, we prepared branched polypropylenes with relatively well-defined structure by a coupling reaction between chain-end functionalized polypropylene and polypropylene with graft functionality.[20] The method involves a multiple step post-polymerization process utilizing amine terminated polypropylenes and maleic anhydride graft copolymers of polypropylene. The molecular weight of branches and density of branches were varied. The grafted branch polymers showed a decrease in solution viscosity as compared to their linear counterparts at the same molecular weight. The ratio between branched and linear intrinsic viscosities at the same molecular weight systematically decreased with the increase of both branch density and branch length.

Synthesis of LCBPP Polymers

Recently, we have developed a new, ''one-pot'' method to synthesize LCBPP via the metallocene mediated polymerization of propylene with T-reagent.[21,22] This unique procedure allowed for the formation of trifunctional branch points with a relatively well-defined LCB structure. Scheme 1 illustrates the reaction mechanism of forming LCBPP polymers via metallocene-mediated propylene polymerization, using isospecific rac-$Me_2Si[2\text{-}Me\text{-}4\text{-}Ph(Ind)]_2ZrCl_2$/MAO catalyst, in the presence of T-reagent, p-(3-butenyl)styrene (BSt) that serves as both comonomer and chain transfer agent.[23–26] Copolymerization of the but-3-ene moiety of BSt via 1,2-insertion results in the formation of a copolymer (III) with pendant styrene functionality. On the other hand, incorporation of the styrene moiety of BSt via 2,1-insertion results in a dormant catalyst site (IV) due to steric hindrance from the bulky aromatic ring and confined catalyst site.[24] Hydrogen can relieve the dormant catalyst site via a subsequent chain-transfer reaction to produce a macromonomer with the α-olefin-like but-3-ene at the chain-end.



Scheme 1.

Table 1.
Comparison of linear and LCBPP polymers prepared by *rac*-$Me_2Si[2\text{-}Me\text{-}4\text{-}Ph(Ind)]Zr_2Cl_2/MAO$ mediated propylene polymerizations.

Sample	[BSt]	Cat. Act.[a)]	$M_n/M_{w,LS}$[b)]	F_{BSt}[c)]	Bran Den[d)]	$\eta_{0,190\,°C}$	Ea (kJ/mol)	T_m
	(mol/L)		($\times 10^3$ g/mol)	(mol%)		(Pa · s)		(°C)
PP	0.000	210	160/430	0.00	0.0	17,250	39	158
LCBPP1	0.007	225	94/249	0.07	1.0	3,200	48	157
LCBPP2	0.013	190	91/240	0.13	1.8	3,890	49	155
LCBPP3	0.020	100	94/247	0.15	2.2	5,700	50	153
LCBPP4	0.030	64	87/256	0.21	3.3	9,030	61	153

[a)] Catalyst activity: [kg of PP/(mmol of Zr · h)];
[b)] Measured by SEC with light scattering detector;
[c)] mol% of incorporated BSt;
[d)] ^{1}H NMR branch density: [branch points/10,000 carbon].

Theoretically, branches in LCBPP (VI) can be formed when a growing polymer chain either incorporates the but-3-ene chain-end of a macromonomer (IV) or chain transfers to the pendant styrene of a copolymer (III). As discussed later, the predominate route for the formation of branches involves the pendant styrene of the copolymer (III), which serves as the chain transfer agent to form the LCBPP (VI) in the presence of hydrogen. The branch point density was proportional to the concentration of T-reagent and the catalyst maintained high activity due to an effective chain transfer reaction to styrene and then hydrogen. To maintain the high temperature stability of LCBPP (VI), residual pendant styrene units were hydrogenated to form saturated LCBPP (VII) for melt rheology study.

Table 1 summarizes the results of several polymerization reactions using various amounts of T-reagent (BSt). Catalyst activities of LCBPP1 and LCBPP2 were comparable to the homopolymerization of propylene. With higher BSt concentrations in LCBPP3 and LCBPP4, the catalyst activity was proportionally reduced, which may be associated with the slow down in chain transfer reaction to T-reagent/H_2. The branch point density was proportional to the feed concentration of BSt and increased from LCBPP1 to LCBPP4. It is interesting to note that on average 43% of the incorporated T-reagent was associated with branch structure, independent of BSt concentration and reaction time. LCBPP4 was run twice as long as LCBPP3 but contained similar ratios between the amounts of pendant styrene and branch points observed. These results may imply that copolymerized T-reagent was immediately involved in a chain transfer reaction to form a branch point before the polymer precipitated from solution and the incorporated BSt units became inaccessible. Melting temperature, T_m, of LCBPP samples, examined by DSC, showed a gradual reduction of T_m with increase of branch density.

Structure Characterization of LCBPP Polymers

Figure 1 shows a typical ^{1}H NMR spectrum of LCBPP polymer, and peak assignments for the incorporated p-(3-butenyl)styrene "T" units. In addition to three major proton chemical shifts ($\delta = 0.95$, 1.35, and 1.65 ppm) corresponding to $\mathbf{CH_3}$, $\mathbf{CH_2}$, and $\mathbf{CH}$ groups in the PP main and side chains, there are several minor chemical shifts between 2 and 8 ppm, which correspond to the incorporated "T" units in LCBPP polymers (VI). They are from three possible structures 1, 2, and 3 (inset in Figure 1), resulting from copolymerization, chain transfer, and both reactions (LCB mode), respectively. In all runs, an extremely low concentration of structure 2 was observed, indicating either a low percentage of direct chain

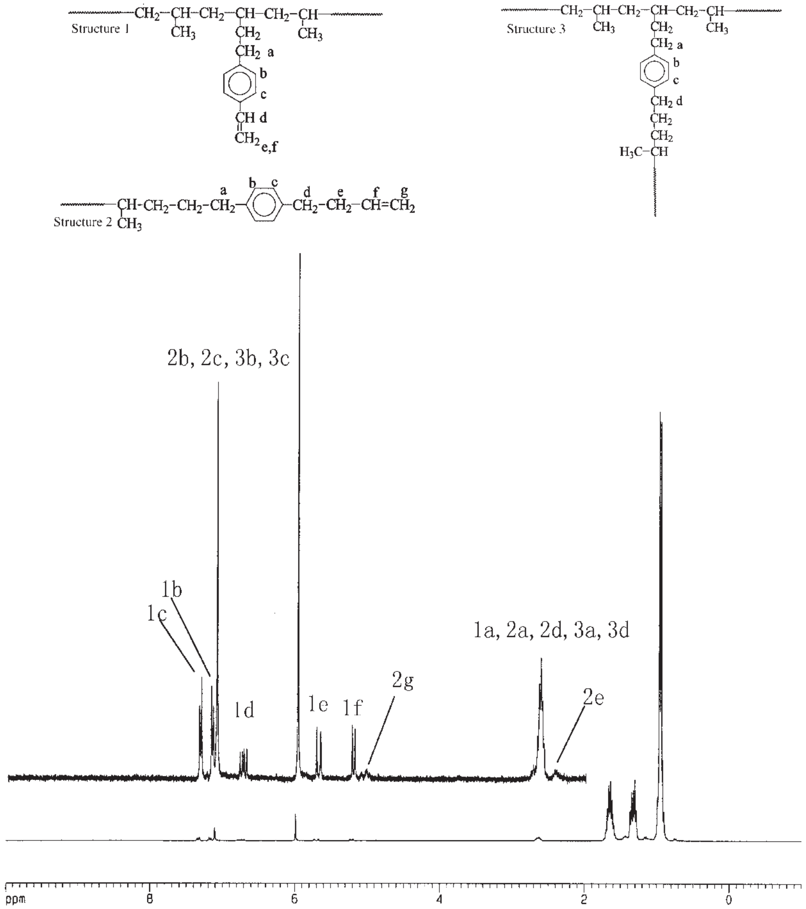


Figure 1.
A typical ^{1}H NMR spectrum of LCBPP polymer.

transfer reaction to "T" reagent or a high copolymerization reactivity of PP macromonomer (structure 2). The PP macromonomer should have high molecular weight and high melting temperature, which should exhibit very low copolymerization reactivity in propylene copolymerization to form the side chain in LCBPP (VI). Therefore, most of "T" reagents must first involve copolymerization with propylene to form a PP copolymer (III) that contains several "T" units, because the vinyl moiety in "T" reagent is much more reactive than styrenic moiety. Then about half of the incorporated "T" units further engage in chain transfer reaction with some propagating PP chains (IV) to form LCBPP product (VI), as illustrated in Scheme 1.

Figure 2 compares the Mark-Houwink plots of two LCBPPs (sample M132 was prepared by solution process and sample X10 was prepared by bulk process, from run A-3 in Table 1) and a linear PP standard (a commercial ExxonMobile capacitor grade PP). Their molecular weights and molecular weight distributions were examined by SEC with triple detectors (refractive index, intrinsic viscosity, and light scattering), which simultaneously measures absolute molecular weight (M_{LS}) and intrinsic viscosity $[\eta]$ for each fraction of polymer separated by the chromatography columns.

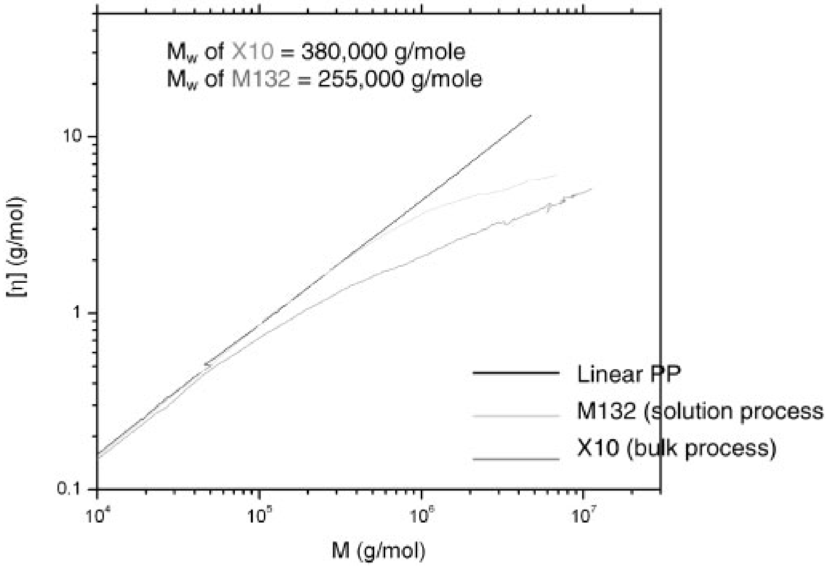


Figure 2.
Comparison of Mark-Houwink plots of linear PP and two LCBPPs prepared by solution (M132) and bulk (X10) reactors under similar conditions.

Mark-Houwink plots, log-log plots of intrinsic viscosity versus absolute molecular weight for each slice of the SEC elution, provide qualitative information about branching in whole molecular weight ranges. Evidenty, the increase of polymer molecular weight extends the LCB structure from only high molecular weight portion (in sample M132) to middle and below middle molecular weight ranges (in sample X10). In other words, the X10 sample contains only a very small portion ($<10\%$) of polymer mixture ($M_w < 50$ k) with linear PP structure. The gradually deviation of Mark-Houwink plot in the X10 sample, from low to high molecular weight, indicates a uniform branch distribution, and the number of branches increases with the polymer molecular weight.

Melt Rheology of LCBPP Polymers

Oscillatory shear measurements were obtained between 170 and 190 °C. Figure 3 (a) shows the storage moduli for LCBPPs and PP. Linear PP with similar molecular weight to that of the LCBPPs, behaved as expected with the slope of G' approaching 2 at low frequency. However, the LCBPPs were observed to have broadened storage moduli with slopes only approaching values of 1.5 at the lowest frequencies measured, indicating the relaxation times increased as the branch density of the polymers increased.

Figure 3 (b) compares complex viscosities between linear PP and LCBPPs. The complex viscosity, η^*, and particularly zero-shear viscosity, η_0, are extremely sensitive to branching.[27–30] The molecular weight of PP was similar to those of the LCBPPs, but the zero-shear viscosities of the LCBPPs were significantly higher. Additionally LCBPPs had broader transitions from shear-thinning behavior at higher frequencies to Newtonian behavior at low frequencies, consistent with broader distributions and branching. Newtonian behavior was harder to obtain in LCBPPs as is clearly illustrated by sample LCBPP4's lack of a frequency independent viscosity in the frequency range measured, which is attributed to the long relaxation times of branched polymers.

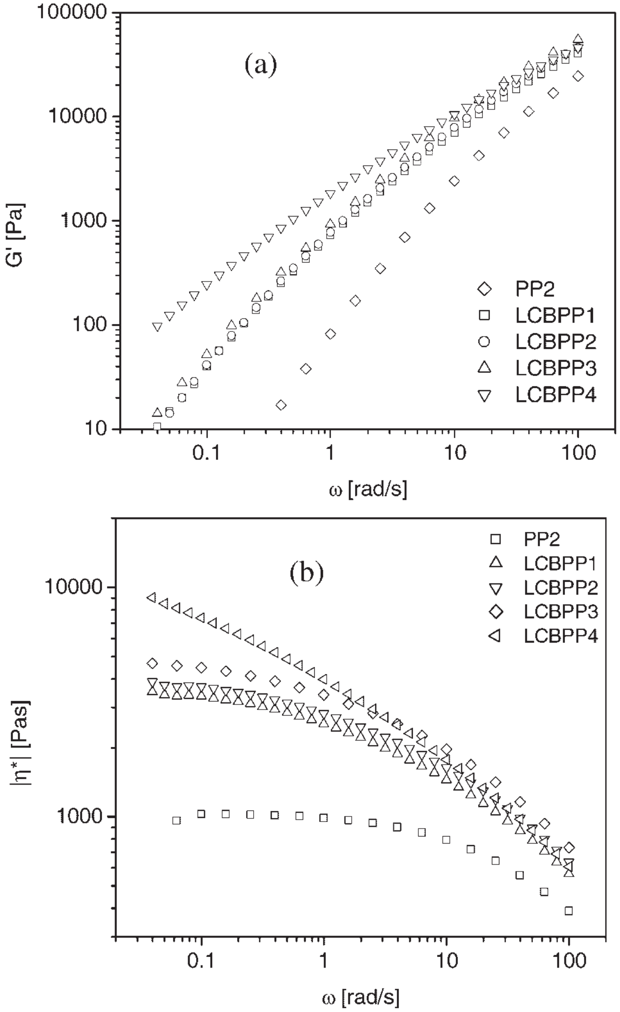


Figure 3.
Comparison of (a) Storage moduli and (b) complex viscosity between linear PP and LCBPPs at 190 °C.

An examination of the extensional flow characteristics of LCBPP4 was performed using an ARES rheometer equipped with the extensional viscosity fixture. The extensional stress growth function, $\eta_E^+(t,\dot{\varepsilon})$,[31,32] is shown in Figure 4 at various Hencky extension rates, $\dot{\varepsilon}$, for LCBPP4. At each extension rate there existed a range of deformation which perfectly tracked linear viscoelastic response. Additionally, at all extension rates studied, with perhaps the exception of $\dot{\varepsilon} = 0.005\ \mathrm{s}^{-1}$, strain hardening was observed. Strain hardening was observed as a sharp increase of $\eta_E^+(t,\ \dot{\varepsilon})$ above the values at $\dot{\varepsilon} = 0.005\ \mathrm{s}^{-1}$.

Conclusion

We have developed a convenient route, i.e. one-pot polymerization process, to prepare isotactic polypropylene with a long chain branched structure (LCBPP). The process is centered on p-(3-butenyl)styrene "T" reagent that can simultaneously perform copolymerization and chain transfer func-

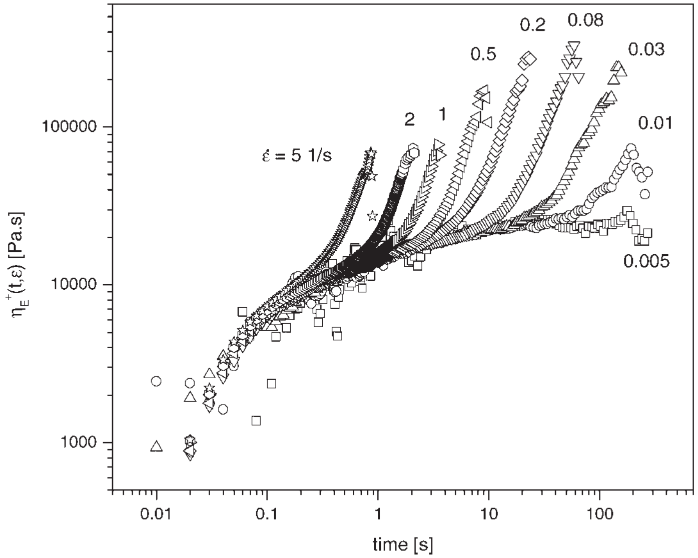


Figure 4.

Extensional stress growth function at various strain rates for LCBPP4 at 180 °C.

tions using an iso-specific rac-$Me_2Si[2\text{-}Me\text{-}4\text{-}Ph(Ind)]_2ZrCl_2$/MAO catalyst. A broad range of LCBPP polymers with good control of molecular structures (branch density and branch length) have been prepared, and their detailed structure information was revealed by a combination of NMR, GPC with triple detectors, and corresponding control reactions. Branch densities affected the slope of the Mark-Houwink plot in the high molecular weight range. Small amplitude oscillatory shear showed control of branch point density allowed for the synthesis of LCBPPs with varying zero-shear viscosities, relaxation times, and Arrhenius activation energies for flow. LCBPP was observed to behave as a strain hardening material under extensional flow, useful for polymer processing operations requiring stability in extension.

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