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Synthesis of Long Chain Branched Polypropylene with Relatively Well-Defined Molecular Structure

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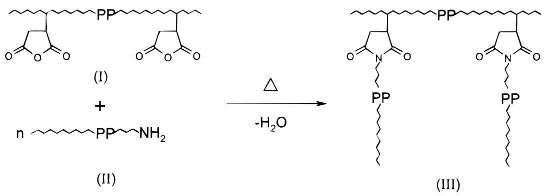
One of the most unique developments in metallocene catalysis is the preparation of polyethylene with a long chain branching molecular structure[1] by using a catalyst with constrained ligand geometry, such as $[C_5Me_4(SiMe_2N^tBu)]TiCl_2/MAO$.[2] Although there are only very low concentration of long chain branched polymer formed and difficulties in determining the detail molecular structure, the long chain branching polyethylene (LCBPE) that exists in the PE product shows many unique rheological properties,[3−5] such as higher viscosity at lower shear rates and lower viscosity at higher shear rates. The shear thinning is very important for improving the processability of the metallocene-produced polyethylene with a narrow molecular weight distribution. In addition, LCBPE polymers also showed significantly higher melt strength, which is essential in blow molding processes.[6,7]

So far, there is no example of a long chain branched polypropylene (LCBPP) prepared via in situ polymerization. The polypropylene (PP) products, prepared by both Ziegler−Natta and metallocene catalysts, currently available have a predominantly linear structure. Although linear PP polymers have many desirable physical properties, they show low melt strength. As a result, PP has been limited in some end-use fabrications, for example, in extrusion coating and blow molding. The processability is also a major concern in the metallocene-prepared PP with narrow molecular weight distribution.

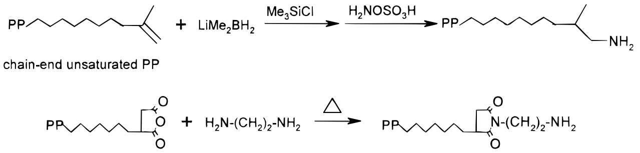
Scheve et al.[7] explored the preparation of LCBPP polymers using high-energy radiation of a linear solid polypropylene in a reduced active oxygen environment for a specific period of time. As expected, the combination of solid state reaction conditions and many competing side reactions (i.e., degradation, cross-linking, disproportional, and so on) severely limits the extent of branching reaction, and in no way can the reaction be controlled to achieve a polymer with a well-defined branching structure. In general, there is a strong scientific and technological interest to develop a new synthetic route that can prepare long chain branching polyolefins with a controllable molecular structure.

In this communication, we report a new method that can be used to prepare long chain branched PP with a relatively well-defined molecular structure, i.e., known backbone molecular weight, graft length, and graft density. The chemistry involves a graft-onto reaction between a maleic anhydride-grafted PP (PP-*g*-MA) (I) and several amine-group terminated PP (PP-*t*-NH_2) (II) chains as shown in Scheme 1. The formed LCBPP (III) has an imide linkage that connects the PP backbone and each PP side chain. Because molecular structures of both the backbone and side chains are predetermined before the graft-onto reaction and the extent of the reaction can be controlled by the MA concentration in the PP-*g*-MA and the ratio between PP-*g*-MA and PP-*t*-NH_2, an effective imidization reaction will produce a long chain branched PP polymer (III) with a relatively well-defined molecular structure.

Scheme 1



Scheme 2



Maleic anhydride-terminated and -grafted PP polymers, i.e., PP-*t*-MA[8,9] and PP-*g*-MA,[10] respectively, were synthesized from the corresponding borane-containing polymers, using the previously reported method. Amine-terminated PP (PP-*t*-NH_2) polymers were prepared by two methods, as shown in Scheme 2. The first method involved hydroboration[11] of chain-end unsaturated PP with dimethylborane that was prepared in situ from lithium dimethylboronhydride and then amination using hydroxyamine-*o*-sulfonic acid. The second method is to react MA-terminated PP with 10-fold excess ethylenediamine at 130 °C for 6 h. The unreacted diamine was completely removed after the imidization reaction. The graft-onto reaction was carried out by intensive mixing between MA- and NH_2-modified PP polymers in xylene solution at 130 °C for 5 h. The final product was precipitated in acetone, washed, and dried at 50 °C in a vacuum oven for 24 h.

To determine the effectiveness of the imidization reaction, a maleic anhydride-terminated PP (PP-*t*-MA), having $M_w \sim 52\,000$ and $M_w/M_n = 2.6$, was reacted with a NH_2-terminated PP (PP-*t*-NH_2), having $M_w \sim 12\,000$ and $M_w/M_n = 2.2$, with a 1/1 mole ratio of MA/NH_2 units in a xylene solution at 130 °C for 5 h. The molecular weight change in the resulting diblock polymer offers very useful information about this coupling reaction. Figure 1 compares the GPC curves of the starting PP-*t*-MA and the resulting diblock PP containing both PP blocks.

The homogeneous increase of polymer molecular weight without significant broadening of the molecular weight distribution strongly suggests the formation of a PP-*b*-PP diblock polymer and indicates an effective imidization coupling reaction.

The same coupling reaction was applied to the graft-onto reaction between PP64K-*g*-MA ($M_w \sim 64\,000$) and PP12K-*t*-NH_2 ($M_w \sim 12\,000$) with a 1/1 mole ratio of MA/NH_2 to produce the LCBPP polymer (III), containing on average one PP backbone and six PP side chains. Figure 2 compares the IR spectrum of PP-*g*-MA, LCBPP sample formed at 130 °C for 5 h and the LCBPP film

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Table 1. Summary of Long Chain Branched PP Polymers and Their Corresponding Mixtures

samples	backbone (wt %)	branch (wt %)	graft density[a]	M_w ($\times 10^3$)	$[\eta]$ (dl/g)[b]	$\langle r^2\rangle^{1/2}$ (nm)[c]	g'[d]
PP64K-*g*-MA				64	0.68	27.5	
PP52K-*t*-NH_2				52	0.62	24.8	
PP23K-*t*-NH_2				23	0.32	15.2	
PP12K-*t*-NH_2				12	0.24	11.1	
PP64K/PP12K-1	73	27			0.62		
PP64K-*g*-PP12K-1	73	27	2	136	0.42	26.1	0.48
PP64K/PP12K-2	47	53			0.48		
PP64K-*g*-PP12K-2	47	53	6	88	0.37	28.8	0.31
PP64K/PP23K	32	68			0.45		
PP64K-*g*-PP23K	32	68	6	202	0.31	31.1	0.20
PP64K/PP52K	29	71			0.66		
PP64K-*g*-PP52K	29	71	3	220	0.39	34.4	0.21

[a] Graft density is the average number of PP grafts in each PP backbone, assuming 100% coupling reaction. [b] Intrinsic viscosity is measured in decahydronaphthalene at 135 °C. [c] $\langle r^2\rangle^{1/2} = (M[\eta]/\Phi)^{1/3}$, where M is molecular weight and Φ is the Flory constant (2.1×10^{21} dL g^{-1} cm^3). [d] $g' = [\eta]_b/[\eta]_l$; $[\eta]_l = KM^a$, where $K = 1.05 \times 10^{-4}$ dL g^{-1}, $\alpha = 0.80$, and $M = M_w$ (backbone) + M_w (branches).

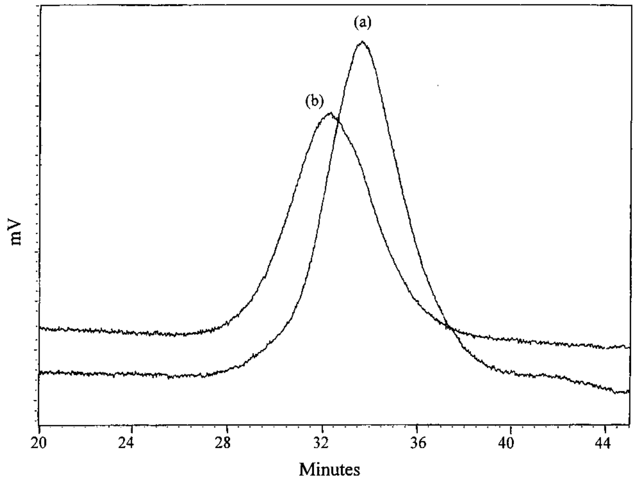

Figure 1. GPC curves of (a) PP-*t*-MA containing a terminal succinic anhydride group and (b) PP-*b*-PP diblock polymer formed by imidization coupling reaction. (Solvent, trichlorobenzene; temp., 135 °C.)

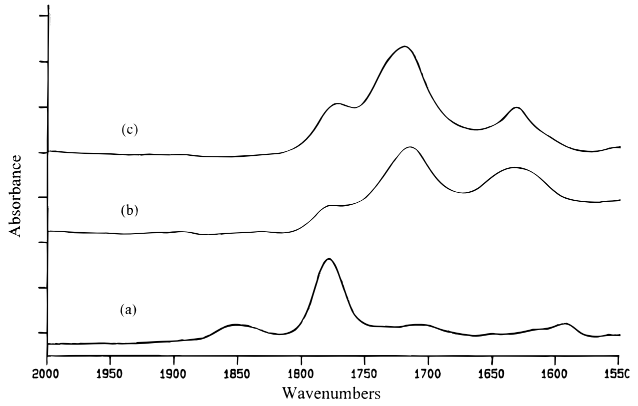

Figure 2. FTIR spectrum of (a) starting PP-*g*-MA polymer, (b) LCBPP formed by reacting PP-*g*-MA with PP-*t*-NH_2 in xylene solution at 130 °C for 5 h, and (c) LCBPP formed after further coupling reaction in a vacuum oven at 130 °C for 24 h.

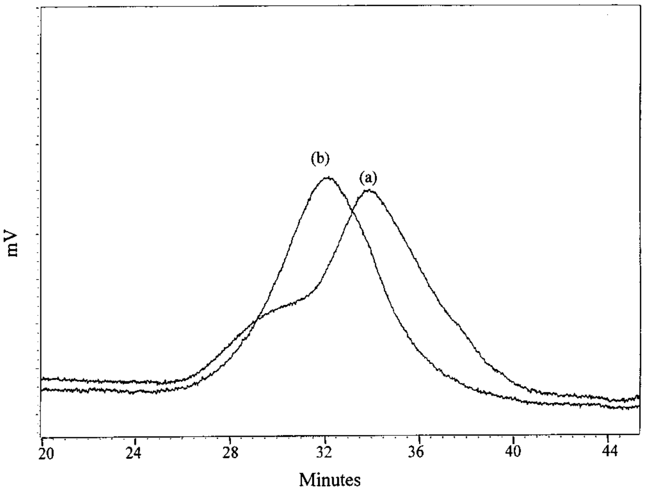

Figure 3. GPC curve comparison between (a) physical mixture of the corresponding PP backbone and side chains and (b) corresponding LCBPP polymer.

further heat-treated at 130 °C in a vacuum oven for 24 h (sample PP64K-*g*-PP12K-2 in Table 1).

In Figure 2a, the starting PP-*g*-MA shows two absorbency peaks at 1860 and 1780 cm^{-1}, corresponding to the symmetric and asymmetric stretching modes, respectively, of the two carbonyl groups in succinic anhydride. After reacting with PP(12K)-*t*-NH_2, Figure 2b shows the disappearance of both succinic anhydride absorbencies and the appearance of three new absorbencies, including a weak peak at 1770 and two strong peaks at 1710 and 1630 cm^{-1}, corresponding to the carbonyl vibration modes of imide, carboxylic acid, and amide groups, respectively. It appears that the succinic anhydride groups in PP-*g*-MA react with the NH_2 groups in terminal PP to form a product containing some imide groups, but mainly amide and carboxylic acid groups. After further heat treatment, Figure 2c shows the decrease of absorbency at 1630 cm^{-1} and the increase of two strong peaks at 1770 and 1730 cm^{-1}, corresponding to the imide group. The cyclization reaction took place to form imide groups as the linkages between the PP backbone and PP side chains.

Figure 3 compares GPC curves for the LCBPP polymer (PP64K-*g*-PP12K-2) and the corresponding physical mixture (PP64K/PP12K) with a same mole ratio of backbone PP64K and branch PP12K.

As expected, the physical mixture shows a bimodel and broad molecular weight distribution. On the other hand, the LCBPP shows a single GPC peak with a relatively narrow molecular weight distribution. It is very interesting to note that the GPC peak of the branched PP64K-*g*-PP12K polymer (with expected molecular weight of 138K) is located between two peaks of the much lower molecular weight backbone PP64K and branch PP12K polymers. The results clearly imply the formation of long chain branched PP polymers. The long chain branching structure reduces the radius gyration and overall hydrodynamic volume of polymer.

The reduction of hydrodynamic volume of LCBPP polymers was further supported by rheological study. Table 1 summarizes the intrinsic viscosity results of long chain branched PP polymers with various graft lengths and densities. It is also very interesting to compare their results with the corresponding physical mixtures.

All of the long chain branched PP polymers show significantly lower intrinsic viscosity than that of their corresponding physical mixtures with identical compositions. The intrinsic viscosity of the physical mixture is roughly equal to the sum of the weight fraction of the intrinsic viscosity of each of the components. It is very interesting to note that the intrinsic viscosity of the LCBPP polymers shown in Table 1 systematically reduces with the increase of both graft density and graft length. Comparing the samples of PP-64K, PP64K-*g*-PP12K-1, and PP64K-g-PP12K-2, having the same backbone and graft length but increased graft densities (0, 2, 6 grafts/backbone, respectively), the intrinsic viscosity decreases from 0.68 to 0.42 to 0.37 dL/g. A comparison of the samples of PP-64K, PP64K-*g*-PP12K-2, and PP64K-*g*-23K, having the same polymer backbone and graft density (6 grafts/each backbone) but increased graft length (0, 12K, and 23K g/mol, respectively) shows that the intrinsic viscosity decreases from 0.68 to 0.37 to 0.31 dL/g. Zimm and Kilb[12] introduced a branching parameter, g', that is defined as $g' = [\eta]_b/[\eta]_l$, where $[\eta]_b$ and $[\eta]_l$ are the intrinsic viscosity of branched and linear polymers with the same molecular weight. Thus, all LCBPP polymers produced have a $g' \ll 1$, and the g' value proportionally decreases with the increases in both graft density and graft length.

In summary, we have shown a versatile method to prepare long chain branched polypropylene with a relatively well-defined molecular structure; i.e., predetermined PP backbone and side chains as well as graft density. The long chain branching structure is strongly supported by the formation of imide linkages and the reduction of overall hydrodynamic volume.

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