One-Pot Process of Preparing Long Chain Branched Polypropylene Using C_2-Symmetric Metallocene Complex and a “T” Reagent

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Introduction. One of the most unique developments in metallocene technology is the preparation of polyethylene with long chain branched structure (LCBPE)[1] by using constrained geometry catalyst (CGC), such as $[C_5Me_4(SiMe_2N^tBu)]TiCl_2$/MAO. The branching mechanism involves the incorporation of vinyl-terminated PE macromonomers that are in situ generated via β-H elimination during ethylene polymerization. Although these LCBPE polymers have very low concentration of long chain branches (estimated branch density ~ 3.0 LCB/10 000 carbons) and are difficult to characterize in detail, the polymers show an excellent combination of properties,[2] including good processability and high melt strength, which are essential in blow-molding applications.[3]

Commercial isotactic polypropylene (PP) has a predominantly linear molecular structure. Despite the huge commercial success with many desirable properties, PP shows a variety of melt-processing shortcomings, especially metallocene-prepared PP with narrow molecular weight distribution. The low melt strength causes local instability in thermoforming, blow molding, extrusion coating, and coextrusion of laminates. As a result, PP has been limited in some end-use fabrications. Unfortunately, the in-situ LCB reaction happened in the PE case is ineffective in the PP case due to the complicated PP macromonomer structures. There are two possible monomer insertion modes (including 1,2- and 2,1-insertions) and multiple chain termination mechanisms[4] that can lead to polypropylene with various chain ends, while only the vinyl chain end is active for LCB reaction. Furthermore, the preparation of isotactic polypropylene requires isospecific catalysts, such as *rac*-$Me_2Si[2\text{-}Me\text{-}4\text{-}Ph(Ind)]_2ZrCl_2$/MAO, which have limited spacial opening at the active site for incorporating macromonomers, especially involving isotactic PP macromonomers.[5]

Most of the early prior art of increasing melt strength of PP was based on postreactor free radical processes,[6] involving the ionizing radiation and peroxide treatments of linear isotactic polypropylene. Many works have been focused on optimizing reaction conditions or extruder parameters to promote branch formation while suppressing undesired degradation and cross-linking. However, because of the inherent complexity of free radical reactions, the final product is usually a complicated mixture. Another approach of using α,ω-diene comonomers, such as 1,7-octadiene, 1,9-decadiene, 1,11-dodecadiene, and 1,13-tetradecadiene, during propylene polymerizations also yielded mixed results. Some results[7] showed only a single enchainment of α,ω-dienes by heterogeneous Ziegler−Natta catalyst to form the linear PP structure. However, other results[8] based on metallocene catalyst indicated that the diene-incorporated polyolefins enhanced melt strength and shear thinning. As expected, the polymer structure is very complicated. The double enchainment of symmetric α,ω-diene units, with increasing crossover structures in the polymer matrix, will result in some unprocessable (cross-linked) polymer networks.

A few years ago, we reported a coupling reaction between side-chain and chain-end functionalized PP polymers to form LCBPP with well-controlled molecular structure[10] (molecular weight, branch density, and branch length). The comparison of intrinsic viscosity between LCBPP and its corresponding linear main and side chains clearly showed a significant reduction of intrinsic viscosity due to the long chain branched structure. The increases of both branch density and branch length proportionally reduced the branching parameter, g' (the ratio of intrinsic viscosity of branching and linear polymers with the same molecular weight). The major drawback of this method is the multiple reaction steps. Despite intense interest and many research attempts, so far there is no commercially viable process for preparing LCBPP polymers.

Results and Discussion. In this paper, we discuss a new one-pot polymerization process to in-situ prepare LCBPP polymers, which employs a novel branching “T” reagent, i.e., *p*-(3-butenyl)styrene, as illustrated in Scheme 1. This asymmetric diene serves as comonomer and chain transfer agent during 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 a small amount of hydrogen. The incorporated “T” units are located right at the junction points between polypropylene main and side chains.

During polymerization, the isospecific propagation site $C{-}Zr^+A^-$ (**I**) is formed[11] by reacting *rac*-$Me_2Si[2\text{-}Me\text{-}4\text{-}Ph(Ind)]_2ZrCl_2$ with MAO, which then copolymerizes propylene and the α-olefin moiety of *p*-(3-butenyl)styrene (**II**) to form a linear PP copolymer (**III**)[12] containing some pendent styrene units. On the basis of our previous results,[13] these pendent styrene units in the copolymer (**III**) can serve as chain transfer agents in the presence of hydrogen. The propagating PP chain (**IV**) reacts with a pendent styrene unit via the 2,1-insertion mode to form a long chain branched PP polymer (**V**) that contains a dormant $C{-}Zr^+A^-$ species[14] incapable of continuing polymerization due to steric hindrance between the active site ($C{-}Zr^+$) and the incoming monomer (propylene with 1,2-insertion) and the formation of complex between the adjacent phenyl group and the Zr^+ ion. In the presence of hydrogen, the dormant species reacts with hydrogen to form LCBPP (**VI**) and regenerates the $H{-}Zr^+$ species (**I**) which is capable of reinitiating the polymerization of propylene, thus continuing the polymerization cycle. In other words, the ideal chain transfer reaction will not significantly affect the rate of polymerization but will produce LCBPP polymers. Both branch density and branch length can be conveniently controlled by a *p*-(3-butenyl)styrene “T” reagent, higher concentration higher branch density, and lower branch length.

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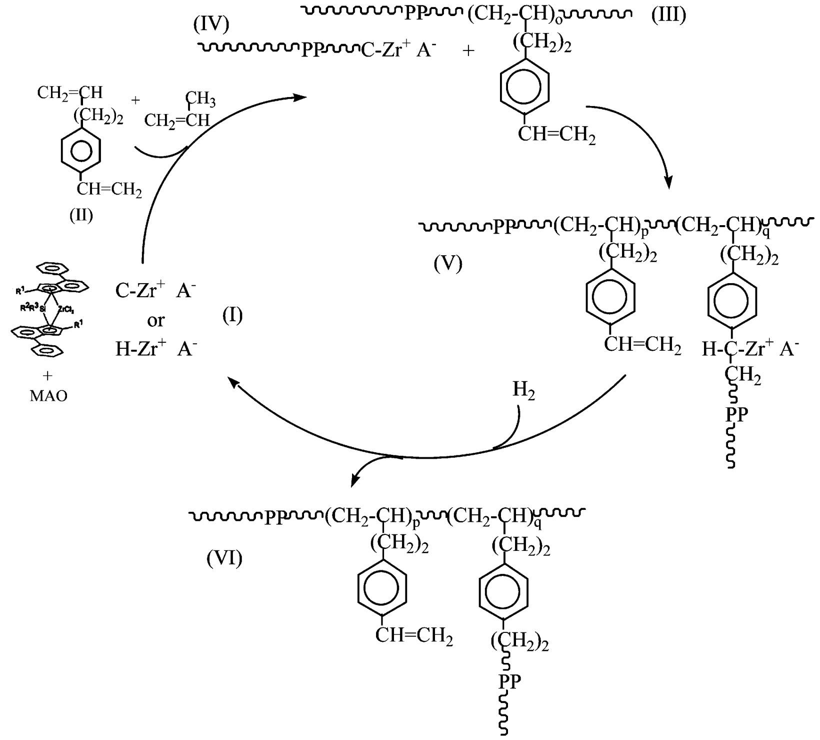
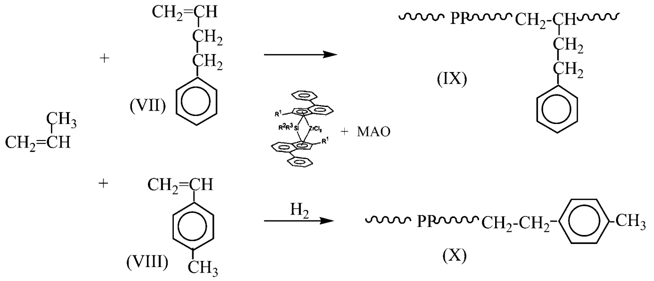
Scheme 1



Scheme 2



Two control reactions were also carried out to understand the separate functions of copolymerization and chain transfer reaction of a *p*-(3-butenyl)styrene "T" reagent (**II**). As illustrated in Scheme 2, copolymerization of propylene and 3-butenylbenzene (**VII**) and homopolymerization of propylene in the presence of *p*-methylstyrene[12,13] (**VIII**) were performed under the same reaction conditions. The resulting two linear isotactic PP polymers, i.e., poly(propylene-*co*-butenylbenzene) (**IX**) and *p*-methylstyrene-terminated PP (**X**), resemble the main chain and side chains, respectively, of the corresponding LCBPP polymer (**VI**). These two control reactions and their products provide important information on the effects of each moiety (α-olefin and styrene) in the *p*-(3-butenyl)styrene "T" reagent during the polymerization.

Table 1 summarizes the experimental results of several control reactions and two sets of in-situ LCB propylene polymerizations using the *rac*-$Me_2Si[2\text{-}Me\text{-}4\text{-}Ph(Ind)]_2ZrCl_2$ catalyst in the presence of the *p*-(3-butenyl)styrene "T" reagent (**II**) and hydrogen. The resulting polymers were analyzed by ^1H NMR, differential scanning calorimetry (DSC), and gel permeation chromatography with a series of detectors, including deferential reflection index, light scattering, and intrinsic viscosity (GPC triple detectors). The experimental details are discussed in the Supporting Information.

Figure 1 shows a typical ^1H NMR spectrum of LCBPP polymer (run A-10) and peak assignments for the incorporated *p*-(3-butenyl)styrene "T" units. In addition to three major proton chemical shifts (δ = 0.95, 1.35, and 1.65 ppm) corresponding to $C\mathbf{H}_3$, $C\mathbf{H}_2$, and $C\mathbf{H}$ 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**). By comparing LCBPP (**VI**) with two control polymers (**IX**) and (**X**), all the chemical shifts associated with the corresponding protons can be quantitatively determined. 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 transfer reaction to the "T" reagent or a high copolymerization reactivity of PP macromonomer (structure **2**). On the basis of the results from control 4 run, the PP macromonomer should have a 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 (similar to control 2 run) to form a PP copolymer (**III**) that contains several "T" units because the vinyl moiety in the "T" reagent is much more reactive than the 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.

Comparing LCBPP (A-2) and linear PP copolymer (control 2), with similar reaction conditions except using different St−X reagents (*p*-(3-butenyl)styrene/H_2 vs 3-butenylbenzene), we observed similar experimental results in catalyst activity, St−X incorporation, and T_m of the resulting PP polymers, despite the difference in

Table 1. Comparison of the Experimental Results in the *rac*-$Me_2Si[2\text{-}Me\text{-}4\text{-}Ph(Ind)]_2ZrCl_2$/MAO Catalyzed Polymerization of Propylene and Various Styrenic Molecules (St−X)

	reaction conditions						St−X[b] incorporation modes[d]		
run[a]	St−X[b] (M)	H_2 (psi)	temp/time (°C/min)	cat. activity[c] (kg/(mol h))	St−X[b] in PP (mol %)	T_m (°C)	Stru 1	Stru 2	Stru 3
control 1	0	0	30/3	93 000	0	160			
control 2	0.012	0	30/3	96 500	0.65	158			
control 3	0.012	0	30/30	0					
control 4	0.012	6	30/3	97 600	0.11	160			
A-1	0.012	0	30/30	24	0.61	158	45.2	n.d.	54.8
A-2	0.012	6	30/3	96 250	0.67	158	42.3	n.d.	57.7
A-3	0.024	0	30/30	0					
A-4	0.024	6	30/3	97 380	0.89	156	46.5	n.d.	53.5
A-5	0.060	0	30/30	0	1.18	156	46.7	n.d.	53.3
A-6	0.060	6	30/3	45 075	1.06	156	46.8	n.d.	53.2
A-7	0.060	20	30/3	99 210	1.06	156	46.8	n.d.	53.2
A-8	0.120	35	30/30	43 320	1.17	153	46.8	1.9	51.3
A-9	0.240	35	30/30	17 750	1.86	152	47.2	3.6	49.2
A-10	0.361	35	30/30	7 780	2.51	146	46.9	4.8	48.3
B-1	0.012	1	55/15	350 000	0.16	152	55.0	n.d	45.0
B-2	0.012	3	55/15	320 000	0.14	152	55.0	n.d	45.0
B-3	0.012	5	55/15	330 000	0.16	152	51.3	n.d	48.7
B-4	0.012	10	55/15	260 000	0.14	152	58.6	n.d	41.4
B-5	0.012	15	55/15	260 000	0.18	152	56.7	n.d	43.3

[a] Reaction conditions: 50 mL of toluene, propylene (100 psi); [Zr] = 1.25×10^{-6} mol/L and [Al]/[Zr] = 3000 for runs A-1 to A-10 and [Zr] = 2.2×10^{-6} mol/L and [Al]/[Zr] = 25 000 for runs B-1 to B-5. [b] St−X: 3-butenylbenzene in control 2, *p*-methylstyrene in control 3 and control 4, and *p*-(3-butenyl)styrene for runs A-1 to A-10 and runs B-1 to B-5. [c] Catalyst activity = kg of PP/(mol of catalyst h). [d] Determined by ^1H NMR spectra.

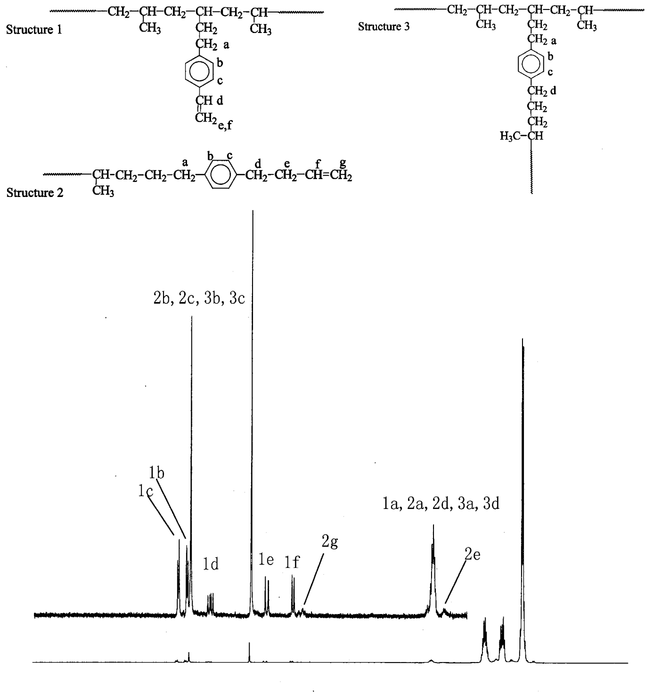


Figure 1. A typical ^1H NMR spectrum of LCBPP polymer (run A-10).

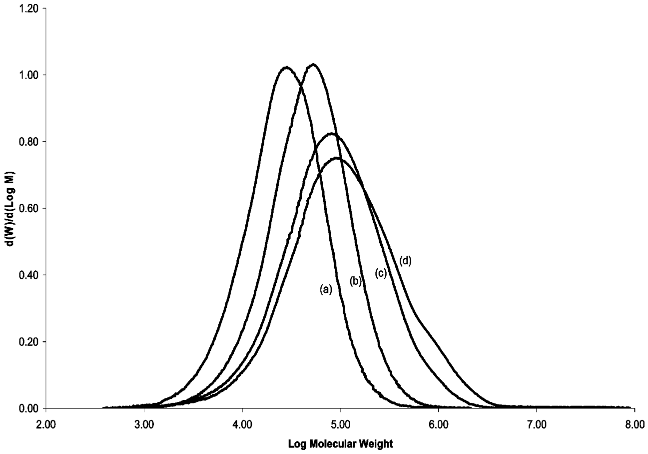


Figure 2. GPC curves of four LCBPP polymers, including (a) run A-2, (b) run A-4, (c) run A-8, and (d) run A-9.

the polymer structure. Their catalyst activities are also very close to that of the corresponding propylene homopolymerization (control 1). The combination implies that the copolymerization reaction is very effective without sign of difficulty due to a bulky comonomer. The ethylene spacer between the olefin and phenyl group in 3-butenylbenzene (**VI**) seems to be sufficient to release the steric congestion. In addition, the chain transfer reaction in A-2 run is also very effective in forming LCBPP structure.

A systematic study (runs A-1 to A-10 and runs B-1 to B-5) was conducted to evaluate the effect of the *p*-(3-butenyl)styrene "T" reagent and hydrogen concentrations on catalyst activity and *p*-(3-butenyl)styrene incorporation modes by varying reaction conditions. All comparative reaction runs (control 3 vs control 4, A-1 vs A-2, A-3 vs A-4, and A-5 vs A-6) show the essential role of hydrogen to complete the chain transfer reaction to form LCBPP structure (**V**). As the "T" reagent concentration increases, an increased amount of hydrogen is needed to maintain high catalyst activity and *p*-(3-butenyl)styrene conversion. Hydrogen is clearly needed to complete the chain transfer cycle during the *rac*-$Me_2Si[2\text{-}Me\text{-}4\text{-}Ph(Ind)]_2ZrCl_2$-mediated propylene polymerization. In general, the "T" reagent incorporation in LCBPP is proportional to the concentration of "T" reagent used during the polymerization. In all A-1 to A-10 runs, more than half of the incorporated "T" reagents involves in chain transfer reaction to form LCB structures. On the basis of the structure **3** content shown in Table 1, we can estimated the average branch density in each LCBPP sample, which is between 15 and 60 per 10 000C in main and side chains and is proportional to the concentration of "T" reagent used during the polymerization. The melting temperature (T_m) of

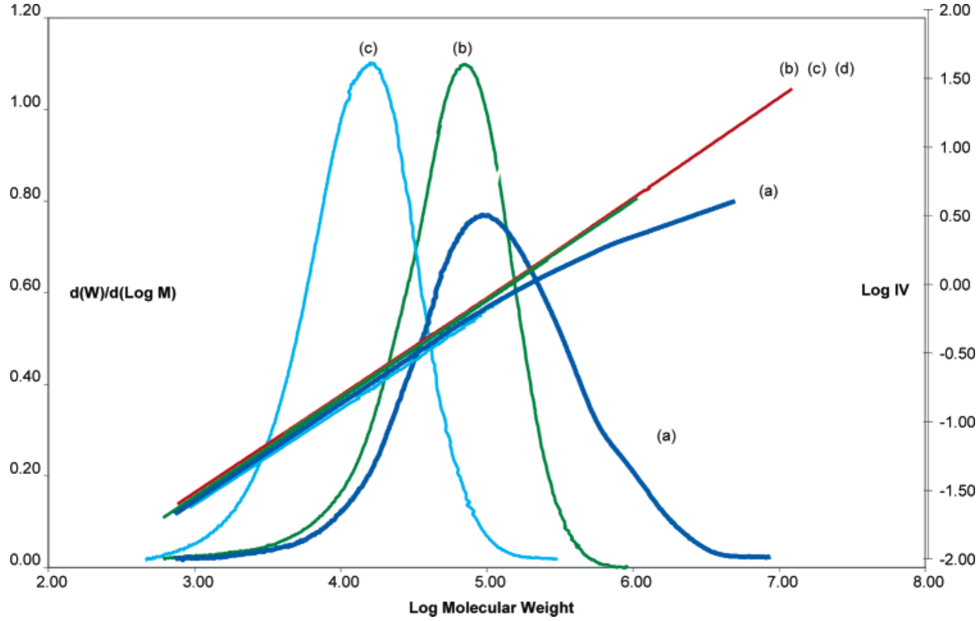


Figure 3. Comparison of GPC curves and Mark–Houwink plots between (a) a LCBPP polymer (run A-9) and three linear PP polymers, including (b) control 2, (c) control 4, and (d) an industrial PP standard.

LCBPP samples, examined by DSC, also shows a consistent trend—graduate reduction of T_{m} with increase of branch density. Comparing with the in-situ LCB reaction in PE case, the "T" reagent provides much more effective branching mechanism in forming LCB polymer structure.

It is interesting to note some experimental results in runs B-1 to B-5, which were carried out at a higher reaction temperature (55 °C) and a higher [Al]/[Zr] = 25 000 ratio. The catalyst reactivity significantly increases with lower incorporation of the "T" reagent and a slight reduction of converting the "T" reagent into LCB structure. However, the branch density of about 4 per 10 000 C is still slightly higher than that in commercial LCBPE polymers. The slightly lower T_{m} of LCBPP polymer implies lower isotacticity due to high reaction temperature.

All resulting polymers, including LCBPP polymers and linear PP polymers obtained from control reactions, were subjected to gel permeation chromatography with three detectors (reflection index, light scattering, and intrinsic viscosity) (GPC triple detectors) to determine their molecular structure. This method provides an absolute polymer molecular weight and molecular weight distribution, as well as Mark–Houwink plot (log–log plot of intrinsic viscosity vs molecular weight). Figure 2 shows GPC curves of several LCBPP polymers (runs A-2, A-4, A-8, and A-9), and Figure 3 compares Mark–Houwink plots of a LCBPP (run A-9) with three linear PP polymers (control 2, control 4, and an industrial PP standard). Two complete sets of GPC curves and Mark–Houwink plots for linear PP and LCBPP polymers, respectively, are also presented in the Supporting Information.

All linear polymers, including an industrial standard PP polymer and two control polymers representing LCBPP main and side chains, exhibit the overlapped Mark–Houwink plots with the same slope and the same linear relationship from low to high molecular weight. The molecular weight of PP copolymer (control 2 run) is several times higher than that of *p*-MS-terminated PP (control 4 run) due to chain transfer reaction. With the increase of *p*-(3-butenyl)styrene concentration, GPC curves show the increase of LCBPP's molecular weight, and Mark–Houwink plots deviate from a linear relationship, especially in the high molecular weight region. The combination clearly indicates a high concentration of LCB structure, which is also consistent with the NMR results showing the exact branch densities. It is interesting to note that the polymer's molecular weight distribution stayed relatively narrow, indicating a single site copolymerization with a clean chain transfer reaction.

Conclusion. This paper shows 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 the *p*-(3-butenyl)-styrene "T" reagent that can simultaneously perform copolymerization and chain transfer functions using an isospecific *rac*-Me$_2$Si[2-Me-4-Ph(Ind)]$_2$ZrCl$_2$/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.

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Supporting Information Available: Experimental procedures and detailed characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Lai, S. Y.; Wilson, J. R.; Knight, G. W.; Hackon, L.; Stevens, J. C. US Patent 5,272,236, 1993, (b) Gibson, V. C.; Bercaw, J. E.; Bruton, W. J., Jr.; Sanner, R. D. *Organometallics* **1986**, *5*, 976, (c) Wang, W. J.; Yan, D.; Zhu, S.; Hamielec, A. E. *Macromolecules* **1998**, *31*, 8677. (d) Jacovic, M. S.; Pollock, D.; Porter, R. S. *J. Appl. Polym. Sci.* **1979**, *23*, 517.

(2) (a) Graessley, W. W. *Acc. Chem. Res.* **1977**, *10*, 332. (b) Vega, J. F.; Santamaria, A.; Munoz-Escalona, A.; Lafuente, P. *Macromolecules* **1998**, *31*, 3639. (c) Yan, D.; Wang, W. J.; Zhu, S. *Polymer* **1999**, *40*, 1737. (d) Markel, E. J.; Weng, W.; Peacock, A. J.; Dekmezian, A. D. *Macromolecules* **2000**, *33*, 8541.

(3) (a) Goyal, S. K. *Plast. Eng.* **1995**, *51*, 25. (b) Scheve, B. J.; Mayfield, J. W.; DeNicola, A. J., Jr. US Patent 5,731,362, 1998.

(4) (a) Burger, B. J.; Thompson, M. E.; Cotter, W. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1990**, *112*, 1566. (b) Hajela, S.; Bercaw, J. E. *Organometallics* **1994**, *13*, 1147. (c) Alelyunas, Y. W.; Guo, Z.; LaPointe, R. E.; Jordan, R. F. *Organometallics* **1993**, *12*, 544. (d) Guo, Z.; Swenson, D.; Jordan, R. *Organometallics* **1994**, *13*, 1424. (e) Resconi, L.; Cavallo, L.; Fait, A.; Piemontesi, F. *Chem. Rev.* **2000**, *100*, 1253.

(5) (a) Weng, W.; Markel, E. J.; Dekmerzian, A. H. *Macromol. Rapid Commun.* **2000**, *21*, 103. (b) Weng, W.; Hu, W.; Dekmerzian, A. H.; Ruff, C. J. *Macromolecules* **2002**, *35*, 3838. (c) Shiono, T.; Azad, S. M.; Ikeda, T. *Macromolecules* **1999**, *32*, 5723.

(6) (a) DeNicola, A. J., Jr. U.S. Patent 5,047,485, 1991. (b) DeNicola, A. J., Jr.; Smith, J. A.; Felloni, M. U.S. Patent 5,541,236, 1996. (c) Raetzsch, M.; Hesse, A.; Reichelt, N.; Panzer, U.; Gahleitner, M.; Wachholder, M.; Kloimstein, K. U.S. Patent 6,077,907, 2000. (d) Gahleitner, M. *Prog. Polym. Sci.* **2001**, *26*, 895.

(7) (a) Lal, J.; Senyek, M. L. U.S. Patent 4,551,503, 1985. (b) Etherton, B. P.; McAlpin, J. J.; Huff, T.; Kresge, E. N. U.S. Patent 5,504,171, 1996.

(8) (a) Meka, P.; Kunihiko, I.; Licciardi, G. F.; Gadkari, A. C. U.S. Patent 5,670,595, 1997. (b) Rosch, J.; Mach, H.; Gruber, F. U.S. Patent 5,929,185, 1999.

(9) Walter, P.; Trinkle, S.; Lilge, D.; Friedrich, C.; Mulhaupt, R. *Macromol. Mater. Eng.* **2001**, *286*, 309.

(10) Lu, B.; Chung, T. C. *Macromolecules* **1999**, *32*, 8678.

(11) Kaminsky, W.; Kulper, K.; Brintzinger, H. H.; Wild, F. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 507.

(12) Resconi, L.; Cavallo, L.; Fait, A.; Piemontesi, F. *Chem. Rev.* **2000**, *100*, 1253.

(13) (a) Chung, T. C.; Dong, J. Y. U.S. Patent 6,479,600, 2002. (b) Chung, T. C.; Dong, J. Y. *J. Am. Chem.* Soc. **2001**, *123*, 4871. (c) Dong, J. Y.; Chung, T. C. *Macromolecules* **2002**, *35*, 1622, (d) Dong, J. Y.; Wang, Z. M.; Han, H.; Chung, T. C. *Macromolecules* **2002**, 35, 9352.

(14) Chung, T. C.; Lu, H. L. *J. Polym. Sci., Polym. Chem. Ed.* **1999**, *37*, 2795.

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