1622 *Macromolecules* **2002,** *35,* 1622−1631

Synthesis of Polyethylene Containing a Terminal *p*-Methylstyrene Group: Metallocene-Mediated Ethylene Polymerization with a Consecutive Chain Transfer Reaction to *p*-Methylstyrene and Hydrogen

J. Y. Dong and T. C. Chung*

Department of Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania 16802

Received September 12, 2001

ABSTRACT: This paper discusses a novel polymerization process for preparing polyethylene having a terminal *p*-methylstyrene (*p*-MS) group. The chemistry involves metallocene-mediated ethylene polymerization in the presence of *p*-MS and hydrogen. Apparently, the reaction mechanism, including the copolymerization and chain transfer reactions, can be controlled with a favorable combination of metallocene catalyst and hydrogen concentration. Under some specific reaction conditions, the Cp_2ZrCl_2/MAO catalyst selectively forms PE with a terminal *p*-MS terminal group (PE-t-*p*-MS) via a consecutive chain transfer reaction to *p*-MS and then hydrogen. The catalyst activity increases with the hydrogen concentration, and the polymer molecular weight is inversely proportional to the *p*-MS concentration. In contrast, $[C_5Me_4(SiMe_2N^tBu)]TiCl_2$/MAO initiates a copolymerization reaction between ethylene and *p*-MS, and hydrogen has little effect on the catalyst activity. The terminal *p*-MS unit at the PE chain end is a valuable reactive group that can be metalated to form a stable polymeric anion, which can be used to prepare functionalized PE polymers containing a polar terminal group or diblock copolymers.

Introduction

The in situ chain transfer reaction during polymerization presents a very convenient route for introducing a reactive terminal group to the polymer chain end.[1] It also offers an opportunity for the preparation of diblock copolymers.[2] This approach is particularly interesting in polyolefin cases due to the long-standing scientific challenge of finding an effective and convenient route to prepare functionalized polyolefins. The lack of functionality and poor compatibility with other materials has imposed limitations on the application of polyolefin[3] in many areas, such as in polymer blends and composites.

In our recent paper,[4] we described the first example of consecutive chain transfer reaction, first to *p*-methylstyrene (or styrene) and then to hydrogen, during metallocene-catalyzed propylene polymerization by *rac*-$Me_2Si[2\text{-}Me\text{-}4\text{-}Ph(Ind)]_2ZrCl_2$/MAO complex. The chemistry centered on the formation of a dormant propagating species after 2,1-insertion of a *p*-MS unit. The steric jamming completely stalled the polymerization process. However, this sluggish propagating chain end allowed a reaction with hydrogen, which produced PP polymer with a terminal *p*-MS group and reenergized the propagation process. The polymer molecular weight was inversely proportional to the molar ratio of [*p*-methylstyrene]/[propylene], and the terminal *p*-MS group was further metalated for preparing PP-*b*-PS diblock copolymers.

It is very desirable to extend this convenient reaction process to other polyolefin systems, especially polyethylene—another important material. However, at first glance, the application of this chemistry in the case of PE seems very doubtful since there is no dormant propagating species formed after 2,1-insertion of *p*-MS (or styrene). In the presence of ethylene, the *p*-MS (styrene) capped propagating site usually further react with ethylene and continues the propagation process.[5] However, in many ethylene/*p*-MS (or styrene) copolymerizations,[6] the catalyst activity and *p*-MS (styrene) incorporation in the copolymer are very dependent on the catalyst used. It is very possible that the low levels of catalyst activity in some systems may also relate to the sluggish *p*-MS (or styrene) capped propagating site, which slows the propagation process and opens the opportunity for reacting with hydrogen.

Results and Discussion

In this paper, we will discuss the reaction conditions that can yield a polyethylene chain with a terminal *p*-MS group (PE-t-*p*-MS). In general, the research benefited greatly from a large pool of metallocene catalysts with various active site openings that are very reactive in ethylene polymerization and that can be guided toward activity involving styrenic monomers[5,6] and chain transfer agents.[7] The combination provides the opportunity to find the proper conditions under which to direct the polymerization reaction into the selective consecutive *p*-MS and hydrogen chain transfer reaction discussed in the case of polypropylene, which results in PE polymer with a terminal *p*-MS group. Scheme 1 illustrates the ideal reaction process.

During the course of ethylene insertion, the propagating $M^+{-}C$ site (II) eventually will react with a *p*-MS unit (k_{12}) (via 2,1-insertion)[4] to form a *p*-MS capped propagating site (III) with an adjacent phenyl group interacting with metal cation.[8] The new propagating site (III) faces several possible choices, dependent on the reaction conditions. In most metallocene systems, this active site (III) is a very difficult place in which to continue the insertion of *p*-MS unit (k_{22}); however, it can react with ethylene (k_{21}) (i.e., copolymerization reaction) to continue the polymerization process or can react with hydrogen ($k_{2,\text{hydrogen}}$) to complete the chain transfer reaction. This consecutive reaction with *p*-MS

---

* To whom all correspondence should be addressed.

10.1021/ma011622n CCC: \$22.00

Scheme 1

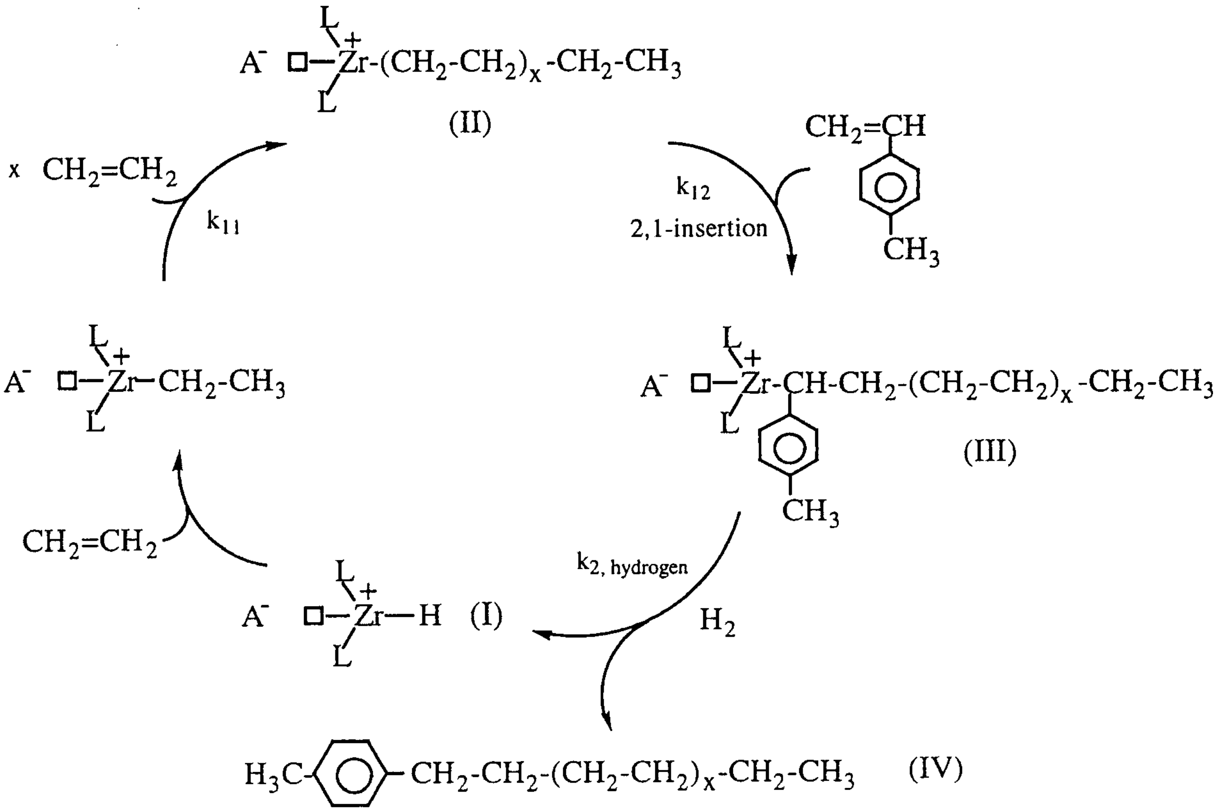


Table 1. Summary of Metallocene-Mediated Polymerization[a] in the Presence of Ethylene and *p*-Methylstyrene (*p*-MS)

run	cat.[b]	*p*-MS (mol/L)	catalyst efficiency (kg P/(mol M h))	*p*-MS in copolymer (mol %)	M_w	M_w/M_n	incorporated *p*-MS strucutres (%)		
							structure 1	structure 2	structure 3
A-1	I	1.12	1758	0	75 400	2.7			
A-2	I	1.44	1212	0	73 200	2.5			
B-1	II	1.12	885	0.71	58 900	2.4	34	20	46
B-2	II	1.44	840	0.92	40 400	2.7	30	18	52
C-1	III	0.28	1764	0.29	87 700	2.1	50	14	36
C-2	III	0.56	1803	0.55	71 300	2.4	42	15	43
C-3	III	1.12	1795	1.13	53 600	2.3	33	14	53
C-4	III	1.44	1706	1.47	30 100	2.2	34	18	48
D-1	IV	0.28	1095	0.74	133 100	2.3	100	0	0
D-2	IV	1.12	1284	3.11	105 800	2.4	100	0	0
D-3	IV	1.44	1499	3.79	89 700	2.4	95	0	5
E−1	V	0.28	1105	3.56	233 400	2.2	100	0	0
E−2	V	1.44	1776	21.34	187 900	2.3	100	0	0

[a] Catalyst = 2.5 μmol with [MAO]/[Zr] = 3000; toluene = 50 mL; ethylene pressure = 45 psi; temperature = 60 °C; reaction time = 10 min. [b] I: $Cp^*_2ZrCl_2$/MAO; II: $(n\text{-}BuCp)_2ZrCl_2$/MAO; III: Cp_2ZrCl_2/MAO; IV: $Et(Ind)_2ZrCl_2$/MAO; V: $[(C_5Me_4)SiMe_2(Nt\text{-}Bu)]TiCl_2$/MAO.

and hydrogen results in a PE-t-*p*-MS polymer chain (IV) and the regenerated Zr−H species (I) that reinitiates the polymerization of ethylene and continues the polymerization cycles. Therefore, the overall rate of polymerization is very similar to that of ethylene homopolymerization, and the polymer molecular weight is linearly proportion to the molar ratio of [ethylene]/[*p*-MS].

In addition to concerns about competing copolymerization reaction (k_{21}), the direct chain transfer reactions from the propagating chain end (II) to hydrogen ($k_{1,\mathrm{hydrogen}}$) results in a polymer chain without a terminal *p*-MS unit (discussed later). Obviously, the major task of this research is to identify the reaction conditions that can suppress both side reactions. The reaction mechanism under each reaction condition can be understood by considering the incorporated *p*-MS structures and through an end analysis that greatly benefits from the low molecular weight polymers.

Catalyst Effects. The first research objective was to focus on the catalyst systems that show favorable chain transfer reaction after incorporating a *p*-MS unit. Several control reactions (without hydrogen) were carried out to understand the normal modes of copolymerization and chain transfer reactions during the metallocene-mediated polymerization in the presence of ethylene and *p*-MS. In addition, styrene was employed to help the interpretation of the experimental results and to find the reaction trend. Tables 1 and 2 summarize the results for the *p*-MS and styrene cases, respectively. This investigation involves five metallocene/MAO systems, including three sandwiched $Cp^*_2ZrCl_2$, $(n\text{-}BuCp)_2ZrCl_2$, and Cp_2ZrCl_2, a bridged $Et(Ind)_2ZrCl_2$, and a half-sandwiched $[(C_5Me_4)SiMe_2(N^tBu)]TiCl_2$, with progressive opening at the active sites.

The polymer structure analysis (measured by NMR) focused on the incorporated *p*-MS (or styrene) units, i.e., their concentration and structures (end groups or

Table 2. Summary of Metallocene-Mediated Polymerization[a] in the Presence of Ethylene and Styrene (Sty)

run	cat.[b]	Sty (mol/L)	catalyst efficiency (kg P/(mol M h))	sty in copolymer (mol %)	M_w	M_w/M_n	incorporated Sty structures (%) structure 1	strucutre 2	structure 3
A′-1	I	1.44	1019	0	76 900				
B′-1	II	1.12	846	0.66	53 500	2.3	28	22	50
B′-2	II	1.44	743	0.83	41 300	2.4	26	24	50
C′-1	III	0.28	1797	0.22	75 500	2.5	40	21	39
C′-2	III	1.12	1860	0.88	43 600	2.3	27	25	48
C′-3	III	1.44	1797	1.25	23 300	2.1	20	26	54
D′-1	IV	0.28	1183	0.61	155 900	2.3	~100	0	0
D′-2	IV	1.12	1526	2.43	104 900	2.4	98	0	2
D′-3	IV	1.44	1469	3.30	67 600	2.1	91	0	9

[a] Catalyst = 2.5 μmol with [MAO]/[Zr] = 3000; toluene = 50 mL; ethylene pressure = 45 psi; temperature = 60 °C; reaction time = 10 min. [b] I: Cp*$_2$ZrCl$_2$/MAO; II: (n-BuCp)$_2$ZrCl$_2$/MAO; III: Cp$_2$ZrCl$_2$/MAO; IV: Et(Ind)$_2$ZrCl$_2$/MAO.

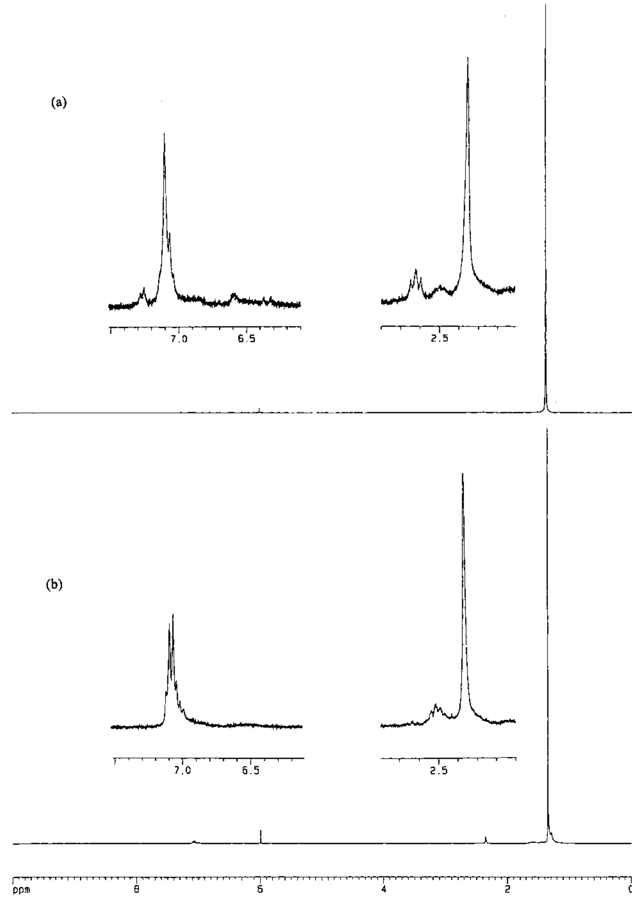


Figure 1. ^{1}H NMR spectra of two PE/p-MS samples: (a) runs C-4 and (b) D-3, prepared by Cp$_2$ZrCl$_2$ and Et(Ind)$_2$ZrCl$_2$, respectively, without hydrogen. The insets show the expanded regions (solvent: C$_2$D$_2$Cl$_4$; temperature: 110 °C).

comonomer units). It is very clear that the incorporation of p-MS (styrene) is governed by the opening of an active site. Cp*$_2$ZrCl$_2$/MAO has the most closed active site and shows no incorporation of p-MS (or styrene) at all. On the other hand, the constrained geometry [(C$_5$Me$_4$)-SiMe$_2$(N^{t}Bu)]TiCl$_2$/MAO with the most opened active site[9] exhibits very high levels of copolymerization activity between ethylene and p-MS (or styrene). Both extremes are unsuitable for the chain transfer reaction to p-MS (styrene) unit.Figure 1 compares two ^{1}H NMR spectra (with an inset of the expanded region) of samples C-4 and D-3, prepared by Cp$_2$ZrCl$_2$ and Et(Ind)$_2$-ZrCl$_2$, respectively, under similar reaction conditions. Detailed structure information was obtained by 2-D ^{1}H and ^{13}C (DEPT-135) NMR spectra. Figure 2 shows the aliphatic region of sample C-4. The concentration of the incorporated p-MS units was determined by the integrated intensity ratio between the chemical shift at 1.35 ppm, corresponding to C**H**$_2$ in ethylene units, and the chemical shifts between 7.0 and 7.3 ppm, corresponding to aromatic protons in p-MS units, and the number of protons both chemical shifts represent. The major differences are in the minor peaks at 2.37 ppm (singlet), 2.49 ppm (multiplet), 2.63 ppm (triplet), and 6.2−6.7 ppm (multiplet), corresponding to φ-C**H**$_3$, −CH$_2$−C**H**(φ)−CH$_2$−, −C**H**$_2$−φ-CH$_3$, and −C**H**=**CH**-φ. They are associated with the incorporation modes of p-MS units as illustrated in Scheme 2.

Under the current reaction condition (with ethylene and p-MS and without hydrogen), Cp$_2$ZrCl$_2$/MAO and (n-BuCp)$_2$ZrCl$_2$ are clearly the better catalyst systems to form PE having a terminal p-MS group. Up to two-thirds of the incorporated p-MS units are located at the polymer chain ends. On the other hand, Et(Ind)$_2$ZrCl$_2$ appears almost exclusively in the copolymerization mode. There is no detectable direct chain transfer reaction from the ethylene-capped propagating chain (II), which usually forms a −C**H**=**CH**$_2$ terminal group via β-hydride elimination.[10] In fact, the systematic reduction of polymer molecular weight with the increase of p-MS (or styrene) concentration (shown in Tables 1 and 2) also implies the promotion of chain transfer reactions by styrenic molecules. After incorporating the p-MS group (2,1-insertion), the active site may interact with π-electrons in the adjacent phenyl group, which slows the propagation and offers the opportunity for chain transfer reaction. It is also interesting to note the different chain transfer modes between the p-MS capped propagating site (III) and the ethylene-capped propagating chain (II). The former prefers the chain transfer reaction to MAO, instead of the β-hydride elimination usually observed in ethylene homopolymerization.Similar results were observed in the case of styrene. Compared to p-MS, styrene exhibits lower reactivity and a slightly higher percentage of the styrene terminal group. The favorable incorporation of p-MS may be due to the cationic nature of the active site. Figure 3 shows ^{1}H NMR spectra (with inset of magnified region) of samples C′-3 and D′-3, prepared by Cp$_2$ZrCl$_2$ and Et(Ind)$_2$ZrCl$_2$, respectively, under similar reaction condition. In Figure 3a, the chemical shifts at 2.35 ppm (multiplet), 2.63 ppm (triplet), and 6.2−6.7 ppm (multiplet), corresponding to −C**H**$_2$−CH=CH−φ, −C**H**$_2$−φ, and −C**H**=**CH**−φ, indicate the favorable chain transfer reactions to MAO and β-hydride elimination after incorporating styrene by Cp$_2$ZrCl$_2$/MAO catalyst. On the other hand, the dominate peak at 2.55 ppm (multiplet), corresponding to CH$_2$−C**H**(φ)−CH$_2$−, reflects the preference of the copolymerization mode in the Et(Ind)$_2$ZrCl$_2$/MAO system.

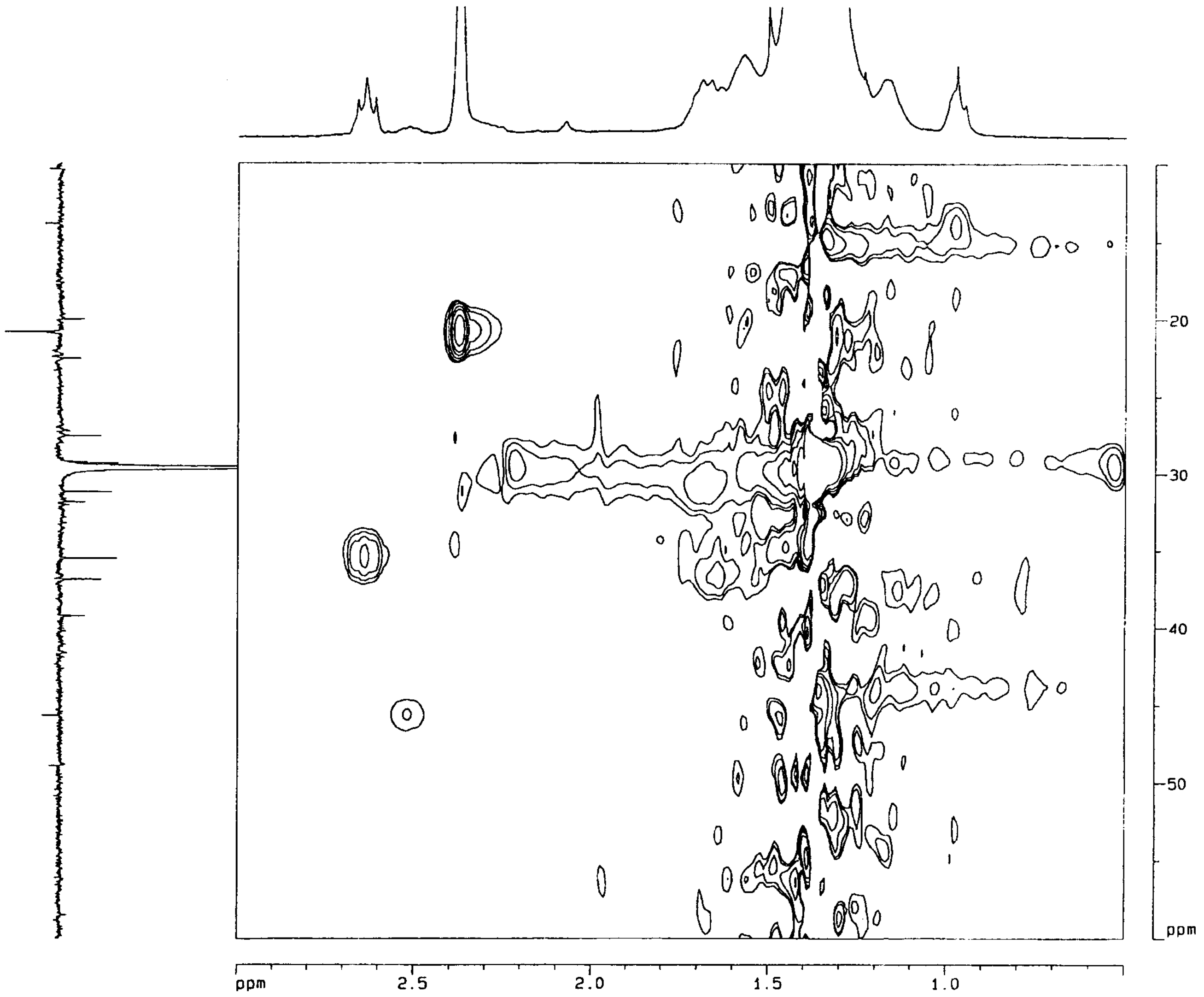
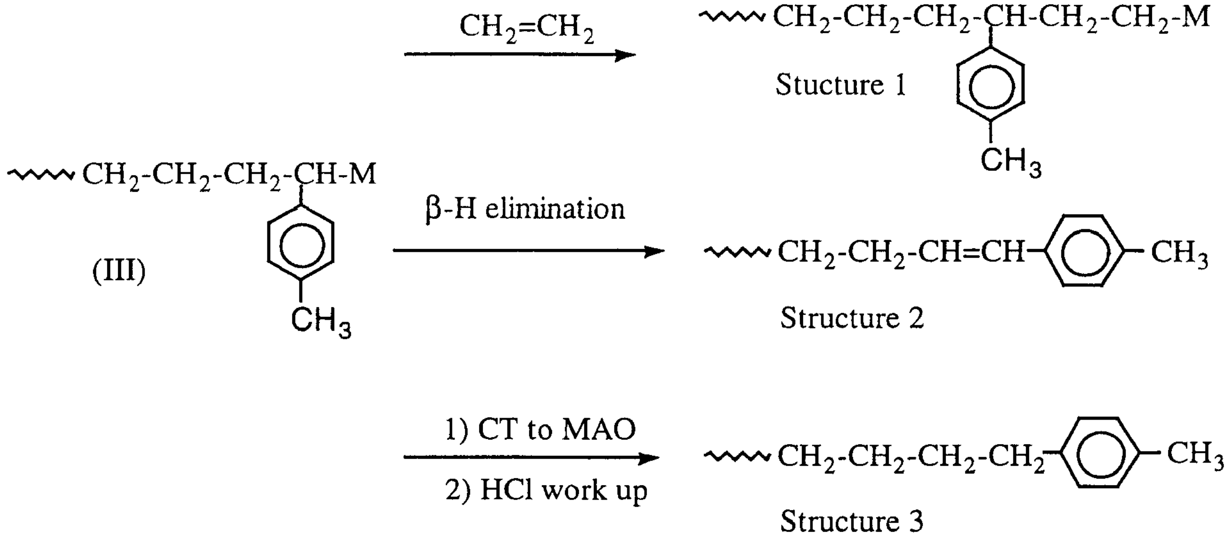


Figure 2. 2-D ^1H and ^{13}C (DEPT-135) NMR spectrum of the aliphatic region of sample C-4 (solvent: $C_2D_2Cl_4$; temperature: 110 °C).

Scheme 2



Hydrogen Effects. The presence of hydrogen should significantly increase the chain transfer reaction. The ideal case is the propagating site (III) reacting with hydrogen directly, or in other words, replacing all three reactions shown in Scheme 2. Based on the previous results,[11] both chain transfer reactions (including β-hydride elimination and chain transfer to MAO) will be diminished if a moderate amount of hydrogen is present. The copolymerization activity may also be depressed due to the favorable reaction of the propagating site (III)

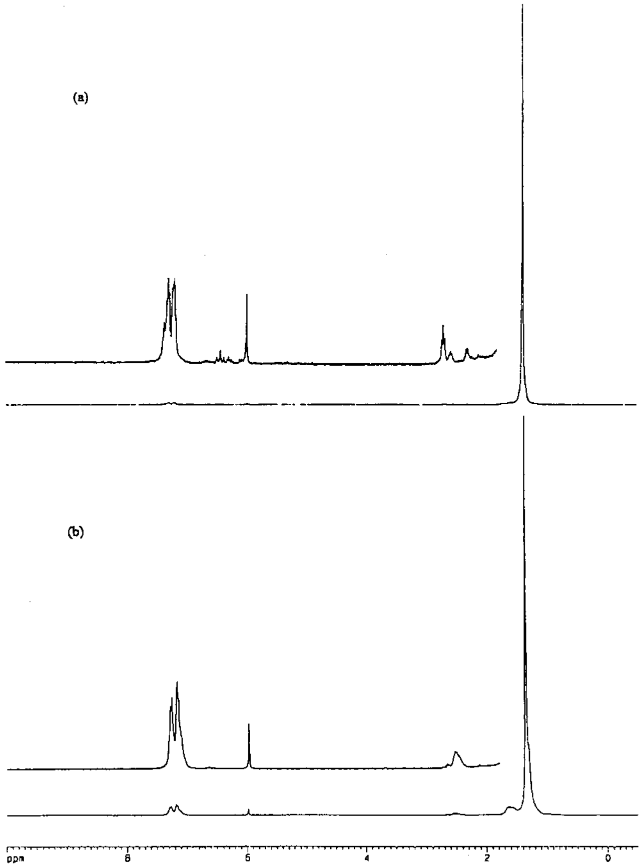


Figure 3. ^{1}H NMR spectra of two PE/styrene samples: (a) runs C′-3 and (b) D′-3, prepared by Cp_2ZrCl_2 and $Et(Ind)_2ZrCl_2$, respectively, without hydrogen. The insets show the magnified regions. (solvent: $C_2D_2Cl_4$; temperature: 110 °C).

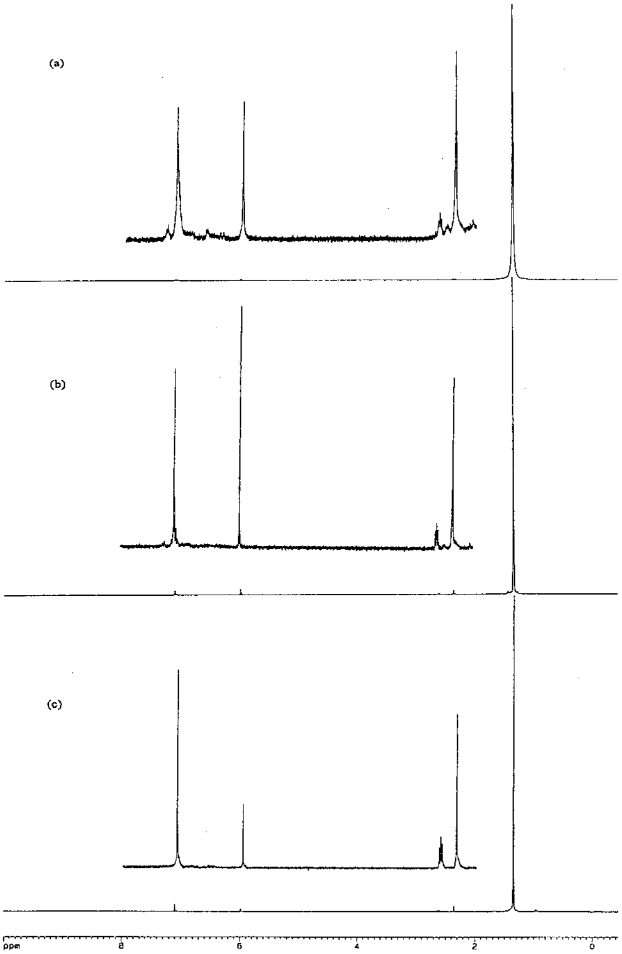


Figure 4. ^{1}H NMR spectra of three PE-t-*p*-MS samples: (a) runs C-4, (b) C-4-a, and (c) C-4-c, prepared by Cp_2ZrCl_2 with various hydrogen pressures (solvent: $C_2D_2Cl_4$; temperature: 110 °C).

with hydrogen. However, there is a real concern with the potential chain transfer reaction involving the propagating site (II) with hydrogen. Such a reaction results in a CH_3 terminal group. The extent of each reaction is governed by kinetic factors, including $k_{1,\mathrm{hydrogen}}$, $k_{1,2}$, [H_2], and [*p*-MS], as illustrated in Scheme 3.

All of these reaction paths can be quantitatively determined by NMR measurement. Figure 4 shows the ^{1}H NMR spectra of three PE-t-*p*-MS samples (runs C-4, C-4-a, and C-4-c in Table 3) prepared by Cp_2ZrCl_2/MAO catalyst under the same reaction conditions (including catalyst concentration, ethylene pressure, *p*-MS concentration, etc.), except for varying hydrogen pressures of 0, 12, and 35 psi. The comparison is focused on the incorporation modes of *p*-MS units. For detailed structure analysis, Figure 5 shows the aliphatic region of the 2-D ^{1}H and ^{13}C (DEPT-135) NMR spectra of sample C-4-c.

In the presence of hydrogen (<6 psi), the broad peak at 6.2−6.7 ppm (multiplet) corresponding to $-C\mathbf{H}{=}\mathbf{CH}-\varphi$ quickly disappears as shown in Figure 4b. The other broad peak at 2.49 ppm (multiplet), corresponding to $-CH_2-C\mathbf{H}(\varphi)-CH_2-$, gradually diminished to un-

Scheme 3

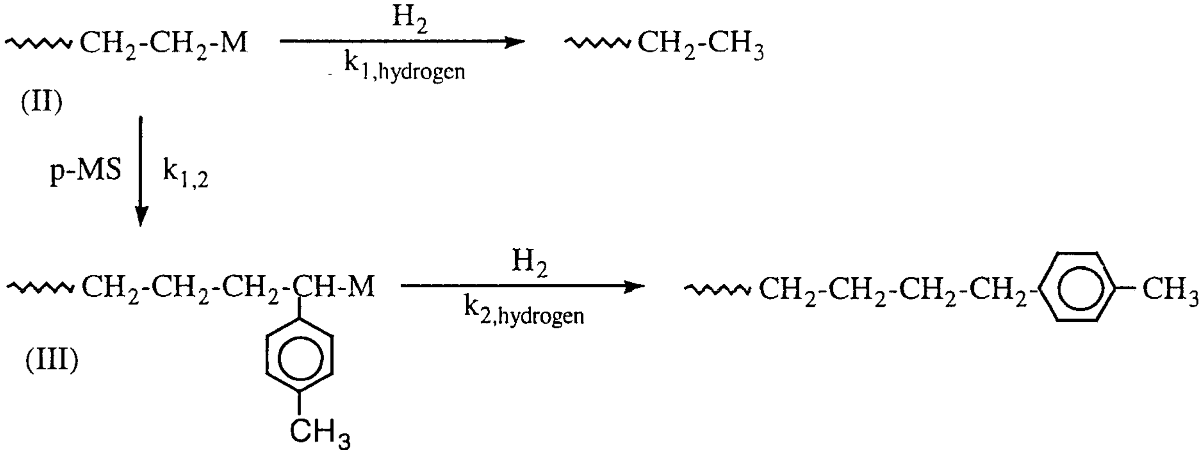


Table 3. Summary of PE-t-*p*-MS Polymers Prepared by Metallocene-Mediated Ethylene Polymerization[a] with *p*-MS and H_2

run	cat.[b]	*p*-MS (mol/L)	H_2 (psi)	cat.[c] eff	*p*-MS in polymer (mol %)	M_w	M_w/M_n	incorp *p*-MS strucutres (%) str 1	str 2	str 3	chain ends (%) $-CH_3$	$-\varphi-CH_3$
B-1	II	1.12	0	885	0.71	58 900	2.4	34	20	46		
B-1-a	II	1.12	12	903	0.74	31 500	2.4	12	0	88	58	42
B-1-b	II	1.12	20	989	0.81	13 000	2.0	0	0	100	72	28
B-2	II	1.44	0	840	0.92	40 400	2.7	30	18	52		
B-2-a	II	1.44	12	871	0.95	11 600	2.1	25	0	75	55	45
B-2-b	II	1.44	20	867	1.01	9 900	2.3	10	0	90	64	36
B-2-c	II	1.44	35	911	1.05	6 400	1.9	0	0	100	70	30
control	III	0	0	1659	0	111 300	2.6	-				
C-1	III	0.28	0	1764	0.29	87 700	2.1	50	14	36		
C-1-a	III	0.28	6	1832	0.33	69 300	2.3	8	0	92	46	54
C-1-b	III	0.28	12	1943	0.41	65 400	2.4	0	0	100	50	50
C-1-c	III	0.28	20	2008	0.47	62 700	2.4	0	0	100	60	40
C-2	III	0.56	0	1803	0.55	71 300	2.4	42	15	43		
C-2-a	III	0.56	12	1912	0.61	40 500	2.2	10	0	90	47	53
C-2-b	III	0.56	17	2013	0.72	41 300	2.2	0	0	100	50	50
C-3	III	1.12	0	1795	1.13	53 600	2.3	33	14	53		
C-3-a	III	1.12	20	1937	1.27	18 700	2.2	0	0	100	48	52
C-3-b	III	1.12	35	2123	1.38	18 300	2.4	0	0	100	54	46
C-4	III	1.44	0	1706	1.47	30 100	2.2	34	18	48		
C-4-a	III	1.44	12	1923	1.51	19 900	2.3	24	0	76	44	56
C-4-b	III	1.44	20	2155	1.53	11 300	2.3	15	0	85	48	52
C-4-c	III	1.44	35	2460	1.55	8 800	2.5	0	0	100	50	50
C-4-d	III	1.44	45	3208	1.55	8 900	2.2	0	0	100	50	50
C-4-e	III	1.44	60	3530	1.63	8 400	2.1	0	0	100	54	46
C-4-f	III	1.44	75	3821	1.67	7 800	2.3	0	0	100	64	36

[a] Catalyst = 2.5 μmol with [MAO]/[Zr] = 3000; toluene = 50 mL; ethylene pressure = 45 psi (0.309 M); temperature = 60 °C; reaction time = 10 min. [b] II: $(n\text{-BuCp})_2ZrCl_2$/MAO; III: Cp_2ZrCl_2/MAO. [c] Catalyst efficiency (kg P/(mol Zr h)).

detectable levels at hydrogen pressure >35 psi, as shown in Figure 4c. On the other hand, the peaks at 2.37 ppm (singlet) and 2.63 ppm (triplet), corresponding to $-\varphi-C\mathbf{H}_3$ and $C\mathbf{H}_2-\varphi-CH_3$, respectively, are clearly visible with only very small changes in their intensities. Overall, the results show the strong effects of hydrogen, which not only stop both β-hydride elimination and chain transfer to MAO but also alter the copolymerization mode to the chain transfer reaction with hydrogen at the propagating site (III), as illustrated in Scheme 3.It is very important to know the effect of hydrogen on the potential direct hydrogen chain transfer reaction at the ethylene-capped propagating site (II), especially under high hydrogen pressure. Such a reaction will significantly increase the mole ratio between two $-CH_2-CH_3$ and $-CH_2-\varphi-CH_3$ terminal groups. The end group analysis greatly benefited from the low molecular weight polymers. Figure 6 shows three *p*-MS-terminated PE samples, including two (runs C-4-d and C-4-f in Table 3) prepared by Cp_2ZrCl_2/MAO catalyst under 45 and 75 psi hydrogen pressures, respectively, and one (run B-2-c) prepared by $(n\text{-BuCp})_2ZrCl_2$/MAO catalyst under 35 psi of hydrogen. In Figure 6a the intensity ratio between 0.96 ppm (triplet) and 2.63 ppm (triplet) is about 3/2, indicating a 1/1 mole ratio of two $-CH_2-C\mathbf{H}_3$ and $-C\mathbf{H}_2-\varphi-CH_3$ terminal groups. Without showing structures 1 and 2 (Scheme 2), we can conclude that the polymer chain formed has an ideal molecular structure of PE-t-*p*-MS (IV) with a $-CH_2-CH_3$ group at the beginning and a $-CH_2-\varphi-CH_3$ group at the end of the polymer chain, respectively. Under moderate hydrogen pressure (35−45 psi), hydrogen does not engage in the direct chain transfer reaction at the ethylene-capped propagating site (II) but rather assists in the completion of the reaction cycle at the *p*-MS capped propagating site (III), as shown in Scheme 1.

On the other hand, with high hydrogen pressure (75 psi), the intensity ratio between 0.96 ppm (triplet) and 2.63 ppm shown in Figure 6b shifts to about 9/4. Apparently, some direct chain transfer reaction involving the ethylene-capped propagating site (II) to hydrogen did take place. Obviously, it is very important to know the level of hydrogen pressure needed in each reaction to achieve pure PE-t-*p*-MS (IV) polymer. Table 3 summarizes the experimental results using $(n\text{-BuCp})_2ZrCl_2$ and Cp_2ZrCl_2/MAO catalysts under different *p*-MS and hydrogen concentrations.

As predicted in Scheme 3, the desirable hydrogen pressure is proportional to the *p*-MS concentration. Comparing runs C-1-b, C-2-b, C-3-a, and C-4-c (with *p*-MS concentration of 0.28, 0.56, 1.12, and 1.44 M, respectively), the Cp_2ZrCl_2/MAO-mediated polymerizations require 6, 17, 20, and 35 psi hydrogen pressure, respectively, to direct the reaction mechanism to the consecutive chain transfer reaction. However, the excess hydrogen in the system (runs C-1-c, C-3-b, C-4-e, and C-4-f) caused an undesirable direct chain transfer reaction between the propagating site (II) and hydrogen. It is very interesting to study this hydrogen effect in the $(n\text{-BuCp})_2ZrCl_2$/MAO system,[12] which is known to be very sensitive to hydrogen during ethylene homopolymerization. As shown in the comparative run sets B-1 and B-2 in Table 3 (with various hydrogen pressures) and Figure 6c, the content of $-CH_2-CH_3$ is always higher than that of $-CH_2-\varphi-CH_3$. Apparently, in the $(n\text{-BuCp})_2ZrCl_2$/MAO system it is very difficult to prevent the undesirable direct chain transfer reaction between the propagating site (II) and hydrogen.

In general, both the catalyst efficiency and *p*-MS incorporation increase with greater hydrogen pressure. The formation of *p*-MS capped propagating site (III) may slow the polymerization process, especially in the Cp_2ZrCl_2/MAO system. Hydrogen is needed to complete the chain transfer reaction, which allows the active site to continue the polymerization and chain transfer cycles. The effect of hydrogen on the polymer molecular weight is very dependent on the catalyst system. As shown in the comparative run sets B-1 and B-2, a strong effect

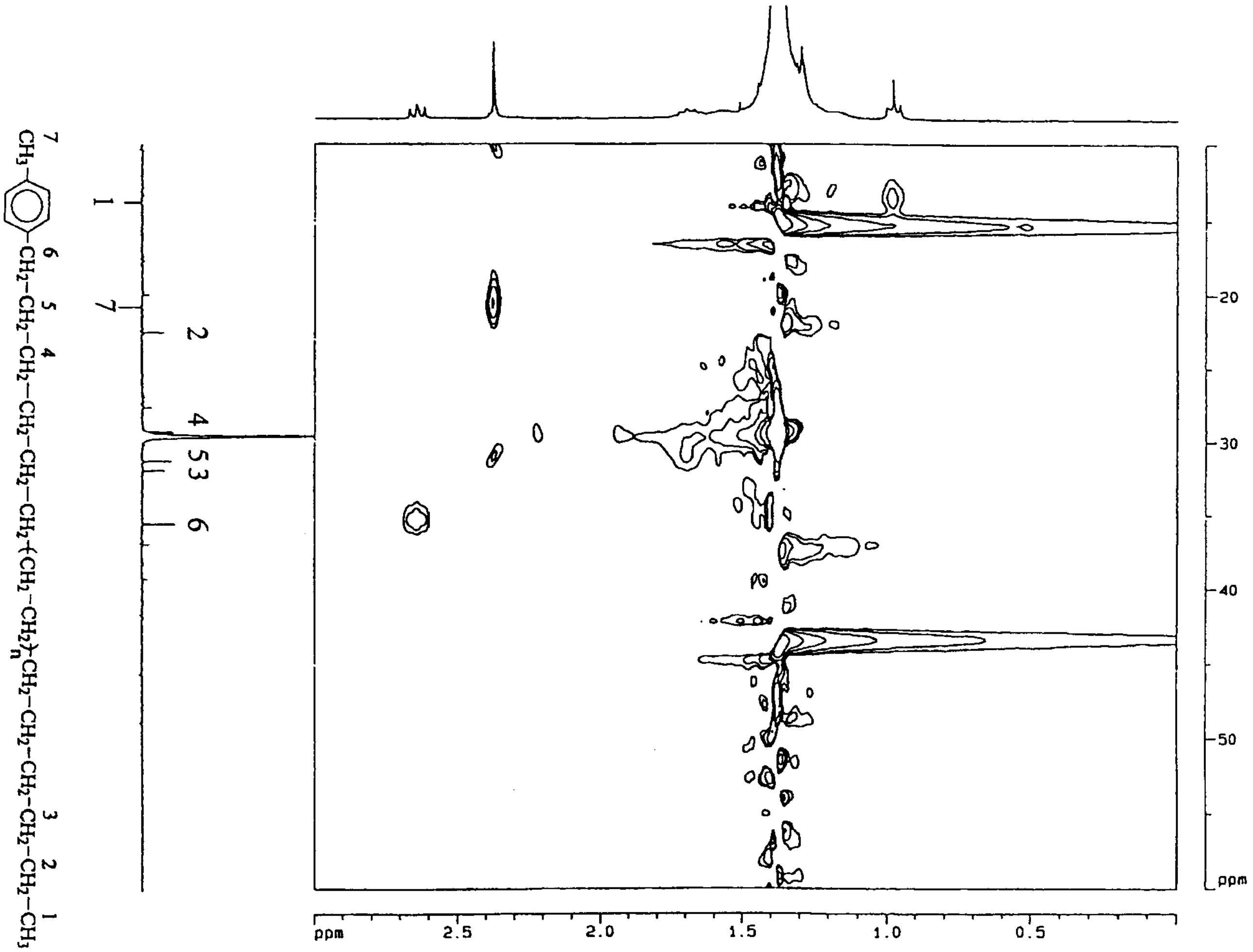


Figure 5. 2-D ^{1}H and ^{13}C (DEPT-135) NMR spectrum of the aliphatic region of PE-t-*p*-MS polymer (run C-4-c) (solvent: $C_2D_2Cl_4$; temperature: 110 °C).

was observed in the $(n\text{-BuCp})_2ZrCl_2$/MAO system—the higher the hydrogen pressure, the lower the molecular weight of the resulting polymer. Such an effect clearly reflects the existence of the direct chain transfer reaction at the propagating site (II). On the other hand, all the comparative runs in each C-1, C-2, C-3, and C-4 sets (in Table 3) show that the polymer molecular weight in the Cp_2ZrCl_2/MAO system is very much governed by *p*-MS concentration. Hydrogen has only a very small effect except in the very high concentration conditions in which the direct chain transfer reaction also occurs. Polymer with very low molecular weight (just a few thousand) has been obtained, and the molecular weight distribution is generally narrow, which is consistent with single site polymerization processes.Figure 7 shows the GPC curves of PE-t-*p*-MS polymers (control run, C-1-b, C-2-b, C-3-a, and C-4-c in Table 3) prepared by the Cp_2ZrCl_2/MAO catalyst. Figure 8 shows the plot of the polymer molecular weight (M_n) vs the mole ratio of [ethylene]/[*p*-MS]. There is a linear proportionality between the polymer molecular weight and molar ratio of [ethylene]/[*p*-MS]. It is clear that the chain transfer reaction to *p*-MS (with rate constant $k_{1,2}$) is the dominant termination process and that it competes with the propagating reaction of ethylene (with rate constant k_{11}). The degree of polymerization (X_n) follows a simple comparative equation $X_n = k_{11}[\text{ethylene}]/k_{12}[p\text{-MS}]$ with the chain transfer constant $k_{1,2}/k_{1,1} \sim 1/376$.

PE-*b*-PS Diblock Copolymers. The existence of a terminal *p*-MS unit in the PE chain is further supported by chain end functionalization and chain extension reactions, as shown in Scheme 4. The terminal *p*-MS group was selectively metalated by *sec*-BuLi/TMEDA reagent[13] and transformed to a stable polymeric anion, which serves as the reactive site for preparing the OH-terminated PE (PE-t-OH) and silane-terminated PE (PE-t-Si) and also for living anionic polymerization to prepare PE-*b*-PS diblock copolymer. The resulting PE-*b*-PS diblock copolymer was subjected to Soxhlet extraction by boiling THF to gain no detectable soluble PS homopolymer. The insoluble fraction (soluble in 1,1,2,2-tetrachloroethane at elevated temperatures) is the PE-*b*-PS diblock copolymer.

Figure 9 compares the GPC curves of the starting PE-t-*p*-MS polymer ($M_n = 27.3 \times 10^3$; $M_w/M_n = 2.4$) with two PE-*b*-PS diblock copolymers ($M_n = 52.3 \times 10^3$ and $M_n = 83.6 \times 10^3$, respectively) sampled after 1.5 and 3 h reaction time. Despite the heterogeneous reaction condition, most of the styrene monomers were incorporated into diblock copolymer within 3 h. The inset plots the polymer molecular weight vs monomer conversion during the chain extension process. The polymer linearly increased its molecular weight with the consumption of styrene monomers, an indication of living anionic polymerization process. The same hydrodynamic volume[14] increase would not be observed if the copolymer were the graft copolymers. This combination of a monochromatic increase of the copolymer molecular weight (with only a slight broadening in the molecular weight distribution) and no detectable PE homopolymer

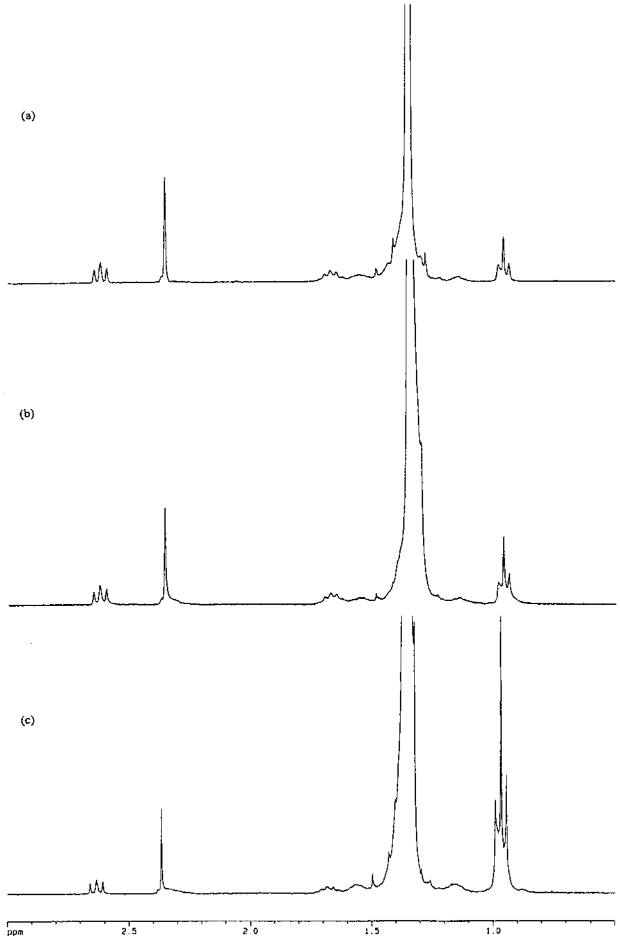


Figure 6. ^{1}H NMR spectra of three PE-t-*p*-MS samples: (a) runs C-4-d and (b) C-4-f samples prepared by Cp_2ZrCl_2/MAO catalyst and (c) run B-2-c sample prepared by $(n\text{-}BuCp)_2ZrCl_2$/MAO (solvent: $C_2D_2Cl_4$; temperature: 110 °C).

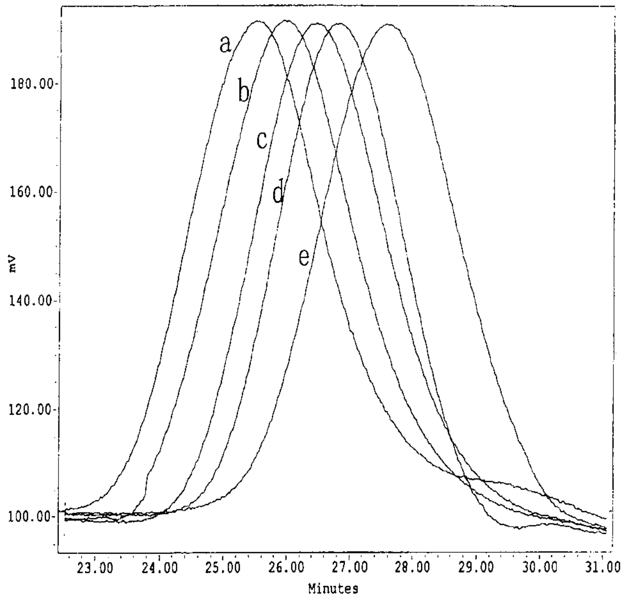


Figure 7. GPC curves of PE-t-*p*-MS polymers prepared by Cp_2ZrCl_2/MAO catalyst and various *p*-MS concentrations: (a) 0, (b) 0.28, (c) 0.56, (d) 1.12, and (e) 1.44 M (control run, C-1-b, C-2-b, C-3-a, and C-4-c in Table 3).

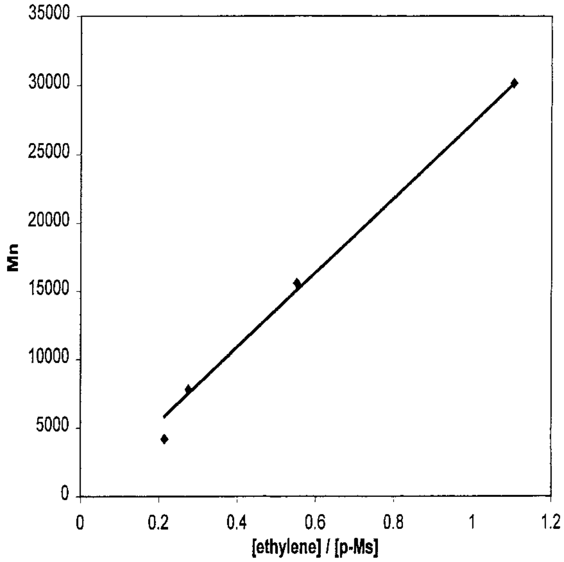


Figure 8. Plots of number-average molecular weights (M_n) of PE-t-*p*-MS polymers prepared by Cp_2ZrCl_2/MAO catalyst vs the mole ratio of [ethylene]/[*p*-MS].

clearly points to the existence of a *p*-MS group at each PE chain end.Figure 10 shows the ^{1}H NMR spectra of PE-t-OH, PE-t-Si, and PE-*b*-PS diblock copolymer. New chemical shifts at 3.65 (Figure 10a) and 0.05 ppm (Figure 10b), corresponding to $C\mathbf{H}_2{-}OH$ and $\phi{-}CH_2{-}Si(C\mathbf{H}_3)_3$, respectively, indicate the effective metalation reaction despite the heterogeneous reaction condition. Most of the terminal *p*-CH_3 groups with good mobility had to be located on the surface or in the amorphous phases and were readily accessible for the reaction. Figure 10c shows the ^{1}H NMR spectrum of a PE-*b*-PS copolymer ($M_n = 48 \times 10^3$; $M_w/M_n = 2.5$). Compared with the ^{1}H NMR spectrum of the initial PE-t-*p*-MS shown in Figure 4, three additional chemical shifts appear at 1.55, 2.0, and 6.4−7.3 ppm, corresponding to $C\mathbf{H}_2$, $C\mathbf{H}$, and aromatic protons in polystyrene. The quantitative analysis of the copolymer composition was calculated using the ratio of two integrated intensities between the aromatic protons ($\delta = 6.4{-}7.3$ ppm) in the PS block and methylene protons ($\delta = 1.35{-}1.55$ ppm) and the number of protons both chemical shifts represent. A nearly 2/1 mole ratio of [ethylene]/[styrene] in the PE-*b*-PS copolymer is consistent with the polymer molecular weight estimated by GPC measurements.

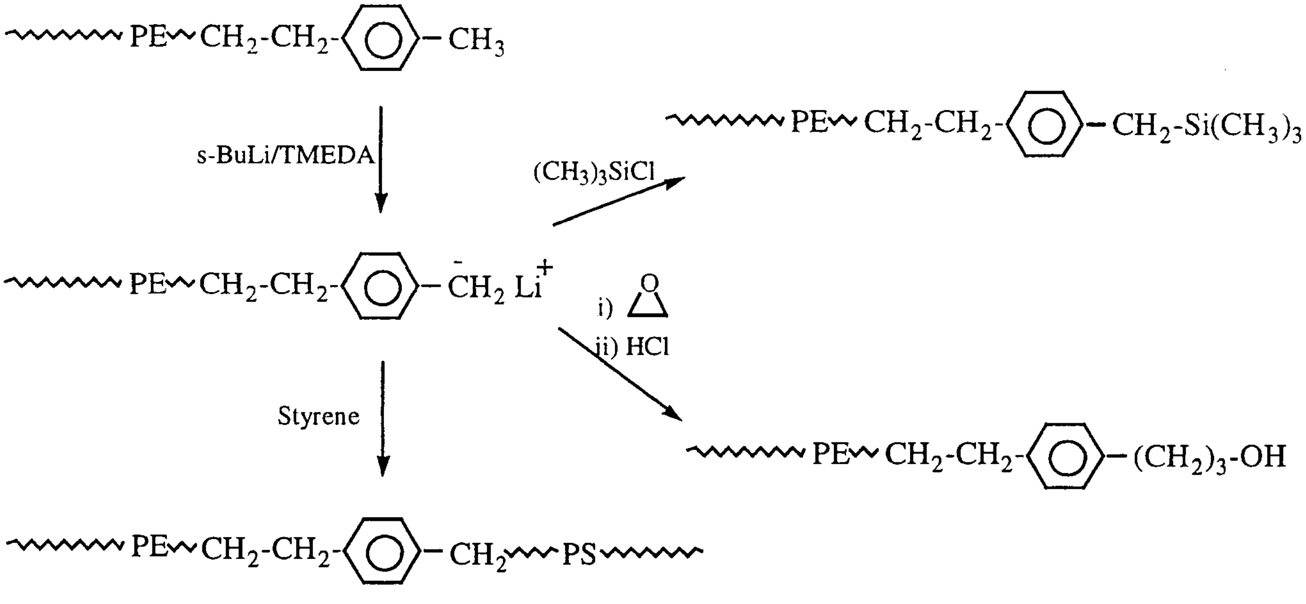
Experimental Details

Instrumentation and Materials. All ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM 300 instrument in 1,1,2,2-tetrachloroethane-d_2 at 110 °C. The molecular weight and molecular weight distribution of the polymers were determined by gel permeation chromatography (GPC) using a Waters 150 C with a refractive index (RI) detector and a set of u-Styragel HT columns of 10^6, 10^5, 10^4, and 10^3 pore size in series. The measurements were taken at 140 °C using 1,2,4-trichlorobenzene (TCB) as solvent and a mobile phase of 0.7 mL/min flow rate. Narrow molecular weight PS samples were used as standards for calibration.

All O_2- and moisture-sensitive manipulations were carried out inside an argon-filled Vacuum Atmosphere drybox. Toluene, cyclohexane, and *p*-methylstyrene (Wiley Organics) were distilled over CaH_2 under argon. High-purity grade (>99.5%) ethylene (MG Industries), methanol, *N,N,N′,N′*-tetramethyethylenediamine (TMEDA), *sec*-BuLi (Aldrich), methylaluminoxane (MAO) (Ethyl), Cp_2ZrCl_2, $Cp^*{}_2ZrCl_2$, $Et(Ind)_2ZrCl_2$ (Aldrich), $(n\text{-}BuCp)_2ZrCl_2$ (Strem), and $[(C_5Me_4)SiMe_2(N^tBu)]TiCl_2$ (Boulder Scientific) were purchased and used as received.

Chain-Transfer Reaction in Metallocene-Mediated Ethylene Polymerization. In a typical reaction (run A-1 in

Scheme 4



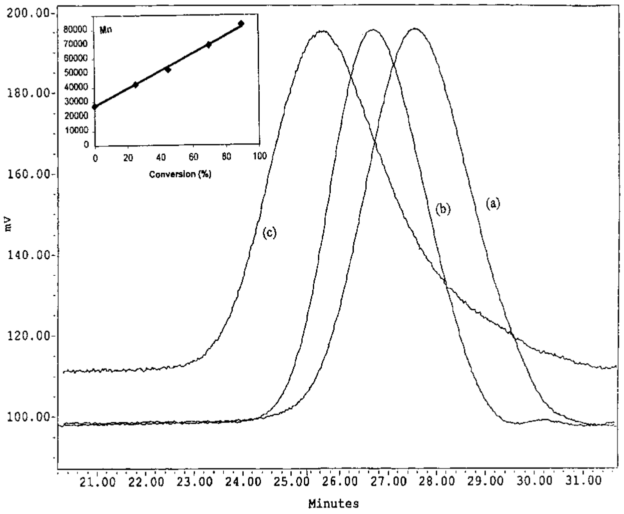


Figure 9. GPC curve comparison between (a) PE-t-*p*-MS ($M_n = 27.3 \times 10^3$ g/mol; $M_w/M_n = 2.4$) and two PE-*b*-PS diblock copolymers with (b) $M_n = 52.3.1 \times 10^3$; $M_w/M_n = 2.2$ and with (c) $M_n = 83.6 \times 10^3$ g/mol; $M_w/M_n = 2.9$ (solvent: trichlorobenzene; temperature: 135 °C). Inset: molecular weight of PE-*b*-PS vs styrene monomer conversion.

Table 1), a Parr 450 mL stainless autoclave equipped with a mechanical stirrer was charged with 50 mL of toluene and 4.5 mL of MAO (10 wt % in toluene) before purging with hydrogen (12 psi). The reactor was then injected with 1.5 g (0.28 M) of *p*-MS and charged with 45 psi (0.309 M) of ethylene to a total pressure of 57 psi at ambient temperature. About 2.5×10^{-6} mol of Cp_2ZrCl_2 in toluene solution was then syringed into the rapidly stirring solution under ethylene pressure to initiate the polymerization. Additional ethylene was fed continuously into the reactor to maintain a constant pressure (57 psi) during the course of the polymerization. To minimize mass transfer and to maintain the constant feed ratio, the reactions were carried out by rapid mixing and short reaction time. After 10 min of reaction at 60 °C, the polymer solution was quenched with methanol. The resulting PE-t-*p*-MS was washed with THF to remove excess styrene and then vacuum-dried at 50 °C. About 0.81 g of PE-t-*p*-MS polymer was obtained with a catalytic activity of 1943 kg of PE/(mol of Zr h).

Synthesis of PE-*b*-PS Diblock Copolymer. The first reaction step is a lithiation reaction of PE-t-*p*-MS polymer. In an argon-filled drybox, 5 g of PE-t-*p*-MS (sample C-1-b in Table 3) was suspended in 80 mL of cyclohexane in a 250 mL air-free flask with a magnetic stirrer bar. Next, 1 mL (1.3 mmol) of 1.3 M *sec*-BuLi solution and 0.2 mL (1.3 mmol) of TMEDA were added to the flask, and the flask was brought out of the drybox and heated to 60 °C for 4 h under N_2. The reaction was then cooled to room temperature and moved back to the drybox. The resulting lithiated PE-t-*p*-MS polymer was filtered and washed with cycohexane a few times to remove excess *sec*-BuLi and TMEDA.

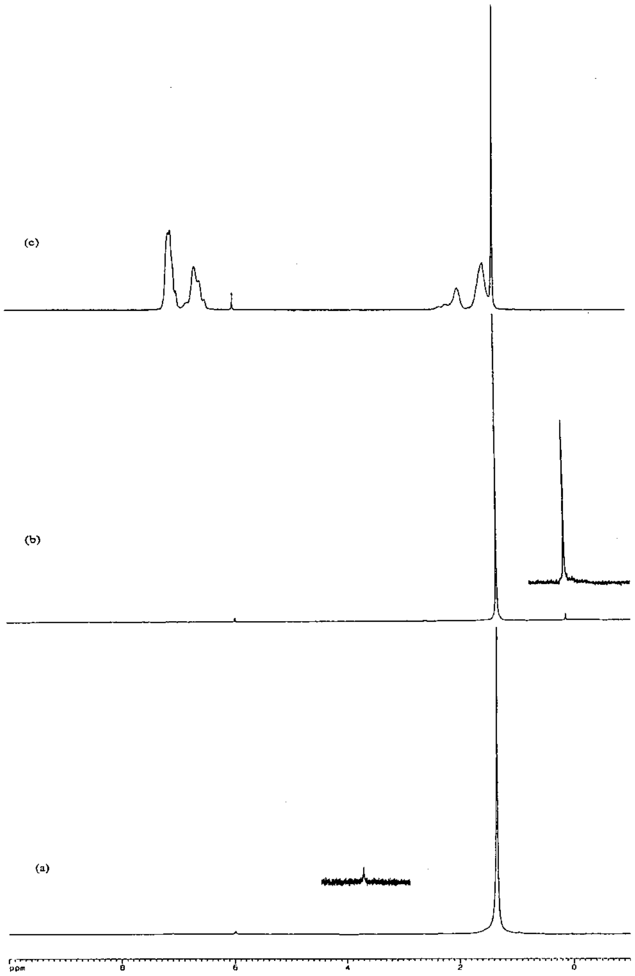


Figure 10. ^1H NMR spectra of (a) PE-t-OH, (b) PE-t-Si, and (c) PE-*b*-PS samples (solvent: $C_2D_2Cl_4$; temperature: 110 °C).

The lithiated PE-t-*p*-MS polymer (3 g) was then again suspended in 100 mL of anhydrous cyclohexane, and the anionic polymerization was carried out at ambient temperature in a slurry solution by introducing 5 mL of styrene. After 3 h, 10 mL of methanol was added to terminate the reaction. The precipitated polymer was filtered and then subjected to fractionation. A good solvent (THF) for PS side chain polymers was used in a Soxhlet apparatus under N_2 for 24 h, resulting in almost no soluble fractions. The THF-insoluble fraction was a PE-*b*-PS diblock copolymer that was completely soluble in 1,1,2,2-tetrachloroethane at elevated temperatures.

Conclusion

The systematic study of metallocene-mediated ethylene polymerization in the presence of *p*-MS (styrene), with varying catalysts and hydrogen pressures, provides the details in the reaction mechanism. Under some specific reaction conditions, with a combination of Cp_2ZrCl_2/MAO catalyst and a controlled hydrogen pressure, it is possible to direct the ethylene polymerization into a consecutive chain-transfer reaction, first to *p*-MS and then to hydrogen, to form high-purity *p*-MS-terminated polyethylene (PE-t-*p*-MS). The PE-t-*p*-MS polymer molecular weight is inversely proportional to the *p*-MS concentration. On the other hand, the terminal *p*-MS group provides an efficient route for preparing chain-end functionalized PE and PE diblock copolymers, such as PE -*b*-PS, that would be very difficult to obtain using other existing methods.

Acknowledgment. The authors thank the Office of Naval Research and the National Institute of Standards and Technology for their financial support.

References and Notes

(1) (a) Koo, K.; Marks, T. J. *J. Am. Chem. Soc.* **1998**, *120*, 4019. (b) Fu, P.-F.; Marks, T. J. *J. Am. Chem. Soc.* **1995**, *117*, 10747. (c) Koo, K.; Fu, P.-F.; Marks, T. J. *Macromolecules* **1999**, *32*, 981. (d) Ringelberg, S. N.; Meetsma, A.; Hessen, B.; Teuben, J. H. *J. Am. Chem. Soc.* **1999**, *121*, 6082. (e) Byun, D. J.; Kim, S. Y. *Macromolecules* **2000**, *33*, 1921. (f) Byun, D. J.; Shin, D. K.; Kim, S. Y. *Macromol. Rapid Commun.* **1999**, *20*, 419.

(2) (a) Xu, G.; Chung, T. C. *J. Am. Chem. Soc.* **1999**, *121*, 6763. (b) Xu, G.; Chung, T. C. *Macromolecules* **1999**, *32*, 8689.

(3) (a) Chung, T. C.; Rhubright, D. *Macromolecules* **1991**, *24*, 970. (b) Chung, T. C.; Rhubright, D.; Jiang, G. J. *Macromolecules* **1993**, *26*, 3467. (c) Chung, T. C.; Lu, H. L.; Janvikul, W. *J. Am. Chem. Soc.* **1996**, *118*, 705. (d) Chung, T. C.; Lu, H. L.; Ding, R. D. *Macromolecules* **1997**, *30*, 1272. (e) Lu, H. L.; Hong, S.; Chung, T. C. *Macromolecules* **1998**, *31*, 2028.

(4) Chung, T. C.; Dong, J. Y. *J. Am. Chem. Soc.* **2001**, *123*, 4871.

(5) (a) Stevens, J. C.; Timmers, F. J.; Wilson, J. R.; Schmidt, G. F.; Nickias, P. N.; Rosen, R. K.; Knight, G. W.; Lai, S. Y. Eur. Pat. Appl. 416,815 A2, 1991. (b) Longo, P.; Grassi, A.; Oliva, L. *Makromol. Chem.* **1990**, *191*, 2387. (c) Oliva, L.; Caporaso, L.; Pellecchia, C.; Zambelli, A. *Macromolecules* **1995**, *28*, 4665. (d) Pellecchia, C.; Pappalardo, D.; D'Arco, M.; Zambelli, A. *Macromolecules* **1996**, *29*, 1158. (e) Oliva, L.; Longo, P.; Izzo, L.; DiSerio, M. *Macromolecules* **1997**, *30*, 5616.

(6) (a) Chung, T. C.; Lu, H. L. U.S. Pat. 5,543,484, 1996. (b) Chung, T. C.; Lu, H. L. *J. Polym. Sci., Part A: Polym. Chem. Ed.* **1997**, *35*, 575. (c) Lu, H. L.; Chung, T. C. *J. Polym. Sci., Polym. Chem. Ed.* **1998**, *36*, 1017. (d) Lu, H. L.; Chung, T. C. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 2795.

(7) (a) Kaminsky, W.; Luker, H. *Makromol Chem., Rapid Commun.* **1984**, *5*, 225. (b) Chien, J. C. W.; Wang, B.-P. *J. Polym. Sci., Part A: Polym. Chem.* **1990**, *15*, 28. (c) Alameddin, N. G.; Ryan, M. F.; Eyler, J. R.; Siedle, A. R.; Richardson, D. E. *Organometallics* **1995**, *14*, 5005. (d) Richardson, D. E.; Alameddin, N. G.; Ryan, M. F.; Hayes, T.; Eyler, J. R.; Siedle, A. R. *J. Am. Chem. Soc.* **1996**, *118*, 11244.

(8) (a) Zambelli, A.; Pellecchia, C.; Oliva, L.; Longo, P.; Crassi, A. *Makromol. Chem.* **1991**, *192*, 223. (b) Zambelli, A.; Pellecchia, C.; Proto, A. *Macromol. Symp.* **1995**, *89*, 373. (c) Longo, P.; Proto, A.; Zambelli, A. *Macromol. Chem. Phys.* **1995**, *196*, 3015.

(9) Stevens, J. C. *Stud. Surf. Sci. Catal.* **1994**, *89*, 277.

(10) (a) Tsutsui, T.; Mizuno, A.; Kashiwa, N. *Polymer* **1989**, *30*, 428. (b) Soga, K.; Uozumi, T.; Nakamura, S.; Toneri, T.; Teranishi, T.; Sano, T.; Arai, T. *Macromol. Chem. Phys.* **1996**, *197*, 4237.

(11) Kokko, E.; Malmberg, A.; Lehmus, P.; Lofgren, B.; Seppala, J. V. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 376.

(12) Andersen, A.; Blom, R.; Dahl, I. M. *Macromol. Chem. Phys.* **2001**, *202*, 726.

(13) Chung, T. C.; Lu, H. L.; Ding, R. D. *Macromolecules* **1997**, *30*, 1272.

(14) Lu, B.; Chung, T. C. *Macromolecules* **1999**, *32*, 8677.

MA011622N