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Chain transfer reaction in metallocene catalyzed ethylene copolymerization with allyltrimethylsilane

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Summary

In order to investigate the polymerization behavior of allytrimethylsilane as a comonomer, ethylene was copolymerized with allyltrimethylsilane at 80°C in toluene using methylaluminoxane (MAO) activated metallocene catalysts. The catalytic activity of the polymerization strongly depended on both the type of the catalysts and the concentration of allyltrimethylsilane. End group analysis of the copolymers by means of ^{1}H and ^{13}C NMR spectroscopy revealed that allyltrimethylsilane rather act as a chain transfer agent in the copolymerization, even though considerable amount of allyltrimethylsilane was incorporated in the polymer chain with rac-Et(Ind)$_2$ZrCl$_2$ catalysts. The chain transfer reaction influence strongly the molecular weight and comonomer content of the copolymers.

Introduction

In the field of coordination polymerization of olefin monomers with heterogeneous or homogeneous catalysts, an understanding of chain transfer reactions is the basis for the control of molecular weight and chain end structure of the polymers. Two chain transfer processes, β-hydride elimination and chain transfer to aluminum, are known as major chain transfer reactions in metallocene catalyzed polymerization,[1] and it is reported that β-hydride elimination is the dominant chain transfer process during ethylene polymerization with metallocene catalysts.[2] However, we found recently that chain transfer to aluminum is the dominant chain transfer process during ethylene-allylbenzene copolymerization with rac-Et(Ind)$_2$ZrCl$_2$/MAO catalyst.[3] It describes that the chain transfer to aluminum in the copolymerization is induced by steric bulkiness of the allylbenzene units incorporated at the propagating chain end. Recently, Mark et al. reported that organosilanes function as chain transfer agents in metallocene-mediated

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polymerizations to afford sily-terminated olefin polymers.[4,5] Also, Resconi et al. reported that the attempt to polymerize allyltrimethylsilane with metallocene catalysts produced the allyltrimethylsilane oligomers due to the severe chain transfer reaction.[6,7]

In this paper, the chain transfer behavior of allyltrimethylsilane in the metallocene catalyzed ethylene polymerization was studied through the analysis of the chain end structure of the obtained polymers. If the bulky allyl monomer could act in the polymerization as a chain transfer agent for chain transfer to aluminum or β-hydride elimination, the resulting polymer would contain the functional end group, aluminum terminal group or allylsilane group. It is known that allylsilane react readily with electrophiles.[8] The reaction takes place at the γ-carbon atom with migration of the double bond and displacement of silicone from the α-carbon. Thus, the terminal allyltrimethylsilane group of the polymer can be readily converted to other functional end groups.

Experimental

Materials & Instruments

Polymerization grade ethylene was deoxygenated and dried by passing through columns of oxygen scavenging catalyst and activated molecular sieve (4Å). Metallocene catalysts obtained from Strem were used as received. MAO was purchased from Akzo as a toluene solution (11.6wt-% aluminum, density 0.89g/ml) and used without further purification. Allyltrimethylsilane was purchased from Aldrich, and was distilled over calcium hydride prior to use. Chromatography grade toluene was distilled over calcium hydride and stored under nitrogen. All manipulations were carried out with standard Schlenk and vacuum techniques under a dry nitrogen atmosphere.

Molecular weight and molecular weight distribution of the copolymers were determined by means of gel-permeation chromatography (GPC; Waters 150C) at 135°C using 1,2,4-trichlorobenzene as a solvent. The weight-average molecular weight and polydispersity (M_w and M_w/M_n, respectively) were calculated on the basis of a polystyrene standard. ^{1}H and ^{13}C NMR spectra of polymers were recorded on a Bruker AMX-500 spectrometer operating at 500MHz for proton and 125MHz for carbon spectroscopy. Samples were run as a solution in $C_2D_2Cl_4$ at 110°C.

Polymerization

Polymerizations were performed in a 100ml jacketed glass reactor. The reactor dried at 80°C *in vacuo* was charged with toluene under ethylene stream. The prescribed amounts of cocatalysts and allyltrimethylsilane were added to the reactor, then the mixture was stand for 10min at 80°C. After the toluene solution was saturated with ethylene, 2.5×10^{-6} mole of the zirconocene was injected at constant ethylene pressure (1.2bar). After the certain time of polymerization, the reaction mixture was poured into a mixture of methanol and a small amount of concentrated hydrochloric acid, and filtered. The filtered polymer was then adequately washed with plenty of methanol and dried *in vacuo* at 60°C.

Results and discussion

Table 1 compiles the copoymerization results of ethylene and allyltrimethylsilane with various metallocene catalysts. Different polymerization behavior was observed depending on the catalysts and allyltrimethylsilane concentration. While the catalytic activity of CP_2ZrCl_2 catalyst decreased as the concentration of allyltrimethylsilane increase, increase of the activity was observed with $Cp^*_2ZrCl_2$ and rac-Et(Ind)$_2$ZrCl$_2$ catalysts. This difference can be rationalized in terms of the different binding character between the catalysts and allyltrimethylsilane.[9]

Table 1 also shows the incorporation percentage of allyltrimethylsilane and molecular weight of the copolymer with various concentration of allyltrimethylsilane in the feed. The molecular weights of the copolymers obtained with Cp_2ZrCl_2 and rac-Et(Ind)$_2$ZrCl$_2$ catalysts decrease with increasing allytrimethylsilane concentration. The molecular weight change indicates that allyltrimethylsilane acts as a chain transfer agent that facilitates β-hydride elimination or chain transfer to aluminum.[10~14]

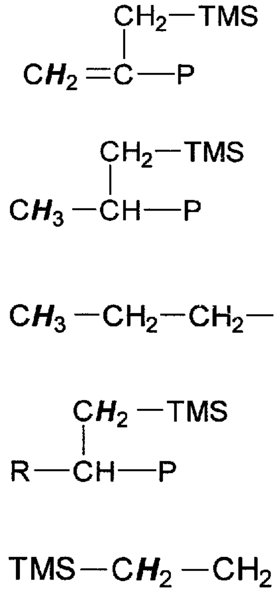
End group analysis by ^{1}H NMR reveals various end groups corresponding to the structures shown in Scheme 1. While structure 2 in Scheme 1 is produced by chain transfer to aluminum at allyltrimethylsilane chain end or by allyltrimethylsilane insertion to Zr-CH_3 complex, structure 1 is only produced by β-hydride elimination at allyltrimethylsilane chain end.

Table 1. The conditions and results of the ethylene copolymerization with allyltrimethylsilane (allylTMS)[a]

run	catalyst	allylTMS conc. (mol/L)	yield (g)	activity[b]	allylTMS in copolymer[c] (mol%)	M_w[d] (g/mol)	M_w/M_n
1	Cp_2ZrCl_2	0.0	3.15	1,050	0.0	14,000	1.9
2	Cp_2ZrCl_2	0.2	3.06	1,020	3.2	2,800	1.7
3	Cp_2ZrCl_2	0.4	2.88	960	5.1	2,100	1.5
4	Cp_2ZrCl_2	0.6	2.64	880	7.2	1,700	1.4
5	Cp_2ZrCl_2	0.8	1.83	610	9.0	1,300	1.3
6	Cp_2ZrCl_2	1.0	1.74	580	10.3	1,200	1.2
7	$Cp^*_2ZrCl_2$	0.0	0.75	250	0.0	2,000	1.5
8	$Cp^*_2ZrCl_2$	0.2	2.91	970	1.1	2,100	1.5
9	$Cp^*_2ZrCl_2$	0.4	3.54	1,180	2.3	2,000	1.4
10	$Cp^*_2ZrCl_2$	0.6	4.44	1,480	4.0	1,700	1.4
11	$Cp^*_2ZrCl_2$	0.8	5.10	1,700	6.4	2,000	1.4
12	$Cp^*_2ZrCl_2$	1.0	4.86	1,620	8.9	1,700	1.4
13	Et(Ind)$_2$ZrCl$_2$	0.0	3.99	1,330	0.0	13,000	3.1
14	Et(Ind)$_2$ZrCl$_2$	0.2	3.72	1,550	3.8	2,900	1.8
15	Et(Ind)$_2$ZrCl$_2$	0.4	5.37	1,790	7.4	2,200	1.6
16	Et(Ind)$_2$ZrCl$_2$	0.6	5.58	1,860	13.2	2,200	1.6
17	Et(Ind)$_2$ZrCl$_2$	0.8	5.88	1,960	22.2	2,100	1.6
18	Et(Ind)$_2$ZrCl$_2$	1.0	6.54	2,180	23.5	2,200	1.5

[a]Polymerization conditions: amount of catalyst = 2.5×10^{-6} mol, Al/Zr = 2000, ethylene pressure = 1.2 bar, solvent = toluene, volume of total solution = 50 ml, temperature = 80 ℃, polymerization time = 1 h. [b]Activity = kg polymer per mol Zr per h per bar, [c]Calculated by ^{1}H NMR. [d]Weight average molecular weight determined by GPC

Scheme 1. Chain end structures formed by chain transfer reaction in ethylene-allyltrimethylsilane copolymerization. The P and TMS denote a polymer chain and a trimethylsilane group, respectively.



(a). β-H elimination on allylTMS unit $\mathit{CH_2}{=}C(CH_2{-}TMS){-}P$ **1**

(b). Al-transfer on allylTMS unit & allylTMS insertion to Zr-CH_3 $\mathit{CH_3}{-}CH(CH_2{-}TMS){-}P$ **2**

(c). Ethylene insertion to Zr-H & Zr-CH_3 $\mathit{CH_3}{-}CH_2{-}CH_2{-}P$ **3**

(d). Al-transfer on allylTMS unit, and allylTMS insertion to Zr-P & Zr-CH_3 $R{-}CH(\mathit{CH_2}{-}TMS){-}P$ **4**

(e). AllylTMS insertion to Zr-H $TMS{-}\mathit{CH_2}{-}CH_2{-}P$ **5**

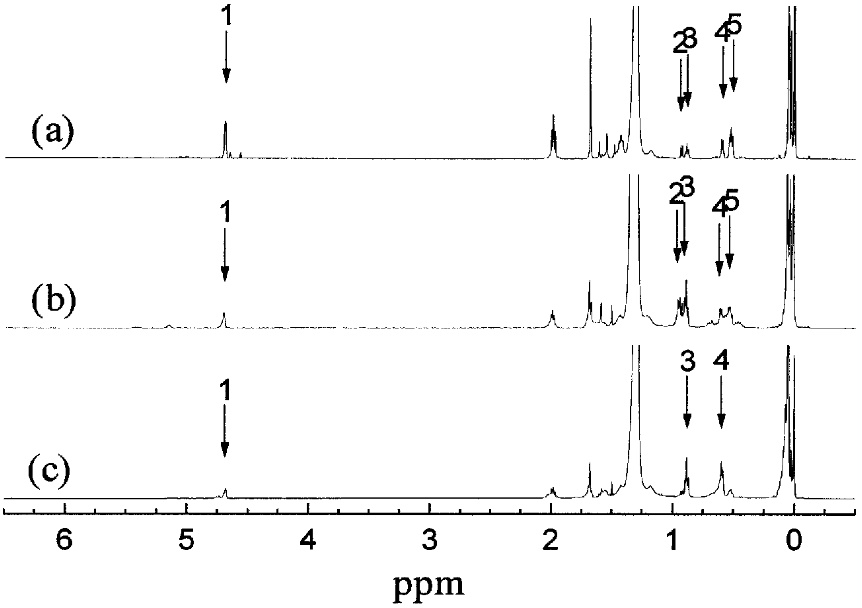


Figure 1. ^{1}H-NMR spectra of poly(ethylene-co-allyltrimethylsilane) obtained with (a): Cp_2ZrCl_2/MAO (run no. 4) (b): $Cp^*{}_2ZrCl_2$/MAO (run no. 11) (c): rac-Et(Ind)$_2$ZrCl$_2$/MAO (run no. 15). Arabic numbers denote the chain end structures in Scheme 1.

Thus, content of structure 1 and 5 increases as β-hydride elimination increases during the copolymerization. The ^{1}H NMR spectrum of the copolymer prepared with Cp_2ZrCl_2 catalyst exhibits the characteristic methylene peaks of $-CH_2-CH_2-TMS$ (structure **5**) and $-CH-CH_2-TMS$ (structure **4**) resonance at δ = 0.05ppm (triplet and doublet, respectively) and the vinylidene peaks of $CH_2=C-CH_2-TMS$ (structure **1**) resonance at δ = 4.75ppm in Figure 1(a). The ^{1}H NMR spectrum of the copolymer (Figure 1(a)) prepared with Cp_2ZrCl_2 catalyst shows that most allyltrimethylsilane units are incorporated at the chain ends, which is also consistent with the explanation that allyltrimethylsilane acts as a chain transfer agent for β-hydride elimination.

However, the polymers prepared with $Cp^*_2ZrCl_2$ catalyst don't show any dependency of molecular weight on the allyltrimethylsilane concentration (cf. Figure 2). This behavior can be explained in terms of chain transfer to aluminum at ethylene chain end which is independent of allyltrimethylsilane, and caused by the steric effect of the hindered catalyst.[3,15~17] The ^{1}H NMR spectrum of the copolymer prepared with $Cp^*_2ZrCl_2$ catalyst shows two intense peaks in methyl region (δ = 0.9ppm) and other peaks in vinylidene (δ = 4.7ppm), silylmethylene region (δ = 0.5ppm). While structure 2 and 3 in methyl region reflect the terminal structures resulting from chain transfer to aluminum, structure 1 in vinylidene region and structure 5 in silylmethylene region reflect the terminal structure resulting from β-hydride elimination. Also in the ^{13}C NMR spectra of the homo-polyethylene and copolymer obtained with $Cp^*_2ZrCl_2$ catalyst, n-butyl structure as a chain end group is readily assigned in both spectra, which indicates the chain transfer to aluminum occurred at the ethylene propagating end (cf. Figure 3). In the ^{13}C NMR spectra of the copolymer, additionally vinylidene structure as a chain end group can be assigned, which indicates β-hydride elimination occurred at allyltrimethylsilane propagating end during the copolymerization. (cf. No. 1', 2', 3' in Figure 3)

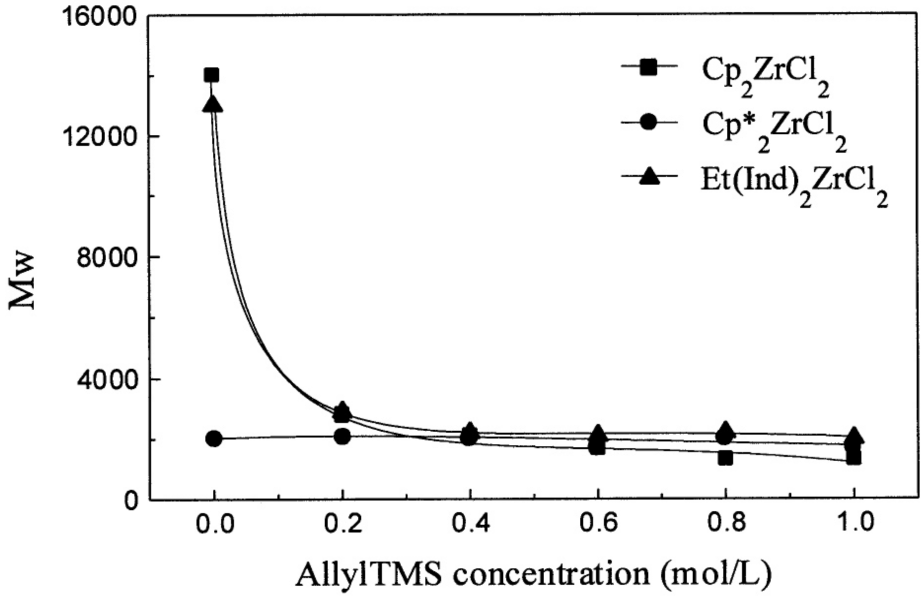


Figure 2. Dependence of the molecular weight on the allyltrimethylsilane concentration in the feed

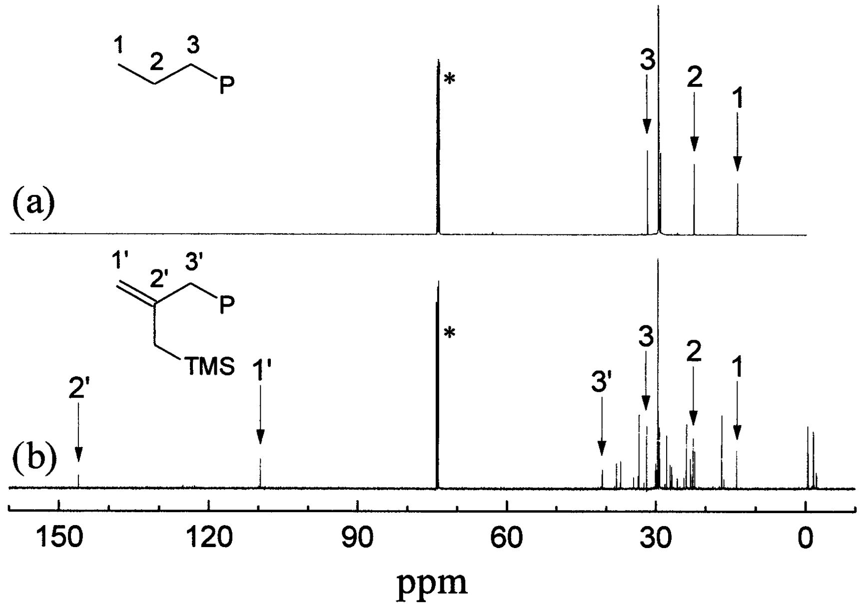


Figure 3. ^{13}C-NMR spectra of polyethylene (a), and poly(ethylene-co-allyltrimethylsilane) (b) obtained with Cp*$_2$ZrCl$_2$/MAO (run no.7 & 12). The P and TMS denote a polymer chain and a trimethylsilane group, respectively, and the asterisk denotes a solvent peak.

Both observations are consistent with the coexistence of the two chain transfer processes in the copolymerization with Cp$^*_2$ZrCl$_2$/MAO catalyst, β-hydride elimination at the allyltrimethylsilane propagating end and chain transfer to aluminum at the ethylene propagating end (cf. Figure 4).

In case of rac-Et(Ind)$_2$ZrCl$_2$ catalyst, molecular weight of copolymer shows deep decrease by using a small amount of allyltrimethylsilane. It indicates allyltrimethylsilane acts as an effective chain transfer agent for β-hydride elimination since the copolymers always show vinylidene end group that was formed by β-hydride elimination at the allyltrimethylsilane chain end. However, the molecular weight of the copolymers doesn't show any additional decrease with the higher allyltrimethylsilane concentration in spite of the high incorporation content of allyltrimethylsilane.

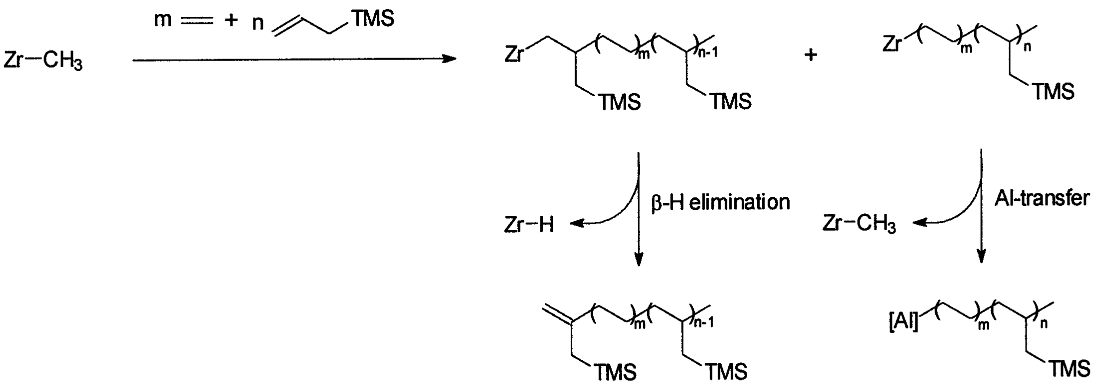
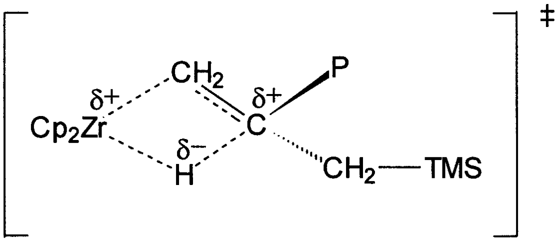


Figure 4. Chain transfer processes for ethylene-allyltrimethylsilane copolymerization with Cp*$_2$ZrCl$_2$/MAO catalyst. TMS denotes a trimethylsilane group.



Scheme 2. Proposed charge buildup for transition states of β-hydride elimination at Cp_2ZrR centers

As shown in Figure [1](c), the ^{1}H NMR spectrum of the copolymer prepared with rac-$Et(Ind)_2ZrCl_2$ catalyst displays relatively intense resonance of inserted allyltrimethylsilane unit (structure <u>4</u> in Scheme 1). The above result indicate that with rac-$Et(Ind)_2ZrCl_2$ catalyst allyltrimethylsilane acts not only as a chain transfer agent but also as a real comonomer in the copolymerization. It seems that bridged metallocene catalyst favors comonomer incorporation during the copolymerization.[12,18]

The chain transfer behavior of allyltrimethylsilane observed in this study show a contrary aspect compared with those obtained with allylbenzene in rac-$Et(Ind)_2ZrCl_2$/MAO catalyzed ethylene polymerization.[3] In the previous study, chain termination in ethylene-allylbenzene copolymerization occurred almost exclusively via chain transfer to aluminum as a result of steric interaction between the bulky allylbenzene unit at the propagating chain end and the indenyl ligand of the catalyst. The different effect of allyltrimethylsilane as a chain transfer agent can be explained by the electronic effect of silicone to the β-carbon. Burger et al. reported that the β-hydride elimination rate was quite sensitive to the nature of the substituent on the β-carbon of the catalytic propagating chain end. Their finding was consistent with a positive charge buildup in the transition state for β-hydride elimination.[19] The stabilization of the partial positive charge on the β-carbon by the silicon of trimethylsilane group promotes β-hydride elimination (cf. Scheme 2).

Thus, allyltrimethylsilane can be used a useful chain transfer agent for synthesis of allylsilane terminated polyethylene.

Conclusions

Chain transfer behavior of allyltrimethylsilane comonomer in metallocene catalyzed ethylene polymerization was studied. End group analysis of the produced polymers revealed that allyltrimethylsilane act as a chain transfer agent that facilitates β-hydride elimination rather than chain transfer to aluminum owing to electronic effect of silicone. It was also found that chain transfer reaction in the copolymerization was significantly effected depending on catalysts.

Most allyltrimethylsilane units in low molecular poly(ethylene-co-allyltrimethylsilane) produced by Cp_2ZrCl_2/MAO or $Cp^*_2ZrCl_2$/ MAO catalyst were incorporated as vinylidene terminal groups. It indicates that allyltrimethylsilane acts as an effective chain transfer agent that makes allylsilane terminated polyethylene in the case of using Cp_2ZrCl_2 and $Cp^*_2ZrCl_2$ catalysts. However, the results obtained from $Cp^*_2ZrCl_2$/MAO catalyst was consistent with the coexistence of the two chain transfer processes, β-hydride elimination at the allyltrimethylsilane chain end and chain transfer to aluminum at ethylene chain end.

On the other hand, the copolymer prepared with rac-Et(Ind)$_2$ZrCl$_2$/MAO catalyst showed that many allyltrimethylsilane units were inserted into ethylene backbone and relatively small amount of allyltrimethylsilane units were incorporated as a terminal group.

References

1. Chien JCW, Wang BP (1990) J Polym Sci Polym Chem 28: 15
2. Thorshaug K, Rytter E, Ystenes M (1997) Macromol Rapid Commun 18: 715
3. Byun DJ, Shin DK, Kim SY (1999) Macromol Rapid Commun 20: 419
4. Koo K, Marks TJ (1998) J Am Chem Soc 120: 4019
5. Koo K, Fu PF, Marks TJ (1999) Macromolecules 32: 981
6. Resconi L, Piemontesi F, Franciscono G, Abis L, Fiorani T (1992) J Am Chem Soc 114: 1025
7. Zeigler R, Resconi L, Balbontin G, Guerra G, Venditto V, De Rosa C (1994) Polymer 35: 4648
8. Carruthers W (1985) "Some modern mothods of organic synthesis", Cambridge Texts
9. Quijada R, Dupont J, Miranda MSL, Scipioni RB, Galland GB (1995) Macromol. Chem. Phys. 196: 3991
10. Michelotti M, Altomare A, Ciardelli F, Ferrani P (1996) Polymer 37: 5011
11. Bergemann C, Cropp R, Luft G (1996) J Mol Cat A. 105: 87
12. Quijada R, Dupont J, Miranda MSL, Scipioni RB, Gallend GB (1995) Macromol Chem Phys 196: 3991
13. Heiland K, Kaminsky W (1992) Makromol Chem 193: 601
14. Cruz VL, Escalona AM, Salazar JM (1998) J Polym Sci Polym Chem 36: 1157
15. Mogstad AL, Waymouth RM (1992) Macromolecules 25: 2282
16. Resconi L, Coates GW, Mogstad A, Waymouth RM (1991) J Macromol Sci Chem A28: 1225
17. Byun DJ, Shin DK, Kim SY (1999) Polym Bull 42: 301
18. Shiono T, Moriki Y, Soga K (1995) Macromol Chem Macromol Symp 97: 161
19. Burger BJ, Thompson ME, Cotter D, Bercaw JE (1990) J Am Chem Soc 112: 1566