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Copolymerization of Ethylene with Styrene Catalyzed by the [η^1:η^5-*tert*-Butyl(dimethylfluorenylsilyl)amido]methyltitanium "Cation"

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ABSTRACT: Titanocene complexes based on an amido-fluorenyl ligand bridged by a dimethylsilylene group, (η^1:η^5-$C_{13}H_8SiMe_2NCMe_3$)$TiCl_2$ (**3**) and (η^1:η^5-$C_{13}H_8SiMe_2NCMe_3$)$TiMe_2$ (**5**), have been synthesized. Reaction of **5** with 1 equiv of $[Ph_3C][B(C_6F_5)_4]$ (**2**) was almost quantitative to give the "cationic" compound $[(\eta^1:\eta^5\text{-}C_{13}H_8SiMe_2NCMe_3)TiMe]^+[B(C_6F_5)_4]^-$ (**1**), as identified on the basis of elemental analyses and spectroscopic properties. The "cation" **1** was highly active and stereoselective in the copolymerization of ethylene (E) and styrene (S), depending upon the polymerization conditions, to produce predominantly a new microstructural E−S copolymer (together with some polyethylene homopolymer) with an activity of (0.65−1.58) × 10^5 g of bulk polymer/(mol of Ti·mol of total monomers·h). As thoroughly characterized by solvent extraction, GPC, ^{13}C NMR, DSC, and DMA, the E−S copolymer obtained by catalyst **1** proved to be a perfectly alternating copolymer with well-defined isotactic polystyrene structure, together with a single glass transition ($T_g = 30$ °C) and melting temperature of 118 °C. The findings obtained by catalyst **1** suggest that the structure of the active species with the bulkier fluorenyl substituent and the following alternating site migratory insertion of comonomer in the chain propagation is responsible for the preferentially alternating, isotactic comonomer incorporation.

Introduction

The utilization of group 4 metallocene compounds as homogeneous Ziegler−Natta catalysts is well established for the polymerization of olefins[1] or styrene.[2] Compared to traditional Ziegler−Natta catalysts, the active site homogeneity and the tailorability of this new generation of catalysts markedly promotes the stereospecific homo- and copolymerization of α-olefins and offers unprecedented control over the properties of polymeric products.[1] Therefore, it is believed that the metallocene catalytic systems might promote the copolymerization of ethylene (E) and styrene (S) in which many technical problems remain unresolved with traditional Ziegler−Natta catalysts. The syntheses of E−S copolymers with tailored microstructures, prepared by using metallocene catalysts, have greatly attracted attention as new materials or important components for novel polyolefin blends and composites. Until recently, several homogeneous catalyst systems based on zirconocene and titanocene with methylaluminoxane (MAO) have been reported to copolymerize ethylene with styrene and, depending upon the catalyst performances and the polymerization conditions, to produce alternating, block, and pseudorandom ethylene−styrene copolymers.[3] Obviously, ligand modifications have played a key role in the development of new catalytic systems that control such copolymer properties as tacticity, microstructure, the level of incorporation of a comonomer, and even end use of E−S copolymers. Given the impact of ligand structure (both steric and electronic) on the microstructure of the copolymer produced, catalyst design remains an extremely active and important facet of the research in the copolymerization of styrene and ethylene.

More recently, strong interest has been generated regarding the synthesis of alternating ethylene−styrene copolymer with isotactic or syndiotactic structure by the design of new catalysts. Although this structural alternating E−S copolymer has been reported by Kakugo et al.[4a,b] by using titanium complexes with the substituted bis(phenolate) ligand 2,2′-thiobis(6-*tert*-butyl-4-methylphenol), inconsistent results on the synthesis of this kind of E−S copolymer, reported by Mulhaupt et al.[4c] by using the identical titanium complexes, have caused much controversy. It was found that the identical catalysts, composed of the titanium complexes with the substituted bis(phenolate) ligand 2,2′-thiobis(6-*tert*-butyl-4-methylphenol) and MAO, afforded only a ran-

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dom poly(ethylene-*co*-styrene) but no alternating E−S copolymer with isotactic structure. Oliva et al.[4d] reported recently the synthesis of this alternating E−S copolymer with isotacticity by using the C_s symmetric complex of isopropylidene(1-cyclopentadienyl)(9-fluorenyl)zirconium and MAO. However, both the activity of catalyst and styrene incorporation are quite low in the copolymerization of ethylene and styrene. As a matter of fact, the E−S copolymer reported by Oliva is not a perfect alternating copolymer but a mixture of alternating copolymer and E−S copolymer with a long sequence of polyethylene. To my best knowledge, little attempt has been made on the copolymerization of ethylene and styrene with the well-defined cationic metallocenium species.[3k] In this paper we synthesized a new, well-defined cationic titanocene complex **1** and reported that the title "cation" **1** is highly active and stereoselective in the copolymerization of styrene (S) and ethylene (E) to produce an alternating ethylene−styrene (E−S) copolymer with isotactic polystyrene.

Experimental Section

Materials. All operations were performed using Schlenk tube and/or glovebox techniques under a nitrogen atmosphere. Polymerization-grade ethylene and extra-pure-grade nitrogen were further purified before use by passing them through a DC-IB gas purification instrument. Toluene, hexane, diethyl ether, and tetrahydrofuran (THF) were refluxed 48 h over sodium−benzophenone and distilled before use. Monomer grade styrene was treated over Al(*i*-Bu)$_3$ and CaH$_2$, respectively, and then distilled under reduced pressure. B(C_6F_5)$_3$,[5] $Ph_3CB(C_6F_5)_4$ (**2**),[2g,6] and (*tert*-butylamino)dimethyl(9-fluorenyl)silane[7] were prepared according to literature procedures. *n*-Butyllithium, BCl_3, C_6F_5Br, Ph_3CCl, Me_2SiCl_2, $TiCl_4(THF)_2$, and fluorene were purchased from Aldrich and Fluka.

[η^1:η^5-*tert*-Butyl(dimethylfluorenylsilyl)amido]titanium Dichloride (3). To a solution of analytically pure (*tert*-butylamino)dimethyl(9-fluorenyl)silane (4.79 g, 16.2 mmol) in diethyl ether (150 mL) was added 2 equiv of *n*-butyllithium in hexane (13.0 mL of a 2.5 M solution, 32.4 mmol) at −78 °C within 30 min. Stirring the solution for 2 h at −78 °C and then 4 h at room temperature quantitatively yielded a yellow powder of the dilithium "salts" $Li_2[C_{13}H_8SiMe_2NCMe_3]$ (**4**). After removal of all of the solvents under vacuum, the resulting orange residue redissolved in toluene. To the solution of **4** in toluene was added $TiCl_4(THF)_2$ at −78 °C over a period of 1 h. After stirring for 3 h at −78 °C, the reaction mixture was gradually warmed to room temperature and stirred for an additional 48 h and then filtered. All volatitles were removed under vacuum. The solid was recrystallized from a mixture of hexane (100 mL) and toluene (50 mL) by slowly cooling to −40 °C overnight, followed by cooling to −78 °C for 24 h. After decanting off at −78 °C and washing with −78 °C hexane, the titanium complex **3** was obtained by drying in vacuo (yield 37.2%) as slightly air-sensitive, orange crystals. ^{1}H NMR (C_6D_6): δ 7.98 (d, 2H, 1-, 8-H), 7.78 (d, 2H, 4-, 5-H), 7.40 (dt, 2H, 2-, 7-H), 7.18 (dt, 2H, 3-, 6-H), 1.42 (s, 9H, $NCCH_3$), 0.53 (s, 3H, $SiCH_3$), 0.85 (s, 3H, $SiCH_3$). Anal. Calcd for $C_{19}H_{23}NSiTiCl_2$: C, 55.38; H, 5.58; N, 3.40. Found: C, 55.42; H, 5.60; N, 3.45.

[η^1:η^5-*tert*-Butyl(dimethylfluorenylsilyl)amido]dimethyltitanium (5). A solution of methylmagnesium chloride in hexane (2.5 mL of a 2.5 M solution, 6.25 mmol) was added via syringe to a solution of the titanium dichloro complex **3** (1.28 g, 3.1 mmol) in 100 mL of dry hexane at −78 °C within 30 min. After stirring for 2 h at −78 °C, the reaction mixture was gradually warmed to 0 °C and left stirring for 5 h. The solvent was removed under vacuum, leaving an orange powder. Extraction of the residue with hexane (100 mL), filtration, concentration, and crystallization at 0 °C afforded a thermal and light-sensitive orange needles of **5** with the yield of 55.1%. ^{1}H NMR (C_6D_6 at 25 °C): δ 7.97 (d, 2H, 1-, 8-H), 7.78 (d, 2H, 4-, 5-H), 7.41 (dt, 2H, 2-, 7-H), 7.20 (dt, 2H, 3-, 6-H), 1.39 (s, 9H, $NCMe_3$), 0.74 (s, 3H, $SiCH_3$), 0.95 (s, 3H, $SiCH_3$), 1.25 (s, 6H, $TiCH_3$). ^{13}C NMR (C_6D_6): δ 142.2 (C-10, -13), 135.8 (C-11, -12), 126.8 (C-3, -6), 126.5 (C-1, -8), 123.7 (C-4, -5), 122.8 (C-2, -7), 87.9 (C-9), 58.1 ($NCMe_3$), 34.8 ($NCMe_3$), 4.4 ($SiCH_3$), 2.5 ($SiCH_3$), 75.4 ($TiCH_3$). Anal. Calcd for $C_{21}H_{29}NSiTi$: C, 69.95; H, 7.81; N, 3.77. Found: C, 68.10; H, 7.92; N, 3.81.

[η^1:η^5-*tert*-Butyl(dimethylfluorenylsilyl)amido]methyltitanium Tetrakis(pentafluorophenyl)borate (1). To a solution of the compound **5** (0.37 g, 1.0 mmol) in hexane (15 mL) was added $[Ph_3C]^+[B(C_6F_5)_4]^-$ (0.92 g, 1.0 mmol) as a solid at −78 °C. After stirring for 1 h at −78 °C, the resulting suspension was gradually warmed to room temperature and stirred for 2 h. The solvent was then removed under vacuum, and the solid was washed with toluene (2 × 15 mL) and pentane (2 × 20 mL). The Ph_3CMe byproduct was obtained analytically pure from the combined mother liquor and extracts (97.5% yield). The product of this reaction was isolated as an air-sensitive yellow-mustard powder and characterized as cationic complex **1** with the yield of 96.3%. Anal. Calcd for $C_{44}H_{26}BF_{20}NSiTi$: C, 51.05; H, 2.51; N, 1.35. Found: C, 51.63; H, 2.92; N, 1.43. ^{1}H NMR (CD_2Cl_2 at 0 °C): δ 0.54 (s, 3H, $TiCH_3$), 7.82 (d, 2H, 1-, 8-H), 7.73 (d, 2H, 4-, 5-H), 7.24 (dt, 2H, 2-, 7-H), 7.02 (dt, 2H, 3-, 6-H), 1.22 (s,9H, $NCMe_3$), 0.64 (s, 3H, $SiCH_3$), 0.96 (s, 3H, $SiCH_3$). ^{13}C NMR (CD_2Cl_2 at 0 °C): δ 135.2 (C-10, -13), 128.8 (C-11, -12), 125.2 (C-3, -6), 123.5 (C-1, -8), 122.2 (C-4, -5), 120.8 (C-2, -7), 85.4 (C-9), 54.5 ($NCMe_3$), 34.2 ($NCMe_3$), 6.5 ($SiCH_3$), 2.8 ($SiCH_3$), 78.4 ($TiCH_3$). ^{13}C NMR data for C_6F_5 of $[B(C_6F_5)_4]^-$: δ 123−125 (br m, ipso-C), 135.8 (br d, *o*-C), 143.5 (br d, *m*-C), 152.0 (br d, *p*-C).

Copolymerization Procedure. In the glovebox, the copolymerization runs were performed at a given ethylene pressure (∼1 atm) in a 150 mL glass reactor equipped with a magnetic stirring bar at various polymerization temperatures in an oil bath. The reactor was attached to the high vacuum line for 2 h at 100 °C and charged under purified nitrogen sequentially with toluene, styrene, and triisobutylaluminum (TIBA) (when specified) afterward. After the inert gas was removed, the reactor was saturated with ethylene and then equilibrated at the desired reaction temperature using an external constant-temperature bath. A prescribed amount of titanium dicholoro complex **5,** activated with equimolar amounts of $Ph_3CB(C_6F_5)_4$ in toluene for 5 min at room temperature to produce in situ active species, was quickly condensed into the reactor by a syringe with rapid stirring, and then the copolymerization started at the desired temperature. The reactor was continuously fed with ethylene to keep the monomer concentration constant. After a measured time interval of 1 h, the polymerization was terminated by the addition of 150 mL of 10% HCl in methanol. The polymer was collected by filtration and washed liberally with methanol. The copolymerization products were then dried in vacuo at 60 °C for 48 h to remove solvent and monomer entrapped in the crude materials. The obtained copolymerization products were next extracted with boiling THF to give homopolymers (insoluble) and the S−E copolymers (soluble), as detailed elsewhere.[3a] The concentration of ethylene in solution at 50 °C and 1 atm was experimentally measured and found to be ∼0.11 M.

Characterization. NMR spectra were recorded on a JEOL FX-100 spectrometer. Chemical shifts for ^{1}H and ^{13}C spectra were referenced using internal solvent resonances and are reported related to tetramethylsilane. Elemental analyses were performed on a PE-2400 spectrometer. The glass transition temperature and melting temperature were determined with a Perkin-Elmer DSC-2 system at 10 °C/min. Any thermal history difference in the polymers was eliminated by first heating the specimen to above 280 °C, cooling at 20 °C/min to room temperature, and then recording the second DSC scan. Dynamic mechanical analysis (DMA) was carried out on a Rheovibron DDV-II-EA analyzer to measure the glass transition temperature of polymers. Gel-permeation chromatography (GPC) of the polymers was conducted on a Water 150C using standard PS as reference and 1,2,4-trichlorobenzene as

Table 1. Copolymerization of Ethylene and Styrene Catalyzed by Titanocene Catalysts[a]

run no.	catalyst Ti	catalyst amt, μmol	cocatalyst	Ti:B:Al mole ratios	[styrene], in the feed, mol/L	activity,[b] $\times 10^{-5}$	comp of copolym products,[c] % w/w PE	S−E	sPS	S−E copolymer[d] T_g,[e] °C	T_m,[f] °C	M_w,[g] $\times 10^{-4}$ g/mol	M_w/M_n
1[h]	**5**	15	**2**	1:1:0	2.92	0							
2[h]	**5**	15	**2**/TIBA	1:1:100	2.92	0							
3[i]	**5**	15	**2**	1:1:0	0	2.40	>99			−68	135	17.4	2.1
4[j]	**5**	15	**2**	1:1:0	0	0.48	>99						
5	**5**	15	**2**	1:1:0	5.83	0.65	3	97	nd[n]	30.5	118	6.5	2.1
6	**5**	15	**2**/TIBA	1:1:50	5.83	0.84	2	98	nd[n]	30.2	116	6.7	2.3
7	**5**	15	**2**	1:1:0	4.38	0.78	14	86	nd[n]				
8	**5**	15	**2**/TIBA	1:1:50	4.38	1.07	12	88	nd[n]	30.1	118	7.2	2.0
9	**5**	15	**2**	1:1:0	2.92	1.06	22	78	nd[n]	30.0	117	8.5	2.2
10	**5**	15	**2**/TIBA	1:1:50	2.92	1.58	24	76	nd[n]	30.2	118	8.7	2.1
11	**5**	30	**2**	1:1:0	4.38	1.06	12	88	nd[n]	30.1	118	7.8	2.1
12	**5**	15	**2**/MAO	1:1:50	4.38	0.17	20	80	nd[n]				
13	**5**	15	**2**/MAO	1:1:1	4.38	0.38	21	79	nd[n]				
14[k]	**5**	15	**2**	1:1:0	4.38	0.73	13	87	nd[n]	30.0	117	7.6	2.2
15[l]	**5**	15	**2**	1:1:0	4.38	0.75	11	89	nd[n]	30.2	118	7.8	2.2
16[m]	**5**	15	**2**	1:1:0	4.38	0							
17	**3**	8	MAO	1:0:1200	4.38	0.27	23	77	nd[n]				
18	**3**	15	MAO	1:0:1000	4.38	0.32	24	76	nd[n]	31.4	nd[n]	7.6	2.2

[a] Polymerization conditions: total volume (styrene + toluene), 30 mL; T_p, 50 °C; polymerization time (tp), 1 h; ethylene pressure, 1 atm; catalyst prepared in situ in the absence of the monomers and aged 5 min at 50 °C. [b] Activity in units of g of bulk polymer/[mol of Ti·mol of total monomers (styrene + ethylene)·h]. [c] Estimated from elemental analyses and ^{13}C NMR spectra of THF-soluble and THF-insoluble fractions. [d] THF-soluble fractions. [e] Glass transition temperature determined by dynamic mechanical analysis (DMA). [f] Melting temperature determined by differential scanning calorimetry (DSC). [g] Weight-average molar mass determined by gel permeation chromatography (GPC) vs polystyrene standard. [h] Styrene homopolymerization. [i] Ethylene homopolymerization at 20 °C. [j] Ethylene homopolymerization at 50 °C. [k] Catalyst prepared in situ in toluene at room temperature but without aging. [l] Using pure "cation" **1** as catalyst obtained by recrystallization in hexane. [m] Catalyst prepared in situ in the absence of the monomers and aged 1 h at 50 °C or 3 h at room temperature. [n] Not detected.

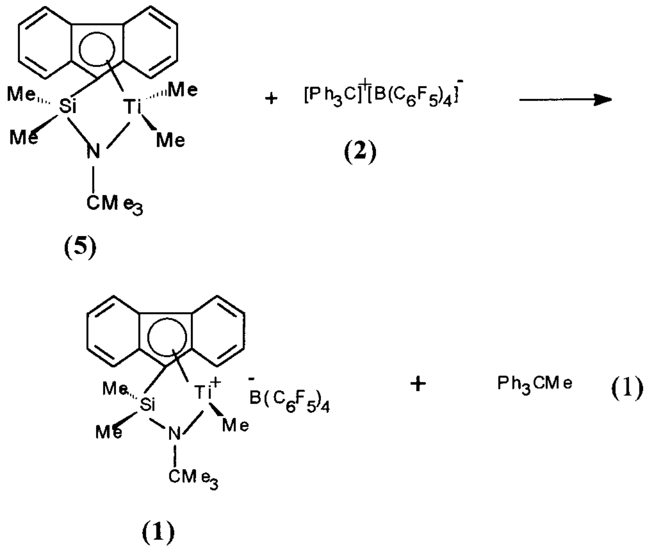
eluent at 135 °C. The molecular weights were determined by a universal calibration technique.

Result and Discussion

Synthesis of "Cationic" Complex 1. Addition of $[Ph_3C]^+[B(C_6F_5)_4]^-$ (**2**) to a hexane suspension of the compound **5** at −78 °C, followed by slowly warming to room temperature, afforded the "cationic" compound $[(\eta^1{:}\eta^5\text{-}C_{13}H_8SiMe_2NCMe_3)TiMe]^+[B(C_6F_5)_4]^-$ (**1**) as a yellow-mustard solid in almost quantitative yield (Scheme 1), as identified on the basis of elemental analyses and spectroscopic properties (see Experimental Section). As also anticipated, the ^{19}F NMR spectra of the complex **1** exhibit well-resolved, single resonances for each of the ortho, meta, and para fluorine sites, consistent with the proposed ionic formulation. The Ph_3CMe byproduct was isolated (97% yield) analytically pure from the mother liquor of this reaction. It was found that complex **1** was highly air-sensitive but thermally stable at room temperature as a solid in more than 30 min. Aging the complex **1** either as a solid or as a solution (3 h to room temperature or 1 h to 50 °C) exhibited no insolubility in hexane or aromatic solvents, as might have been expected since complex **1** appears to be unstable enough to form a stable and dark precipitate, which is unclear in its structure. Like other titanocene or zirconocene alkyl cations reported,[2g,h,3k] since $[B(C_6F_5)_4]^-$ is readily displaced, complex **1** behaves in solution as a source of the cationic species $[(\eta^1{:}\eta^5\text{-}C_{13}H_8SiMe_2NCMe_3)TiMe]^+$, which might be expected to behave as an excellent homogeneous olefin polymerization or copolymerization catalyst.

Copolymerization of Ethylene and Styrene with "Cation" 1. Copolymerization of ethylene (E) and styrene (S) was carried out under variable conditions in the presence of "cation" **1** catalyst, prepared in situ by reacting **5** with 1 equiv of **2** in the toluene. The copolymerization was quenched with methanol, and the polymer was worked up and then fractionated by THF solvent as detailed elsewhere.[3a] According to the results of the control fractionations, together with the ^{13}C NMR spectra and the molecular weight distribution (GPC) of the corresponding fractions, it was found that the THF-soluble fraction of the copolymerization products was an E−S copolymer without contamination of any homopolymer or homopolymer mixtures. The results are summarized in Table 1, while details of the polymerizations are reported in the Experimental Section.

Scheme 1



As seen from Table 1, the $\mathbf{5}/[Ph_3C]^+[B(C_6F_5)_4]^-$ catalyst system was inactive for the syndiospecific polymerization of styrene at 50 °C (runs 1 and 2). As previously demonstrated for syndiospecific styrene polymerization,[2] in addition to one η^2-coordinated styrene through both the vinylic double bond and the aromatic ring to the metal center, there is η^6 coordination of the aromatic ring of the last inserted monomer to the metal center in the chain propagation of styrene polymerization, which accounts for the formation of a benzyl-type growing chain due to 2,1 insertions.[2i] Therefore, the present findings indicate that the geometric requirement for the multihapto interactions/coordinations of styrene is not met by the titanium metal with the sterically "constrained geometry" of Flu−Si−N chelate in "cation" **1**, thus producing no styrene homopolymer. A similar result has been recently observed in the MAO-activated $Me_2Si(Me_4Cp)$(*N*-*tert*-butyl)$TiCl_2$ system.[3d] "Cation" **1** was found to have different catalytic behaviors for the ethylene homopolymerization and the copolymerization of ethylene with styrene, dependent upon the polymerization temperature. The activity of ethylene homopolymerization decreased from 2.40×10^5 at 20 °C to 0.48×10^5 g of bulk polymer/(mol of Ti·mol of ethylene·h) at 50 °C (runs 3 and 4), but in contrast, the title "cation" **1** was found to be highly active for the copolymerization of styrene with ethylene to produce predominantly an E−S copolymer at 50 °C. This suggests that the active species promoting the copolymerization result from a reaction requiring a higher temperature. It was also found that the activity of **1** was over 3 times greater than that of the **3**/MAO system under the same polymerization conditions (runs 5−10 and 17−18), although the extraction of chloride ion from **3** and methylation of the resulting complex by MAO gave the same cation with a different counteranion.[1]

As compared with MAO-cocatalyzed copolymerization of ethylene with styrene,[3] the application of reaction 1 to catalyze copolymerization was found to require higher threshold amounts of **5**, some of which was probably consumed to scavenge impurities because the cationic metallocene complexes were prone to coordination with impurities from the solvents or monomers in the polymerization system to form incatalytical complexes.[3g,h,8] Therefore, an optimum amount of extra-additional triisobutylaluminum (TIBA) may play the more important role of stabilizing the active species and extending the catalyst lifetime in order to obtain high catalytic activity and reproducible copolymerization if rigorous exclusion of air, moisture, and other impurities in the solvents and monomer feeds is not maintained. The activity of this catalytic system significantly increased when TIBA was used to scavenge monomers or solvent impurities. But the role of TIBA should not be essential, since an E−S copolymer is also obtained without using any Al compound, provided that the catalyst concentration is high enough to scavenge impurities in the polymerization medium (runs 5, 7, and 9). What is more, the use of a 2-fold concentration of the catalyst precursors (run 11) resulted in a polymer producticity and composition almost analogous to that of run 8 obtained in the presence of TIBA.

It is well-known that MAO is currently so far the most effective metallocene cocatalyst, and there is always a small but definite amount of trimethylaluminum (TMA) present along with MAO.[9] Consequently, it occurred to me that not only may MAO be used to activate the **5** but also TMA in MAO may be used to scavenge impurities in the polymerization medium. MAO was found, however, to be detrimental to the copolymerization of styrene with ethylene. The addition of a mixture of **5**, **2**, and MAO to the reactor containing monomers in toluene resulted in the significant decrease of activity; it is over 5 times less than the activity of the **5**/**2** system when the mole ratio of Ti:B:Al is 1:1:50 (run 12). The activity was also almost 2 times less than that of the **5**/**2** system even in the presence of a small amount of MAO (Ti:B:Al = 1:1:1) (run 13). It is probably related to complicated compositions and the structure of MAO oligomers that unavoidably contaminate the active species for the copolymerization catalyzed by **1**. In fact, except TMA in MAO, various structures (e.g., linear, cyclic, ladder, even three-dimensional cages with different coordinative aluminum centers analogous to that in butylaluminoxane[9]) were found to exist at the same time with MAO. These various compositions and structures controlled the formation of different active species for the copolymerization of ethylene and styrene with the MAO-cocatalyzed titanocene system[3a] and for olefin homopolymerization.[9a,10] ^1H, ^{13}C, and ^{19}F NMR showed that **5** reacted with MAO in the presence of **2** and gave a complex beyond explanation.

Table 2. Effect of Polymerization Medium and Temperature (T_p) on the Copolymerization of Ethylene and Styrene Catalyzed by "Cation" 1[a]

run no.	[styrene] in the feed, mol/L	T_p, °C	solvent	activity,[b] $\times 10^{-5}$	comp of copolym products,[c] % w/w PE	S−E	s-PS
19	2.92	0	toluene	0.51	>95		
20	2.12	25	toluene	0.72	63	37	nd[d]
21	1.73	50	toluene	1.05	20	80	nd[d]
22	1.33	75	toluene	0.67	12	63	25
23	1.10	90	toluene	0.55	10	23	67
24	4.38	50	*o*-dichlorobenzene	0.95	19	81	nd[d]
25	4.38	50	chlorobenzene	0.87	21	79	nd[d]

[a] Polymerization conditions: Ti compound **5**, 15 μmol; $[Ph_3C]^+$-$[B(C_6F_5)_4]^-$, 15 μmol; total volume (styrene + toluene), 27 mL; ethylene pressure, 1−1.2 atm depending on T_p; tp, 1 h. [b] Activity in units of g of bulk polymer/[mol of Ti·mol of total monomers (styrene + ethylene)·h]. [c] Estimated from elemental analyses and ^{13}C NMR spectra of THF-soluble and THF-insoluble fractions. [d] Not detected.

Run 14 was initiated by injecting simultaneously solutions of the catalyst precursors into the reactor containing the solution of the monomers, while run 15 was initiated by the pure "cation" **1** obtained by recrystallization in hexane. It can be seen that, combined with the results already discussed above, the activity of the copolymerization and the composition of copolymerization products were independent of the treatment of the catalyst precursors. These findings suggest that "cation" **1** can be formed in situ after the introduction of equimolar amounts of the catalyst precursors, thus immediately initiating the copolymerization. However, it is notable that the catalyst prepared in situ in the absence of the monomers, aged 3 h at room temperature or aged 1 h at 50 °C, shows no catalytic activity, probably due to its thermal stability, as explained before.

The compositions of the copolymerization products were also strongly dependent on the feed composition: in particular, the E−S copolymer fraction increased with increasing concentration of styrene. However, the E−S copolymer composition is independent of the feed ratio (vide infra). Similar behavior has been recently observed by Pellecchia[3k] in the $Cp^*Ti(CH_2Ph)_3/B(C_6F_5)_3$ catalytic system. It was found that the polymerization activity was greatly reduced with increasing styrene concentration. As can be also seen in Table 1, the weight-average molar mass (M_w) decreased with increasing styrene concentration from 174 000 g/mol for polyethylene to 65 000 g/mol, possibly attributable to a slower rate of polymerization for the styrene monomer, as it also lowers polymerization activity (*vide ante*). It must be pointed out that the styrene strongly coordinated the catalytic species and its insertion is slow due to its more nucleophilic character and the steric hindrance. Therefore, the catalytic species takes a longer time to coordinate with styrene at higher styrene concentrations, possibly conducive to the coordination−insertion of styrene, and so at a higher S:E ratio in the feed ranging from 29:1 to 58:1 or more it offset the difference of the rate of the coordination−insertion into the metal−polymer bond between two monomers. As a result, it makes sure that the last inserted ethylene monomer unit will be followed by subsequent styrene insertion, and a perfect alternating E−S coplymer can be formed.

Runs 19−23 in Table 2 were performed at increasing temperature in toluene with ethylene at atmospheric pressure and decreasing styrene concentrations to keep the feed composition approximately constant. The polymerization temperature controlled the compositions of the copolymerization products. Little, if any, of the E−S copolymer was obtained at 0 °C, and the amount of E−S copolymer has a maximum value near 50 °C. The ethylene homopolymerization became more and more significant at temperatures below 25 °C, while the syndiospecific polymerization of styrene became favored at temperatures above 75 °C although the styrene homopolymerization did not occur at temperatures below 70 °C. It is because the catalyst system can be decomposed into a third complex. The NMR study indicated that, as expected, there occurred a decomposition reaction in the catalyst system examined when the temperature rose to over 70 °C. The ESR study detected a Ti(III) complex present along with the catalyst system at 75 °C.[11] The Ti(III) complex may promote styrene polymerization, as also suggested in other catalyst systems.[2e,g,h] These results provide further evidence that the active species for the formation of PE, sPS, and S−E copolymer are quite different.[3a,c,k]

The effect of polymerization medium has been tested by substituting *o*-dichlorobenzene ($\epsilon = 9.93$), and chlorobenzene ($\epsilon = 5.62$) for toluene ($\epsilon = 2.38$) (runs 21, 24, and 25 in Table 2). It is notable that the electron-withdrawing substituents on the aromatic solvent ring have an effect on the activity of the cationic complex and the composition of copolymerization products, although the $B(C_6F_5)_4^-$ counterion is uncoordinative. This observation is different from that observed previously in the syndiospecific styrene polymerization.[2g,h] For the syndiospecific polymerization of styrene, the catalytic activity of the catalytic system with this uncoordinative counterion, $B(C_6F_5)_4^-$, was not elevated by using a medium of high dielectric constant, in which the dissociation of the ion couple with the coordinative counterion may be facilitated to form catalytically cationic species.

Characterization and Microstructure of the E−S Copolymer. The copolymerization products, obtained by "cation" **1** in various conditions (runs 5−16 and 20−25), are analyzed by ^{13}C NMR. The spectra of all samples show the same resonances, but with different relative abundances at δ 29.9 ppm. The aliphatic region of the ^{13}C NMR spectrum of sample 7 is displayed in Figure 1a as an example. According to the literature,[3] the resonances observed are diagnostic of the presence of long methylene sequences (EEE) and S−E sequences.

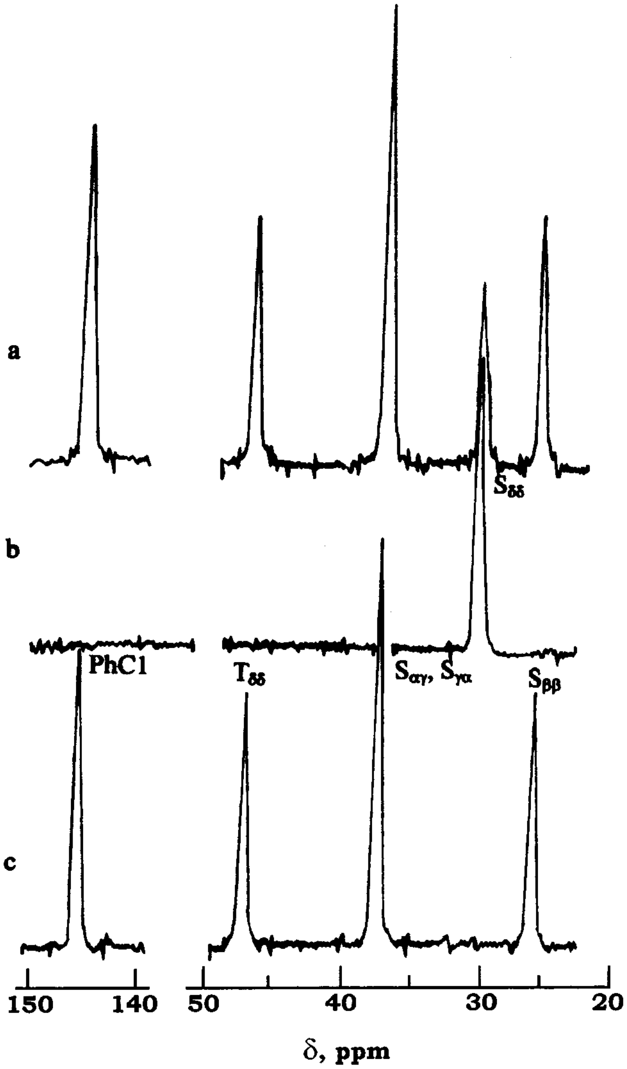


Figure 1. ^{13}C NMR spectra of ethylene−styrene copolymerization products obtained by using [η^1:η^5-*tert*-butyl(dimethylfluorenylsilyl)amido]methyltitanium "cation" **1** (sample 7): (a) E−S copolymerization product; (b) THF-insoluble fraction; (c) THF-soluble fraction.

Samples were fractionated with boiling THF. The THF-insoluble fraction and the THF-soluble fraction were characterized by ^{13}C NMR, as shown in Figure 1b,c as an example. In the ^{13}C NMR spectrum of the THF-insoluble fraction (Figure 1b), only one peak could be found at δ 29.9 ppm, which was assigned to the $S_{\delta\delta}$ carbon in the ethylene sequence of polyethylene, indicating that the THF-insoluble fraction is polyethylene homopolymer. However, the ^{13}C NMR spectrum of the THF-soluble fraction was quite different from that of the THF-insoluble fraction (Figure 1c), indicating that THF-soluble fraction was an E−S copolymer without contamination of any homopolymer. Three resonances centered at δ 45.4, 36.6, and 25.2 ppm are assigned, respectively, to the $T_{\delta\delta}$, $S_{\alpha\gamma}$, and $S_{\beta\beta}$ carbons of an E−S copolymer according to the improved Grant and Paul empirical method through calculated chemical shifts.[12] All these patterns of resonances are diagnostic of an E−S coplymer containing SES and ESE sequences. It is notable that the three resonances attributed to $T_{\delta\delta}$, $S_{\alpha\gamma}$, and $S_{\beta\beta}$ carbons were observed with a peak intensity ratio of 1:2:1. This indicates clearly that styrene units and ethylene units are incorporated alternately in the

Table 3. Relative Abundance of the Backbone Carbons in the E−S Copolymer Fractions Obtained by "Cation" 1 in Various Polymerization Conditions

δ, ppm from TMS	carbon[a]	sequence	area of the resonances[b]							
			sample 5	sample 7	sample 8	sample 9	sample 13	sample 14	sample 15	sample 25
25.2	$S_{\beta\beta}$	SES	25.0	25.2	24.9	25.1	25.8	24.9	25.0	24.7
36.6	$S_{\alpha\gamma}$	SES	50.0	49.8	50.0	49.9	49.5	50.0	49.8	50.0
45.4	$T_{\delta\delta}$	ESE	25.0	25.0	25.1	25.0	24.7	25.1	25.2	25.3

[a] S = secondary carbon; T = tertiary carbon; the Greak letter indicates the nearest tertiary carbon. [b] The areas are normalized to unity.

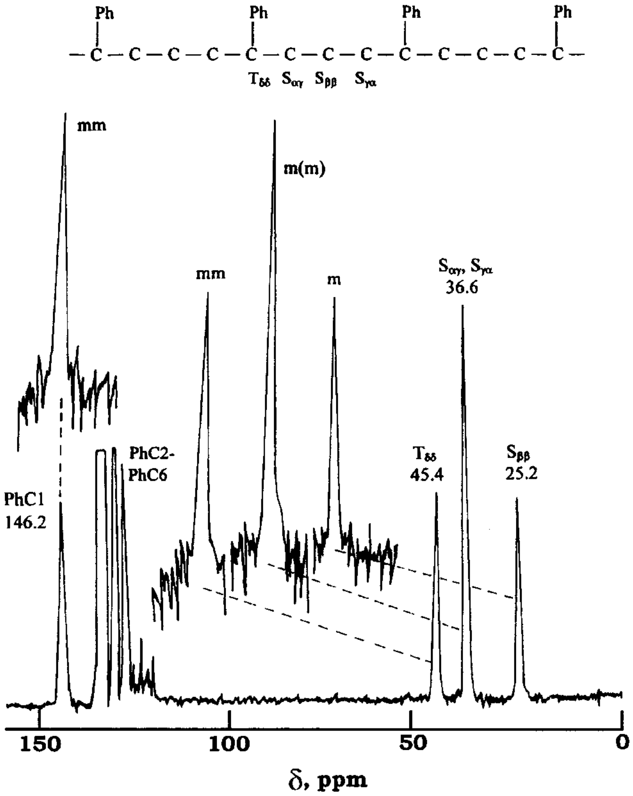


Figure 2. ^{13}C NMR spectra of ethylene−styrene copolymer (THF-soluble) obtained by "cation" **1** catalyst (sample 5 or 7).

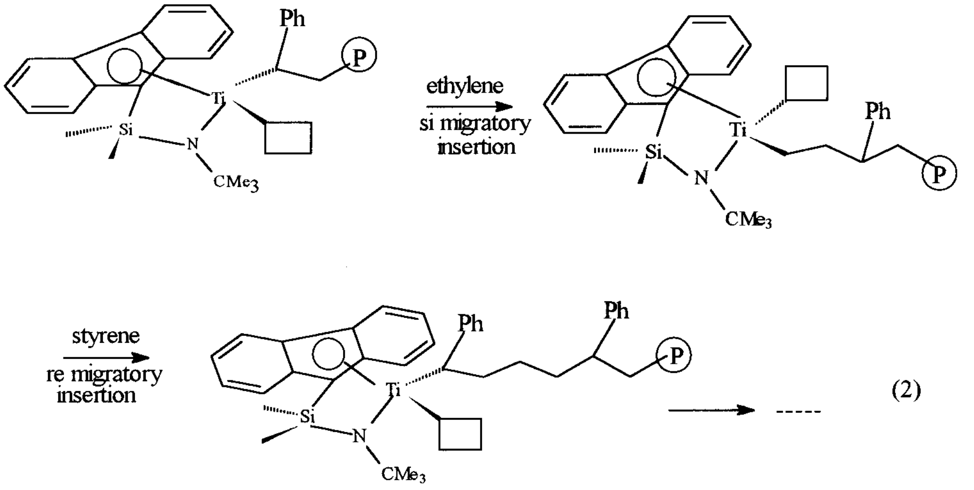
polymer sequence. From these findings, the peak at δ 146.2 ppm can be assigned to the *ipso* carbon of the phenyl group (PhC1) attached to the $T_{\delta\delta}$ carbon.

The microstructure and composition of E−S copolymers (THF-soluble fractions) were found to be independent of the feed composition, reaction temperature, extra-additional TIBA, and even additional MAO, although these reaction conditions had an important effect on the catalytic activity of copolymerization and the composition of the copolymerization products, as already discussed (vide ante). As shown in Table 3, ^{13}C NMR analyses of the THF-soluble fractions showed little change in the peak intensity ratio and/or the composition of the E−S copolymer, all having almost the same alternating structure: e.g., the relative abundance of the $S_{\beta\beta}$ carbons is close to 25%, while the mole fraction of styrene in the copolymers is about 0.50. These findings indicate that "cation" **1** is apparently more prone to incorporate styrene to form the alternating E−S copolymer under given polymerization conditions, as shown in Table 1.

As shown in Figure 1c, the ^{13}C NMR spectra of the THF-soluble fractions of samples obtained are similar to those of the poly(ethylene-*alt*-styrene) synthesized by Suzuki et al.[13] by hydrogenating 1,4-poly(1-phenylbutadiene) or 1,4-poly(2-phenylbutadiene). But the present E−S alternating copolymers have a unique stereochemical placement of the phenyl substituents without the splittings, due to tacticity effects, of the ^{13}C NMR resonances of the $T_{\delta\delta}$, $S_{\alpha\gamma}$, and $S_{\beta\beta}$ backbone and phenyl *ipso* carbons (Figure 2), thus significantly different from that of the poly(ethylene-*alt*-styrene), all being substantially atactic, synthesized by Suzuki et al.[13] and by Pellecchia et al.[3k] Therefore, the E−S alternating copolymer obtained by **1** is proposed to be an isotactic structure on the basis of the coincidence with those of the diad (m) and triad (mm) assignments.[13] The present copolymer is also significantly different from those obtained in the presence of catalysts based on either zirconocenes or monocyclopentadienyltitanium derivatives.[3a−j,4c] As a matter of fact, the E−S copolymer obtained by "cation" **1** is not similar to that obtained by the Et(Ind)$_2$ZrCl$_2$/MAO or (*i*-Pr[Cp][Flu]ZrCl$_2$/MAO catalytic system,[4d] although the latter is a crystalline alternating E−S copolymer with the minor incorporation of styrene and a long sequence of polyethylene. The properties of the alternating E−S copolymer with isotactic structure are different from those of other S−E copolymers reported.[3] It was found that the melting point of the present E−S copolymer was about 118 °C, and the glass transition temperature (T_g) was about 30 °C, dependent upon the polymerization conditions, according to the analytical results from DSC and DMA, respectively. The T_m and T_g of the present E−S copolymer are lower than those of the E−S copolymer obtained by Oliva.[4d] It is believed that the E−S copolymer obtained by Oliva shows some properties similar to those of the polyethylene homopolymer due to its having a long sequence of polyethylene segments with only a minor amount of styrene.

From the ^{13}C NMR of the present S−E copolymer (Figure 2) it can be seen that the regiospecificity of styrene insertion is higher than for another system, as evidenced by almost no abundance of the $S_{\alpha\beta}$ carbons assigned to tail-to-tail enchainments in the E−S copolymer. It is evident that, as shown in Figure 2, in the copolymerization as in the previously described E−S copolymerization,[3,4] the regioregular insertion of the styrene into the M−St··· bond is forbidden. As previously described in the literature,[3,14] the benzyl-type growing chain end obtaining from 2,1 insertion of styrene is weakly bound to the electron-deficient metal center by η^n coordination of the aromatic ring. As a result, a following styrene insertion seems to be impossible to form polystyrene homopolymer due to the steric hindrance of active species of cation **1**. However, the bonding mode of the last inserted monomer unit in the active species, which affects the competitive monomer coordination, becomes favored for the alternate incorporation of two monomers, taking into account steric hindrance and the electronic effect in the initiation step or the chain-propagating active species in the copolymerization of ethylene and styrene.[3k,4d] To form the

Scheme 2



alternating copolymer with isotactic stereostructure by "cation" **1**, the possible chain propagation of alternating site migratory insertion of comonomer (Scheme 2) is responsible for the predominant m diad and mm triad distribution in the resulting copolymer. On the basis of the stereocontrol mechanism proposed in the literature[15] for the syndiospecific propylene homopolymerization, my hypothesis is that, in the sterically geometry-contrained complex **1**, repulsive interactions between the aromatic ring on the prochiral face of the incoming styrene and the bulkier substituents on the C_5 ring reinforce the prochiral monomer orientation, which leads to the formation of isotactic polymer. That is to say, in the strictly alternating copolymerization, the prochiral styrene is coordinated and inserted to its re-face side of the cation **1** complex and, as a consequence, has the same enantiofacial orientation, while the ethylene monomer is coordinate-inserted to its other side (si-face), as shown in Scheme 2.

Conclusion

Titanocene complexes based on an amido-fluorenyl ligand bridged by a dimethylsilylene group, $(\eta^1{:}\eta^5\text{-}C_{13}H_8SiMe_2NCMe_3)TiCl_2$ (**3**) and $(\eta^1{:}\eta^5\text{-}C_{13}H_8SiMe_2NCMe_3)TiMe_2$ (**5**), have been synthesized in good yield. Reaction of **5** with 1 equiv of $[Ph_3C][B(C_6F_5)_4]$ (**2**) affords a "cationic" compound $[(\eta^1{:}\eta^5\text{-}C_{13}H_8SiMe_2NCMe_3)TiMe]^+[B(C_6F_5)_4]^-$ (**1**) in almost quantitative yield, as identified on the basis of elemental analyses and spectroscopic properties. "Cation" **1** was found to be highly active and stereoselective in the copolymerization of ethylene (E) and styrene (S), which produces predominantly a new microstructural E−S copolymer without contamination of any homopolymer or homopolymer mixtures, as thoroughly characterized by solvent extraction, GPC, ^{13}C NMR, DSC, and DMA. The present S−E copolymer obtained by catalyst **1** has a unique stereochemical placement of the phenyl substituents without the splittings, due to tacticity effects, of the ^{13}C NMR resonances of the $T_{\delta\delta}$, $S_{\alpha\gamma}$, and $S_{\beta\beta}$ backbone and phenyl ipso carbons. And the copolymer was proposed to be a perfectly alternating copolymer with well-defined isotactic structure, significantly different from those of the styrene−ethylene copolymer as reported elsewhere.[3] The alternate incorporation of two monomers in the active species relates directly to the bonding mode of the last inserted monomer unit, taking into account steric hindrance and the electronic effect in the initiation step or the chain propagating active species. As to the stereostructure of the E−S copolymer, it is believed that, in the strictly alternating copolymerization in the geometry-constrained "cation" **1** catalytic system, the prochiral styrene is coordinated and inserted to its re-face side of the cation **1** complex and, as a consequence, has the same enantiofacial orientation to give isotactic polymer, while the ethylene monomer is coordinate-inserted to its other side (si-face), as shown in Scheme 2. From the findings obtained by using cation **1**, one can see that ligand modifications have played a key role in the development of new catalytic systems that significantly control such copolymer properties as tacticity, microstructure, the level of incorporation of a comonomer, and even end use of E−S copolymers.

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References and Notes

(1) For recent reviews, see, for example: (a) Kaminsky, W.; Kulper, K.; Brintzinger, H. H.; Wild, F. R. W. P. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 507. (b) Kaminsky, W. *Catal. Today* **1994**, *20*, 257. (c) Mohring, P. C.; Coville, J. N. *J. Organomet. Chem.* **1994**, *479*, 1. (d) Fink, G., Mulhaupt, B., Brintzinger, H. H., Eds. *Ziegler Catalysts*; Springer: Berlin, 1995. (e) Brintzinger, H. H.; Fischer, D.; Mulhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143 and references therein.

(2) See, for example: (a) Ishihara, N.; Seimiya, T.; Kuramoto, M.; Uoi, M. *Macromolecules* **1986**, *19*, 2464. (b) Zambelli, A.; Pellecchia, C.; Oliva, L.; Longo, P.; Grassi, A. *Makromol. Chem. Phys.* **1991**, *192*, 223. (c) Ready, T. E.; Day, R. O.; Chien, J. C. W.; Rausch, M. D. *Macromolecules* **1993,** *26*, 5822. (d) Xu, G. X.; Liu, Z. J.; Lin, S. A. *Chin. Polym. Bull.* **1993,** *1*, 21. (e) Foster, P.; Chien, J. C. W.; Rausch, M. D. *Organometallics* **1996**, *15*, 2404. (f) Grassi, A.; Lamberti, C.; Zambelli, A.; Mingozzi, I. *Macromolecules* **1997**, *30*, 1884. (g) Xu, G. X.; Lin, S. A. *Acta Polym. Sin.* **1997**, *3*, 380. (h) Xu, G. X. *Macromolecules* **1998,** 31. (i) Flores, J. C.; Wood, J. S.; Chien, J. C. W.; Rausch, M. D. *Organometallics* **1996,** *15*, 4944.

(3) (a) Xu, G.; Lin, S. *Macromolecules* **1997,** *30*, 685. (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) Sernetz, F. G.; Mulhaupt, R. *Macromol. Chem. Phys.* **1996**, *197*, 1071. (e) Stevens, J.

C.; Timmers, F. J.; Wilson, D. R.; Schmidt, G. F.; Nickias, P. N.; Rosen, R. K.; Knight, G. W.; Lai, S. Eur. Pat. Appl. 416815, 1990 (to Dow Chemical Co.); *Chem. Abstr.* **1991**, *115*, 93163. (f) Inoue, N.; Shiomura, T.; Kouno, M. Eur. Pat. Appl. 572990, 1993 (to Mitsui Toatsu Chemicals Inc.); *Chem. Abstr.* **1994**, *121*, 58212. (g) Devore, D. D. Eur. Pat. Appl. 514828, 1991 (to Dow Chemical Co.); *Chem. Abstr.* **1993,** *118*, 169790. (h) Naganuma, A.; Tazaki, T.; Machida, S. Jpn. Kokai Tokkyo Koho JP 04130114, 1992 (to Polyplastics Co., Ltd.); *Chem. Abstr.* **1994**, *121*, 109890. (i) Inoe, N.; Jinno, M.; Shiomura, T. Jpn. Kokai Tokkyo Koho JP 0687937, 1994 (to Mitsui Toatsu Chemicals Inc.); *Chem. Abstr.* **1994**, *121*, 109890. (j) Canich, J. A. M. US 5096867, 1990 (to Exxon Chemical Patents Inc.); *Chem. Abstr.* **1991**, *115*, 95183. (k) Pellecchia, C.; Pappalardo, D.; D'Arco, M.; Zambelli, A. *Macromolecules* **1996**, *29*, 1158.

(4) (a) Kakugo, M.; Miyatake, T.; Mizunuma, K. *Stud. Surf. Sci., Catal.* **1990**, *56*, 517. (b) Miyatake, T.; Mizunuma, K.; Kakugo, M. *Makromol. Chem., Macromol. Symp.* **1993**, *66*, 203. (c) Sernetz, F. G.; Mulhaupt, R.; Fokken, S.; Okuda, J. *Macromolecules* **1997**, *30*, 1562. (d) Oliva, L.; Longo, P.; Izzo, L. *Macromolecules* **1997**, *30*, 5616.

(5) Massey, A. G.; Park, A. J. *J. Organomet. Chem.* **1964**, *2*, 245.

(6) (a) Chien, J. C. W.; Tsai, W. M.; Rausch, M. D. *J. Am Chem. Soc.* **1991,** *113*, 8570. (b) Massey, A. G.; Park, A. J. *J. Organomet. Chem.* **1966,** *5*, 218.

(7) Okuda, J.; Schattenmann, F. J.; Wocadlo, S.; Massa, W. *Organometallics* **1995**, *14*, 789.

(8) (a) Bochmann, M.; Lancaster, S. J. *J. Organomet. Chem.* **1992,** *434*, C1. (b) Vizzini, J. C.; Chien, J. C. W.; Babu, G. N.; Newmark, R. A. *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*, 2049. (c) Chien, J. C. W.; Song, W.; Rausch, M. D. *J. Polym. Sci., Part A: Polym. Chem.* **1994,** *32*, 2387.

(9) For recent reviews, see, for example: (a) Reddy, S. S.; Sivaram, S. *Prog. Polym. Sci.* **1995**, *20*, 309 and references therein. (b) *Macromol. Symp.* **1995**, *97* (Alumoxanes) (Kaminsky, W., Sinn, W., Eds.).

(10) Giannetti, E.; Nicoletti, G.; Mazzochi, R. *J. Polym. Sci., Polym. Chem. Ed.* **1985**, *23*, 2117.

(11) A quantitative analysis of the Ti(III) ESR signals was carried out by comparing the areas with the areas of the ESR signals of standard TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy free radical) toluene solutions with a concentration in the range of $1.0 \times 10^{-3} \sim 5.0 \times 10^{-5}$ M.

(12) Randall, J. C. *J. Polym. Sci., Polym. Phys. Ed.* **1975**, *13*, 901.

(13) Suzuki, T.; Tsuji, Y.; Watanabe, Y.; Takegami, Y. *Macromolecules* **1980**, *13*, 849.

(14) (a) Jordan, R. F.; LaPointe, R. E.; Bajgur, C. S.; Echols, S. F.; Willett, R. *J. Am. Chem. Soc.* **1987**, *109*, 4111. (b) Pellecchia, C.; Immirzi, A.; Pappalardo, D.; Peluso, A. *Organometallics* **1994**, *13*, 3773.

(15) (a) Ewen, J. A.; Jones, R. L.; Razavi, A.; Ferrara, J. D. *J. Am. Chem. Soc.* **1988**, *110*, 6255. (b) Giardello, M. A.; Eisen, M. S.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1995**, *117*, 12114.

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