Syndiospecific Polymerization of Styrene. 3. Catalyst Structure[1]

James C. W. Chien,* Zdenek Salajka,[2] and Sizhong Dong

Department of Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts 01003

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ABSTRACT: The active oxidation state of Ti in the cyclopentadienyltributoxyltitanium methylaluminoxane ($CpTi(OBu)_3$/MAO) catalyst has been determined by electron paramagnetic resonance (EPR) and redox titration. The results, together with previously reported active species concentrations measured by radiolabeling techniques, showed that all the catalytic species are trivalent Ti. The syndiospecific species (78% Ti) is characterized by a sharp EPR resonance at $g = 1.989$ ($^{H}a = 7$ G) which corresponds to a titanium(III) hydride. The nonspecific species (13% Ti) has a g value at 1.995.

Introduction

Until a few years ago stereospecific olefin polymerization research was concerned mainly with heterogeneous Ziegler–Natta (ZN) catalysts.[3] Two important discoveries greatly expanded the scope of scientific investigation on stereospecific polymerizations. The first discovery was that homogeneous stereorigid *ansa*-metallocene catalysts can promote isospecific polymerization of α-olefins.[4,5] The second findings were the homogeneous syndiospecific catalysts for the polymerization of propylene[6] and of styrene (S).[7] These discoveries opened up the possibility of elucidating stereochemical control in olefin polymerization at the molecular level[8] and making use of it to produce polymers with new microstructures. For instance, homopolypropylene having outstanding thermoplastic elastomeric properties was obtained with a nonsymmetric *ansa*-metallocene catalyst.[9] These polymers[4-7,9] are in fact new materials derived from abundant and inexpensive monomers; thus, no new technologies regarding processing, stabilization, disposal, recycling, etc., need to be developed.

Organometallic compounds of the transition element were first employed by Ballard and co-workers[10] to polymerize styrene. This type of catalyst is both inefficient and nonstereospecific. For instance, only about 1% Bz_4Zr (Bz = benzyl) was catalytically active and produced only atactic polystyrene (a-PS). The authors proposed a coordinated anionic propagation mechanism. We found that tetrakis(neopentyl)titanium initiated nonstereospecific homopolymerization of S[11] and copolymerization of styrene and methyl methacrylate. The reactivity ratios of the latter copolymerization are consistent with free-radical propagation. Ishihara and co-workers[7] first reported the syndiospecific polymerization of S by organotitanium compounds with methylaluminoxane (MAO) as the cocatalyst; the catalytic activities decreased in the order $CpTiCl_3$ (Cp = η^5-cyclopentadienyl) ~ Cp^*TiCl_3 (Cp^* = η^5-pentamethylcyclopentadienyl) > $CpTiCl_2H$ ~ $Ti(OEt)_4$ > $Ti(OMe)_4$ ~ $TiCl_4$ > $TiBr_4$. Even the Bz_4Ti/MAO catalyst[12] produced syndiotactic polystyrene s-PS. But analogous Zr, V, Nb, Ta, Cr, and Co compounds produced either a-PS or none.

We have investigated two syndiospecific styrene polymerization catalysts in detail: a low-activity Bz_4Ti/MAO catalyst[1a,12] and a high-activity $CpTi(OBu)_3$/MAO catalyst.[1b] The latter is 360-fold more active than the former. This difference can be quantitatively accounted for by the measured kinetic rate constants and concentrations of syndiospecific and nonspecific catalytic species, [C_s*] and [C_a*], respectively.[1] Expressed in percent Ti, the Bz_4Ti/MAO catalyst has [C_s*] = 1.7% and [C_a*] = 17% with corresponding rate constants of propagation: $k_{p,s} = 1.38$ $(M\cdot s)^{-1}$ and $k_{p,a} = 0.056$ $(M\cdot s)^{-1}$ at 45 °C temperature of polymerization (T_p). The $CpTi(OBu)_3$/MAO system has [C_s*] = 79%, [C_a*] = 13%, $k_{p,s} = 10.8$ $(M\cdot s)^{-1}$, and $k_{p,a} = 6.2$ $(M\cdot s)^{-1}$.

Virtually nothing is known about the chemical structure of the catalytic species. In this work we determined the oxidation states of titanium by redox titration and by EPR (electron paramagnetic resonance), investigated the ionic charge on titanium by electrodialysis polymerization, and considered the state of ligation of MAO to titanium. The results showed that a hydridotitanium(III) complex catalyzes the syndiospecific propagation of S and that the atactic PS is produced by another Ti(III) complex.

Experimental Section

Materials. Bz_4Ti[1a] (1), $CpTi(OBu)_3$[1b] (2), $CpTi(OPh)_3$[1b] (3), MAO,[14] and triphenylcarbenium tetrakis(pentafluorophenyl)-borate (trityl fluoroborate, 4)[13,15] were prepared as previously described. $CpTiCl_2Me$ was synthesized by the method of Eiskine et al.[16] except trimethylaluminum was used instead of dimethylzinc. All chemicals were purchased from Aldrich except the 95% H_2SO_4 which was from Fisher. Styrene was distilled from CaH_2 and stored at −25 °C under argon in the dark. Aqueous 0.1 N solutions of $NH_4Fe(SO_4)$ and $K_2Cr_2O_7$ were made up with deionized distilled water and stored under Ar. The sodium salt of diphenylamine-4-sulfonic acid was used as received.

Titanium Oxidation States. The procedures for the determination of Ti oxidation states, [Ti(n)] (n = II–IV), are the same as described previously.[17] Two redox titrations, A and B, were performed. The Ti(II) ion was titrated as two electron-reducing species in "titration A"; the titer corresponds to 2[Ti(II)] + [Ti(III)]. In "titration B" the Ti(II) ions were first oxidized to the Ti(III) ion by proton and subsequently titrated as a one-electron-reducing species. Therefore, the titer B is the simple sum of [Ti(II)] + [Ti(III)]. The total Ti was analyzed by atomic absorption. The only modification of the published method is the indicator used in titration A. The one employed previously was *N,N'*-diphenylbenzidene which worked well for various heterogeneous ZN catalyst as well as the Bz_4Ti/MSO[1a] systems. But in the case of $CpTi(OBu)_3$/MAO, the color change of this indicator was an indistinct one of yellow to muddy brown and it was not reversible. This difficulty appeared to be associated with the Cp ligand for some unknown reasons. When sodium diphenylaminesulfonate was used as the indicator, the end point became a sharp color change from purple to green within ±2 drops of 0.1 N $K_2Cr_2O_7$.

Electrodialysis Polymerization. An electrodialysis apparatus was constructed comprised of two Schlenk-type chambers each equipped with a 1-cm^2 Pt electrode. The chambers are separated by a glass frit of 5-μm pores; the distance between the electrodes is about 1 cm. The contents in the chambers varied from one experiment to another.

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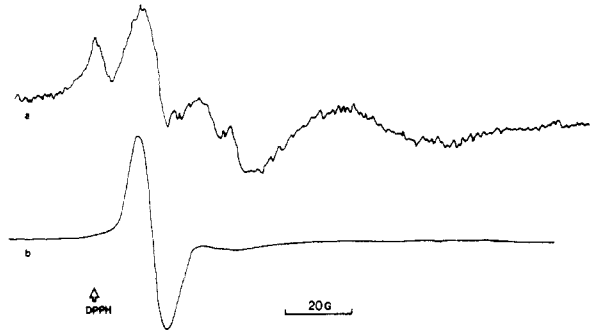

Figure 1. EPR spectra of (a) Bz_4Ti/MAO, [Ti] = 0.83 mM, [Al]/[Ti] = 100, and (b) after styrene (0.73 M) was added to the catalyst.

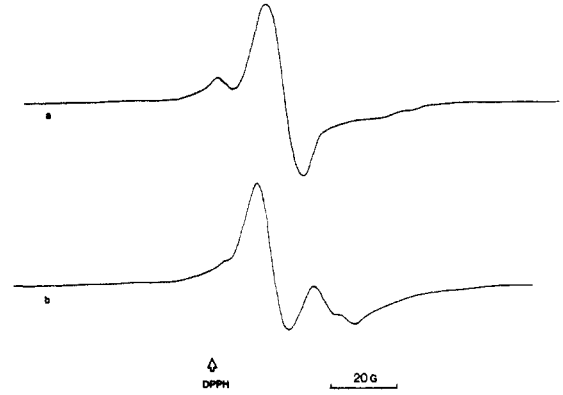

Figure 2. EPR spectra of (a) Bz_4Ti/MAO; [Ti] = 25 mM, [Al]/[Ti] = 100, and (b) after styrene (0.73 M) was added to the catalyst.

EPR. The spectrometer used and the quantitative determination of EPR-observable Ti(III) species were the same as given before.[18]

Results

Bz_4Ti/MAO. The EPR spectrum of a mixture of Bz_4Ti (0.88 mM) with MAO (Al/Ti = 100) is shown in Figure 1a. It contains four signals with g values of 1.993, 1.982, 1.976, and 1.946. An additional signal at $g \sim 2$ is probably due to a radical species. Previously we have reported[19] that the EPR of $Ti(OBu)_4/AlEt_3$ is characterized by four resonances having g values of 1.981, 1.976, 1.965, and 1.945. Therefore, the two catalysts have three Ti(III) species sharing common g values but differ in the fourth species which has g = 1.993 in the Bz_4Ti/MAO but g = 1.965 in the $Ti(OBu)_4/AlEt_3$ systems. The spectral intensity of Figure 1a corresponds to 24% of Bz_4Ti which agrees with the amount of Ti(III) found by redox titration (vide infra).

The effect of S on the EPR spectra was a pronounced one (Figure 1b). Addition of S caused the disappearance of all the high-field signals; only a symmetric singlet g = 1.993 remained. The spectrum integrates to a [Ti(III)] equal to 35.2% Bz_4Ti; this quantity is much greater than the amounts of syndiospecific and aspecific sites previously determined to be $[C_s^*]$ = 1.7% and $[C_a^*]$ = 17%, respectively.[1a] Therefore, some species in the EPR spectrum is due to catalytically inactive Ti(III) ions.

A mixture containing a high concentration of Bz_4Ti (25 mM) and Al/Ti = 100 exhibited a single EPR resonance with several inflections (Figure 2a). The integrated intensity of this resonance corresponds to only 3.7% Ti (Figure 2a). Addition of S to this catalyst gave the EPR spectrum shown in Figure 2b with g values of 1.993, 1.983, and 1.979. The amount of Ti(III) in this figure is 14%, which is almost 4-fold greater than that in the absence of S. Changing the solvent from toluene to a 1:1 toluene/*o*-dichlorobenzene solvent mixture caused no change in the EPR spectrum. The weak EPR spectrum in Figure 2a is attributable to dipolar and Heisenberg exchange interactions which caused excessive line broadening. These interactions are significantly diminished by the addition of styrene. Styrene can break up electron-deficient bonds between Ti(III) ions, occupy vacant coordination positions, and insert into Ti–alkyl bonds, all of which have the effect of physically separating Ti(III) ions from each other.

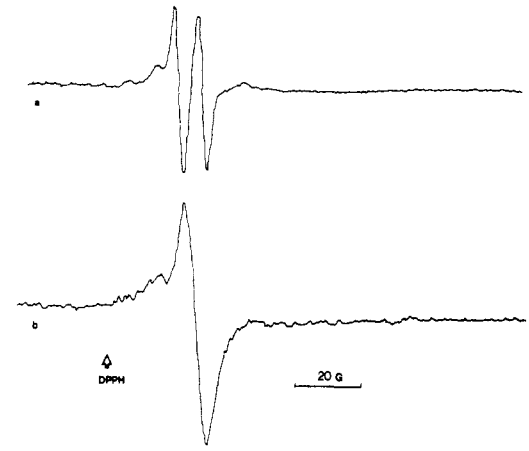

Figure 3. EPR spectra of (a) $CpTi(OBu)_3$/MAO, [Ti] = 83 μM, [Al]/[Ti] = 1,000, and (b) after styrene (0.73 M) was added to the catalyst.

Redox titration blanks were determined on 0.15 mmol of Bz_4Ti transferred directly into a Schlenk-type Erlenmeyer flask. Duplicate analysis of blanks gave 0.2 mL of a 0.1 N $K_2Cr_2O_7$ solution without MAO in titration A and no consumption of $K_2Cr_2O_7$ in titration B. A solution of Bz_4Ti (0.15 mmol) and MAO (0.87 g) (Al/Ti = 100) in 180 mL of toluene was stirred at 60 °C for 10 min to simulate the polymerization conditions. The solution was cooled to 0 °C and titrated. The distribution of oxidation states of Ti in this catalyst was found to be Ti(IV):Ti(III):Ti(II) = 53.3%:26.6%:20%. The effect of S on the Ti oxidation state was investigated by adding 3 mL of S (0.24 M) to the above catalyst solution. Assay of this mixture found [Ti(IV)] to be significantly lowered to 36% and [Ti(III)] raised to 48%. [Ti(II)] was found to be 16%, which is only slightly smaller than it is in the absence of S.

$CpTi(OBu)_3$/MAO. Figure 3a shows the EPR spectrum of a solution of $CpTi(OBu)_3$ (83 μM) and MAO (Al/Ti = 1000). This is the same mixture employed to polymerize S. The main EPR signal is a doublet at g = 1.989 attributable to a hydridotitanium(III) species with ^{H}a = 7.0 G (Table I). Hyperfine splitting of ca. 7 G for the ^{47}Ti ($I = {}^5/_2$) and ^{49}Ti ($I = {}^7/_2$) isotopes can also be seen. The integrated intensity of this spectrum corresponds to 94% of the $CpTi(OBu)_3$. The spectrum is essentially the same as that described for $CpTiCl_3$/MAO[20] which has g = 1.989 and ^{H}a = 7.4 G. In addition, there is a peak at g = 1.995. Addition of styrene converted the doublet into a broad singlet at g = 1.989 with a shoulder at g = 1.995 (Figure 3b). Integration of the spectrum in Figure 3b gave a [Ti(III)] of 98%.

It will be presented below that redox titrations gave unexpected results when [Ti] is high and Al/Ti is low. We have recorded EPR spectra for this solution which has a low polymerization activity.[1,2] Figure 4a shows the spectrum of a catalyst solution of 0.83 mM Ti and 83 mM Al. The main spectral feature is still a doublet (g = 1.990, H_a = 7.7 G). However, there are now additional resonances

Table I
EPR of $CpTi(OBu)_3$/MAO

Figure	$[CpTi(OBu)_3]$ (M)	Al/Ti	S (M)	[Ti(III)] (%)	g values (hyperfine splitting)
3a	8.4×10^{-5}	1000	0	94	1.995, 1.989 (^{H}a = 7 G)
3b	8.4×10^{-5}	1000	0.73	98	1.995, 1.987
	8.4×10^{-5}	1000	0.73[a]	90	1.993, 1.989
4a	8.4×10^{-4}	100	0	91	1.994, 1.990 (^{H}a = 7 G)
4b	8.4×10^{-4}	100	0.73	96	1.995, 1.990, 1.982, 1.977, 1.968, 1.952
	2.81×10^{-3}	100	0	84	1.995, 1.990 (^{H}a = 7 G)
5a	2.9×10^{-2} (10 min)[b]	20	0	35	1.992, 1.987, 1.980 (^{H}a = 9 G), ^{Al}a = 2.5 G), 1.965, 1.960, 1.945
	2.9×10^{-2} (60 min)[c]	20	0	42	1.980 (^{H}a = 9 G), ^{Al}a = 2.5 G), 1.965, 1.960, 1.945
5b	2.9×10^{-2}	20	0.73	43	1.992, 1.980 (^{H}a = 9 G), 1.974 (^{Al}a = 2.5 G), 1.965, 1.960, 1.949

[a] α-Methylstyrene. [b] 10 min after mixing. [c] 60 min after mixing.

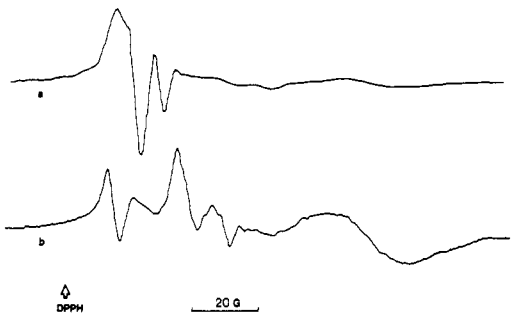

Figure 4. EPR spectra of (a) $CpTi(OBu)_3$/MAO, [Ti] = 84 mM, [Al]/[Ti] = 100, and (b) after styrene (0.73 M) was added to the catalyst.

at g = 1.989 and higher fields. The total integrated intensity corresponds to 91% Ti. Addition of styrene to this catalyst solution caused the collapse of the doublet as before.

Addition of S caused the following spectral changes. The number of resolved ^{27}Al shfs (superhyperfine splitting) lines increased to 11 as shown in Figure 5b, which suggests that the unpaired spin is coupled to two ^{27}Al nuclei instead of one when S is absent. The center of this shfs resonance was shifted to higher field to g = 1.974. The monomer had no apparent effect on that resonance associated with the proton shfs interaction, and the overall integrated EPR spectral intensity is the same as without the monomer. The spectrum obtained in a 1:1 toluene/chlorobenzene solvent is essentially the same as that in Figure 5b but has a lower [Ti(III)] of 32%.

The lowering of the amount of Ti(III) observable by EPR may be either due to excessive line broadening caused by various types of interactions between paramagnetic ions at high concentration or due to change of the Ti oxidation states to diamagnetic Ti(IV) or Ti(II). The latter was investigated by redox determinations of [Ti(n)]. Table II and Figure 6 show the results at several $[CpTi(OBu)_3]$. In the presence of S, Ti(III) increases with a decrease of $[CpTi(OBu)_3]$ while Ti(IV) showed the opposite dependence. [Ti(II)] remained relatively independent of $[CpTi(OBu)_3]$. The variations of [Ti(n)] with $[CpTi(OBu)_3]$ were more modest in the absence of S. One cannot correlate [Ti(III)] values obtained with redox titration and EPR. At [Ti] < 1 mM, the [Ti(III)]'s determined by EPR are greater than the titration results. For [Ti] > 10 mM, the [Ti(III)] observed by EPR was smaller than that obtained by titrations. Similar differences were also found for the Bz_4Ti/MAO system.

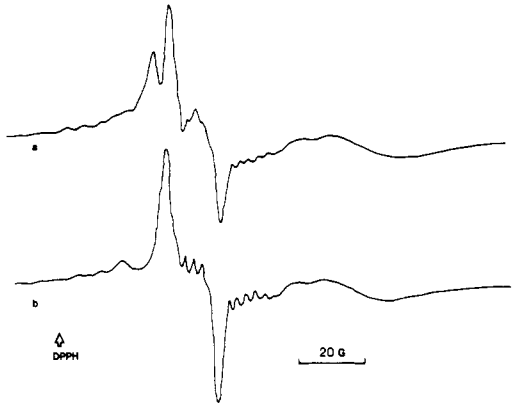

Figure 5. EPR spectra of (a) $CpTi(OBu)_3$/MAO, [Ti] = 29 mM, Al/Ti = 20, and (b) after styrene (0.73 M) was added to the catalyst.

Ionic Initiation of Styrene Polymerization. Recently, group IVb metallocene cation alkyls had been shown[13] to be very active and to be stereospecific catalysts for propylene polymerizations and that probably such species were produced by the reaction between metallocene alkyls and MAO.[13] We looked into the possible participation of ionic initiators in the present catalyst system.

The electrodialysis polymerization method was used to show the formation of cationic ethylene polymerization species by $Cp_2TiCl_2/AlEt_2Cl$.[20] The apparatus was described in the Experimental Section. It was first checked out for ethylene polymerization. Without applying any potential to the system (+)|Cp_2TiCl_2 (0.125 mM), Et_2AlCl (1 mM), 1,1-dichloroethane (CH_3CHCl_2)‖Et_2AlCl (1 mM), C_2H_4 (1 bar), CH_3CHCl_2|(−), there was no ethylene polymerization. Application of a 500-V potential resulted in the production of 0.36 g of polyethylene in 20 min. In comparison, Dyachkovski and co-workers[20] used 17–20 mM Cp_2TiCl_2 and 12–33 mM Et_2AlCl in dichloroethane at 1 kV and obtained only 50–70 mg of polyethylene in the cathodic chamber. Their lower polymerization yield obtained at a higher catalyst concentration and electric potential may be attributable to their usage of a less permeable cellophane membrane as the partition and/or to the presence of impurities.

A blank was tested for styrene polymerization using the arrangement (+)|$CpTi(OPh)_3$ (42 μM), MAO (83 mM), toluene (55 mL)‖MAO (83 mM), S (5 mL), toluene (55 mL)|(−). No PS was isolated after 1 h without an imposed electric potential. Therefore, there is free diffusion neither of S from the cathodic into the anodic compartment nor of $CpTi(OPh)_3$ in the opposite direction during the time of the experiment. A 500-V electric potential was then applied; the results are given in Table III. Experiment 1 is like the blank above but with the 500-V potential. Again there was no styrene polymerization. $CpTi(OPh)_3$ was added into the cathodic chamber in experiment 2. The same amount (0.43 ± 0.01 g) of s-PS was produced in both compartments. This indicates that the catalyst must have been formed also in experiment 1 and that there was no migration of catalytic species in either direction. To

Table II
Titration of $CpTi(OBu)_3$/MAO

[Ti] × 10^5 (M)	MAO [Al] (mM)	MAO [Al]/[Ti]	S (M)	[Ti(IV)] (%)	[Ti(III)] (%)	[Ti(II)] (%)
10	10	100	0	36.6	56.6	6.7
83	83	100	0	35.3	58.0	6.6
83	83	100	0	34.6	57.3	8.0
			av	35.6 ± 0.83	57.3 ● 0.54	7.1 ● 0.63
83	83	100	0.24	40.0	56.6	3.3
41.6	83	200	0	33.3	60.0	6.6
41.6	83	200	0.12	33.3	64.6	2.0
160	83	50	0	26.6	60.0	13.3
160	83	50	0.12	40.0	56.6	3.3
8.3	83	1000	0	(35)[a]	(60)[a]	(5)[a]
8.3	83	1000	0.12	(30)[a]	(68)[a]	(2)[a]

[a] Extrapolated value from Figure 3.

Table III
Results of Electrodialysis Polymerizations under a Potential of 500 V at Room Temperature

expt	solvent[a] (55 mL)	anodic	cathodic	t_p (h)	yield of PS[b] (g) anodic	yield of PS[b] (g) cathodic
1	T	Ti,[c] MAO[d]	MAO, S[e]	2	0	0
2	T	Ti, MAO, S	Ti, MAO, S	0.5	(s) 0.44[f]	(s) 0.42[f]
3	DCB	Ti, MAO	MAO, S	0.5	0.01	0.11
4	DCB	MAO, S	Ti, MAO	0.5	0.22	0
5	DCB	Ti, MAO, S	Ti, MAO, S	0.5	(s + a) 0.23[f]	(s + a) 0.27[f]

[a] Solvent, 55 mL in each chamber, T = toluene, DCB = *o*-dichlorobenzene, DCE = CH_3CHCl_2. [b] a-PS unless otherwise stated. [c] $CpTi(OPh)_3$, 42 μM unless otherwise stated. [d] 83 mM Al unless otherwise stated. [e] Styrene, 5 mL. [f] s-PS was produced. [g] Duplicate results.[h] The |Ti, MAO||MAO| system was allowed to stand and diffuse for 4 h, after which S was added to the cathodic chamber, all without electric potential.

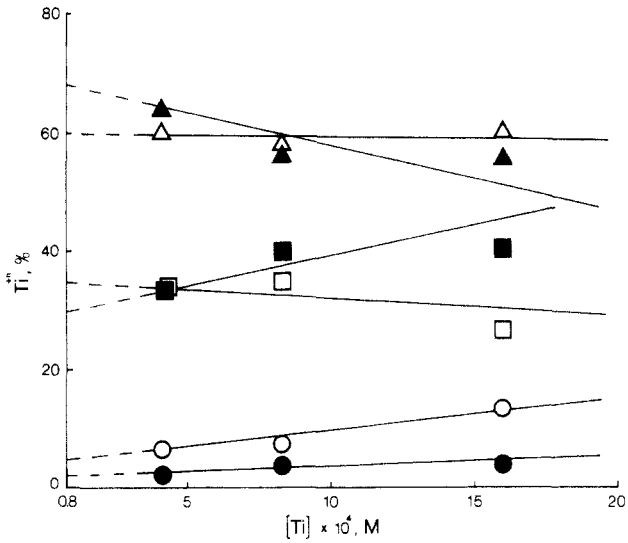

Figure 6. Variation of the distributions of the Ti oxidation states in a $CpTi(OBu)_3$/MAO mixture as a function of [$CpTi(OBu)_3$] at a constant [Al] = 83 mM: (○) Ti(III); (△) Ti(III); (□) Ti(IV). Open symbols are without monomer; filled symbols are with styrene.

promote the migration of possible charged species, toluene was replaced with *o*-dichlorobenzene (DCB) in experiments 3–5 for a higher medium dielectric constant (ε). Experiment 3 had the configuration (+)|Ti, MAO, DCB||MAO, S, DCB|(−). There was produced a-PS in both compartments, the amount of which in the cathodic chamber was 10 times greater than that in the anodic section. The phenomenon can have more than one cause. So experiment 4 was performed, reversing the ingredients in the cells. Now all the a-PS was produced in the anodic compartment, which means there is aspecific S polymerization in a mixture of MAO, S, and DCB without $CpTi(OPh)_3$. If one introduced the titanium compound to this mixture (experiment 5), then both s-PS and a-PS were isolated. Two kinds of catalysts were formed in this case, one from $CpTi(OPh)_3$/MAO and the other from MAO/DCB for syndiospecific and aspecific S polymerizations, respectively.

Table IV
"Cation" Initiation of Styrene Polymerization[a]

	expt 117a	expt 117b	expt 117c	expt 117d	expt 117e
$CpTiMeCl_2$ (μmol)	0	5	5	5	5
MAO (mmol)	0	0	0	0	5
TIBA (mmol)	0	0	0.5	0.5	0
TFB (4)[b] (μmol)	5	0	0	5	0
[Al]/[Ti]	0	0	10^2	10^2	10^3
yield (g)	3.2	0	0	0.42	0.89
SY (%)	0			0	99

[a] Polymerization conditions: T = 50 mL, S = 5 mL, T_p = 50 °C, t_p = 30 min. [b] Trityl fluoroborate.

Other styrene polymerizations were carried out in glass reactors under an argon atmosphere. The results are summarized in Table IV. Experiment 117a showed that the trityl cation (4) alone caused rapid but random S polymerization. The catalyst system $CpTiMeCl_2$/4 produced a low yield of a-PS (experiment 117d). In this table only the $CpTiMeCl_2$/MAO (experiment 117e) catalyst produces exclusively s-PS.

Discussion of Results

Very high polymerization activity is achieved only at conditions of very low [Ti] (≤83 μM)[1b] and a very high Al/Ti ratio (≥1000) with the $CpTi(OBu)_3$/MAO catalyst. Virtually all the Ti are catalytically active: [C_s*] + [C_a*] corresponds to 92% of Ti according to radio labeling.[1b] Nearly all the Ti (96 ± 2%) are in the trivalent state and observable by EPR. The principal EPR species with g = 1.989 is a proton doublet. Earlier we had investigated with EPR the reduction of $CpTiCl_3$ by MAO.[21] A spectrum of the proton doublet was obtained which had the same spectral parameters as Figure 3b. In that case,[21] the EPR doublet collapsed to a broad singlet without a change in g value when the catalyst solution was equilibrated with deuterium gas. This is consistent with a rapid exchange equilibrium between D_2 and Ti(III)–H species to form Ti(III)–D species and concomitant loss of the superhy-

perfine splitting. Since C_s* amounted to 79% of the Ti, we can safely assume that it is a hydridotitanium(III) complex. This interpretation is further supported by the observation that upon introduction of S the proton doublet is transformed into a singlet consistent with π-complexation of the monomer and its migratory insertion.

Following the discovery of the Cp_2TiCl_2·AlR_2Cl catalyst,[22] Long and co-workers[23] obtained spectroscopic evidence for an ionic active species. This was supported by the electrodialysis experiments.[20] Recently, a number of cationic tetravalent metallocene complexes were synthesized and shown to polymerize ethylenes[24-28] and propylene.[13,18] Because of these significant findings, we felt it necessary to consider the possibility of cationic catalytic intermediates in the present systems. None of the polymerizations in the electrodialysis apparatus gave any indication of free charged catalytic species. The $CpTiMeCl_2$/4 system has a much lower activity than 4 alone; both of them produce only a-PS. The reaction between alkyls with 4 is a convenient pathway to a cationic metallocene alkyl.[13] However, this reaction has not yet been studied for monocyclopentadienyltitanium alkyl.

$CpTi(OBu)_3$/MAO is definitely not a "single-site" catalyst. The s-PS fraction has $\bar{M}_w/\bar{M}_n$ values lying between 4 and 6.[1b] The MW distribution of the total polymer, including the a-PS, would be even broader. Thus there must be at least two or maybe even more syndiospecific active species. The $\bar{M}_w/\bar{M}_n$ ratio also varies with the temperature of polymerization,[1b] which indicates thermal equilibria between the various catalytic species. A possible explanation for the multiplicity of catalytic species is that CpTi(OBu)H is coordinatively unsaturated. It can complex one or more MAO molecules via a unident, bident, or trident mode. If these postulated complexes are in equilibria and catalytically active, they would produce PS with a broad MW distribution.

The nature of the aspecific species is unknown except that it is also a Ti(III) complex. More of it is present at a low [Al]/[Ti] ratio.[1a,b] This suggests that the aspecific species is more coordinatively unsaturated than the syndiospecific species.

The catalytic species in the Bz_4Ti/MAO system are also Ti(III) complexes. The low catalyst activity is probably attributable to the stability of benzyl transition-metal compounds toward reduction.

References and Notes

(1) This is Part 3 of the series Syndiospecific Polymerization of Styrene. (a) Part 1: Chien, J. C. W.; Salajka, Z. *J. Polym. Sci. A* **1991**, *29*, 1243. Part 2: Chien, J. C. W.; Salajka, Z. *J. Polym. Sci. A* **1991**, *29*, 1253.

(2) On leave from the Research Institute of Macromolecular Chemistry, BRNO, Czechoslovakia.

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