# Metallocene-catalyzed olefin polymerizations using triphenylcyclopropenium tetrakis(pentafluorophenyl)borate as the activator

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**Abstract:** Triphenylcyclopropenium (TPCP) tetrakis(pentafluorophenyl)borate activates bis(cyclopentadienyl)dimethyl titanium resulting in a highly reactive initiating system for the polymerization of styrene. In contrast to triphenylmethyl tetrakis(pentafluorophenyl)borate which is quite active in the absence of the metallocene, TPCP borate shows no activity for styrene polymerization in the absence of bis(cyclopentadienyl)dimethyl titanium. TPCP is the most efficient activator in the carbonium ion – borate class. We propose, based on <sup>1</sup>H NMR evidence that reaction of  $Cp_2TiMe_2$  and TPCP borate leads to the formation of the cationic Ti complex  $[Cp_2TiMe]^+B(C_6F_5)_4^-$ . Evidence for the latter is also provided by UV–vis spectroscopy in that we found a bathochromic shift of the  $Cp_2TiMe_2$  LMCT absorption band from 361 to 482 nm in  $CH_2Cl_2$  and 487 nm in toluene, respectively. Thermal decomposition of the cationic complex  $[Cp_2TiMe]^+B(C_6F_5)_4^-$  leads to less activity. The systems are good catalysts for ethylene polymerization as well, but are less active when using propylene. A conventional Ziegler–Natta coordination polymerization mechanism accounts for ethylene and propylene polymerization while a carbocationic polymerization mechanism is proposed for styrene.

*Key words:* triphenylcyclopropenium tetrakis(pentafluorophenyl)borate, bis(cyclopentadienyl)dimethyl titanium, activator, olefin polymerization.

**Résumé :** Le tétrakis(pentafluorophényl)borate de triphénylcyclopropénium (TPCP) active le bis(cyclopentadiényl)diméthyltitane qui conduit à un système très réactif pour initier la polymérisation du styrène. Par opposition au tétrakis(pentafluorophényl)borate de triphénylméthyle qui est très actif en l'absence de métallocène, le borate de TPCP ne présente aucune activité vis-à-vis de la polymérisation du styrène en l'absence du bis(cyclopentadiényl)diméthyltitane. Le TPCP est l'activateur le plus efficace de la classe borate – ion carbonium. On suggère, sur la base de données de RMN du <sup>1</sup>H, que la réaction du Cp<sub>2</sub>TiMe<sub>2</sub> et du borate de TPCP conduit à la formation du complexe cationique du Ti,  $[Cp_2TiMe]^+B(C_6F_5)_4^-$ . Ce résultat est également appuyé par des mesures effectuées par spectrométrie UV–vis qui démontrent un déplacement bathochrome de la bande d'absorption du LMCT du Cp<sub>2</sub>TiMe<sub>2</sub> de 361 nm vers 482 nm pour le CH<sub>2</sub>Cl<sub>2</sub> et vers 487 nm pour le toluène, respectivement. Une décomposition thermique du complexe cationique  $[Cp_2TiMe]^+B(C_6F_5)_4^-$  conduit à une perte d'activité. Les systèmes sont aussi de bons catalyseurs pour la polymérisation de l'éthylène, mais ils sont moins réactifs pour le propylène. Un mécanisme de polymérisation conventionnel de Ziegler–Natta par coordination permet d'expliquer la polymérisation de l'éthylène et du propylène alors qu'on propose un mécanisme de polymérisation carbocationique pour le styrène.

*Mots clés :* tétrakis(pentafluorophényl)borate de triphénylcyclopropénium, bis(cyclopentadiényl)diméthyltitane, activateur, polymérisation d'oléfine.

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## Introduction

Metallocene coordination polymerization catalyst systems for olefins are an important research and development topic

(1). Successful catalysts invariably consist of transition metal complexes called *catalyst precursors* and activators also called *co-catalysts*. The partners react forming an active species that is comprised of a cation–anion ion pair. The struc-

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It is a sincere pleasure to recognize the career-long contributions to the photochemical sciences of Professor Don Arnold on the occasion of his retirement. Through the application of the principles of physical organic chemistry to the study of the emerging field of reactions catalyzed by ultraviolet light, Professor Arnold and his students enhanced predictive power in organic photochemistry. His colleagues are most grateful for his insights.

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ture of the activator significantly influences catalytic activity, the character of the polymerization, and polymer properties.

The number of viable co-catalysts for metallocene polymerizations is rather limited (2). Methylaluminoxane (MAO) is an important industrial co-catalyst, but must be used in huge excess to achieve high activity. Triphenylmethyl carbenium ion ("trityl") if paired with  $B(C_6F_5)_4^-$  (1) has been reported to be a highly efficient activator for group 4 dimethylmetallocenes (3) at low co-catalyst to catalyst ratios (1:1). A number of other borates have also been developed to improve properties such as solubility in organic solvents and thermal stability (4).



We have recently discovered that triarylcyclopropenium salts may be used as cationic initiators for both the thermal and photochemical polymerization of epoxides (5, 6). Triphenylcyclopropenium (TPCP) cation is a strong electrophile (7) and when TPCP salts paired with weakly nucleophilic anions tetrakis(pentafluorophenyl)gallate are dissolved in ketones with active  $\alpha$ -hydrogens such as cyclohexanone we found that super acids (presumably H-Ga(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>) form. Super acids also result from irradiation of TPCP<sup>+</sup>Ga(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup> in various solvents (8).

In view of this new discovery we wished to explore further the advantages of cyclopropenium salts in various polymerization reactions. We report herein results of olefin polymerization catalyzed by bis(cyclopentadienyl)dimethyl titanium (3) using TPCP borate (2) as the activator (Fig. 1).

## **Experimental section**

#### Materials

All chemicals were used as received from Aldrich unless otherwise noted. Benzene and toluene were distilled over sodium under argon.  $CH_2Cl_2$  was freshly distilled over  $CaH_2$ under argon.  $\alpha,\alpha$ -Dichlorotoluene was purchased from Acros Organics and used as received. Bis(cyclopentadienyl)titanium dichloride was purchased from Strem Chemicals Inc. and used as received. Styrene was distilled over  $CaH_2$  at  $50^{\circ}C$  under vacuum and kept over molecular sieves (4 Å) under argon in a refrigerator. Potassium tetrakis(pentafluorophenyl)borate was prepared as reported (9). Bis(cyclopentadienyl)dimethyltitanium (**3**) was prepared according to the literature (10) and kept in a freezer as a solution (~36%) in toluene.

#### Measurements

<sup>1</sup>H and <sup>19</sup>F NMR spectra were recorded either with a Varian Gemini 200 NMR or a Varian Unity plus 400 NMR spectrometer. Chemical shifts are in ppm with TMS as the internal standard (<sup>1</sup>H NMR) or CFCl<sub>3</sub> as the external standard (<sup>19</sup>F NMR). Melting points were determined with a Thomas Hoover capillary melting point apparatus and were uncorrected. UV–vis spectra were recorded on a Shimadzu

Fig. 1. Structure of the activator and the catalyst.



UV-2401PC UV-vis recording spectrophotometer. Numberand weight-average molecular weights ( $M_n$  and  $M_w$ ) and polydispersity ratios ( $M_w/M_n$ ) were estimated by gel permeation chromatography (GPC) on a Shimudzu HPLC system equipped with a Plgel 5 µm MIXED-C 300 × 7.5 mm column (Polymer Laboratories), using THF as the eluent with a flow rate of 1.0 mL min<sup>-1</sup> by polystyrene calibration, and a RID-10A refractive index (RI) detector.

#### Synthesis of TPCP tetrakis(pentafluorophenyl)borate (2)

To a suspension of TPCP chloride (11) (1.51 g, 5 mmol) in acetonitrile (25 mL) was added a solution of potassium tetrakis(pentafluorophenyl)borate (4.00 g, 5 mmol) in acetonitrile (15 mL) and the reaction mixture stirred at room temperature for 2 h. The solid thus formed was removed by filtration and the filtrate concentrated to give a brown viscous substance that was further purified using a silica gel column with CH<sub>2</sub>Cl<sub>2</sub> as the eluent. After washing with pentane, the product was obtained as white crystals (62%), mp 209 to 210°C. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 7.88 (dd, <sup>3</sup>J<sub>H-H</sub> = 7.6, 7.8 Hz, 6H, 3,5-H on phenyl), 8.06 (t, <sup>3</sup>J<sub>H-H</sub> = 7.8 Hz, 3H, 4-H on phenyl), 8.42 (d, <sup>3</sup>J<sub>H-H</sub> = 7.6 Hz, 6H, 2,6-H on phenyl). <sup>19</sup>F NMR (CDCl<sub>3</sub>)  $\delta$ : -133.12 (s, 2, 6-F on C<sub>6</sub>F<sub>5</sub>), -163.40 (sm, 4-F on C<sub>6</sub>F<sub>5</sub>), -167.20 (s, 3,5-F on C<sub>6</sub>F<sub>5</sub>). Anal. calcd. for C<sub>45</sub>H<sub>15</sub>F<sub>20</sub>B: C 57.11, H 1.60; found: C 57.02, H 1.66.

#### **Polymerization of styrene**

In a typical polymerization, 2 (0.03 mmol) was dissolved in solvent (2 mL) (TPCP tetrakis(pentafluorophenyl)borate dissolved in  $CH_2Cl_2$  and is partially soluble in toluene) and the solution degassed (freeze-thaw) for three cycles. 3 (0.03 mmol, 36% in toluene) was also dissolved in styrene (2 mL) and the solution degassed as above. The catalyst solution in styrene was then transferred into the solution of 2 under dry argon at room temperature and the mixture stirred for 30 min. Subsequently, the polymerization mixture was quenched with MeOH (containing 1% HCl). The resulting polymer was purified twice from  $CH_2Cl_2$ -MeOH or until a white powder of the polymer was obtained. The polymer was dried under vacuum overnight. The activity of the catalyst system was calculated by the following:

Activity = weight of polymer (g)/(Ti (mol) monomer (mol) time (h))

# Polymerization of styrene with preactivated initiating systems

In a typical polymerization run, **3** (36% in toluene) was mixed with  $CH_2Cl_2$  (2 mL), and the solution degassed using freeze-thaw techniques for three cycles. This initiating solu-

tion in  $CH_2Cl_2$  was then transferred into the polymerization tube (prevacuum evacuated) containing **2** under dry argon (the reactions are quite sensitive to spurious moisture) at room temperature and the mixture stirred (aged) for 10 min. The mixture turned from yellow to dark red. Styrene (predegassed) was next introduced into the system, and the polymerization mixture stirred at room temperature for 15– 30 min. It was next quenched by MeOH (containing 1% HCl). The resulting polystyrene (PS) was purified twice from  $CH_2Cl_2$ –MeOH or until a white powder of the polymer was obtained, and the polymer then dried under vacuum overnight.

#### **Polymerization of ethylene**

In a typical polymerization run, a solution of **3** (1.5–3.0 mmol, 36% in toluene) in  $CH_2Cl_2$  (2 mL) was degassed for three cycles and then transferred into a polymerization tube (25 mL, prevacuumed) containing **2** (1.5–3.0 mmol) under an ethylene atmosphere. The catalyst system was preactivated for 10 min at room temperature and then ethylene at 1 atm (1 atm = 101.325 kPa) was bubbled through the solution. Polyethylene (PE) precipitated from the solution immediately. After 5 min, the polymerization reaction was quenched with MeOH (containing 1% HCl, 5 mL). The polymer was collected by filtration. After washing with MeOH, the polymer was dried under vacuum overnight. The resulting polymer did not dissolve in THF or in 1,1,2,2-tetrachloroethane.

#### **Polymerization of propylene**

Polymerization of propylene resulted if a similar procedure to that used for ethylene polymerization was employed. Propylene was bubbled through the catalyst solution at 1 atm (1 atm = 101.325 kPa) for 30 min at room temperature. After quenching with MeOH (1% HCl), the resulting polypropylene (PP) (viscous oil) was collected by carefully decanting the solvent and subsequently dried under vacuum overnight.

### <sup>1</sup>H NMR studies

To complete the reaction of Cp<sub>2</sub>TiMe<sub>2</sub> with TPCP salts, a mol ratio of 1.1:1.0 for TPCP:Ti was used in this experiment. In a typical experiment, CD2Cl2 was vacuum distilled over CaH<sub>2</sub>, trapped at 78 K, and then degassed by freezethaw techniques for three cycles. The catalyst (0.03 mmol, 36% solution in toluene) was dissolved in the above CD<sub>2</sub>Cl<sub>2</sub> and the solution transferred to a vacuum evacuated tube containing TPCPB (0.032 mmol) at -78°C. The solution was subsequently warmed to room temperature and held there for 5 min. During this period, the catalyst system turned from yellow to dark red. The dark red solution was next transferred into an NMR tube that had been degassed by passing dry argon through it for 30 min. The NMR tube was cooled to -78°C again and taken to the NMR. The sample temperature was equilibrated for 1 h at 0°C and the NMR data collected.

#### **UV-vis studies**

Absorption spectra of the catalyst systems were recorded under dry argon in a quartz cuvette (1.0 cm path length). In a typical experiment, a solution of **3** ( $4.2 \times 10^{-4}$  M) in  $CH_2Cl_2$  (containing traces of toluene) was degassed for three cycles. 2 was placed in a quartz cuvette and the cuvette degassed with bubbling dry argon for 20 min. Catalyst solution was introduced using a two-tipped needle and the vessel sealed under dry argon. UV–vis spectra of the resulting solutions were recorded at room temperature at various times.

# **Results and discussion**

#### Synthesis of TPCP borate

Anion exchange of TPCP chloride with  $\text{KB}(\text{C}_6\text{F}_5)_4^-$  afforded triphenylcyclopropenium tetrakis(pentafluorophenyl)borate **2** as a white solid, mp 209 to 210°C. **2** is stable under air at room temperature and soluble in  $\text{CH}_2\text{Cl}_2$  but only slightly soluble in toluene.

### **Polymerization of styrene**

Styrene polymerizations were carried out in toluene or CH<sub>2</sub>Cl<sub>2</sub> at 23°C under dry argon (Table 1). Control experiments show neither 2 nor 3 had significant activity when used alone in CH<sub>2</sub>Cl<sub>2</sub> or toluene. Following the prescribed period of preactivation, 2 was among the most active activators for styrene polymerization (entry 6) of the type carbonium ion - borate (12). The solvent had little effect on initiation activity (entries 1 and 2), but polystyrene obtained from toluene solution was of lower weight average molecular weight  $(M_w)$ , presumably because of the limited solubility of 2 and the active species. The activity of a preactivated initiating system was much higher than that without preactivation. If the preactivation time was increased to 20 min (entry 4), the activity of the initiating system was reduced by about 50%. We presume this is due to the thermal decomposition of the catalytic cationic complex at room temperature.

The efficiency of **2** in the polymerization of styrene is compared to that of the trityl salt **1** in toluene. Titanocene **3** shows a high activity of  $6.04 \times 10^6$  g (PS)/mol (Ti) × mol (styrene) × h in the presence of **1** (entry 11), however, from control experiments, **1** itself is a rather active initiator for the polymerization of styrene with the activity of  $5.60 \times 10^6$  g (PS)/mol (Ti) × mol (styrene) × h (entry 12). This is not the case with **2**.

All polystyrene samples obtained in our reactions are soluble in 2-butanone indicating only atactic polystyrene (a-PS) is formed. This was confirmed by <sup>13</sup>C NMR spectroscopy (13).

#### Polymerization of ethylene and propylene

Polymerization was carried out at room temperature by bubbling of ethylene (1 atm, (1 atm = 101.325 kPa)) through a preactivated solution of **4** (1.5–3.0 mmol) formed by reaction of an equimolar concentration of **2** and **3** in CH<sub>2</sub>Cl<sub>2</sub> (2 mL) (Table 1). PE immediately precipitated from the solution. After 5 min, quenching the reaction mixture with acidic methanol yielded lightly yellow polymers with  $T_m$  127 ~ 130°C. The PE obtained was not soluble in organic solvents such as CH<sub>2</sub>Cl<sub>2</sub>, THF, and 1,1,2,2-tetrachloroethane.

Bubbling of propylene into the catalyst system for 30 min, followed by quenching of the polymerization mixture with acidic methanol, gave polypropylene as a viscous oil of relatively low molecular weight  $(4.0-7.2) \times 10^3$  g mol<sup>-1</sup>. Though the quantity of catalyst used had little affect on the yield of

Run	Catalyst (mmol)	Polymerization time (min)	Monomer	Yield (g)	Activity $(\times 10^6)^b$	$M_{ m w}$ (kg mol <sup>-1</sup> )	$M_{\rm w}/M_{\rm n}$
$1^c$	3.0	30	Styrene	1.23	4.68	20.6	2.13
2	3.0	30	Styrene	1.06	4.05	65.3	1.93
$3^d$	3.0	30	Styrene	1.80	7.15	50.8	2.31
$4^e$	3.0	30	Styrene	0.92	3.50	50.5	2.14
$5^d$	3.0	15	Styrene	1.78	13.5	40.2	2.38
$6^d$	1.5	15	Styrene	1.43	21.8	54.8	2.27
$7^d$	3.0	5	Ethylene	0.17	0.068	f	
$8^d$	1.5	5	Ethylene	0.17	0.14	_	_
$9^d$	3.0	30	Propylene	0.037	0.0035	3.97	1.46
$10^d$	5.0	30	Propylene	0.038	0.0015	7.18, 5.56	2.68, 2.14
$11^c$	$3.0^{g}$	30	Styrene	1.59	6.04	6.3	2.48
$12^c$	h	30	Styrene	1.46	5.60	8.3	4.14

**Table 1.** Polymerization of styrene, ethylene, and propylene by  $Cp_2TiMe_2$ -TPCP<sup>+</sup>B( $C_6F_5$ )<sub>4</sub><sup>-</sup> in CH<sub>2</sub>Cl<sub>2</sub>.<sup>*a*</sup>

<sup>*a*</sup>Polymerization conditions: Styrene polymerization: temperature =  $23^{\circ}$ C, styrene = 2 mL, solvent = 2 mL, [Styrene] = 4.4 M. Ethylene and propylene polymerization: temperature =  $23^{\circ}$ C, solvent = 2 mL, monomer pressure = 1 atm (1 atm = 101.325 kPa).

<sup>b</sup>Unit: g (PS)/(mol Ti × mol styrene × h); g (PE or PP)/(mol Ti × atm × h) (1 atm = 101.325 kPa). <sup>c</sup>Toluene was used as the solvent.

<sup>d</sup>Preactivation time: 10 min.

<sup>e</sup>Preactivation time: 20 min.

<sup>f</sup>The polymers were not soluble in CH<sub>2</sub>Cl<sub>2</sub>, THF, and CHCl<sub>2</sub>CHCl<sub>2</sub> for  $M_{w}$  measurement.

<sup>g</sup>Trityl tetrakis(pentafluorophenyl)borate was used as the activator.

<sup>h</sup>Only trityl tetrakis(pentafluorophenyl)borate was used.

PE and PP, the use of a large amount of catalyst (5.0 mmol) for propylene resulted in polymers that exhibited a bimodal molecular weight distribution pattern.

#### Formation of the cationic complex

The dimethyl Ti(IV) complex reacts with a stoichiometric amount of TPCPB at room temperature to yield the cationic titanium – monomethyl complex  $[Cp_2TiMe]^+[B(C_6F_5)_4]^-$  (4) as a dark red solution. If the reaction is carried out at 0 or  $-23^{\circ}$ C, it takes longer (>30 min) to form the red solution. On the basis of its NMR spectrum taken at 0°C, the cationic complex 4 exhibits resonances at  $\delta$  6.38 (s, 10H), 1.30 (s, 3H) attributed to the Cp and Ti-Me hydrogens, respectively. The spectrum of 4 differs from that of the parent  $Cp_2TiMe_2$  $(^{1}\text{H NMR in CD}_{2}\text{Cl}_{2} \text{ at } 25^{\circ}\text{C} \delta: 6.07 \text{ (s, 10H)}, -0.15 \text{ (s, 6H)})$ and the integrated ratio of Cp to methyl evolved to 10:3 in the activated complex as compared to a value for the parent compound of 10:6. Bochmann et al. (14) reported a similar complex was generated by reaction of the parent complex with dimethylanilinium tetraphenylborate and that it exhibits resonances at  $\delta$  6.28 (s, 10H), 1.26 (s, 3H). We presume that the resonance differences from the two cationic complexes are due to differences in ion pairing. There were also small resonances in the ranges of 0.20-2.00 and 6.40-6.70 which could not be assigned.

If the catalyst solution is warmed to 25°C and equilibrated for 30 min, the resonances at  $\delta$  6.38 and 1.30 decrease slightly, and the resonances at  $\delta$  0.22 and 6.56, 6.64, 6.72 grow presumably because of decomposition of the cationic complex. One of the deactivation processes of the metallocenium cation that may occur results from Cl<sup>-</sup> abstraction from the solvent if the reaction is carried out in CH<sub>2</sub>Cl<sub>2</sub> (15). During our NMR studies no by-products such as CH<sub>3</sub>-CD<sub>2</sub>Cl were observed.

#### UV-vis spectroscopy

There are a number of reports of spectroscopic studies of the reactions of zirconocene precursors with MAO (16) and  $PhMe_2NH^+B(C_6F_5)_4^-$  (17) but few such reports with activated titanocene catalysts (18). In the zirconocene studies, the activated complex formed is easily distinguished by changes in the positions of the ligand-to-metal charge transfer (LMCT) bands in the optical spectra. Though UV–vis spectroscopy is not suitable for catalyst systems containing trityl cation owing to the overlap of absorption of the cation with the LMCT bands of the complexes formed in the activation process (Fig. 2), TPCP cation has no absorption beyond 320 nm. Thus, one may examine the LMCT bands formed from catalyst systems containing TPCP cation using UV–vis spectroscopy.

In the absence of **2**, **3** shows a LMCT band at 361 nm in both  $CH_2Cl_2$  and toluene. The LMCT absorption band of **3** is shifted to 482 nm in  $CH_2Cl_2$  in the presence of **2** and to 487 nm in toluene, respectively, corresponding to a decrease of electron density on the metal center (16*a*). This is consistent with the formation of cationic Ti(IV) complex observed by NMR spectroscopy. During styrene polymerization, we found that with preactivation, a deep approximately dark red solution of initiator was required in order for the system to exhibit the highest activity. Yellow solutions showed little or no activity as polymerization initiators. Therefore, the corresponding species, which absorbs at 482 nm, must be the actual active species.

In the case of the 2, 3 couple, formation of the active species 4 was followed by observing the absorption changes in dichloromethane at 482 nm (Fig. 3). In the absence of monomer at fixed concentrations of reagents, the maximum concentration of 4 was observed after 17 min (Fig. 3*a*). The absorption then decayed presumably because of the thermal

Fig. 2. UV-vis spectra of catalyst  $Cp_2TiMe_2$  (3) and a mixture of 2 and 3 in  $CH_2Cl_2$ . Concentration of catalyst and activator: [3] =  $4.2 \times 10^{-4}$  M, [2] =  $4.8 \times 10^{-4}$  M; spectrum of the mixture of 2 and 3 was taken after being mixed for 17 min.



decomposition of the active cationic complex. Consistent with results obtained in the polymerization of styrene in that if the initiation system was preactivated for times greater than 17 min (e.g., 20 min, entry 4, Table 1), one observes decreased activity. Consistent with the lower activity observed for the polymerization of styrene when the initiator is prepared in its presence, the growing in of the absorption at 482 nm was much slower in the presence of styrene than in its absence (Fig. 3b). This can be explained if styrene consumes the active species during its formation. A rapid decay of **4** also results from the addition of styrene to the initiation system (Fig. 3c). We presume this to be from the reaction of styrene at the Ti center resulting in a decreased concentration of the cationic complex **4** (Scheme 1).

The formation and decay of cationic complex **4** was studied by following the absorption changes at 482 nm. The formation and decay lifetimes of the active species were obtained by fitting the experimental data to a double exponential decay function using ORIGIN 6.1 software. The species grew in rapidly with  $\tau_1$  of 7.96 min and then decayed slowly with  $\tau_2$  of 28.9 min.

### Mechanism of olefin polymerization

The mechanism we propose for olefin polymerization is that dimethyl Ti(IV) complex reacts with a stoichiometric amount of TPCPB at room temperature to yield the cationic titanium – monomethyl complex  $[Cp_2TiMe]^+[B(C_6F_5)_4]^-$  (4). The system is active for nonfunctionalized olefins like ethylene, propylene, and styrene with polymerization of ethylene and styrene being much faster in  $CH_2Cl_2$  at room temperature than the polymerization of propylene. That ethylene polymerization is faster than that of propylene is consistent with a coordination polymerization mechanism (Scheme 2).

It has recently been found that some well-characterized Ziegler–Natta catalysts can also initiate carbocationic poly-

Fig. 3. Variation of the absorption of 2 and 3 at 482 nm with time in CH<sub>2</sub>Cl<sub>2</sub>. [3] =  $4.2 \times 10^{-4}$ M, ratio of 2:3:styrene in mol (*a*) in the absence of styrene; (*b*) in the presence of styrene; and (*c*) styrene added at 17 min.



Scheme 1. Electrophilic attack of 4 on styrene.







merization of olefins (19) and that styrene may undergo polymerization via both coordination and carbocationic mechanisms. Using Cp\*TiMe<sub>3</sub>–B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> as the catalyst and if the polymerization is carried out at a low temperature, only atactic polystyrene was produced. If the polymerization temperature rises to above  $-10^{\circ}$ C, highly syndiotactic polystyrene is obtained (20). At high temperature Ti(III) complex formed by reductive decomposition was confirmed to be the active catalyst for production of syndiotactic polystyrene (21). At lower temperatures, cationic Ti(IV) complex Scheme 3. Cationic polymerization of styrene.



initiates a carbocationic process for the production of atactic polystyrene.

Our spectroscopic studies indicate that cation  $[Cp_2TiMe]^+$ is more stable than  $[Cp^*TiMe_2]^+$  but that it decomposes, though moderately, at room temperature on the polymerization time scale. The decay lifetime of the cationic complex is 28.9 min indicating that most of the cationic complex survived during the polymerization process. Each of the PS samples prepared using our initiating system is soluble in 2butanone, suggesting no syndiotactic PS (s-PS) forms. Therefore, we assume that the cationic Ti(IV) complex is the actual active species in the system reacting as a carbocationic initiator with styrene and producing atactic polystyrene (Scheme 3). The relatively narrow polydispersities of the resulting PS samples (1.92–2.56) is further evidence for a carbocationic polymerization process.

In summary, TPCP borate efficiently reacts with bis(cyclopentadienyl) dimethyltitanium to form cationic Ti complex  $[Cp_2TiMe]^+B(C_6F_5)_4^-$  (4). The formation of cationic Ti complex 4 was confirmed by NMR spectroscopy. The reaction was also studied using UV-vis spectroscopy and observed the bathochromic shift of the Cp2TiMe2LMCT main absorption band from 361 to 482 nm in CH<sub>2</sub>Cl<sub>2</sub>. The kinetic profile showed the cationic species grew in rapidly and then decayed slowly. Though the cationic complex  $[Cp_2TiMe]^+B(C_6F_5)_4^-$  was observed to be thermally unstable and its activity in the polymerization of styrene decreased with time, the system shows generally high polymerization activity for both ethylene and styrene. It is less active for the polymerization of propylene. The cationic Ti(IV) complex is proposed to be a conventional Ziegler-Natta coordinative catalyst for ethylene and propylene polymerization, while it acts as a carbocationic initiator for styrene polymerization.

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