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Carbocationic Initiation of Polymerization of Vinyl Ethers and *N*-Vinylcarbazole Induced by (η^5-C_5Me_5)$TiMe_2$(μ-Me)$B(C_6F_5)_3$. The First Examples of Polymerization of This Class of Electron-Rich Olefins by a Metallocene-like Initiator

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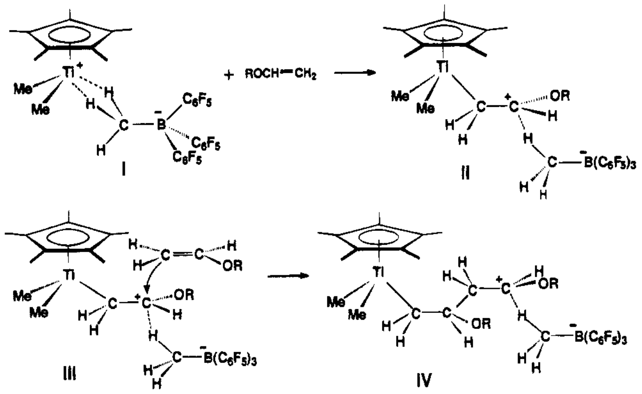
ABSTRACT: Addition of Cp^*TiMe_3 and $B(C_6F_5)_3$ (1:1 ratio; Cp* = η^5-pentamethylcyclopentadienyl) to toluene or methylene chloride solutions of *N*-vinylcarbazole or the vinyl ethers CHR′CHOR″ (R′ = H, R″ = Me, Et, CH_2CHMe_2; R′ = Me, R″ = Et) and 2,3-dihydrofuran at room temperature or −78 °C results in the formation of polymers which generally exhibit unusually high molecular weights and narrow molecular weight distributions. The materials, which are formed *via* carbocationic initiation by the titanium-containing cationic complex $[(\eta^5\text{-}C_5Me_5)TiMe_2]^+$ rather than *via* Ziegler–Natta processes, are in all cases characterized by GPC and $^{13}C\{^1H\}$ and ^{1} NMR spectroscopy, some by DSC and IR spectroscopy. The neutral borane, $B(C_6F_5)_3$, is also a carbocationic polymerization initiator, but is generally less active than the titanium-containing cation.

Introduction

Since the mid-1980s, the utilization of metallocene compounds of the Group 4 metals as catalysts for olefin polymerization has been very extensively developed.[1–3] In general, the active species are believed to be cationic complexes containing a coordinated alkyl group and either a vacant site or a labile ligand, and the mechanism of polymerization involves classical Ziegler-Natta processes. The nature of active initiator sites[4,5] and the factors affecting tacticities of polymeric products[6–8] have been elucidated, and the relevance of key steps such as olefin insertion[9,10] and β-hydrogen and β-methyl elimination[11] processes have been discussed.

Rather more slowly developing has been olefin polymerization catalysis by monocyclopentadienyl compounds,[12] although such species might be expected to exhibit high reactivity for the polymerization of olefins. We have previously established that treatment of the compound Cp^*TiMe_3 with $B(C_6F_5)_3$ results in methyl carbanion abstraction and formation of the complex $[Cp^*TiMe_2][MeB(C_6F_5)_3]$.[13a] The latter exists in methylene chloride solution as the labile, methyl-bridged species $Cp^*TiMe_2(\mu\text{-}Me)B(C_6F_5)_3$ (**I** in Scheme 1), possibly in equilibrium with the solvent-separated ion pair $[Cp^*TiMe_2(CH_2Cl_2)][MeB(C_6F_5)_3]$ and certainly in equilibrium with the methyl-bridged species $[Cp^*TiMe_2(\mu\text{-}Me)TiMe_2Cp^*][MeB(C_6F_5)_3]$.[13b] In aromatic solvents, on the other hand, arene complexes of the type $[Cp^*TiMe_2(\eta^6\text{-arene})][MeB(C_6F_5)_3]$ are formed.[13a] Since the $MeB(C_6F_5)_3^-$, CH_2Cl_2, Cp^*TiMe_3, and arene ligands are readily displaced, these complexes all behave in solution as sources of the cationic, 10-electron species $[Cp^*TiMe_2]^+$, which behaves as an excellent Ziegler-Nata catalyst for the polymerization of ethylene, norbornene, and, possibly, 1,5-hexadiene, but as a carbocationic polymerization initiator for the polymerization of styrene (to atactic polymer in methylene chloride), α-methylstyrene, and isobutylene.[14] In the latter cases, the cationic metal complex presumably activates the olefins *via* η^1-coordination, as depicted in Scheme 1, and polymerization occurs as with other carbocationic initiators.[15]

Scheme 1



It has been generally well established that polymerization of vinyl ethers and *N*-vinylcarbazole proceeds *via* carbocationic initiation,[16–19] and a number of living cationic polymerization systems have been developed.[20–22] Indeed, poly(vinyl ethers) continue to attract attention from both scientific and technological perspectives because of their interesting properties.[16,23] Since *N*-vinylcarbazole and vinyl ethers are more susceptible to carbocationic polymerization than styrene and α-methylstyrene,[15–19] it is to be expected that **I** would be an excellent polymerization initiator for these monomers, and we now describe a series of experiments to this effect. Aspects of this work have appeared previously as a communication.[14a]

Experimental Section

All operations were performed under purified nitrogen, utilizing normal Schlenk techniques or in a Vacuum Atmospheres Dri Lab. Solvents were purified by standard methods, and distilled and degassed before use. All ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded using Bruker AC 200 or Bruker AM 400 spectrometers, chemical shifts being determined by reference to residual ^1H and ^{13}C solvent peaks. IR spectra were measured using a Bruker IFS 25 FT-IR spectrometer, while differential scanning calorimetric (DSC) measurements were recorded using a Mettler TA 3000 system. Gel permeation chromatography (GPC) experiments with the polymers were carried out at room temperature using a Waters Model 440 liquid chromatograph with THF as eluant or at 145 °C in

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Table 1. Effects of Varying Temperature and Solvents on the Weight Average Molecular Weights and Molecular Weight Distributions of the Poly(vinyl ether) Products

expt no.	olefin	temp, (°C)	solvent	M_w ($\times 10^{-4}$)	M_w/M_n
1	MVE	−78	toluene	4.7	1.5
2	EVE	RT	toluene	0.2	broad
3	EVE	−78	toluene	4.6	1.9
4	EVE	−78	1:1 toluene/*n*-hexane	5.0	1.6
5	EVE	−78	CH_2Cl_2	1.6	1.2
6	EVE	−78	10% THF in toluene	3.6	1.6
7	IBVE	−78	toluene	9.3	1.8
8	IBVE	−78	CH_2Cl_2	4.1	2.4
9[a]	IBVE	−78	toluene/5 mL of hexane	10.5	1.7
10	EPE	RT	toluene	2.5	1.5
11	EPE	RT	CH_2Cl_2	2.4	1.5
12	DHF	−78	toluene	4.5	1.6
13	DHF	−78	CH_2Cl_2	5.7	1.7
14	NVC	−78	toluene	10.3	3.5

[a] Except the amount of solvent used in each run, 5 mL of hexane was added additionally.

1,2,4-trichlorobenzene using a Waters Model 150-C GPC, and data were analyzed using polystyrene calibration curves. Crystallinity of polymers was observed using a Nikon Labophat-2 polarizing microscope. Cp^*TiMe_3[24] and $B(C_6F_5)_3$[25] were prepared according to published procedures.

All monomers were purchased from the Aldrich Chemical Co. except for methyl vinyl ether, which was obtained from Matheson. Methyl vinyl ether (MVE) was purified by passing through a column containing 3-Å molecular sieves and was condensed at −78 °C (dry ice−2-propanol bath). The compound 2,5-dihydrofuran was passed through an alumina column, stirred over CaH_2 for about 2 h, and then filtered, degassed, and distilled under reduced pressure. Ethyl vinyl ether (EVE), isobutyl vinyl ether (IBVE), 2,3-dihydrofuran (DHF), and ethyl propenyl ether (EPE, 24% *trans* isomer determined by ^1H NMR spectroscopy)[26] were purified by stirring over CaH_2, degassing, and vacuum distillation, while *N*-vinylcarbazole (NVC) was recrystallized from hexane.

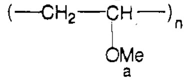
General Polymerization Procedures. Cp^*TiMe_3 (7 mg, 0.03 mmol, purified by recrystallization) was dissolved in the neat liquid monomer (1−1.5 g, 15 mmol), and polymerization was initiated by rapid addition of $B(C_6F_5)_3$ (15 mg, 0.03 mmol) dissolved in toluene or methylene chloride. (In an alternative procedure, utilized for EVE, $[Cp^*TiMe_2][MeB(C_6F_5)_3]$ (**I**) was prepared at low temperatures (<−30 °C), and a solution of the monomer was then added dropwise.) In most cases, the concentration of initiator was 0.01 M and the molecular ratio of monomer and initiator was 500:1 (except for NVC, for which the ratio was 50:1 because of low solubility). The polymerizations were carried out at either −78 °C or room temperature and were terminated by quenching in methanol. Volatile materials were removed under reduced pressure, and removal of residual initiator was accomplished by dissolving the crude products in an appropriate solvent at room temperature and eluting the resulting solution through a column of silica gel. The solvent was then removed under reduced pressure. For polyMVE, 2,6-di-*tert*-butyl-4-methylphenol was added as a stabilizer. Conversions with EVE and IBVE were ~100% according to the ^1H NMR observations, no monomers being detected after about 5 min. Conversions to polyEPE, -NVC, and -DHF were determined gravimetrically; when the polymerizations were allowed to proceed overnight, conversions were in the range 70−80%. The results are presented below and in Tables 1 and 2.

The strongly electrophilic borane co-initiator, $B(C_6F_5)_3$, was also tested for its ability to initiate polymerization of the various monomers. Reaction conditions were as above, with results as in Table 3.

***In Situ* NMR Investigations.** Cp^*TiMe_3 (10 mg, 0.042 mol) in CD_2Cl_2 was placed in an NMR tube sealed with a septum, and the solution was cooled to −78 °C. $B(C_6F_5)_3$ (23 mg, 0.042 mol) in CD_2Cl_2 was added, and the solution turned orange as **I** formed. Ethyl vinyl ether (50 μL, 0.52 mmol) was added by a syringe, the tube was mixed well to give a dark green solution, and the ^1H NMR spectrum was measured immediately at −50 °C. In a complementary experiment, THF (50 μL, 0.62 mmol) was transferred to a solution of **I** at −78 °C. Upon shaking, a pale red solution was generated, and the ^1H NMR spectrum was measured immediately at −50 °C.

Results and Discussion

Poly(methyl vinyl ether) (PolyMVE). The synthesis of polyMVE exhibiting high molecular weights and narrow molecular weight distributions has recently received considerable attention,[27−29] in part because polystyrene and polyMVE form a compatible blend exhibiting a lower critical solution temperature,[27] in part because of the unusual physical properties of polyMVE such as its solubility in both cold water and many common organic solvents other than *n*-alkanes.[28] Polymerization of MVE, initiated by **I**, is very rapid in toluene at −78 °C and results in the formation of sticky yellow liquids (Table 1, expt 1) which were characterized as **A** by NMR spectroscopy.[30] ^1H NMR (298 K in toluene-d_8): δ 3.27 (s, 3H, a), 3.63 (s, 1H, b), 1.38−2.15 (d, 2H, c). $^{13}C\{^1H\}$ NMR (298 K in toluene-d_8): δ 75.7 (s, a), 56.8 (m, b), 38.9−40.9 (m, c). Analysis of the β-methylene resonance[30] in the $^{13}C\{^1H\}$ NMR spectrum indicated the formation of an atactic polymer (47.7% r diads, 52.3% m diads). Pentad sequences were assigned recently by means of well-resolved ^{13}C NMR spectra.[30]



$$(-\overset{c}{C}H_2-\underset{\underset{a}{OMe}}{\overset{b}{C}H}-)_n$$

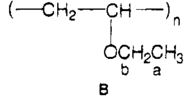
A

The values obtained for M_w and M_w/M_n (Table 1) are comparable with data for polyMVE obtained utilizing some classical Lewis acid initiators,[28,29] but not all.[27]

Poly(ethyl vinyl ether) (PolyEVE). PolyEVE is one of the most useful poly(vinyl ethers), being utilized in hairspray and moisture coating solutions,[17] and in films for paper preservation.[31] Polymerization of EVE by **I** was investigated at −78 °C and room temperature, the reaction being found to be very rapid at both temperatures in various solvents (Table 1, expts 2−6). Higher molecular weight polymers are formed at the lower temperature (Table 1), consistent with normally greater ease of chain termination at higher temperatures,[16] and the values of M_w and M_w/M_n obtained compare well with polyEVE formed utilizing other initiators.[32]

In separate experiments, toluene solutions of EVE were added slowly to toluene solutions containing equimolar amounts of Cp^*TiMe_3 and $B(C_6F_5)_3$, *i.e.*, to preformed **I**. The polyEVE samples formed were found to possess broad molecular weight distributions, with the higher molecular weight fractions exhibiting $M_w \approx 5 \times 10^5$, apparently the first example of polyEVE with $M_w > 10^5$.[32]

PolyEVE forms very sticky liquids in most cases, although the material obtained at −78 °C in 10% THF/toluene was a solid-like material. ^1H NMR (298 K in $CDCl_3$): δ 3.47 (m, 3H, b + c), 1.59−1.77 (d, 2H, d), 1.14 (t, 3H, a). $^{13}C\{^1H\}$ NMR (298 K in $CDCl_3$): δ 73.6−73.8 (b), 63.5−64.5 (c), 39.5−41.5 (d), 15.7 (a).[32d,33]



$$(-\overset{d}{C}H_2-\underset{\underset{b\ \ a}{OCH_2CH_3}}{\overset{c}{C}H}-)_n$$

B

Table 2. Tacticities of PolyEVE and PolyIBVE Prepared at −78 °C

			triads obsd (%)[a]			diads calcd (%)[b]		diads obsd (%)[c]	
expt no.	olefin	solvent	mm	mr	rr	r	m	r	m
3	EVE	toluene	28	50	22	47	53	47	53
4	EVE	1:1 toluene/hexane	28	44	28	47	53	50	50
5	EVE	CH_2Cl_2	36	38	26	55	45	55	45
6	EVE	10% THF in toluene	29	46	25	48	52	48	52
7	IBVE	toluene	0	58	42			45	55
8	IBVE	CH_2Cl_2	0	59	41			56	44
9	IBVE	toluene/5 mL of hexane	0	49	51			33	67

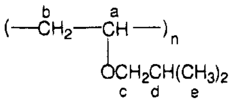
[a] Triads were determined from the ethoxy methylene resonance in the $^{13}C\{^1H\}$ NMR spectra of polyEVE and from the α-proton resonance in the ^1H NMR spectra of polyIBVE. [b] Diad values were calculated by means of the following equations: (m) = (mm) + $^1/_2$(mr); (r) = (rr) + $^1/_2$(mr). [c] Values were determined from β-methylene resonance in the $^{13}C\{^1H\}$ NMR spectra.

Analysis of the OCH_2 multiplets in the $^{13}C\{^1H\}$ spectra (in $CDCl_3$ at room temperature) of the polymers made indicates an approximately 1:2:1 distribution of mm, mr, and rr triads (Table 2).[33] In addition, careful inspection of the ^1H NMR spectra of samples prepared in toluene and quenched with methanol, then water, also revealed weak resonances at δ 9.88 (s), attributable to aldehydic end groups.[34]

EVE was also polymerized by $B(C_6F_5)_3$ in toluene at room temperature: the reaction was completed within a few seconds and gave polyEVE with M_w and M_w/M_n of 1.4 × 10^4 and 1.7, respectively. Polymerization by $B(C_6F_5)_3$ in toluene at −78 °C was, however, extremely slow.

Poly(isobutyl vinyl ether) (PolyIBVE). Considerable research has been carried out on the polymerization of isobutyl vinyl ether, largely in an effort to demonstrate the presence of living polymer systems.[35−37] Polymerization of IBVE by **I** is essentially instantaneous at room temperature and is normally completed within seconds at −78 °C, the temperature at which most reactions with this monomer were therefore carried out (Table 1, expts 7−9). The values of M_w compare well with those of polyIBVE formed utilizing other initiators, but the values of M_w/M_n are relatively high.[35−37] By using a low polarity solvent in expt 9, a material of unusually high molecular weight (>10^5) was obtained and shown to be partially crystalline by means of polarizing microscope.

Most samples of polyIBVE are very sticky, solid-like materials. ^1H NMR (298 K in $CDCl_3$): δ 3.08−3.53 (m, 3H, a + c), 1.48−1.80 (m, 3H, b + d), 0.87 (d, 6H, e). $^{13}C\{^1H\}$ NMR (298 K in $CDCl_3$): δ 76.9 (c), 73.6 (a), 41.1 (b), 29.6 (d), 15.7 (e).[33,35b,37b] Detailed analyses of the



$$\left(-\overset{b}{CH_2}-\underset{\underset{c\quad d\quad e}{OCH_2CH(CH_3)_2}}{\overset{a}{CH}}-\right)_n$$

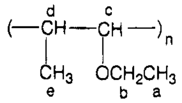
C

O*CH* multiplets in the ^1H NMR spectra demonstrated the presence of approximately 0:3:2 distributions of mm, mr, and rr triads, respectively, indicating a predominance of syndiotactic structures (Table 2).[33]

IBVE was also polymerized by $B(C_6F_5)_3$ in CH_2Cl_2 at room temperature. The reaction was completed within a few seconds and gave polyIBVE with M_w and M_w/M_n of 5.1 × 10^4 and 1.8, respectively.

Poly(ethyl propenyl ether) (PolyEPE). Higashimura *et al.* have previously reported a series of studies concerning polyEPE,[26,38] finding that *cis*-propenyl ether polymerizes several times more rapidly than do vinyl ether counterparts[38a,38f,g] and that the *trans* isomer, being thermodynamically more stable, is less readily polymerized than the *cis* isomer. The monomer used here was a 3:1 mixture of *cis* and *trans* isomers,[26] and even at room temperature polymerization required about 30 min to go to completion (Table 1, expts 10 and 11). For this reason, all polymerization experiments with this monomer were carried out at room temperature rather than at −78 °C. Table 1 contains the GPC results; the values of M_w and M_w/M_n compare well with polyEPE formed utilizing other initiators and reported elsewhere.[26,38a]

PolyEPE is a colorless, glassy solid. ^1H NMR (298 K in $CDCl_3$): δ 2.95−3.95 (d, 3H, b + c), 1.64−2.00 (s, 1H, d), 1.15 (s, 3H, a), 0.83 (s, 3H, e). $^{13}\{^1H\}$ NMR (298 K in $CDCl_3$): δ 80.0−82.5 (c), 65.5−68.2 (b), 37.5−41.5 (d), 15.8 (a), 9.8 (e).[38]



$$\left(-\underset{\underset{e}{CH_3}}{\overset{d}{CH}}-\underset{\underset{b\quad a}{OCH_2CH_3}}{\overset{c}{CH}}-\right)_n$$

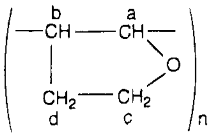
D

It is anticipated that polymers obtained from α,β-disubstituted monomers will exhibit three basic structures: threodiisotactic (threo−meso), erythrodiisotactic (erythro−meso), and disyndiotactic (racemic).[38,39] Assignments of the three structures in the case of polyEPE have been accomplished utilizing $^{13}C\{^1H\}$ NMR spectroscopy,[38c,d,h] and analyses of the OCH_2 multiplets in the $^{13}C\{^1H\}$ NMR spectra of the materials made here indicate that they contain ~62% threo−meso dyads and ~38% racemic dyads. Our results are similar to those obtained with some conventional initiators,[38a,b] but not others.[38e] The reasons for the differences in selectivity are not known.

EPE was also polymerized by $B(C_6F_5)_3$ in CH_2Cl_2 at room temperature, the reaction being complete within 30 min and giving polyEPE with M_w and M_w/M_n of 1.6 × 10^4 and 1.3, respectively.

Poly(2,3-dihydrofuran) (polyDHF). Polymerizations carried out at −78 °C proceeded rapidly and completely to give colorless, solid polyDHF (Table 1, expts 12 and 13). The effects of solvent polarity on the polymerizations of 2,3-dihydrofuran were investigated using toluene and CH_2Cl_2, and Table 1 contains the GPC results. Interestingly, changing the solvent polarity has pronounced effects on the properties of the polyDHF products; the polymer formed in toluene forms a rubbery, partially crystalline film.[40a,b] In contrast, the polyDHF synthesized in CH_2Cl_2 is a very brittle solid. The molecular weights of polyDHF are higher than those in recent literature reports.[32a,40c]

Polymerization of 2,3-dihydrofuran can proceed *via* either head-to-tail addition to the olefinic carbon atoms, to give **E**,as discussed above for MVE, EVE, IBVE, and EPE, or *via* ring opening polymerization, to give **F**.[40c−e] NMR and IR data for the polyDHF formed here suggest



E

$(\text{-O-CH=CHCH}_2\text{CH}_2\text{-})_n$

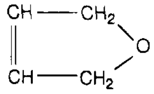
F

that the product is the cyclic ether, **E**. There are no reasonances in either the ^{1}H or the ^{13}C NMR spectra which might be assigned to olefinic groups, and the frequency of $\nu_{as}(C_2O)$, 1060 cm^{-1}, is more consistent with a five-membered ring than with an acyclic product.[41] ^{1}H NMR (298 K in CDCl$_3$): δ 3.80–4.30 (s, 3H, a + b, broad), 1.65–2.20 (s, 3H, c + d, broad). ^{13}C{^{1}H} NMR (298 K in CDCl$_3$): δ 78–88 (a), 65–70 (c), 43–49 (b), 25–32 (d).[40c–e] IR (KBr disk): $\nu_{as}(C_2O)$ 1060 cm^{-1}. T_g 109 °C for product of expt 14.

In contrast to polyEPE (see above), polyDHF can in principle assume only two different stereoisomers, erythrodiisotactic (erythro–meso) and disyndiotactic (racemic); because of the ring structure, the α- and β-substituents of DHF must be in mutually *cis* positions. On the basis of comparison with polyEPE,[38d] the ^{13}C{^{1}H} NMR spectrum suggests that the product of expt 13 is 65% racemic and 35% erythro–meso.

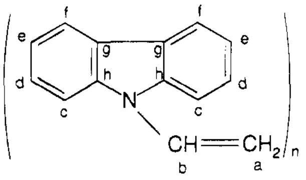
DHF was also polymerized by B(C$_6$F$_5$)$_3$ in CH$_2$Cl$_2$ at −78 °C, the reaction being completed within a few seconds to give polyDHF with M_w and M_w/M_n of 2.5 × 10^4 and 1.4, respectively.

Attempts To Obtain Poly(2,5-dihydrofuran). Polymerizations of 2,5-dihydrofuran (**G**) were attempted in toluene and CH$_2$Cl$_2$, and in the bulk monomer at room temperature and −78 °C. No heat was given off, and after 1 month the volatile materials were removed under reduced pressure and the residues were characterized by ^{1}H NMR spectroscopy. No polymer was detected, although isomerization of 2,5-dihydrofuran and concomitant ring opening polymerization have been observed with other initiator systems.[42] Comparative attempts to polymerize bulk **G** and THF were also made at −78 °C; the reaction mixtures were left for 20 h, after which all volatile materials were removed under reduced pressure. In neither case were resonances of polymeric materials observed in the ^{1}H NMR spectra.



G

Poly(*N*-vinylcarbazole) (PolyNVC). PolyNVC has generated considerable recent interest because it exhibits interesting photoconductivity properties when doped appropriately.[43] Polymerization of NVC is readily accomplished *via* free radical and cationic methods, but anionic and Ziegler–Natta processes are not generally thought to be applicable.[18,19] Polymerization of NVC initiated by **I** in toluene at −78 °C resulted in a white crystalline material (Table 1, expt 14) with a relatively high glass transition temperature and very low solubility in many solvents. Molecular weight distributions, based on polystyrene calibrations, are given in Table 1; the values of M_w and M_w/M_n compare well with those of polyNVC formed utilizing other initiators and reported elsewhere,[32a,43e–k] although molecular weights determined utilizing the universal calibration principle[44] were higher by approximately an order or magnitude. ^{1}H NMR (373 K in C$_2$D$_2$Cl$_4$): δ 4.8–8.0 (m, 4H, c–f), 2.5–3.5 (d, 1H, b), 1.0–2.0 (m, 2H, a). ^{13}C{^{1}H} (363 K in dioxane, external standard diglyme-d_{14} (δ 57.7)): δ 108–161 (m, c–f), 50.0–51.1 (m, b), 36.3 (m, a). T_g 228 °C for product of expt 14. The syndiotactic fraction, X_s, was 68%, determined according to $(T_g - 399)(1 - X_s) + (T_g - 549)X_s = 0$,[45] 61% determined by ^{1}H NMR spectroscopy.[46]



H

NVC was also polymerized by B(C$_6$F$_5$)$_3$ in CH$_2$Cl$_2$ at −78 °C. The reaction was completed within a few seconds and gave polyNVC with M_w and M_w/M_n of 10.2 × 10^4 and 3.6, respectively.

Mechanistic Considerations. We have previously suggested[14a] that polymerization of vinyl ethers initiated by [Cp*TiMe$_2$][MeB(C$_6$F$_5$)$_3$] (**I**) proceeds *via* the mechanism shown in Scheme 1.[14e] Here, the olefin coordinates in **II** in a nonclassical η^1-fashion, the metal–olefin interaction being stabilized by a complementary borate–olefin interaction. The next step in the polymerization process would involve the carbocationic center of the metal ion-activated olefin molecule being attacked by a second olefin monomer (**III**), in a manner normally postulated for carbocationic polymerization processes,[10] followed by chain growth as in **IV**.

Although metallocene compounds of the group 4 elements have been very well studied as catalysts for olefin polymerization, no reports concerning their utilization as initiators for the polymerization of vinyl ethers and *N*-vinylcarbazole have appeared in the literature.[47] However, the ease of polymerization of vinyl ethers containing an ether linkage α to an olefinic group, *i.e.*, in a position to take part in π-bonding with a carbenium ion center, coupled with the failure to polymerize 2,5-dihydrofuran, points to carbocationic initiation. In contrast to 2,3-dihydrofuran, a carbenium ion center cannot be stabilized by an electron pair on an adjacent oxygen atom in 2,5-dihydrofuran. Perhaps surprisingly, **I** induces ring opening polymerization in neither 2,5-dihydrofuran nor THF, although the related complex [Cp*Ti(PhCH$_2$)$_2$][PhCH$_2$B(C$_6$F$_5$)$_3$] has been reported to polymerize THF in this manner.[12p]

End group analyses of the polyEVE obtained on termination with aqueous methanol and a low temperature NMR investigation of the polymerization of EVE both give further support for the carbocationic mechanism shown in Scheme 1, as do observations that tacticities of the products obtained are often similar to those obtained with conventional initiators.

On terminating the formation of polyEVE with first methanol then water, an aldehyde group was formed at the end of the polymer chain and detected by ^{1}H NMR spectroscopy (δ 9.8). The aldehyde group arises *via* hydrolysis of the acetal formed *via* nucleophilic attack by the methanol on the carbenium center of the growing polymer (eqs 1 and 2) and has been observed previously

$$\text{Cp*TiMe}_2[\{\text{CH}_2\text{CH(OR)}\}_n(\text{CH}_2\text{C}^+\text{HOR})] + \text{MeOH} \rightarrow$$
$$\text{Cp*TiMe}_2[\{\text{CH}_2\text{CH(OR)}\}_n(\text{CH}_2\text{CH(OR)OMe}] + \text{H}^+ \quad (1)$$

$$\mathrm{Cp^{*}TiMe[\{CH_2CH(OR)\}_{\mathit{n}}(CH_2CH(OR)OMe)] + H^+ + H_2O \rightarrow CH_3CH(OR)\{CH_2CH(OR)\}_{\mathit{n}-1}CH_2CHO + ROH + MeOH} \quad (2)$$

in samples of polyEVE formed utilizing conventional initiators.[34] Thus, identification of the aldehydic group provides excellent evidence for relevance of a carbocationic process.

Since the successful trapping of the carbenium ion implies a significant steady state concentration of this functional group, not altogether successful tests for the presence of living polyEVE chains were performed by adding incremental amounts of EVE to solutions of **I** in toluene at −78 °C.[20−22] Broadened molecular weight distributions of polyEVE were obtained, the higher molecular weight fractions exhibiting M_w significantly higher than obtained by adding a single aliquot of initiator to a solution of EVE. While rather inconclusive, these results are consistent with a low steady state concentration of a carbenium ion (as in **IV**), although chain transfer processes are clearly a factor in the polymerization process.

Further support for the species proposed in Scheme 1 was achieved by *in situ* NMR investigations. On addition of EVE to a CD_2Cl_2 solution of $[Cp^{*}TiMe_2(\mu\text{-}Me)B(C_6F_5)_3]$ (**I**) (12:1 ratio) at −50 °C, the ^1H resonances of **I** at δ 1.95 (Cp*) and 1.20 (μ-Me) disappeared and were replaced by strong Cp* resonances at δ 2.04 and 2.02, the methyl resonance of the free borate ion, $MeB(C_6F_5)_3^-$ (δ 0.38),[13] and the resonances of polyEVE (δ 0.8−1.9). The terminal TiMe resonance of **I** presumably also disappeared, but the broad polyEVE resonances obscured any new TiMe resonances. A complementary ^1H NMR investigation of the effects of added THF on the initiator system was carried out at −50 °C in CD_2Cl_2; as with EVE, addition of the ether to the solution resulted in the resonances of **I** disappearing and new resonances appearing at δ 2.04 (Cp*), 0.79 (TiMe), and 0.37 (BMe). Since both EVE and THF produce a complex exhibiting a Cp* resonance at $\sim\delta$ 2.04, it appears that the ethers both displaced the borate anion from the titanium cation to form as dominant species complexes of the type $[Cp^{*}TiMe_2(L)_n][BMe(C_6F_5)_3]$ (L = polyEVE, THF; $n = 1$, 2[12p,13a,14b]). Similar titanium and zirconium complexes have been formed with amines and phosphines, and the putative Cp* and TiMe chemical shifts are reasonable.[13a,14b] The Cp* resonance at δ 2.02 in the spectrum of the EVE-containing reaction mixture may possibly be attributable to the neutral, titanium-containing end group of the growing polymer. If so, then a considerable proportion of the titanium in solution is actively involved in polymerization rather than being O-coordinated to vinyl ether molecules.

These conclusions are supported by the results of a $^{13}C\{^1H\}$ NMR study involving the utilization of ^{13}C-enriched $Cp^{*}Ti(^{13}CH_3)_3$.[13c] The $^{13}C\{^1H\}$ NMR spectrum of the neutral complex $Cp^{*}Ti(^{13}CH_3)_3$ in CD_2Cl_2 at room temperature exhibits a TiMe resonance at δ 60.4, while the $^{13}C\{^1H\}$ NMR spectrum of $[Cp^{*}Ti(^{13}CH_3)_2][(^{13}CH_3)B(C_6F_5)_3]$ in CD_2Cl_2 at −30 to −60 °C exhibits resonances at δ 131.1 (w, Cp* ring C), 80.1 (vs TiMe), ~44.3 (br, m, BMe), and 12.6 (w, Cp* methyl). The $^{13}C\{^1H\}$ NMR spectrum of the THF adduct of $[Cp^{*}Ti(^{13}CH_3)_2][(^{13}CH_3)B(C_6F_5)_3]$ in CD_2Cl_2 at −50 °C exhibits a TiMe resonance at δ 75.6.

On the addition of EVE to a solution of $[Cp^{*}Ti(^{13}CH_3)_2][(^{13}CH_3)B(C_6F_5)_3]$ in CD_2Cl_2 at −50 °C, new TiMe *multiplets* appeared at $\sim\delta$ 79 and 64, in addition to the methyl resonance of the free borate anion, $[(^{13}CH_3)B(C_6F_5)_3]^-$, at δ 9.6. Comparison with the $^{13}C\{^1H\}$ given above suggests tentative assignments of the resonances at $\sim\delta$ 79 and 64 to cationic O-bonded ether complexes and neutral trialkyltitanium species, respectively, and the multiplet structure of both resonances presumably reflects the presence in solution of species containing EVE chains of varying molecular weight. Interestingly, the $^{13}C\{^1H\}$ spectrum also exhibited resonances, at δ 20.1 and 17.8, which are attributed to $OCHMe_2$ end groups by analogy with the methyl chemical shift of 2-methoxybutane.[48] This interpretation impies that the neutral trialkyltitanium species of Scheme 1 can transfer a methyl group to a carbenium ion center of the growing polymer chain, either intra- or intermolecularly, a reasonable conclusion since Cp*TiMe has been shown to transfer a methyl group to the trityl carbenium ion.[14b,49]

Table 3. Molecular Weight Data for Polymers Formed *via* Initiation by $B(C_6F_5)_3$

olefin	temp	solvent	time	M_w ($\times 10^{-4}$)	M_w/M_n
EVE	RT	toluene	5 s	1.4	1.7
IBVE	RT	CH_2Cl_2	5 s	5.1	1.8
EPE	RT	CH_2Cl_2	0.5 h	1.6	1.3
DHF	−78 °C	CH_2Cl_2	5 s	2.5	1.4
DHP	RT	CH_2Cl_2	12 h	0.1	1.4
NVC	−78 °C	CH_2Cl_2	5 s	10.2	3.6

As reported elsewhere,[46] polyNVC synthesized *via* cationic polymerization normally contains 50% isotactic, 50% syndiotactic diads, whereas polyNVC obtained *via* radical polymerization normally contains only a 25% isotactic diads fraction. The relative amounts of these fractions may be deduced from the broad methine resonances in the ^1H NMR spectrum; examination of the polyNVC prepared here reveals a 40% isotactic fraction, supporting the proposal that polymerization of NVC initiated by **I** proceeds *via* a carbocationic processes.

Shown in Table 3 are the results of several polymerization reactions by the borane $B(C_6F_5)_3$, itself a very good Lewis acid which might well be expected to be a good carbocationic initiator in the absence of $Cp^{*}TiMe_3$. As is clear, the borane is a good initiator, although it exhibits generally lower activity than the titanium cation. Interestingly, it also produces polymers with generally lower weight average molecular weights but with narrower molecular weight distributions. Under the conditions of the polymerization experiments involving **I**, polymerization by the borane was not a factor.

Summary

The complex $[Cp^{*}(TiMe_2][MeB(C_6F_5)_3]$ (**I**) has been shown to be a very active cationic initiator system for methyl vinyl ether, ethyl vinyl ether, isobutyl vinyl ether, 2,3-dihydrofuran, and *N*-vinylcarbazole; in general, weight average weights of the products are comparable with or higher than weight average weights obtained using more conventional initiators. Coupled with the very high activity which **I** exhibits for the Ziegler−Natta polymerization of ethylene,[14a,b] for the carbocationic polymerization of isobutylene,[14d] styrene (in CH_2Cl_2),[14b] and α-methylstyrene,[14b] for cyclopolymerization of 1,5-hexadiene[14c] and ring opening metathesis polymerization of norbornene,[14c] this titanium complex may well be the most versatile olefin polymerization initiator/catalyst known.

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