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Polymerization of norbornene and 1,5-hexadiene by $[Cp^*TiMe_2][MeB(C_6F_5)_3]$ ☆

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Abstract

Reaction of Cp^*TiMe_3 with $B(C_6F_5)_3$ results in methyl abstraction and formation of the compound $[Cp^*TiMe_2][MeB(C_6F_5)_3]$. The thus formed 10-electron, cationic species $[Cp^*TiMe_2]^+$ is an excellent initiator for polymerization of norbornene via Ziegler and ring opening methasis processes and of 1,5-hexadiene via cyclopolymerization and Ziegler processes.

Keywords: Titanium; Boron; Norbornene polymerization; 1,5-hexadiene polymerization

1. Introduction

There has in recent years been extensive research into the utilization of titanocene, zirconocene and hafnocene derivatives as homogeneous catalysts for olefin polymerization [1], much of this work being derived from the seminal contributions of Brintzinger et al. [2]. On the basis of considerable research [1], it is now widely accepted that the best metallocene catalysts function as coordination (Ziegler) polymerization catalysts and incorporate the following structural features: the presence of a coordinated alkyl ligand, of a vacant site and of a positive charge. Thus 16-electron complexes of the type $[Cp'_2MR(L)]^+$ (M = Ti, Zr, Hf; Cp′ = substituted η^5-cyclopentadienyl group; R = alkyl group; L = labile ligand) form probably the most extensively studied class of homogeneous catalysts for the polymerization of olefins.

Complementing the above-mentioned research on metallocene systems, we [3] and others [4] have demonstrated that electronically less saturated and sterically less hindered monocyclopentadienyl complexes of the type $[Cp'MR_2L]^+$ may also behave as useful catalysts or initiators for olefin polymerization. Indeed, there have recently appeared many publications describing the utilization of monocyclopentadienyl compounds of titanium and zirconium as olefin polymerization catalysts or initiators for a variety of monomers including ethylene [3b,c,4g,h,k,r], α-olefins [4h,k,s], conjugated dienes [3d,4a,q], isobutylene [3d], aromatic olefins [3b,c,4b,f,j,l,m,o], vinyl ethers [3b] and *N*-vinylcarbazole [3b]. The latter two types of olefin are not normally susceptible to polymerization via Ziegler processes because they coordinate via the heteroatoms to the active sites of most types of Ziegler catalysts, and thus act as poisons. However, vinyl ethers and *N*-vinylcarbazole are readily polymerized via carbocationic processes, and the recently recognized ability of the compound $[Cp^*TiMe_2][MeB(C_6F_5)_3]$ to act as a carbocationic initiator for these types of monomer and for aromatic olefins has greatly broadened the scope of olefin polymerization by metallocene-like systems [3b–d].

We have previously shown that reaction of the compound Cp^*TiMe_3 (Cp^* = η^5-pentamethylcyclopentadienyl) with $B(C_6F_5)_3$ results in methyl abstraction and formation of the complex $[Cp^*TiMe_2][MeB(C_6F_5)_3]$ [3a], which appears to exist in methylene chloride solution as the labile, zwitterionic species **A**, in equilibrium possibly with the solvent-separated ionic complex $[Cp^*TiMe_2(CH_2Cl_2)][MeB(C_6F_5)_3]$ [3a]. In aromatic solvents, however, arene complexes of the type $[Cp^*TiMe_2(\eta^6\text{-arene})][MeB(C_6F_5)_3]$ are formed [3a]. Since the $MeB(C_6F_5)_3^-$, CH_2Cl_2 and arene ligands

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☆ Dedicated to Professor Dr. Hans-Herbert Brintzinger on the occasion of his 60th birthday.

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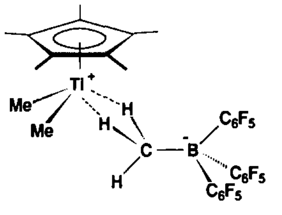


A

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 initiator or initiator precursor for olefin polymerization. We now describe our findings on the use of $[Cp^*TiMe_2]^+$ as an initiator for the polymerization of norbornene (via Ziegler and ring opening methasis processes) and 1,5-hexadiene (via a cyclopolymerization process).

2. Experimental details

All polymerizations were carried out under an atmosphere of nitrogen. In a typical experiment, olefin (1–3 g) and Cp^*TiMe_3 (7 mg, 0.03 mmol, olefin : Ti ratio approx. 500 : 1) were introduced into a flask and polymerization was initiated by the rapid addition of $B(C_6F_5)_3$ (16 mg, 0.03 mmol) in 5 ml toluene. The products formed were maintained at the polymerization temperature for about 15 min, after which time polymerizations were terminated by quenching the reaction mixtures with 1% acidified methanol. The precipitated polymers were washed with methanol and dried to constant weight at 80 °C.

Differential scanning calorimetric (DSC) measurements were recorded using a Mettler TA 3000 system. Gel permeation chromatograms (GPC) of the polymers were obtained at 145 °C in 1,2,4-trichlorobenzene using a Waters model 150-C GPC or in THF at room temperature using a Waters model 440 liquid chromatograph; data were analyzed using polystyrene calibration curves. High temperature (120 °C) ${}^{13}C\{{}^{1}H\}$ NMR spectra of the polymer products were recorded in $C_2D_2Cl_4$ (d^{14}-diglyme internal lock) on a Bruker CXP 200 MHz spectrometer; room temperature ${}^{1}H$ and ${}^{13}C\{{}^{1}H\}$ spectra were recorded in CD_2Cl_2 on a Bruker AM 400 spectrometer; chemical shifts were referenced to residual solvent peaks.

3. Results and discussion

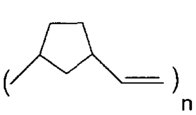
3.1. Norbornene

Polymerization of norbornene is effected by a variety of initiators, the majority of which catalyze ring opening metathesis polymerization (ROMP) to produce poly(1,3-cyclopentenylene vinylene) **B** [5]. In these cases, the reactive species involved in chain propagation is a transition metal carbene complex, and the polymers formed generally exhibit good solubilities in a variety of solvents and have been well characterized by ${}^{1}H$ and ${}^{13}C\{{}^{1}H\}$ NMR spectroscopy [5]. Materials exhibit *cis–trans* isomerism about the C=C double bonds and, since each ring contains two chiral carbon atoms, *m* and *r* dyad structures, as well.

A relatively smaller number of initiators behave, apparently, as classical Ziegler catalysts, producing poly(2,3-bicyclo[2.2.1]heptane) **C** [5e]. These products are generally considerably less soluble in organic solvents at ambient temperature, and do not generally appear to have been well characterized spectroscopically.

Norbornene polymerizations induced by $[Cp^*TiMe_2][MeB(C_6F_5)_3]$ were attempted at −78 °C, 0 °C, 21 °C, 50 °C and 100 °C, the yields of polymeric products being 0%, 25%, 78%, 97%, and 0% respectively. The reaction initiated at 21 °C proceeded very rapidly, and the exothermicity caused a rapid increase in the temperature to about 50 °C. Attempts to purify the resulting elastomeric products of entrained catalyst were made by dissolving in 1,2,4-trichlorobenzene, but the materials failed to dissolve completely and colorless gels were obtained. These, on addition of acidified methanol, afforded white residues which were washed with methanol and dried at 80 °C under vacuum. The white products obtained were of very low solubility in most organic solvents at room temperature, but were sufficiently soluble in 1,2,4-trichlorobenzene at 145 °C that GPC measurements could be made. The products formed at 0 °C, 21 °C and 50 °C exhibited M_w of 83000 (M_w/M_n = 4.8), 9400 (M_w/M_n = 5.2) and 7000 (M_w/M_n = 7.2) respectively; in all cases the GPC traces were quite symmetric.

A ${}^{1}H$ NMR spectrum (400 MHz in $C_2D_2Cl_4$ at 135 °C) of the material prepared at 21 °C exhibited weak olefinic resonances at approx. δ 5.3, which can be assigned to polymer such as **B** [5c,d], and broad multiplets in the region δ 1.0–3.1. The ratio of the total integrated intensity of the high field, aliphatic hydrogen resonances to the intensity of the olefinic hydrogen resonances is approx. 26 : 1, far higher than expected for pure **B**, and thus the polymer presumably contains considerable **C**. A ${}^{13}C\{{}^{1}H\}$ NMR spectrum (100 MHz in



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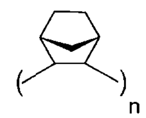


C

benzene-d_6 at 60 °C) supports this conclusion, exhibiting olefinic multiplets at approx. δ 133.2 and 134.3 and more than 50 resonances in the region δ 27–56. The relative intensities of the olefinic resonances suggest that the cis–trans ratio is about 2 : 1, comparable with the products of other ROMP systems [5b], but interpretation of the high field region of the spectrum is impossible. Clearly the chemical shifts expected for all of the aliphatic sites implicit in structures **B** and **C** are met, but the material is highly atactic.

The ^1H NMR spectrum of the polymer prepared at 0 °C did not exhibit olefinic resonances, while that prepared at 50 °C did. Attempts to extract the presumably soluble poly(1,3-cyclopentenylene vinylene) via Soxhlet extraction with toluene from the product formed at 21 °C were successful, however, and thus the material obtained would appear to be a copolymer incorporating the elements of **B** and **C** rather than a mixture of homopolymers. The fact that GPC traces of this material and that produced at 50 °C were symmetric support this conclusion.

3.2. 1,5-hexadiene

The cyclopolymerization of 1,5-hexadiene, as in Fig. 1, has long been known; cyclopolymerization is a chain growth reaction which involves a two-step mechanism, olefin insertion into the transition-metal bond followed by intramolecular cyclization [6d,f]. The poly(methylene-1,3-cyclopentane) products are readily characterized by $^{13}C\{^1H\}$ NMR spectroscopy [7].

Waymouth et al. have recently reported the stereoselective cyclopolymerization of 1,5-hexadiene using chiral group IV metallocenes, and have pointed out that the polymers may assume four microstructures of maximum order, *cis*- and *trans*-isotactic and *cis*- and *trans*-syndiotactic [7], all readily distinguished on the basis of $^{13}C\{^1H\}$ NMR spectroscopy [6,7]. It is believed that tacticity of polymer products is determined by the level of enantioface discrimination for olefin insertion step, and that the *cis* to *trans* ratio is determined by the diastereoselectivity in the cyclization step [6]. Interestingly, while utilization of Group IV metallocene complexes in the polymerization results in complete cyclization, use of $TiCl_4/AlEt_3$ as initiator results in partial 1,2-incorporation of monomer as in **D** [7a].

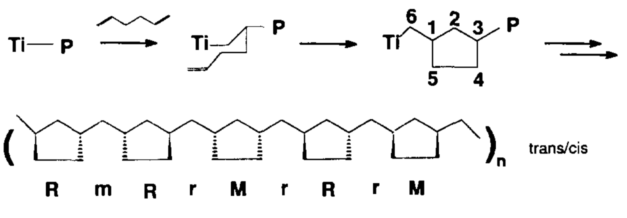
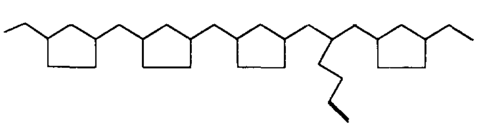


Fig. 1. Cyclopolymerization mechanism for 1,5-hexadiene.



D

Polymerizations of 1,5-hexadiene, initiated by $[Cp^*TiMe_2][MeB(C_6F_5)_3]$ in toluene at 21°C and −78°C proceeded very rapidly, producing insoluble rubbery, elastomeric products. The polymerization processes are highly exothermic, and thus runs initiated at room temperature could not be controlled and became significantly warmer immediately. At temperatures as low as −78°C, in dilute solutions, solidification of the polymer product occurred instantaneously and near quantitatively, resulting in the formation of highly insoluble materials. However, at room temperature under more dilute conditions, polymerization afforded orange gels which, on treatment with 1% HCl in methanol, yielded white precipitates which were soluble in toluene and chloroform at 50 °C. No polymerization was observed to occur when 1,5-hexadiene was reacted with $B(C_6F_5)_3$ in the absence of catalyst.

In general, the products were highly insoluble in toluene but sufficiently soluble in hot 1,2,4-trichlorobenzene that GPC measurements could be made. The materials exhibit relatively high weight average molecular weights ($M_w = (4–5) \times 10^5$) and broad molecular weight dispersions (M_w/M_n of 4–5) compared with those reported in the literature [6,7]. The less soluble fractions formed swollen gels in $C_2D_2Cl_4$ at 120 °C, however, permitting $^{13}C\{^1H\}$ NMR spectra to be recorded. Spectra of several samples were run and, on the basis of the relative intensities of resonances at δ 31.0 and 33.2 in the $^{13}C\{^1H\}$ NMR spectra, corresponding to ring carbons C_4 and C_5 of the *cis* and *trans* repeating units respectively (Fig. 1), the cyclopolymerized products generally contain *trans* : *cis* ratios of 1.4 : 1 to 1 : 1, a result consistent with that obtained by mono Cp^* yttrium complexes [8]. However, the resonances were sufficiently broad that no information concerning tacticity could be obtained.

Resonances in the olefinic region [6], corresponding to residual unsaturation arising from 1,2-incorporation of monomer, were weak and became considerably weaker when the samples were heated to 150 °C, presumably because the materials undergo cross-linking. Interestingly, however, polymerizations carried out by dropping a dilute toluene solution of 1,5-hexadiene to $[Cp^*TiMe_2]^+$ generated in situ at −78 °C resulted in complete cyclopolymerization of the 1,5-hexadiene, no olefin resonances being observed.

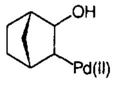
DSC thermograms for most of the products exhibited sharp exotherms at about 160 °C, suggesting that the polymers undergo further cross-linking at that temperature. Consistent with this notion is the fact that polymer samples obtained after DSC analyses were considerably less soluble and less elastomeric. Indeed, such samples could not be solubilized for further $^{13}C\{^1H\}$ NMR analyses or molecular weight determinations.

3.3. Comments on the polymerization mechanisms

We have previously observed that ethylene, styrene and α-methylstyrene are polymerized much faster than is propylene by $[\mathrm{Cp^*TiMe_2}][\mathrm{BMe(C_6F_5)_3}]$, and have suggested that these relative rates appear to be inconsistent with a Ziegler mechanism [3b]. Although ethylene would be expected to coordinate to the sterically congested $[\mathrm{Cp^*TiMe_2}]^+$ ion much more readily than propylene and hence might well polymerize faster, the much more sterically demanding aromatic olefins should coordinate much less effectively than propylene and, in spite of their higher solubilities, would therefore be expected to undergo relatively slow Ziegler polymerization. For this reason, we hypothesized and then established that the strongly electrophilic $[\mathrm{Cp^*TiMe_2}]^+$ can behave as a carbocationic polymerization initiator with aromatic olefins [3b,c], vinyl ethers [3b], *N*-vinylcarbazole [3b] and isobutylene [3d]. However, $[\mathrm{Cp^*TiMe_2}][\mathrm{MeB(C_6F_5)_3}]$ is thermally very labile, decomposing above about 0 °C to give several as yet unidentified species [3b,c]. Thus polymerization of styrene at room temperature and above, which gives syndiotactic polystyrene in high yield, is induced by a product of thermal decomposition of $[\mathrm{Cp^*TiMe_2}][\mathrm{MeB(C_6F_5)_3}]$, probably via a Ziegler process [3c].

As demonstrated above, norbornene polymerization induced at room temperature by $[\mathrm{Cp^*TiMe_2}][\mathrm{MeB(C_6F_5)_3}]$ is sufficiently rapid and exothermic that the temperatures of reaction mixtures increase very rapidly, as observed with styrene. Thus norbornene polymerization also involves a presumably sterically unhindered product of thermal decomposition of $[\mathrm{Cp^*TiMe_2}][\mathrm{MeB(C_6F_5)_3}]$, and its high reactivity is not in conflict with the presumed steric congestion in the cationic "$[\mathrm{Cp^*TiMe_2}]^+$". In contrast to norbornene, cyclohexene and cycloheptene seem completely inert, and the greater reactivity of norbornene presumably arises because this ring-strained olefin can coordinate and thus participate in coordination polymerization much more readily than can the less strained cyclic olefins [9].

On the basis of the ^1H NMR spectra of the polymers obtained, coordination polymerization appears to be the kinetically favoured process, with ROMP becoming of significance only at higher temperatures. However, the fact that the product obtained here at room temperature is an apparent copolymer containing small amounts of the anticipated ROMP product, poly(1,3-cyclopentenylene vinylene), and the anticipated Ziegler product, poly(2,3-bicyclo[2.2.1]heptane), suggests [5] that carbene and related metallacyclobutane intermediates also pertain. Presumably a carbene-containing species is formed via thermal decomposition of the cationic complex $[\mathrm{Cp^*TiMe_2}]^+$, and we note that the related $\mathrm{CpTiMe_3}$ also initiates ROMP with norbornene [5d]. The large number of resonances in the ^1H and $^{13}C\{^1H\}$ NMR spectra indicate no preferred stereochemistry for the polymer growth steps [10].



E

Finally, we note that poly(2,3-bicyclo[2.2.1]heptane) **C** is also obtained using cationic palladium(II) complexes containing no hydride or alkyl ligand which might participate in olefin migratory insertion steps and thus initiate polymerization [5e]. While no route to initiation of polymerization has been suggested, we note that no efforts to exclude water are made, and indeed that polymerization occurs explicitly in the presence of water. On this basis, it seems possible that a σ-bonded 2-hydroxynorbornyl species **E** might be formed via the well understood nucleophilic attack on an η^2-norbornene complex by water [11]. In the presence of free norbornene, the resulting alkylpalladium complex might well be sufficiently stable that polymerization would be possible.

Cyclopolymerization of 1,5-hexadiene by $[\mathrm{Cp^*TiMe_2}][\mathrm{MeB(C_6F_5)_3}]$ is not very rapid, and thus initiation via a normal coordination and migratory insertion process involving $[\mathrm{Cp^*TiMe_2}]^+$ [6] seems feasible. We note that 1,5-hexadiene may also be cyclized without polymerization by a variety of alkylmetal compounds [12a,b] as well as by palladium(II) salts [12c]. Mechanisms similar to that suggested in Fig. 1 undoubtedly pertain, with rapid β-elimination providing a "chain termination" step.

3.4. Summary

The compound $[\mathrm{Cp^*TiMe_2}][\mathrm{MeB(C_6F_5)_3}]$ (and/or the products of its thermal decomposition) induces polymerization of norbornene via Ziegler and ROMP processes and of 1,5-hexadiene via cyclopolymerization and Ziegler processes. Since this initiator system is also an excellent Ziegler catalyst for ethylene [3b,c] and styrene (to syndiotactic polystyrene [3c]) and an excellent carbocationic polymerization initiator for styrene [3c], vinyl ethers [3b], *N*-vinylcarbazole [3b] and isobutylene [3d], it is clearly one of the most versatile and potentially useful olefin polymerization initiators known.

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