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Coupling of Insertion and Ring-Opening Polymerizations on a Pd(II) Center: A Potential Route to Novel Block Co-Polymers

A thesis submitted to the Faculty of Graduate Studies
and Research in partial fulfilment of the requirements
of the degree of Master of Science

by
Ngiap Kie Lim

Department of Chemistry
McGill University, Montreal
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ABSTRACT

The first part of this study concerns the examination of tetrahydrofuran ring-opening polymerization mediated by the palladium insertion polymerization catalysts, (bipy)Pd(CH_3)(L)$^+$ OTf$^-$ (L = $NCCH_3$, PhN=C(H)Tol, ^{t}BuN=C(H)Tol, CH_3N=C(H)Tol). Mechanistic studies reveal a series of metal-based reactions prior to ring-opening, which can be utilized to control polymer molecular weights and end-groups.

The feasibility of combining this ring-opening reaction to insertion polymerization to generate new block co-polymers is subsequently investigated, and it forms the primary objective of the study.

The dual-functional palladium(II) complex (bipy)Pd(CH_3)($NCCH_3$)$^+$ OTf$^-$ is found to mediate a novel, single-step coupling of insertion and ring-opened monomers (CO, norbornene, THF) into new polymers. This coupling process follows an unusual route, involving enol lactone as an intermediate, and facilitated by weak Lewis acid. Similar coupling chemistry has been applied to the synthesis of polyTHF end-capped with a small polynorbornene fragment.

Résumé

La première partie de cette thèse concerne l'étude de la polymérisation par ouverture de cycles tétrahydrofuranes sous l'action de catalystes de polymérisation insertive au palladium : $(bipy)Pd(CH_3)(L)^+$ OTf^- (L = $NCCH_3$, PhN=C(H)Tol, ^{t}BuN=C(H)Tol, CH_3N=C(H)Tol). L'étude mécanistique révèle une série de réactions sur le métal précédant l'ouverture du cycle, et pouvant être utilisée afin de contrôler le poids moléculaire du polymère ainsi que ses groupes terminaux.

La faisabilité de combiner cette reaction d'ouverture de cycle à une polymérisation insertive dans le but de générer de nouveaux co-polymères alternés est examinée par la suite, formant ainsi l'objet principal de cette étude.

Le complexe métallique bi-fonctionnel $(bipy)Pd(CH_3)(NCCH_3)^+$ OTf^- est montré comme le médiateur d'une étape nouvelle et unique de couplage de monomères insertifs ou ouverts (CO, norbornène, THF) dans le nouveaux polymères. Ce procédé de couplage suit une voie inhabituelle avec pour intermédiaire un énol de lactone, facilitée par des acides de Lewis faibles. Des couplages similaires furent appliqués à la synthèse de poly-THF terminés par de petits fragments de polynorbornène.

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CHAPTER ONE.

INTRODUCTION:
TRANSITION METAL-CATALYSTS FOR THE SYNTHESIS OF FUNCTIONALIZED POLYMERS

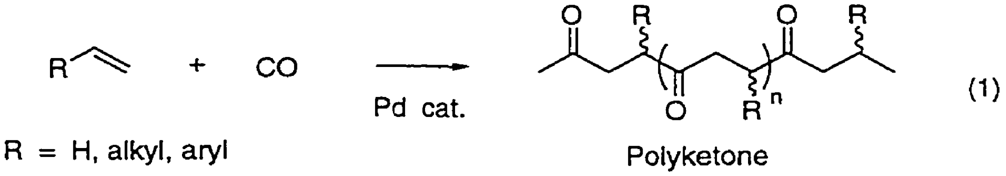
1.0 PERSPECTIVE

The initial discovery of the Ziegler-Natta catalysts[1-2] helped to establish the importance of metal-catalyzed polymerization reactions. Prior to this, most industrial polymerizations of unsaturated substrates were performed using conventional methods involving free radicals, cationic or anionic initiators.[3] These processes often require extreme reaction conditions.[4-6] The newly developed *metal-based* catalysts, on the other hand, offer an efficient and yet versatile route for the polymerization of olefins.[6] In addition, these metal catalysts were found to provide excellent control over polymerization properties, including sequential monomer selectivity, polymer molecular weights and microstructure.[7]

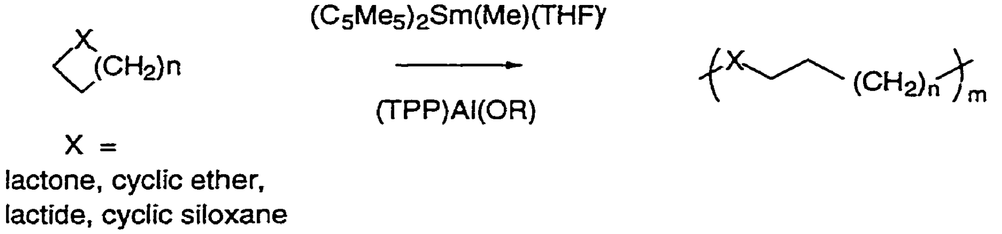
Typically, a Ziegler-Natta catalyst consists of an early transition metal complex (Group IV, V and VI) in a high oxidation state.[8-9] The use of an electron poor (and therefore oxophilic) metal center is necessary to ensure a high degree of polymerization.[9] However, this property makes the catalyst sensitive to any electron-donating functionality that may be present in the olefin substrate.[10] Thus, Ziegler-Natta catalysts are seldom employed in the polymerization of polar olefins, substrates that are deemed as excellent precursors to new polymeric materials.[11]

There is an enormous interest in the development of more versatile metal catalysts which allow the incorporation of functionality into the polymer backbone.[11] A primary area of research into the generation of these new catalysts focuses on the use of late transition metal insertion polymerization catalysts. Late transition metal complexes are known to be less oxophilic,[9,12] and are thus less sensitive to functionalized substrates. However, late metal-alkyl complexes also tend to undergo rapid β-hydride elimination. Since β-hydride elimination is the major termination step for olefin polymerization, late metal catalysts tend to lead to olefin oligomerization rather than generate high molecular weight polymers.[12] This drawback has traditionally restricted their potential utility as polymerization catalysts.

Recently, late transition metal complexes of the form $(L\text{-}L)Pd(R)(L)^+ X^-$ (M = Ni, Pd; L-L = bidentate nitrogen or phosphorus ligand; R = alkyl; L = labile solvent ligand; X^- = weakly coordinating counter-ion) have been reported to not only catalyze the formation of high molecular weight insertion polymers, but also allow the incorporation of functionality into the olefin insertion polymerization reaction.[13] Perhaps the most important example of the use of these catalysts is the *alternating* co-polymerization of carbon monoxide and olefin to produce highly functionalized polyketones, with molecular weights of up to 10^5 (Equation 1).[13,14]



A further step in the development of metal-catalyzed functionalized polymer synthesis is the discovery of metal initiators for the ring-opening polymerization of *saturated heterocycles*. Organolanthanide complexes and metalloporphyrins have recently been reported to catalyze the polymerization of a diverse variety of heterocycles in living fashion to generate high molecular weight polymers (Equation 2).[15] The polymerization of these heterocyclic monomers, containing substituents like oxygen, nitrogen and sulfur, can similarly impart functionality into the *backbone* of polymers.



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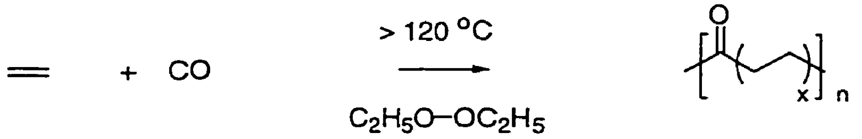
In this chapter, the alternating co-polymerization of CO and olefins to produce polyketones will be first described. A concise review on ring-opening polymerization of heterocycles will be subsequently presented as an alternate route of preparing functionalized polymers.

1.1 METAL-CATALYZED ALTERNATING CO-POLYMERIZATION OF CARBON MONOXIDE AND OLEFIN

1.1.1 SYNTHESIS OF CO/OLEFIN CO-POLYMERS

1.1.1.1 Free Radical Initiated Co-Polymerization

The alternating co-polymerization of carbon monoxide (CO) and olefin to produce polyketones has been known for several decades. Brubaker and co-workers first reported the radical initiated co-polymerization of CO with ethylene, propylene and several other functionalized olefins (CH_2=CHX; X = Cl, OAc, CN) as early as 1950 in a patent.[16] Initiators examined in this study included peroxides, hydroperoxides and O_2. For example, CO and ethylene can be co-polymerized with a di(*tert*-butyl)peroxide initiator at temperature of 120 - 165 °C, and with a combined gas pressure of 1030 bar (Equation 3).[16b] CO-ethylene co-polymers with molecular weights of up to 8000 were obtained in these reactions. However, the resulting polyketone structure is not perfectly alternating (CO incorporation is less than 50 mol %). A monomer mixture consisting of > 70 mol % CO is required to achieve the desired CO incorporation of close to 50 mol %.[16b] This lack of control over the polymer microstructure severely limited the utility of this radical initiated route, and as a result this method is not actively pursued.



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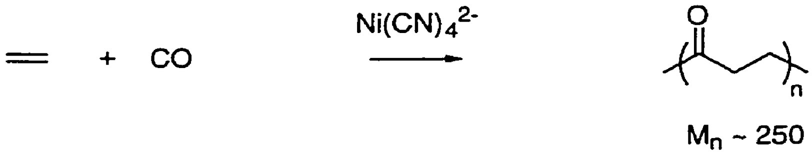
1.1.1.2 Historical Development of Transition Metal Co-Polymerization Catalysts

Reppe and Magin provided evidence in 1952 that CO/olefin co-polymerization can be catalyzed by transition metal complexes (Equation 4).[17] The nickel complex $K_2Ni(CN)_4$ was found to co-polymerize CO and ethylene in water, at 110 °C and a gas pressure of 1500 bar, to afford a strictly alternating CO-ethylene oligomers (M_n ~ 250). However, side products such as diethyl ketone and propionic acid are also observed in this reaction. Following this discovery, there have been numerous attempts to create an efficient catalytic system for this co-polymerization process, with the goal of making high molecular weight, ketone-based polymers. As described below, these efforts have focused primarily upon the development of palladium catalysts.



(4)

Palladium Catalysts

Palladium catalysts for the co-polymerization of CO and olefin were first reported by Gough at ICI in 1967.[18] The catalysts employed were generated *in situ* by reaction of palladium(II) chloride with a variety of chelating phosphine ligands (Figure 1). Co-polymerizations (of CO and ethylene) were performed under extreme conditions, employing a combined gas pressure of up to 2000 bar and a temperature of 150 °C. Molecular weights of CO-ethylene co-polymers ($M_n > 8000$) obtained were significantly higher than those reported by Reppe and Magin with Ni(II) catalysts. However, the catalyst activity was still very low (300 g of polymer / (g of Pd)(h)).

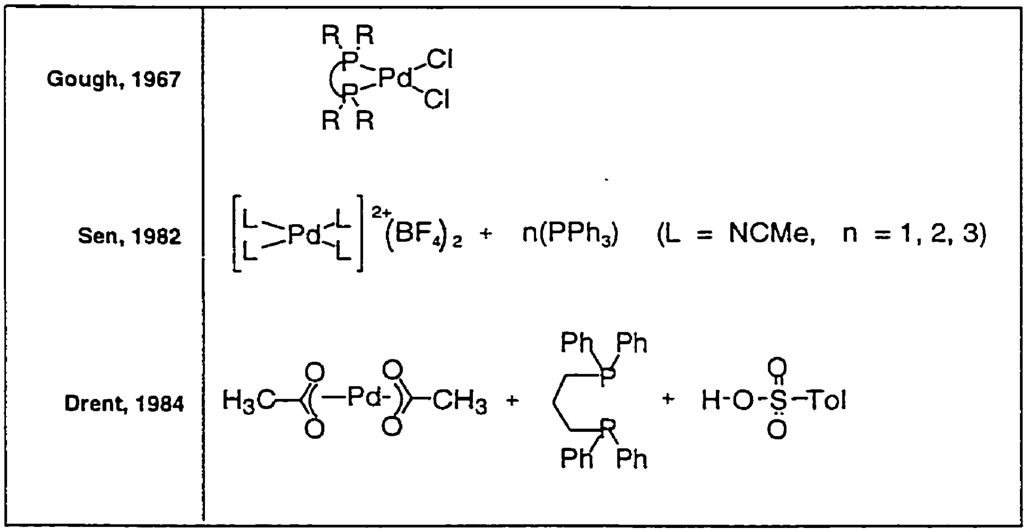
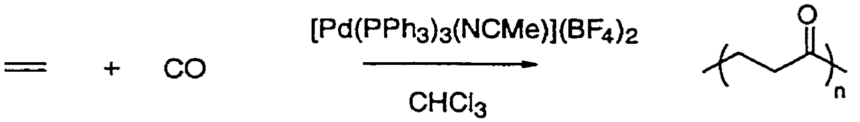


Figure 1. Pd catalyst development

Weakly / Non-Coordinating Counter-Ion

Few advances were made in this field over the next two decades in term of catalyst efficiency. However in the early 1980s, Sen and co-workers demonstrated that cationic Pd(II) complexes of the form $[Pd(PPh_3)_n(NCCH_3)_{4-n}](BF_4)_2$ (n = 1-3) could co-polymerize CO and ethylene under very mild conditions (25 °C, 350 bar).[19] Unlike earlier Pd-based catalysts containing strongly coordinating counter-ions such as CN^- or Cl^-, the new catalysts utilized weakly coordinating BF_4^- counter-ion. The cationic Pd species thus formed had a more accessible coordination sites on the metal center, which likely lead to the increase in catalyst activity. This crucial point is illustrated by the reactions of the corresponding neutral Pd complexes: $Pd(PPh_3)_2(CH_3)(I)$, $Pd(PPh_3)_2(COCH)_3(I)$, $Pd(PPh_3)_2Cl_2$ and $Pd(PPh_3)_4$.[19b] Under similar reaction conditions, they were found to be completely inactive for the co-polymerization of CO and ethylene. In addition, no reaction was observed when a coordinating solvent such as acetonitrile or THF is employed.

A typical co-polymerization reaction with $[Pd(PPh_3)_3(NCCH_3)](BF_4)_2$ involves the dissolution of the catalyst in $CHCl_3$ solvent, followed by exposure to a mixture of ethylene (350 bar) and CO (350 bar) at 25 °C for 1 day (Equation 5).[19] Analysis of the product indicates a CO/C_2H_4 ratio of almost exactly 1 (Anal. Calcd for $C_2H_4.CO$: C, 64.26; H, 7.14. Found: C, 63.97; H, 7.05). The alternating $CO-C_2H_4$ structure in the polymer is further discerned from ^{13}C-NMR which shows only two peaks: δ 211.8 ($CH_2C(O)CH_2$) and δ 38.3 ($C(O)CH_2CH_2C(O)$, and the absence of any resonance at ~ 24 ppm (normally observed in random ethylene-CO co-polymers).



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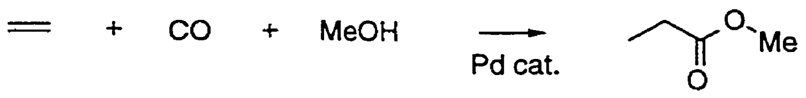
Bidentate Ligand

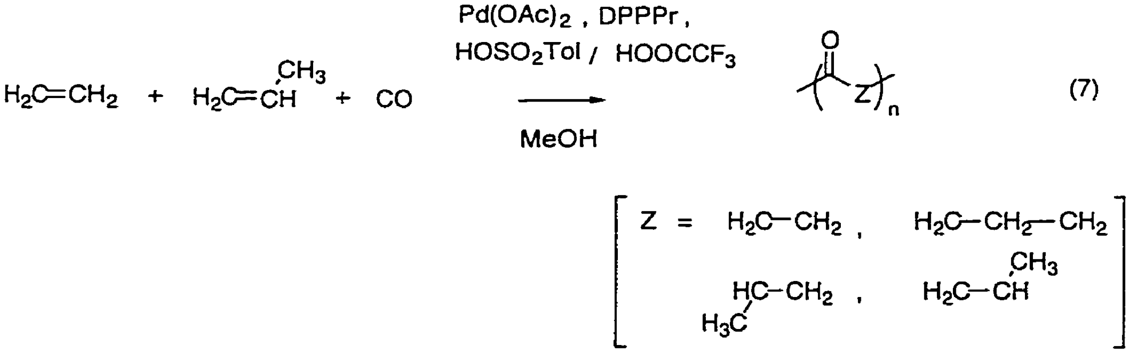
Despite the significant improvement in reaction conditions achieved with these palladium salts, the overall rate of the polymerization is still very low, yielding only 4 g / (g of Pd)(h).[19] This mediocre activity remained unresolved until research at Shell in Amsterdam in 1984 revealed another Pd system which catalyzed the co-polymerization of CO and ethylene at a much higher rate (~ 6000 g / (g of Pd)(h)).[20] This highly active catalyst is prepared *in situ* by adding 1,3-bis(diphenylphosphino)propane) and *p*-toluenesulfonic acid to palladium acetate in methanol (Figure 1). The co-polymerization of CO and ethylene performed with this new catalyst yields more than 10^6 g polymer / g of Pd even under mild reaction conditions (90 °C, 45 bar) .

This Pd catalyst by Drent, which combines the utility of a weakly coordinating counter-ion with a *bidentate* phosphorus ligand, was unexpectedly discovered during the study of ethylene hydrocarboalkoxylation to form methyl propionate (Equation 6).[20b] The catalysts initially examined for ethylene hydrocarboalkoxylation were formed by the combination of palladium acetate with an excess triphenylphosphine and a Bronsted acid (such as HCl). A surprising change in selectivity was observed upon replacement of the excess triphenylphosphine with an equimolar quantity of the bidentate ligand 1,3-bis(diphenylphosphino)propane. Under the same reaction conditions, a perfectly alternating co-polymer of ethylene and CO with essentially 100 % selectivity was produced. The rate of co-polymerization could be further enhanced by substituting the acid component (HCl) with acids of weakly coordinating anion (*p*-toluenesulfonic acid, tetrafluoroboric acid, trifluoromethylsulfonic acid and trifluoroacetic acid).



(6)

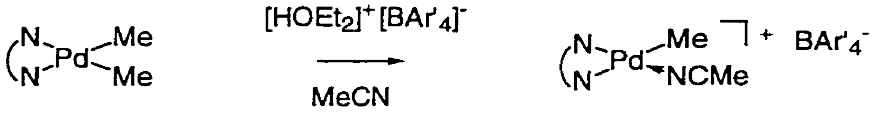
These palladium catalysts were also found to be effective for the terpolymerization of CO with ethylene in combination with other olefins.[20b] For example, the simultaneous co-polymerization of CO, ethylene and propylene yields an alternating CO/olefin terpolymer in which the propylene C_3 units randomly replace ethylene units along the chain according to the general formula: $[-(CO)Z-]_n$ where Z represents the structures: $(-CH_2CH_2-)$, $(-CH_2CH(CH_3)-)$, $(-CH(CH_3)CH_2-)$, $(-CH_2CH_2CH_2-)$ (Equation 7).



Palladium-Alkyl Ligand

In 1992, Brookhart and co-workers prepared the first well-defined catalyst for the the co-polymerizations of CO and olefins.[21] This catalyst system incorporates the two important features described above: a weakly coordinating counter-ion and bidentate ligand, as well as a Pd-alkyl bond. The latter provides a bond into which monomer insertion can occur. The Pd(II) catalysts $(N\text{-}N)Pd(Me)(NCMe)^+\ BAr'_4{}^-$ [N-N = 2,2'-bipyridine or 1,10-phenanthroline, Ar' = $3,5\text{-}(CF_3)_2C_6H_3$] were used for this purpose.[21] These can be easily prepared by protonation of their corresponding di-alkyl Pd complexes $(N\text{-}N)Pd(Me)_2$ by $Et_2OH^+\ BAr'_4{}^-$ in acetonitrile (Equation 8). The co-polymerization of

CO (40 psi) with *tert*-butylstyrene (62 mmol) at 25 °C with 0.02 mmol of catalyst in chlorobenzene yielded co-polymers (T_g = 158 °C) with molecular weight > 10^5. A linear relation was observed between M_n and the degree of monomer conversion, along with M_w / M_n values close to 1.0, which suggest a living polymerization process.



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1.1.2 GENERAL CATALYST STRUCTURE

Current research with well-defined metal catalyzed alternating co-polymerization of CO and olefin employ the basic catalyst features described above: a late transition metal cation, bidentate ligand, non-coordinating counter-ion and a metal-alkyl ligand. While a number of metal systems have been investigated, including Ni(II),[17] Rh(I)[22] and Pd(II),[18-21] the Pd(II) system remains the most thoroughly explored to date.[13a] The general structure of a typical palladium catalyst consists of a Pd(II) center with a bidentate nitrogen or phosphorus ligand, an alkyl ligand, a weakly/non-bonding counter anion and a labile ligand on the Pd center (usually a solvent molecule, the substrate, or the counter-ion) (Figure 2).[13a,21] Each of these features has a unique role critical to the overall catalyst activity. For example, the labile ligand allows easy access to the metal center for the polymerization monomers to coordinate.[21] This is further enforced by the weakly / non-binding nature of the counter-ion which disfavors any close association or interaction between the cationic metal center and the accompanying counter-ion.[19] The weakly / non-coordinating counterion also allows the formation of a cationic metal center upon CO or olefin coordination, further facilitating insertion.

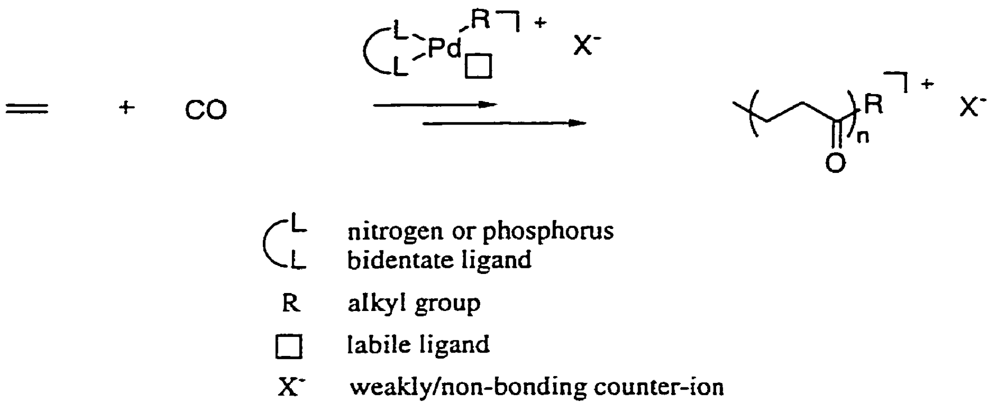
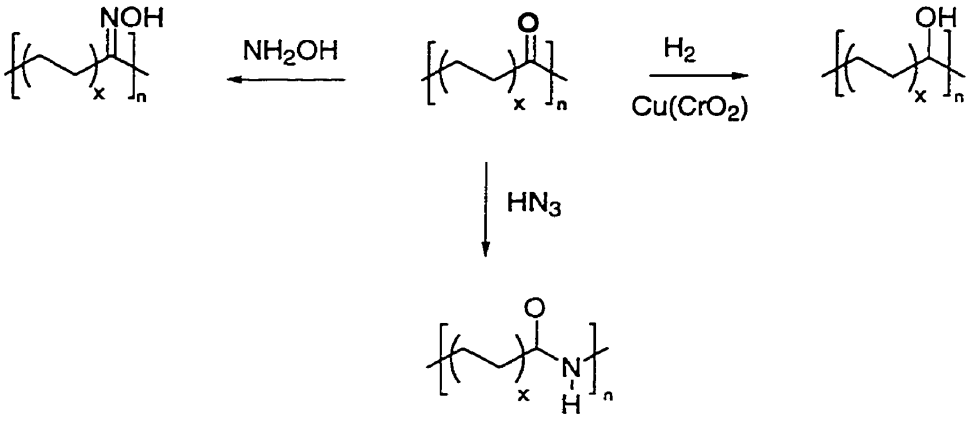


Figure 2. General structure of CO and olefin co-polymerization catalyst

The bidentate ligand on the catalyst serves to ensure that the unsaturated monomer is oriented exclusively in the *cis* configuration with respect to the Pd-C bond,[20b] where the chain growth occurs. This established *cis* regiochemistry facilitates the sequential insertion of coordinated monomers, resulting in polymer chain growth. On the other hand, the use of *monodentate* ligands in place of a bidentate ligand allows the monomer to coordinate in either a *cis* or *trans* configuration, due to isomerization of the ligands on the metal center. Since only the *cis* isomer will permit the anticipated chain growth, the *trans* isomer will impede the progressing insertion of unsaturated monomers into the Pd-C bond. The chain growth is therefore regularly interrupted, and consequently low molecular weight polymers are obtained. The various components of the catalyst incorporated are therefore essential to creating an efficient insertion catalyst system, leading to the formation of high molecular weight polymers.

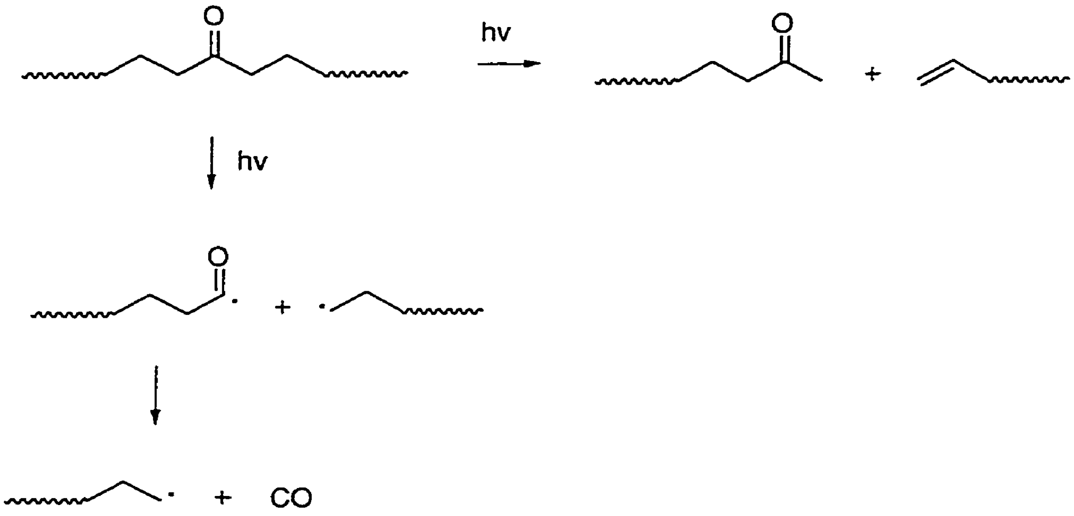
1.1.3 THE INTERESTS IN CO/OLEFIN CO-POLYMERS

The co-polymerization of CO and olefin is considered very attractive from an economic perspective. The base materials required (CO and olefin) are relatively inexpensive and readily available.[13] This alternating co-polymerization process is also rare and yet a convenient method for incorporating functionality into polymers generated with olefins. Brubaker[16] and Michel[23] have shown that the polyketone backbone of these polymers could be easily derivatized into a host of other functionalities: alcohol, carboxyamide and oxime (Scheme 1). Thus, a whole variety of new materials can be assembled.



Scheme 1. Derivatization of ketone-based polymers

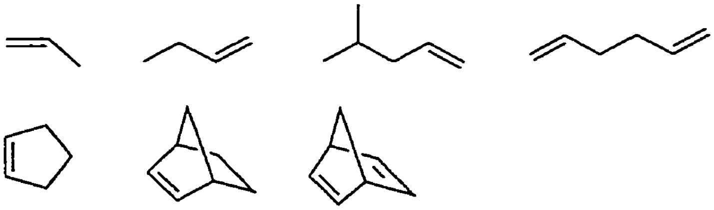
The presence of carbonyl group in the backbone of the polymer has also been shown to render these materials photodegradable. Guillet and co-workers have examined the effect of light in the near-UV region on CO/ethylene co-polymers.[24] The absorption of light results in a decrease of the molecular weight accompanied by the evolution of CO and the generation of terminal vinyl groups in the polymer decomposition products. These results are consistent with Norrish decomposition modes shown below (Scheme 2).



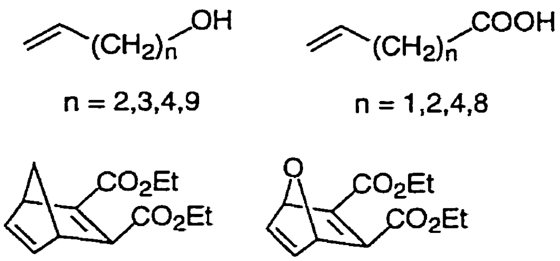
Scheme 2. Degradation of ethylene-CO co-polymer

The co-polymerization process has been very successful in terms of the variety of olefin substrates that can be used. The initial co-polymerization of CO and ethylene by Brubaker and co-workers[16] has been expanded to include a series of α-olefins (Figure 3).[25-27] Later developments have produced co-polymers of *functionalized* olefins and CO.[28] A number of styrene derivatives have also been tested.[21,27,29] As a result, a wide range of ketone-based materials can be easily accessed.

i. propene and higher homologues



ii. functionalized olefins



iii. styrene and its functionalized analogues

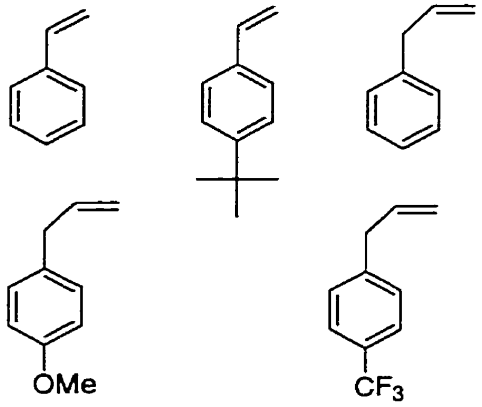


Figure 3. Types of olefins used for co-polymerization with CO

These highly functionalized polyketones formed have been predicted to possess interesting engineering properties.[30] Recent studies on CO/olefin co-polymers show that their properties can range from being crystalline thermoplastics to elastomers, depending on molecular weight and substituents.[14] Carilon, which is a CO-ethylene co-polymer, has an excellent impact resistance at room temperature, and remains ductile even at very low temperature (-20 °C).[30] It also picks up less moisture compared to common engineering thermoplastics such as nylon.[18a] Thus, pre-drying is usually not required, thereby saving a processing step.

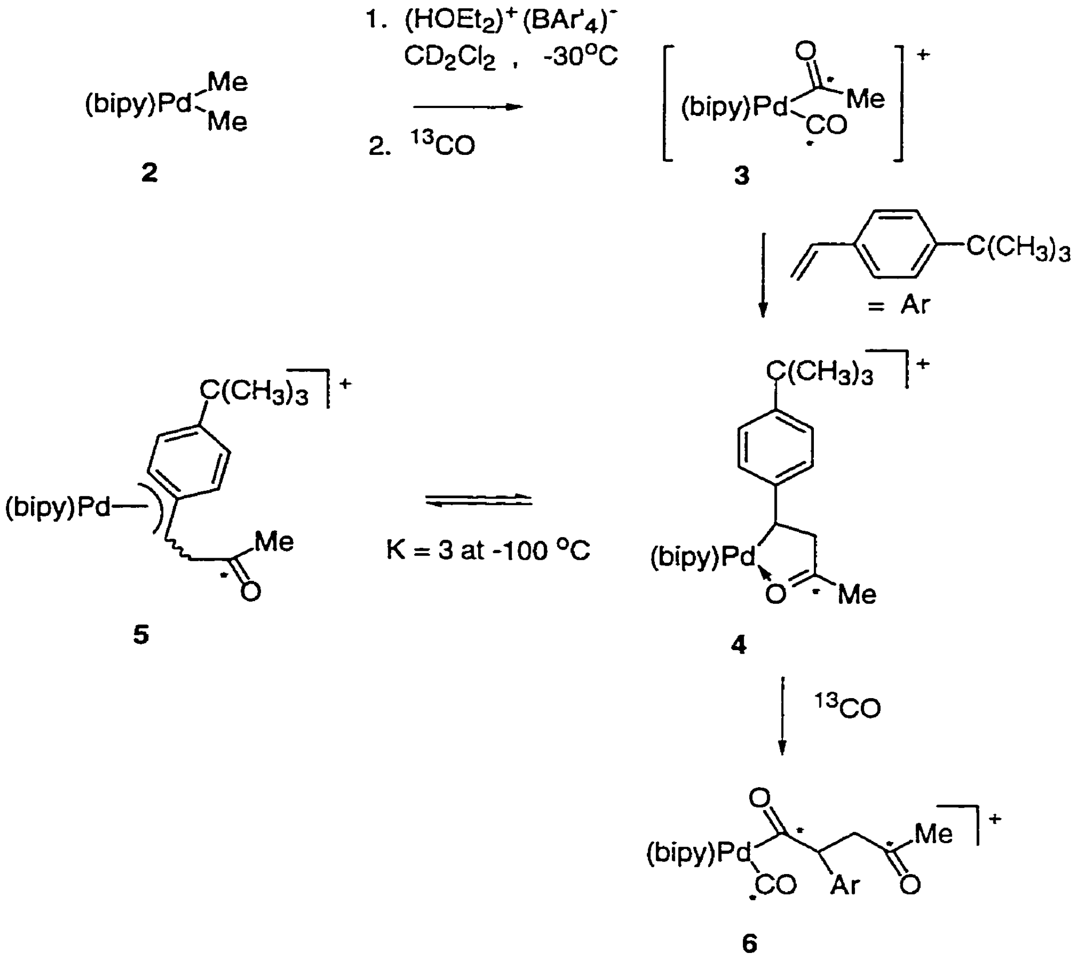
Today, the CO/olefin co-polymers are commercially produced by Shell International. The company is marketing its CO/ethylene co-polymer under the trade name of Carilon.[30] The new thermoplastic is expected to slowly replace older engineering plastics (nylon and acetals) in the automotive industry, particularly in Europe and United States. Shell is also currently planning to open another facility in Geismar, LA to serve the North American market.[30b] Production will start in 1999 with an initial capacity of 25,000 tons per year.

1.1.4 MECHANISM OF THE CO-POLYMERIZATION OF CO AND OLEFIN

Step-wise Alternating Insertion of CO and Olefin

The development and refinement of the Pd catalysts for CO/olefin co-polymerization allowed insights to be obtained in the mechanism of the polymerization reactions. Sen provided the first evidence that polymer chain growth involves the alternating insertion of CO and olefin into a Pd-C bond by trapping out the various palladium intermediates during polymerization.[19b] However, the first direct evidence for this mode of chain growth was provided by Brookhart, who monitored the co-polymerization of ^{13}CO and *tert*-butylstyrene with the complex (bipy)Pd(Me)(NCMe)$^+$ $BAr'_4{}^-$ (**1**) [Ar' = 3,5-$(CF_3)_2C_6H_3$] at low temperature (-80 °C) by ^1H- and ^{13}C-NMR.[21] These spectroscopic studies were able to identify the catalyst resting state, and directly observed the polymer chain growth in step-wise manner.

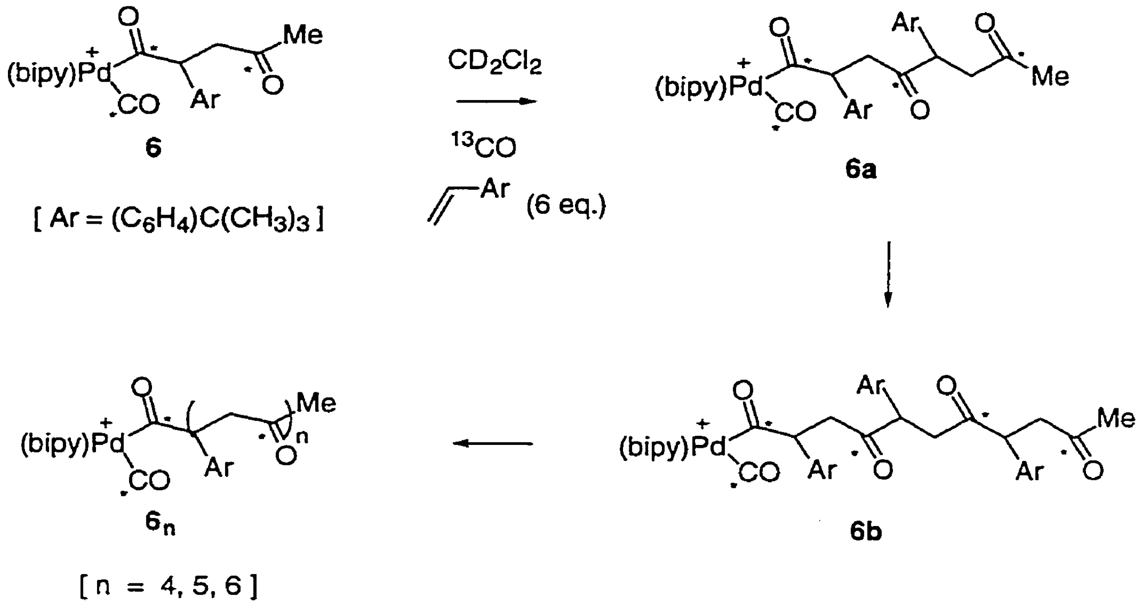
The initial reaction of ^{13}CO with **1** to yield (bipy)Pd($^{13}COMe$)(^{13}CO)$^+$ $BAr'_4{}^-$ (**3**) was obtained via protonation of the complex (bipy)Pd$(Me)_2$ (**2**) in CD_2Cl_2 with $(HOEt_2)^+$ $BAr'_4{}^-$ in the presence of ^{13}CO (Scheme 3a), instead of a direct ^{13}CO addition to **1** in CD_2Cl_2 (in order to produce an *acetonitrile-free* system).[21] Subsequent exposure of this carbonyl acyl complex **3** to one mole equivalent of *tert*-butylstyrene resulted in displacement of the ^{13}CO ligand and insertion of the olefin substrate to afford a five-membered metallacycle (**4**). The complex **4**, which is observed to be in equilibrium with the π-benzyl complex **5**, demonstrates the regiochemistry of insertion of *tert*-butylstyrene substrate into Pd-acyl bond. Exposure of **4** to ^{13}CO at -80 °C to yield a second carbonyl acyl complex **6** (Scheme 3a).



Scheme 3a. Alternating insertion CO and *tert*-butylstyrene to yield catalyst resting state

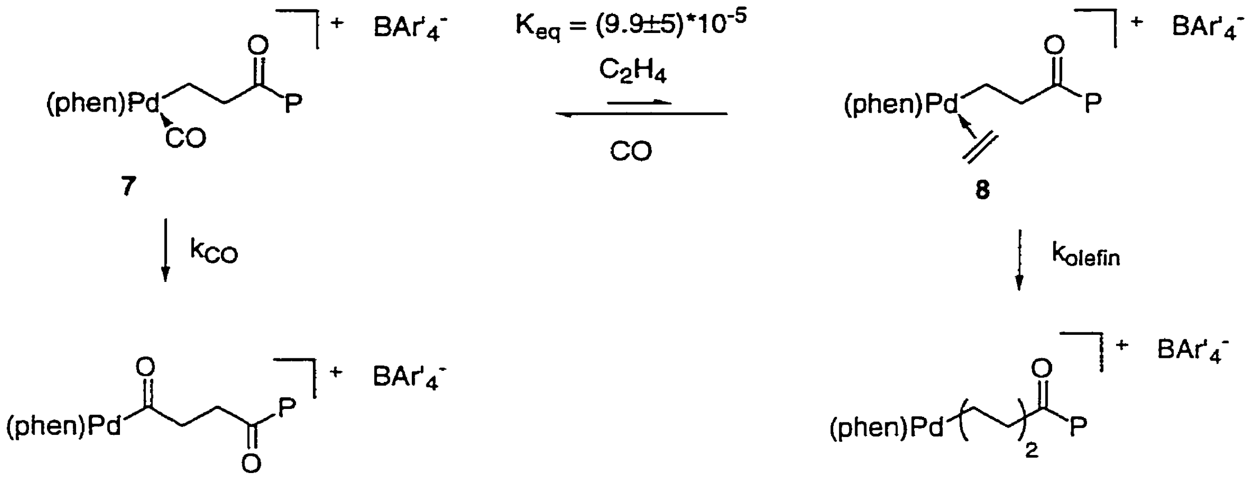
The alternating insertion of CO and olefin can be gradually repeated to propagate chain growth, as demonstrated by the treatment **6** with ~ 6 equivalent *tert*-butylstyrene in

^{13}CO (at -60 to -80 °C).[21] Successive alternating insertion of *tert*-butylstyrene and ^{13}CO to yield **6a**, **6b**...**6**$_n$ are observed, which are evidence in support of the *step-wise chain growth* postulated (Scheme 3b). The detection of only carbonyl acyl complexes (**4**, **6**, **6a**, **6b**...**6**$_n$) during actual co-polymerization conditions indicated that the palladium complex with an acyl ligand and a CO coordinated to the metal is the *resting state* of the catalyst. The favorable formation of these carbonyl acyl complexes is considered to arise from the stronger coordination of ^{13}CO to palladium than *tert*-butylstyrene, and the more facile insertion of ^{13}CO into the Pd-alkyl bond compared to the corresponding insertion of the olefin, *tert*-butylstyrene.[13]



Scheme 3b. Sequential insertion of CO and *tert*-butylstyrene to propagate chain growth

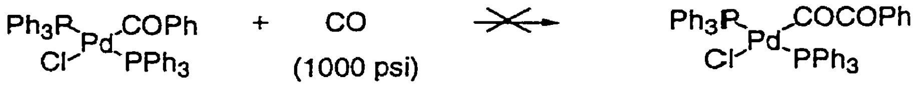
Based upon the above observations, the mechansim of CO/olefin co-polymerization can be considered to consist of two key steps: the insertion of CO into Pd-alkyl bond, followed by insertion of olefin into Pd-acyl bond. In order for these steps to occur selectively, two conditions must be satisfied. First, the insertion of CO into Pd-alkyl bond must be significantly favored over the insertion of olefin into Pd-alkyl bond. Evidence for this postulate can be found by examining the equilibrium between the Pd-carbonyl complex **7** and Pd-olefin complex **8** (Scheme 4). In their studies with the complex (phen)Pd($CH_2CH_2C(O)P)^+$ $BAr'_4{}^-$ [P = $-(CH_2CH_2CO)_n-$], Brookhart and co-workers observed that this equilibrium lay far to the left, favoring the Pd-carbonyl complex **7** over complex **8** in a ratio of approximately 10^4: 1.[31] Furthermore, the rate of CO insertion into Pd-alkyl bond (k_{CO}) relative to olefin insertion (k_{olefin}) was: k_{CO}/k_{olefin} = 2000/1. These two factors, which involve a stronger coordination of CO to palladium and its faster rate of insertion compared to olefin, serve to enforce the required preferential insertion of CO into Pd-alkyl bond.



Scheme 4. Equilibrium between Pd-carbonyl and Pd-olefin complexes, and the kinetics of insertion into Pd-alkyl bond

The second requirement for alternating co-polymerization is the preferential insertion of olefin into Pd-acyl bond over a corresponding insertion of CO. This was demonstrated by Sen who found that CO insertion into Pd-acyl bond is thermodynamically uphill.[32] Treatment of the model complex, $(PPh_3)_2Pd(COPh)(Cl)$, with up to 1000 psi of CO at 25 °C leads to no uptake of CO (Equation 9). Furthermore, the double carbonylation product $(PPh_3)_2Pd(COCOPh)(Cl)$, prepared via oxidative addition of PhCOCOCl to $Pd(PPh_3)_4$, was shown to undergo decarbonylation spontaneously at room temperature to yield $(PPh_3)_2Pd(COPh)(Cl)$. This rate of decarbonylation was found to be independent of CO pressure (of up 700 psi) (Equation 10).

This unfavorable thermodynamics associated with CO insertion into Pd-acyl allows for the slower insertion of olefin into Pd-acyl to occur. Combining this factor with the kinetically favored insertion of CO into Pd-alkyl forces the co-polymerization to occur in a strictly *alternating* fashion.



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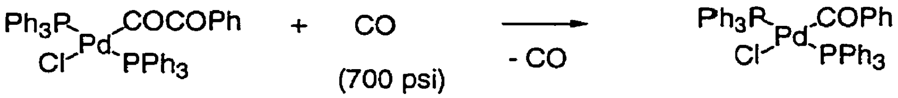
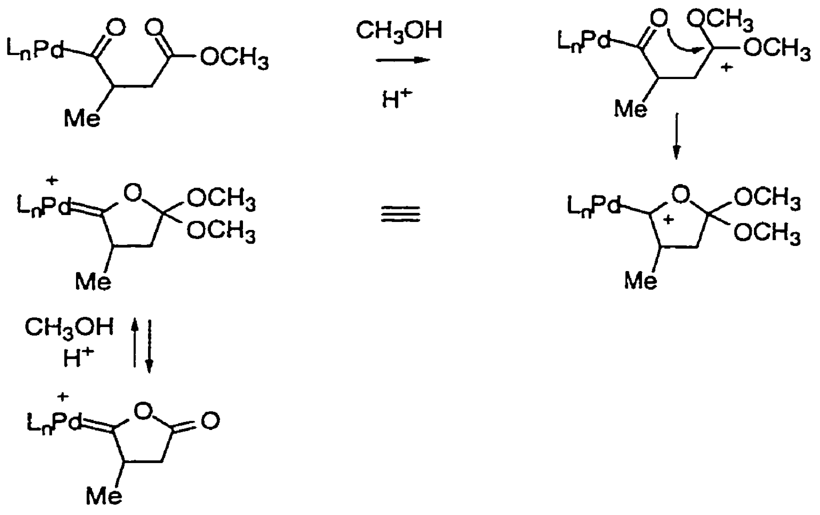


(10)

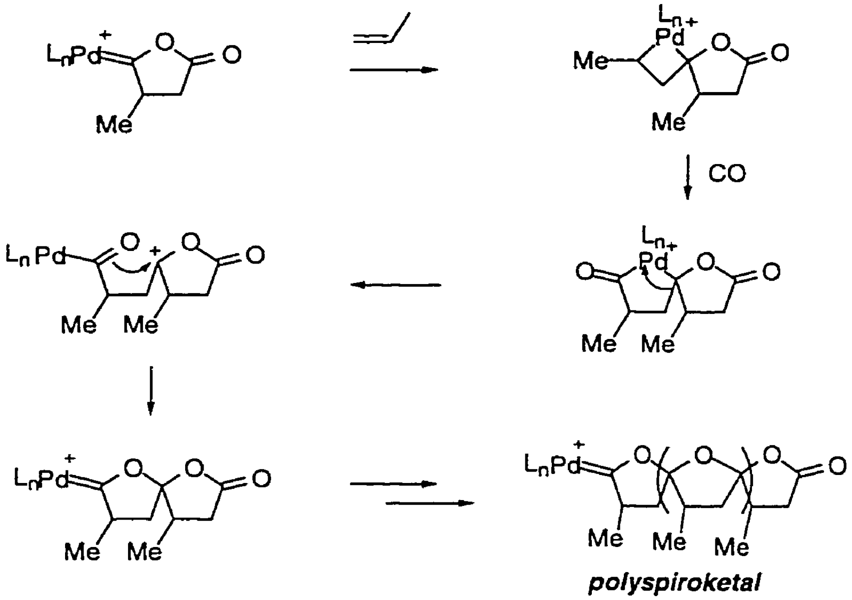
Alternative Mechanism

In a separate mechanistic study, Consiglio and co-workers[33] proposed that chain growth in CO/olefin co-polymerization occurs via the formation of a Pd-carbene intermediate instead of a Pd-carbonyl acyl complex (Scheme 5). This conclusion is based upon the characterization of a poly(spiro-2,5-(3-methyltetrahydrofuran) instead of poly(1-oxo-2-methyltrimethylene) obtained from the co-polymerization of CO and propylene with a palladium acetate catalyst modified with a chiral (*S*)-(6,6'-dimethylbiphenyl-2,2'-diyl)bis(dicyclohexylphosphine) ligand.

Initiation of Pd-carbene complex:



Polymer chain growth:

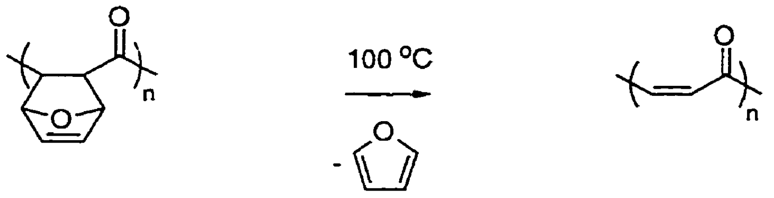


Scheme 5. Mechanism of spiroketal formation (L_n = (S)-(6,6'-dimethylbiphenyl-2,2'-diyl)bis(dicyclohexylphosphine)

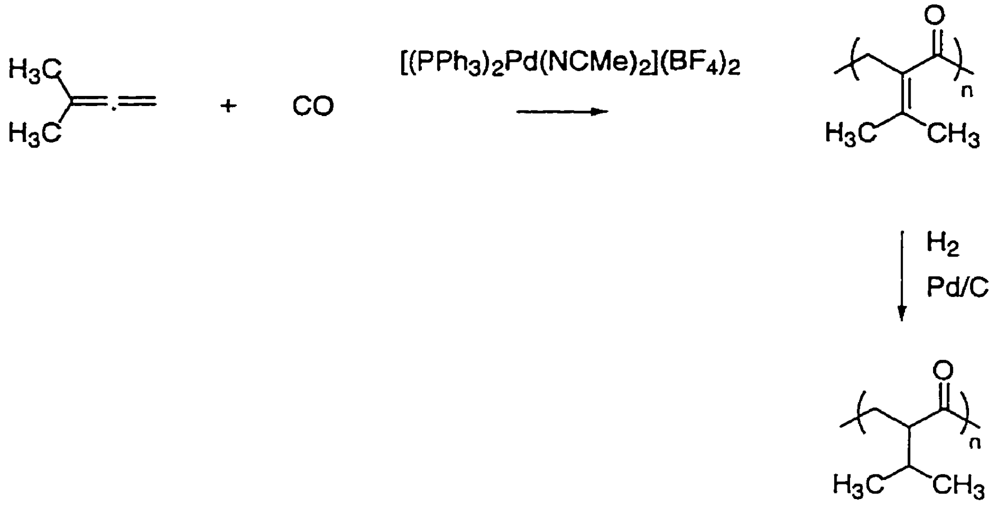
This finding is not the first reported encounter with polyspiroketal, particularly in the co-polymerization of CO with cyclic or aliphatic α-olefins.[34] Consiglio and co-workers suggest that co-polymerization initially yields a polyspiroketal polymer, which then converts to a thermodynamically more stable polyketone form upon acid work-up.[33] Consistent with this hypothesis, poly(spiro-2,5-(3-methyltetrahydrofuran) can be transformed to poly(1-oxo-2-methyltrimethylene) upon dissolution in hexafluoro-2-propanol and precipitation with methanol. Beyond this report by Consiglio, however, there are no further mechanistic details to support this hypothesis, and alternating insertion remains the more generally accepted mechanism for the co-polymerization of CO and olefins.

1.1.5 RELATED DEVELOPMENTS

The palladium catalyzed alternating co-polymerization of CO and olefin creates a new dimension in metal-catalyzed polymerizations. It not only allows the synthesis of a completely new class of functionalized polymers, but also provides potential access to other important functionalized materials through derivatizations.[16,23] Brookhart[21] and Novak[35] have shown that the co-polymerization of CO with *tert*-butylstyrene and functionalized norbornenes respectively can be made living, which is an important feature that can be further utilized for the preparation of block co-polymers. In addition, Novak has also studied the thermolysis of CO-diethyl-7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate co-polymers, which were found to undergo retro Diels-Alder reaction to form a novel, cross-conjugated poly(ketovinylene) (Equation 11).[35] Unsaturated polyketone materials, prepared by the co-polymerization of CO with 3,3-dimethylallene using a $[(PPh_3)_2Pd(NCMe_2)](BF_4)_2$ catalyst, can also be subsequently hydrogenated to yield substituted polyketones which are otherwise not accessible by simple CO/olefin co-polymerization (due to steric bulk of the corresponding olefins) (Scheme 6).[36]

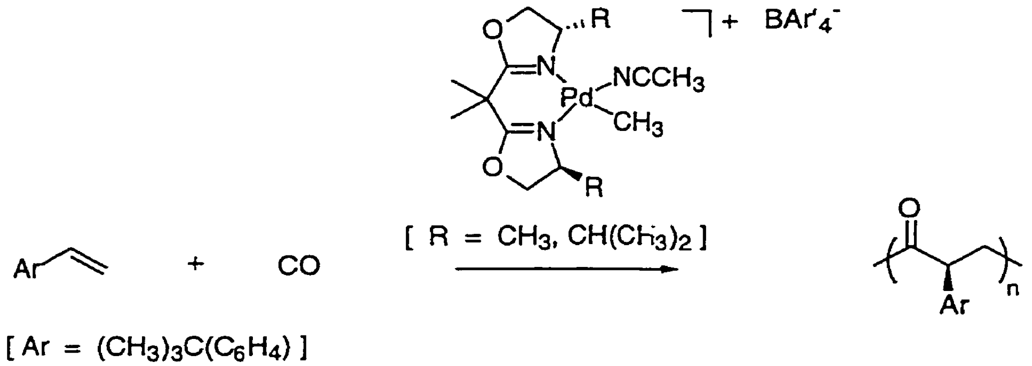


(11)



Scheme 6. Synthesis of unsaturated CO-allene co-polymer, and hydrogenation to substituted polyketone

The synthesis of highly isotactic CO/α-olefin co-polymers such as poly(propylene-*alt*-CO)[37] and poly(4-*tert*-butylstyrene-*alt*-CO),[38] has been reported using chiral bidentate ligands on the palladium catalysts. Since the tertiary carbons along the backbones of these chiral co-polymers are true stereogenic centers, the resulting highly isotactic materials are therefore also optically active (Equation 12).

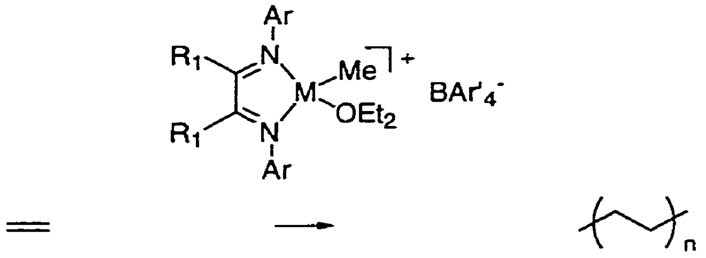


(12)

isotactic,

$[\Phi]^{25}_{589}$ - 536°

More recently, a number of independent research groups have reported similar Fe, Co, Ni and Pd-based systems that are capable of polymerizing ethylene and α-olefins to high molecular weight polymers.[39-40] For example, the polymerization of ethylene with various Ni/Pd-diimine complexes are shown in Equation 13. In some cases, the activity of these catalysts even exceeded metallocene-based catalysts.[40] Although these late metal catalysts undergo facile β-hydride elimination to yield an olefin hydride complex **11**, the bulky diimine ligands employed will hinder the associative displacement of this olefin ligand from the metal center (Scheme 7).[40] This is accomplished by the bulky aryl substituents on the diimine ligands which block the the axial approach of free olefin monomers. The rate of chain transfer is therefore much slower, while the fast rate of propagation allows the polymer to grow to a significant length. These catalysts have also been employed for the co-polymerization of ethylene and propylene with polar monomers such as methyl acrylate, *tert*-butyl acrylate and methyl vinyl ketone. The soft metal centers can tolerate the heteroatom functionalities present within the polar monomers.

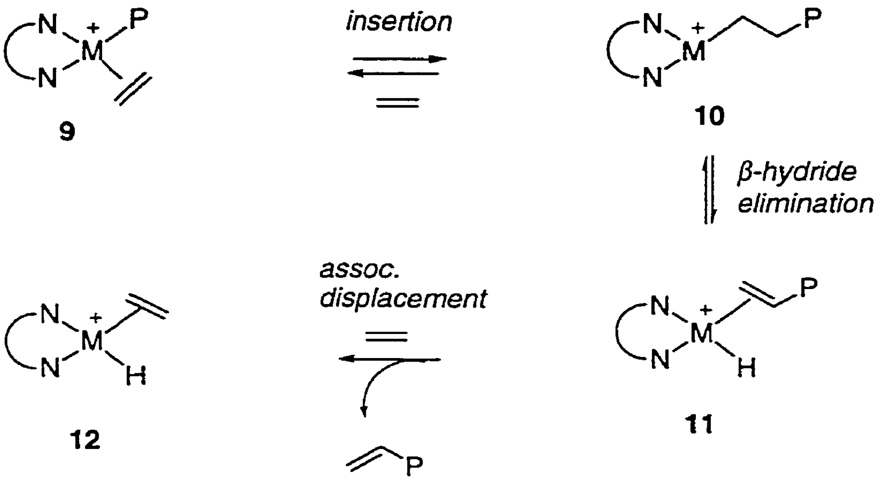


(13)

M = Ni, Pd

R_1 = H, Me]

Ar = 2,6-C_6H_3(i-Pr)$_2$,
2,6-$C_6H_3Me_2$



[P = polymer]

Scheme 7. Chain transfer via associate displacement

1.2 RING-OPENING POLYMERIZATION

1.2.1 INTRODUCTION

The ring-opening polymerization of saturated heterocycles constitutes one of the more important methodologies for the synthesis of polymers.[41] It is a useful technique as it provides a means of introducing functionality into the backbone of a polymer.[42] Unlike polymers which are prepared from olefin monomers, the backbone of these ring-opened polymers is often not wholly carbon-based. This distinctive feature is due to the nature of the monomers, which are typically cyclic compounds containing heteroatoms or functionalities such as ethers, amines, esters, amides, sulfides, carbonates, siloxane and phosphonites (Figure 4).[41-44] The long list of monomers clearly demonstrates that the diversity of ring-opening polymerization chemistry. The scope of materials and polymer properties that can be constructed is hence extensive.

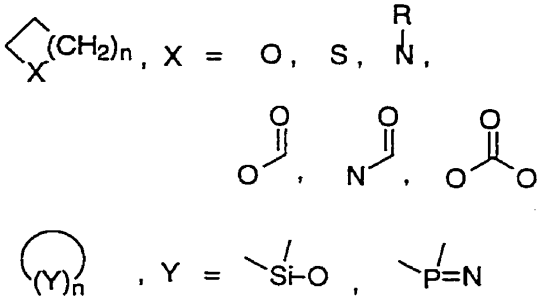


Figure 4. Diversity of ring-opening monomers

Polymers generated through ring-opening polymerizations have found many industrial applications, including textile fibers, thermoplastic resins, high performance elastomers, water-soluble polymers, oil additives, intermediates for thermoplastic elastomers, additives in cosmetics and biomaterials.[41] Some of these polymers are produced commercially in large scale, such as polycaprolactam (Nylon 6), polyacetal resin, polyethylene oxide, polypropylene oxide and polytetrahydrofuran,[41] which is commonly used within thermoplastic segmented polyurethanes and ureas.[45]

1.2.2 THERMODYNAMICS OF RING-OPENING POLYMERIZATIONS

A cyclic monomer can be induced to undergo ring-opening under the influence of a suitable cationic, anionic or radical initiator.[41] The driving force in this reaction is primarily the relief of ring-strain caused by bond angle distortion, conformational strain and non-bonding interactions.[46] The heat of polymerization (ΔH_p) often provides a useful measure of this ring strain.[42,46] Since the conversion of monomers into a polymer results in an entropy loss ($\Delta S_p < 0$), the heat of polymerization in these reactions must be negative ($\Delta H_p < 0$) to favor polymer formation (Equation 14).[42]

$$\Delta G_p = \Delta H_p - T\Delta S_p \tag{14}$$

This heat of polymerization (ΔH_p) is dependent upon the size of the ring in a cyclic monomer as illustrated in Table 1 for a number of cyclic ethers.[46] This table shows that cyclic ethers with smaller ring size have a more negative heat of polymerization (ΔH_p << 0). This is due to greater bond angle distortion in these small rings. The heat of polymerization becomes more positive for larger rings, due to the abatement of bond distortion, leading to a reduction in ring strain.[46] However, five-membered heterocycles experience increased destabilizing non-bonding interactions between the oxygen lone pairs and hydrogen atoms on neighbouring carbons. Hence five-membered cyclic ethers can still undergo ring-opening favorably despite the minimal bond angle distortion present.

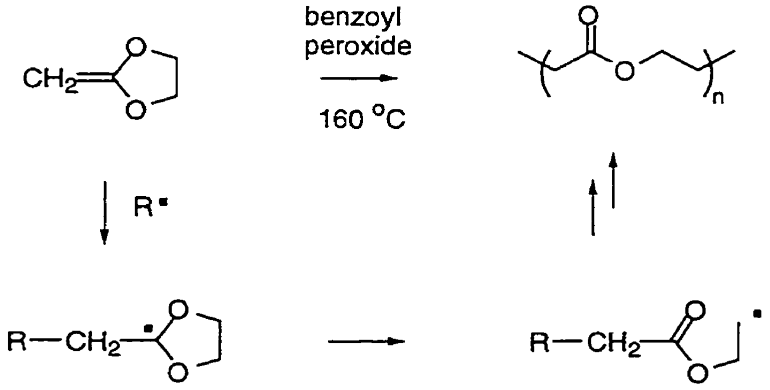
Monomer	Ring Size	ΔH_p (kJ mol^{-1})
ethylene oxide (oxirane)	3	- 94.5
trimethylene oxide (oxetane)	4	- 81
tetrahydrofuran (oxolane)	5	- 15
tetrahydropyran (oxane)	6	~ 0
hexamethylene oxide (oxepane)	7	- 33.5

Table 1. Changes in the heat of polymerization (ΔH_p) versus ring size[46]

A six-membered ring such as tetrahydropyran experiences only a small angular strain and negligible non-bonding interactions due to its non-planar configuration, and does not undergo ring-opening.[46] Seven-membered ring or higher are forced to adopt a highly strained configuration, where each bond is in a gauche conformation. This eventually leads to a conformational strain large enough to induce ring-opening to occur.

1.2.3 INITIATORS FOR HETEROCYCLE RING-OPENING POLYMERIZATION

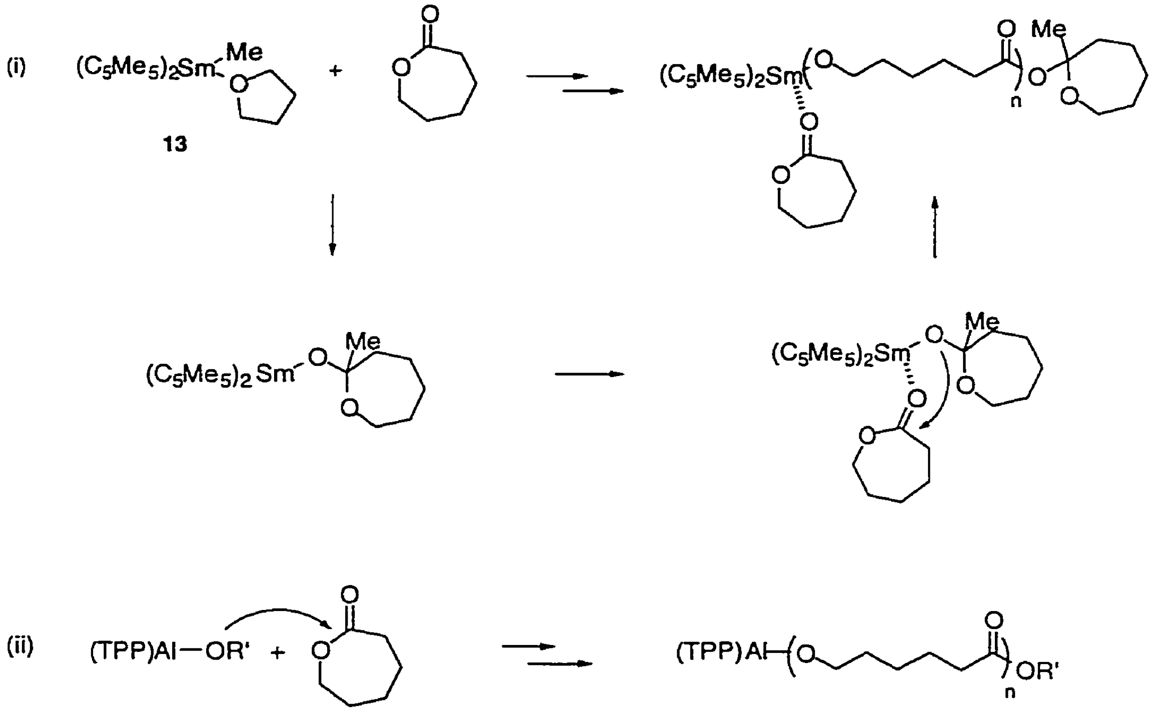
The ring-opening polymerization of heterocycles can be induced by radical, anionic or cationic initiators.[41-43] For example, Bailey and co-workers have reported the *radical* ring-opening polymerization of 2-methylene-1,3-dioxolane (a cyclic ketene acetal) with benzoyl peroxide as initiator (Scheme 8).[43c] This polymerization allows the selective synthesis of high molecular weight polyesters. Remarkably, the cyclic ketene acetal substrate is also susceptible to co-polymerization with styrene and methyl methacrylate, which creates a novel and convenient method to incorporate functionality into the C-C skeletal structure of addition polymers. The radical ring-opening polymerization of other methylene substituted cyclic compounds, as well as vinyl cyclopropane derivatives such as α-cyclopropylstyrene have also been investigated.[43b]



Scheme 8. Radical ring-opening polymerization of cyclic ketene acetal

Other heterocycles which do not contain such vinyl substituents are more easily polymerized by ionic means. For example, ethylene oxide, ethylene sulfide, ε-caprolactone and a number of cylic siloxanes undergo ring-opening in the presence of a suitable anionic or cationic initiator.[41,42] Some of these ionic initiators are known to induce living polymerizations to yield well-defined polymers. For example, Sharkey has reported the anionic ring-opening of pivalolactone in which the propagating terminus was observed to have an exceptionally long lifetime.[41b] The reaction was performed in an aprotic organic solvent such as THF using a variety of tetraalkylamonium carboxylate initiators.

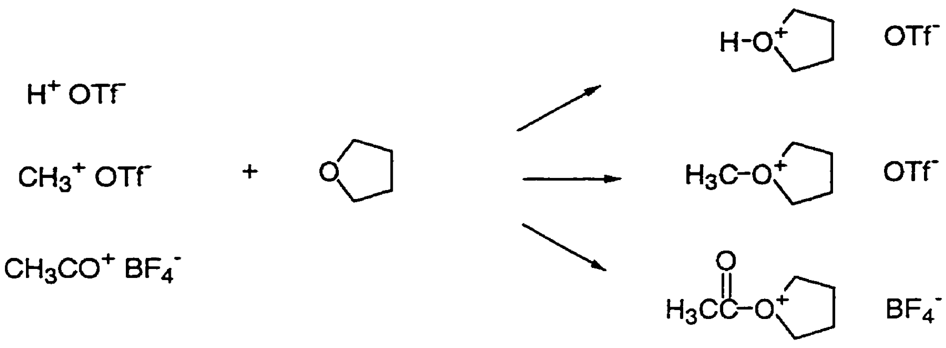
The ring-opening polymerization of lactones via *insertion* has also been achieved using lanthanide metal complexes and metalloporphyrins as described by Yasuda[15a] and Inoue[15b] respectively. The ring-opening polymerization of ε-caprolactone by these metal catalysts is illustrated in Scheme 9. Both ring-opening processes proceeded in a living fashion, forming polymers with extremely narrow distribution ($M_w/M_n < 1.1$). The initiation of the polymerization with **13** occurs via insertion of the unsaturated carbonyl (-C=O) into metal-alkyl bond.[15a] This nucleophilic alkoxide subsequently attacks the carbonyl of a coordinated monomer to propagate chain growth. These metal catalysts are known to be active for the polymerization of other heterocyclics, such as oxiranes, lactides and cyclic carbonates.



Scheme 9. Ring-opening polymerization of ε-caprolactone via insertion

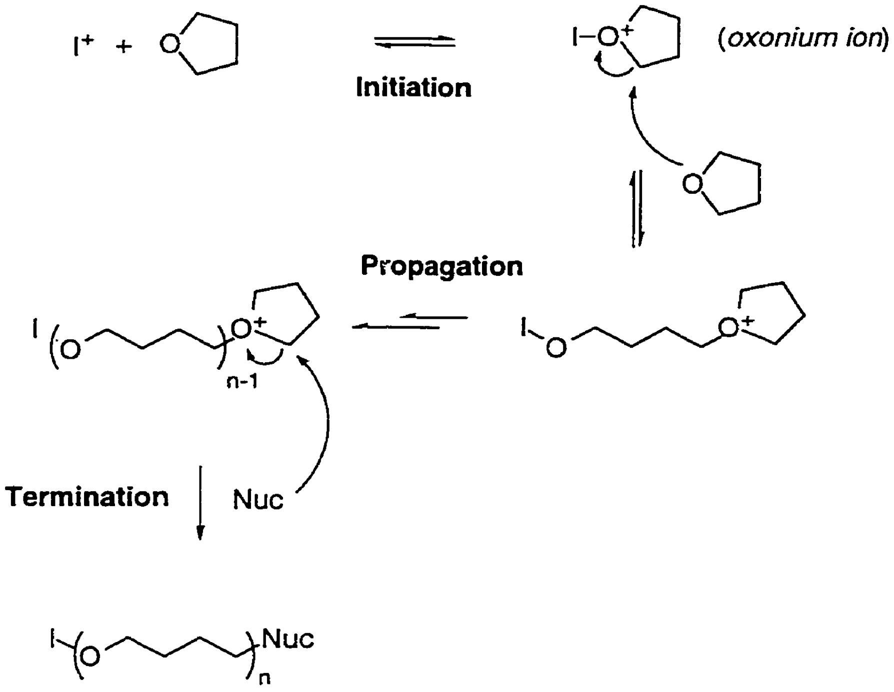
1.2.4 CATIONIC RING-OPENING POLYMERIZATION OF THF

The most rigorously studied mechanism of heterocycle ring-opening is the cationic one.[43a] Here, a concise discussion will be given using THF ring-opening polymerization as a model system. THF polymerization was first reported by Meerwin in the late 1930s using a trialkyloxonium salt as catalyst.[45] It has since become the most extensively studied system within ring-opening polymerization. A variety of cationic initiators have been investigated for the polymerization of THF. These include protic acids (HOTf), oxonium ions (MeOTf) and acylium salts (CH_3COBF_4).[47,48] The corresponding onium ions generated with THF are shown below (Scheme 10).



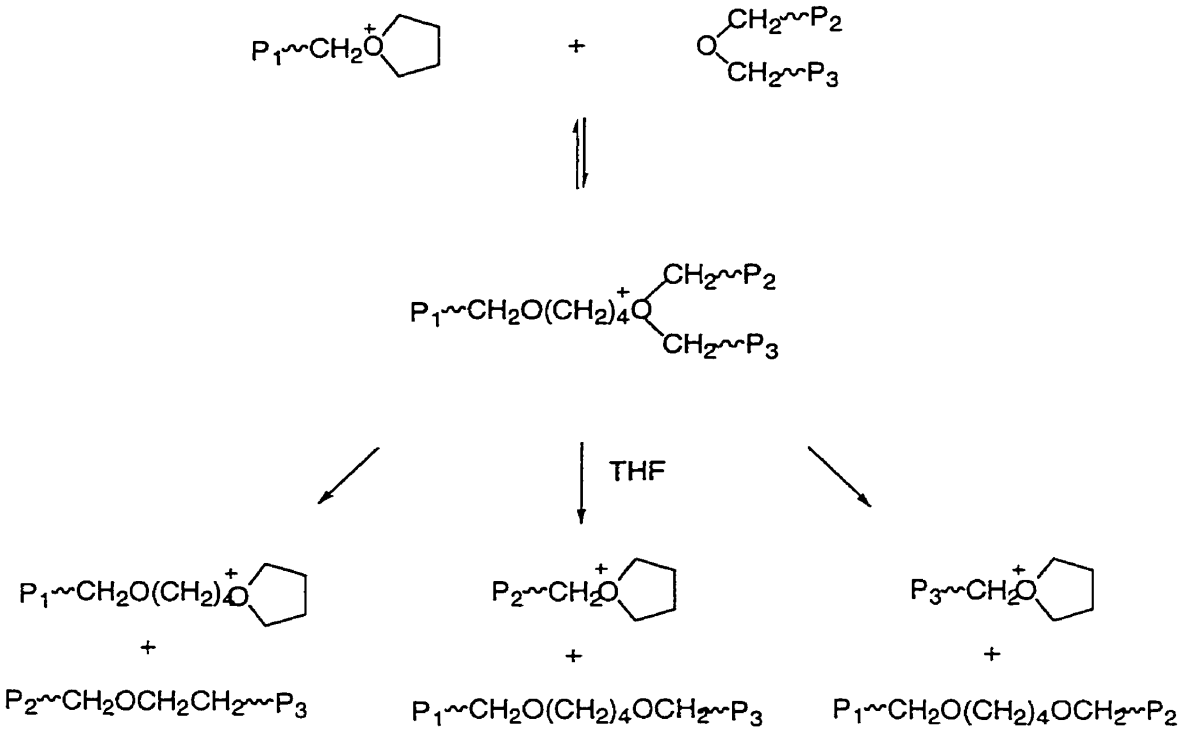
Scheme 10. Types of onium ions generated by various initiators

Like all chain growth reactions, the *cationic ring-opening polymerization of THF* is characterized by three major steps: initiation, propagation and termination.[45] These elementary steps are presented in Scheme 11 below. The initiation is characterized by the coordination of a THF monomer to a cationic initiator (I^+), leading to the formation of an onium ion[42,45] via charge transfer from the initiating species. The formation of this cationic species causes the carbon-oxygen bond to weaken, and makes the α-carbon susceptible to nucleophilic attack by surrounding monomers. This process occurs during the propagation, where addition of THF monomer results in the cleavage of the carbon-oxygen bond and generation of a new oxonium salt. Chain growth continues as further nucleophilic attack occurs on this newly developed charged species. Under favorable conditions, polyTHF chain-growth can go on virtually without termination. In fact, THF polymerization is an excellent example of 'living polymerization'.[45] A strong nucleophile is often introduced to quench the chain growth process to obtain polymers with well-defined end-groups. For example, water can be added to obtain polyTHF with hydroxyl end groups, while ammonia will produce polyTHF with amine end-groups.[45]



Scheme 11. Mechanism of *cationic ring-opening polymerization* of THF

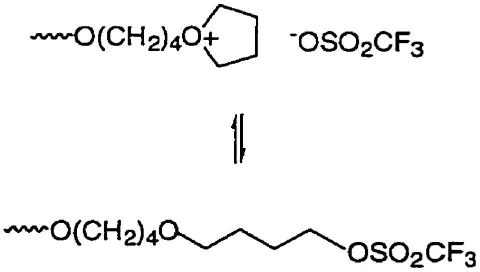
Chain transfer reactions may also take place during THF polymerization. This typically involves nucleophilic attack on the growing end of a polymer chain by an oxygen atom within the main chain (Scheme 12).[42-45] A *branched* ion is produced in the process. Its subsequent reaction with a monomer can occur at any of the three carbon atoms α to the acyclic polymeric oxonium ion. As a result, the original polymer chains may not be re-formed. This chain transfer process causes the molecular weight to be partially randomized, and explains the high polydispersity index (close to 2) obtained in most THF polymerizations.[45]



Scheme 12. Chain transfer via nucleophilic attack on branched onium ion

Role of counter-ion

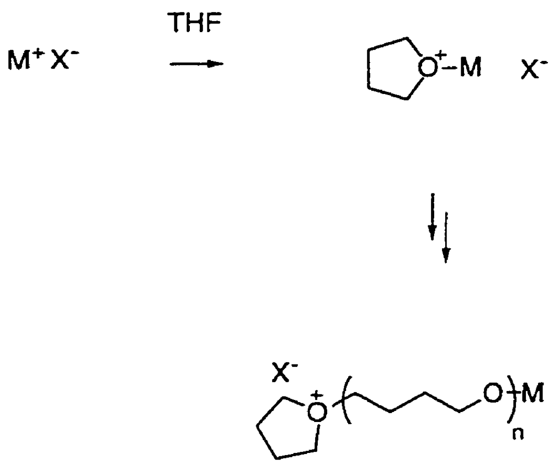
An interesting feature of the ring-opening polymerization of THF is the role played by the counter-ion accompanying the onium species. Certain counter-ions have been found to influence the degree of polymerization through their participation in secondary reactions with the onium ion. An example is shown in Equation 15 for the $CF_3SO_3^-$ counter-ion, which attacks the α-carbon of the oxonium ion to form a weak ester bond.[45] Due to these interactions, a non-bonding counter-ion such as SbF_6^-, BF_4^- and AsF_6^- is required for the formation of high molecular weight polymers.[42,45] On the other hand, small nucleophilic anions such as Cl^- show an extremely rapid termination, since they are capable of undergoing rapid nucleophilic attack on the oxonium ion to generate a stable alkyl chloride end-group.[45]



(15)

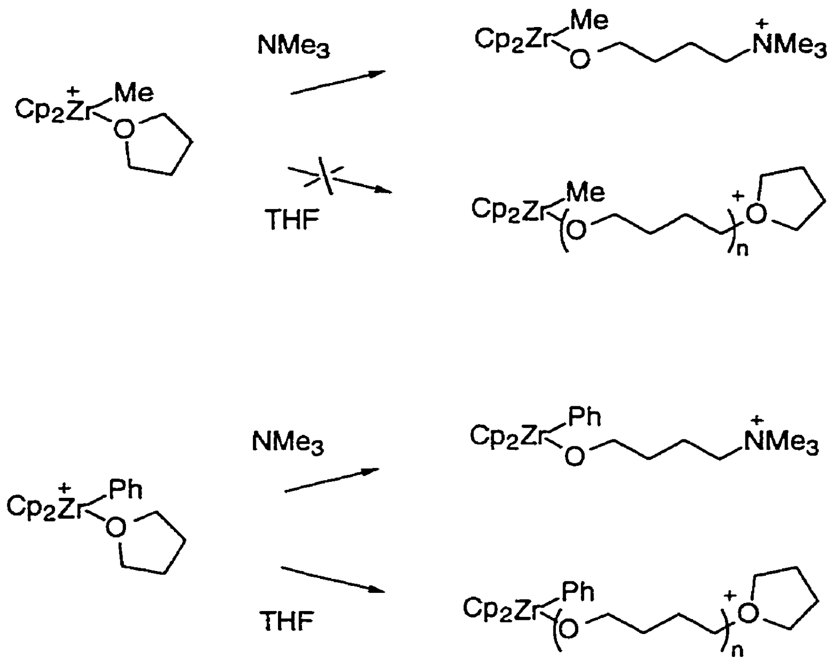
1.2.5 METAL-MEDIATED POLYMERIZATION OF THF

In addition to organic initiators, metal complexes have also been used to initiate the ring-opening polymerization of THF. Typically, these initiators consist of metals which behave as strong Lewis acids (Scheme 13).[47,49] For example, triflate salts of Group IIIA elements[47] ($M(OSO_2CF_3)_3$; M = Al, Ga) and rare earth trifluoroacetate[49] ($Ln(CF_3CO_2)_3$ where Ln = Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er and Tm) have been reported to initiate THF polymerization to a high degree of conversion. There are also examples of metal halide salts which are sufficiently electrophilic to initiate ring-opening directly, such as AsF_6, $NbCl_5$, $TaCl_5$, WCl_6, SeF_6.[50]



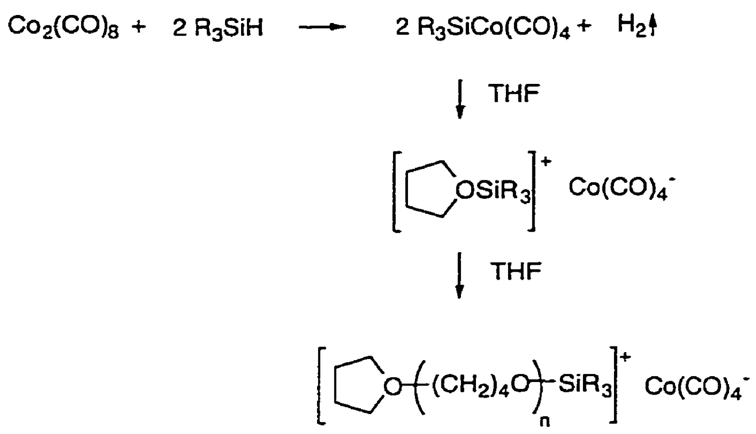
Scheme 13. THF polymerization by metal cation (M^+) associated with a weakly coordinating anion (X^-)

A number of organotransition metal complexes have also been reported to mediate the ring-opening of THF, though this does not necessarily lead to polymerization. These typically consist of oxophilic metal complexes which coordinate strongly to THF, such as $(C_5Me_5)_2Sm(PPh_2)(THF)$, $(C_5Me_5)_2Sm(AsPh_2)(THF)$, $(C_5H_4Me)Zr(H)(THF)^+$ $(BPh_4)^-$, $(C_5Me_5)_2Y(H)(THF)$ and $(C_5Me_5)_3Sm$.[51] Subsequent attack on the α-carbon of the coordinated THF by either THF or an external nucleophile results in ring-opening, as illustrated with the complexes $(C_5H_5)_2Zr(CH_3)(THF)^+$ $(BPh_4)^-$ and $(C_5H_5)_2Zr(Ph)(THF)^+$ $(BPh_4)^-$ (Scheme 14).[51a] Interestingly, the complex $(C_5H_5)_2Zr(Ph)(THF)^+$ $(BPh_4)^-$ can initiate polymerization of THF while its CH_3 analogue, $(C_5H_5)_2Zr(CH_3)(THF)^+$ $(BPh_4)^-$ is completely inactive in the presence of THF (Scheme 14). This was attributed to the stronger coordination of the THF ligand in the complex $(C_5H_5)_2Zr(Ph)(THF)^+$ $(BPh_4)^-$ than in $(C_5H_5)_2Zr(CH_3)(THF)^+$ $(BPh_4)^-$ since the Ph group is more electron-withdrawing ligand than the CH_3 group.



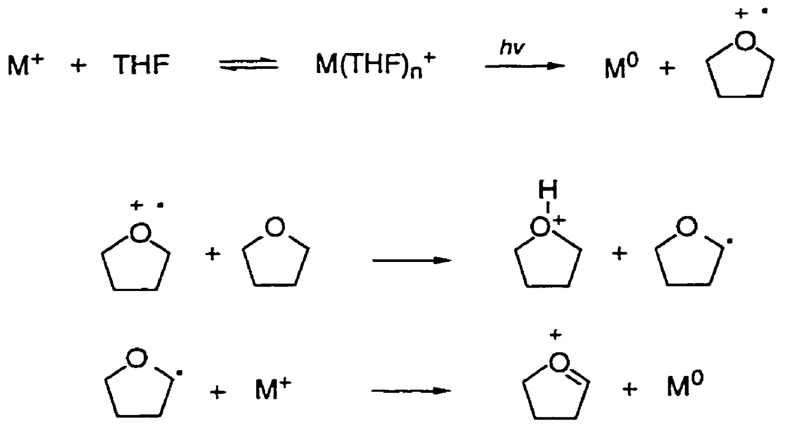
Scheme 14. Ring-opening with Zr(IV) complexes

In addition, there have been several reports of metal complexes that do not initiate the polymerization process directly, but rather undergo a series of reactions before forming the active species.[52] For example, dicobalt octacarbonyl, in the presence of a silane can polymerize THF to give high molecular weight polymer (ca. 50,000) in 20 min at 25 - 40 °C.[52a] However, mechanistic studies have shown that this reaction involves initial generation of $(CO)_4CoSiR_3$, which ionizes to $(CO)_4Co^-$ and the silyl cation, with the latter being the active initiator for THF polymerization (Scheme 15).



Scheme 15. Generation of onium ion by silylation

Marks and co-workers have demonstrated that certain metal salts can polymerize THF under photochemical conditions.[52b] Solutions of Ag(I), Cu(I), Cu(II) and Tl(I) salts (with PF_6^-. SbF_6^-, OTf$^-$ or BF_4^- counter-ion) in anhydrous THF are stable in the dark for an indefinite period of time. However, upon irradiation with 254-nm light at room temperature, the solutions turned viscous as polyTHF is formed. The polymer yield was observed to be dependent upon several factors, such as the identity and concentration of the metal salt, the duration of irradiation and the dark time following this irradiation. The observed dependencies upon metal ion and anion at low conversions are Cu(II) > Ag(I) > Cu(I) >> Tl (I) and PF_6^- > SbF_6^- >> OTf$^-$ > BF_4^- . Initiation of the polymerization was proposed to occur via a ligand-to-metal charge transfer excitation of metal-THF complex to generate an oxidized THF and reduced metal (Scheme 16). The THF radical cation then further reacts with another THF monomer to form an onium ion, known to be the active species in such ring-opening polymerizations. This study constitutes the first example of a transition metal mediated photopolymerization of THF.



Scheme 16. Ligand-to-metal charge transfer excitation

Finally, several metal oxides and zeolite catalysts have recently received considerable interest in industrial applications as initiators for THF polymerizations.[53,54] These complexes have been found to polymerize THF to produce low molecular weight polymers (< 5000) with extremely narrow molecular weight distribution. Such polymers are useful commercially as soft segments for certain thermoplastics.[45] The metal oxides reported comprised of a wide range of metals: Ge, Sn, Pb, B, Ga, In, Cd, Cu, Fe, Mn, Ni, Cr, Mo, Co, Ta, Hf, Y, La, Nb, Ce, Al, Zr, Ti, Zn, W, V, As and Ge.[53] Alternatively, the metal complexes have also been attached onto zeolites of varying structures (β– and L-zeolite, modernite, erionite-offretite)[54] in order to facilitate the purification of the polymer products.

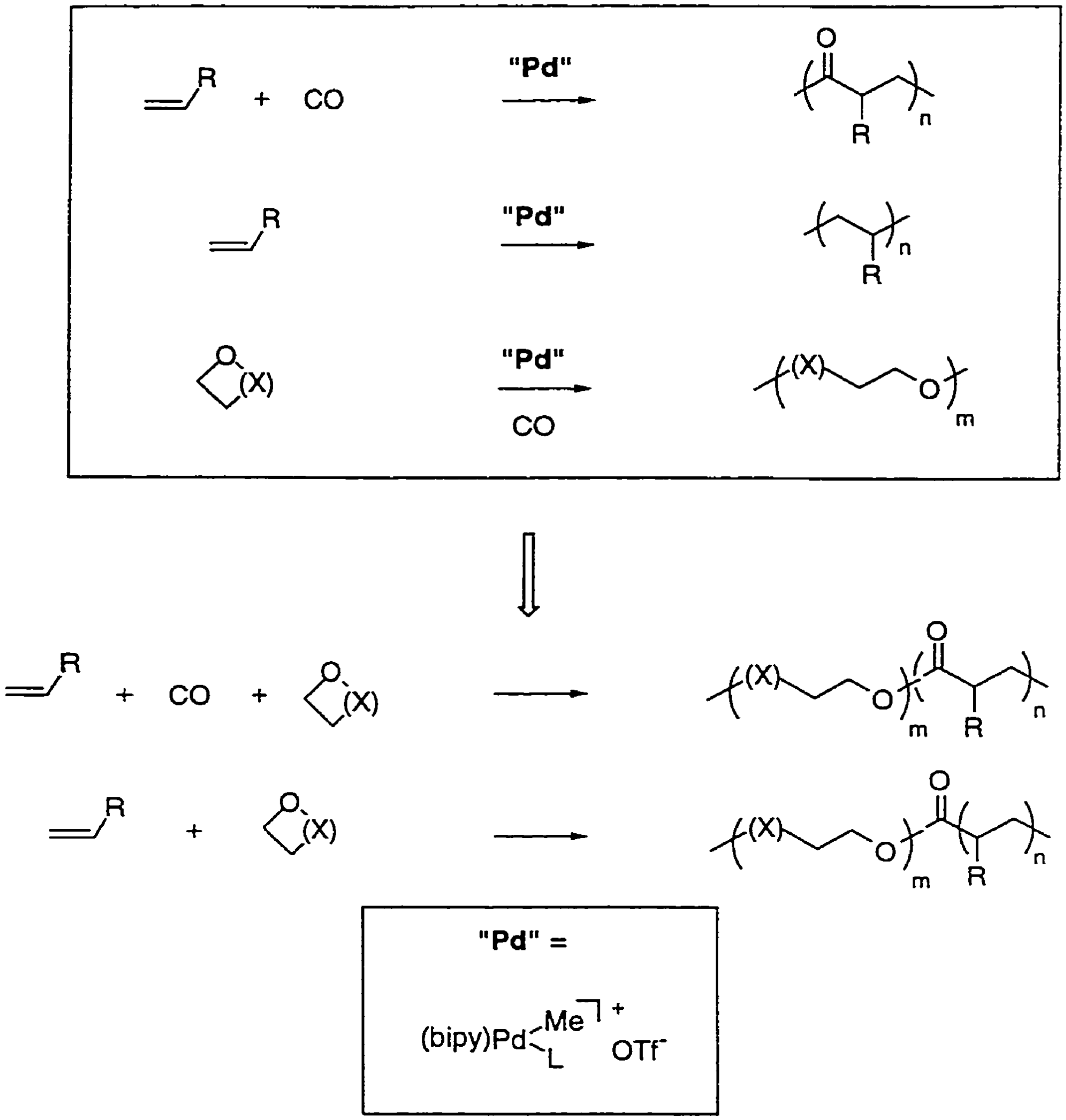
1.3 OVERVIEW OF PROJECT

The alternating co-polymerization of CO and olefins is an excellent example of the significant control offered by metal-based catalysts over polymerization properties.

These transition metal catalysts ensure a perfectly sequential insertions of CO and olefins into metal-carbon bond to generate a strictly alternating ketone polymers.[13] Modifications to the catalysts can further effect polymer microstructures[31] and molecular weights.[21] On the other hand, the synthesis of ring-opened heterocycles is often mediated by compounds whose role is to initiate the polymerization process, providing little opportunity to manipulate polymer properties through catalyst choice.[41-43] This has stimulated research to develop initiators which function beyond simple activation of polymerization, such as living polymerization initiators,[42] chiral initiators[55] and ring-opening insertion systems.[15]

Recent studies in our laboratory have however shown that the palladium insertion polymerization catalysts (bipy)Pd(Me)(L)$^+$ OTf$^-$ (L = NCMe, $(Me_3)_3CN{=}C(H)Tol$, $PhN{=}C(H)Tol$, $MeN{=}C(H)Tol$) (**14-17**) can effectively initiate the ring-opening polymerization of a number of heterocycles (THF, dioxolane, ε-caprolactone and β-butyrolactone) in the presence of CO (Scheme 17).[56] In contrast to typical initiators, preliminary studies suggest this polymerization proceeds via an unusual series of metal-based reactions. The manipulation of these steps provides significant control over polymer molecular weights and end-groups.

Since the complexes **14-17** are known insertion polymerization catalysts,[57] the primary objective of the present study is therefore to investigate the feasibility of combining the insertion process with ring-opening polymerization to generate new block co-polymers (Scheme 17). An initial mechanistic study is aimed at providing better insight into the various metal-based reactions in the polymerization, and the effect of ligands and conditions on the polymers formed (Chapter 2). The research subsequently presented in Chapters 3 and 4 concern our efforts to develop new synthetic routes for the coupling of this ring-opening polymerization to insertion polymerization. These Pd-mediated couplings can be potentially applied to the preparation of ketone-THF and olefin-THF block co-polymers, consistent with the various types of monomers (CO, olefins and heterocycles) that can be polymerized. This coupling process also represents a rare episode in chemistry of polymers where two distinct polymerization mechanisms are found to occur on a single metal site.



Scheme 17. Combining insertion and ring-opening polymerization

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CHAPTER TWO.

RING-OPENING POLYMERIZATION WITH PALLADIUM(II) COMPLEXES

2.0 INTRODUCTION

Recent work in our laboratory has established that the insertion polymerization catalysts (bipy)Pd(Me)(L)$^+$ OTf$^-$ [L = NCMe (**14**), PhN=C(H)Tol (**15**), ^{t}BuN=C(H)Tol (**16**), MeN=C(H)Tol (**17**)] are active for a second class of polymerization reaction: the ring-opening polymerization of heterocycles (eg. THF, 1,3-dioxolane, β-butrolactone, ε-caprolactone) (Scheme 17, Sect. 1.3).[1] Several unusual features were noted about these Pd-mediated reactions. Firstly, unlike the traditional Lewis acid initiators, these Pd complexes are known to interact only weakly with heteroatom substituents (eg. ethers and esters), a feature that has made them of such interest in the insertion polymerization of functionalized olefins.[2] Additionally, **14-17** only initiate the ring-opening polymerization of THF in the presence of 1 atm CO gas; little or no polymer is obtained upon warming **14-17** to 70 °C in THF in the absence of CO (Equation 16).[1] The substitution of the OTf$^-$ counter-ion in these complexes for a more strongly coordinating Cl$^-$ anion is also found to hinder the ring-opening process (Equation 17).[1]

(16)

(17)

Finally, polymer yields and molecular weights are observed to vary with the four complexes studied, as shown in Table 2.[1] The Pd-acetonitrile complex **14** gives the highest yield, followed respectively by complexes **15**, **16** and **17**. Molecular weights of the resulting polymers follow a similar trend. These features suggest a more complex mechanism for the polymerization of heterocycles with **14-17** compared to typical ring-opening polymerization initiators (Chapter 1) with a specific role played by *CO*, the ligand L and the requirement of an *empty coordination site* at the metal center.

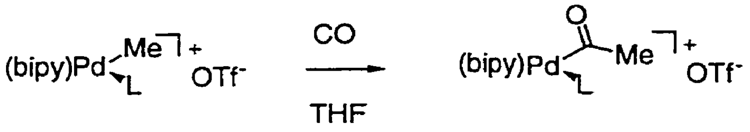
Table 2. Polymer yields and molecular weights

Catalyst	Yield (g)	M_n (10^3)	M_w (10^3)
14	0.92	35.4	78.4
15	0.44	23.9	49.3
16	0.55	32.7	72.3
17	0.06	12.9	18.5

(reaction performed under 1 atm of CO at 70 °C for 24 hours with 10.0 g THF and 0.05 mmol of catalyst)

2.1 OBJECTIVE

The objective of the research described in this chapter is to study the mechanism of THF polymerization by (bipy)Pd(Me)(L)$^+$ OTf$^-$ (**14-17**). Although some of the unusual features described earlier can be readily rationalized, experimental data are unavailable to support any hypothesis proposed. For example, the unusual activation of the ring-opening process by CO can be attributed to insertion of CO into Pd-Me bond to yield the Pd-acyl complexes (bipy)Pd(COMe)(L)$^+$ OTf$^-$ (Equation 18).[3] However, these intermediate species have not been reported in THF polymerization.



(18)

Similarly, the influence of the dative ligand L on the molecular weight is thought to involve participation of L in termination.[1] However, earlier end-group analysis on the polymer product is unsuccessful in accounting for this observed molecular weight variation. The studies presented below are therefore aimed at providing concrete evidence to support these hypotheses, and to clarify the underlying mechanism of ring-opening polymerization by the complexes **14-17**.

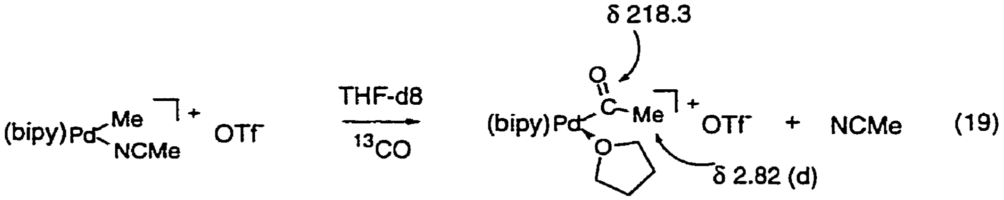
2.2 ELUCIDATION OF MECHANISM

The required addition of CO in the ring-opening polymerization of THF by **14-17** suggests that a multi-step process for initiation. In order to explore this, a practical approach is needed to identify any possible intermediate species generated in the polymerization. The use of NMR spectroscopy was considered since it allows progress in these reactions to be easily monitored. An intermediate species that is not stable can often be briefly detected in NMR time scale. The approach is further re-inforced by the fact that a *neat* NMR scale reaction (with d^8-THF as substrate) is conceivable, thus removing potential solvent effect frequently present in such NMR study.

2.2.1 Monitoring d^8-THF Polymerization by NMR

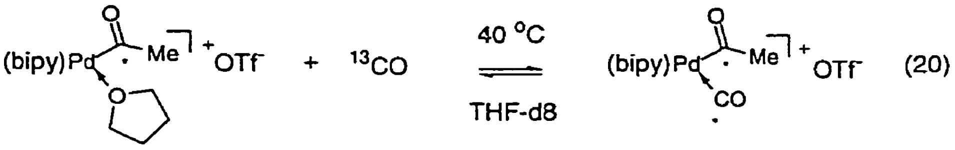
The reaction of (bipy)Pd(Me)(NCMe)$^+$ OTf$^-$ (**14**) in d^8-THF (1 mL) is studied as a *model* for the Pd-mediated ring-opening polymerization of THF with the complexes **14-17**. Upon addition of 1 atm ^{13}CO to **14** (7 mg, 0.02 mmol) in d^8-THF (1 mL) (performed within a J-Young NMR tube), the yellow slurry is observed to convert immediately to a clear, bright yellow solution. ^{1}H- and ^{13}C-NMR spectra taken show the formation of a new complex **5** (^{1}H-NMR: δ 8.57 (d, 2H), δ 8.48 (d, 2H), δ 8.19 (t, 2H), δ 7.70 (t, 2H), δ 2.82 (d, 3H); ^{13}C-NMR: δ 218.3, only ^{13}C-labelled peak) and a quantitative formation of free acetonitrile. The ^{13}C-labelled chemical shift for **18** closely resembles the value of an α-acyl carbonyl in a similar complex (bipy)Pd(^{13}COMe)(^{13}CO)$^+$ BAr'$_4^-$ (Ar' = 3,5-$(CF_3)_2C_6H_3$) (^{13}C-NMR (CD_2Cl_2): δ 217.4).[4] These spectral data are consistent with the formation of a palladium-acyl fragment (bipy)Pd(COMe)$^+$, generated by insertion of CO into the Pd-Me bond of **14**. The analogous insertion of CO into Pd-Me bond in *CH_2Cl_2 solvent* has been previously reported for complexes **15-17**.[2] This structural assignment is supported by the downfield shift observed for the Me resonance in **18** (δ 2.82) and splitting of this resonance into a doublet ($^2J_{C\text{-}H}$ = 6.9 Hz) due to coupling with the ^{13}C-labelled carbonyl carbon.

The insertion of ^{13}CO into the Pd-Me in **14** requires the initial substitution of the NCMe ligand by a ^{13}CO molecule to afford (bipy)Pd(Me)(^{13}CO)$^+$ OTf$^-$.[5] The ensuing insertion of the coordinated ^{13}CO into the Pd-Me bond creates an empty palladium coordination site. Since ^{1}H-NMR analysis shows the initial NCMe ligand is no longer coordinated to Pd, and no resonance due to a coordinated ^{13}CO is observed in the ^{13}C-NMR, this empty coordination site is undoubtedly occupied by a d^8-THF solvent to form **18** (Equation 19). However, attempts to isolate intermediate **18** for complete characterization are unsuccessful, as it decomposes to Pd(0) upon removal of solvent.



14 **18**

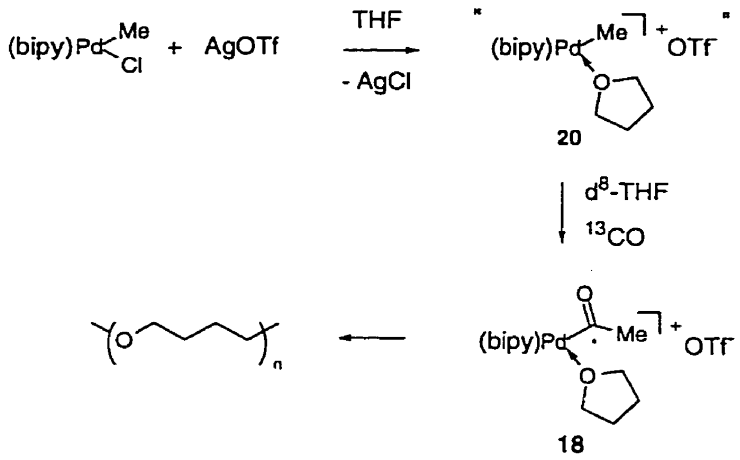
The warming of Pd-THF acyl complex **18** to 40 °C (so as to initiate THF polymerization) leads to the appearance of a second ^{13}C-NMR peak prior to polyTHF formation, in addition to the previous ^{1}H- and ^{13}C-NMR peaks for **18**. This peak at δ 177.0 is broadened, and its chemical shift is between that of a coordinated ^{13}CO in the reported intermediate (bipy)Pd(^{13}COMe)(^{13}CO)$^{+}$ BAr'$_4^-$ (δ 172.5)[4] and free ^{13}CO (δ 183.0), thus indicating that an equilibrium exists between free ^{13}CO and **18** and **19** at this temperature (Equation 20). As heating is continued, the reaction solution gradually turns more viscous due to the formation of polyTHF (^{1}H-NMR: δ 3.31, δ 1.52; ^{13}C-NMR: δ 69.1, δ 26.3).



18 **19**

2.2.2 Independent Generation of 18

The intermediate complex **18**, which is the active palladium species in the ring-opening of THF, can be prepared by an alternate route. The reaction of (bipy)Pd(Me)(Cl) (108 mg, 0.35 mmol) with AgOTf (98 mg, 0.38 mmol) in THF (5 mL) for 45 minutes leads to the generation of a clear yellow solution with white precipitate (AgCl) (Scheme 18). This solution was filtered through celite, and the clear yellow filtrate subsequently concentrated to ~ 1 mL. Upon cooling to -40 °C, a white precipitate was collected in 68.8 % yield. ^{1}H-NMR showed the solid product to be (bipy)Pd(Me)(THF)$_{1/2}^+$ OTf$^-$ (**20**) [^{1}H-NMR: δ 8.65 (d, 1H), δ 8.49 (d, 1H), δ 8.09 (m, 4H), δ 7.52 (m, 2H), δ 3.67 (m, 2H), δ 1.80, 2H), δ 1.07 (s, 3H)]. The presence of only 1/2 of a THF molecule per palladium in **20** implies that OTf$^-$ may be partially coordinated to palladium, or that THF is a bridging ligand. Nevertheless, dissolution of **20** in d^8-THF and addition of ^{13}CO (1 atm) leads to the clean formation of **18**, with identical ^{1}H- and ^{13}C-NMR resonances to those observed in Equation 19. Warming of this complex to 40 °C once again leads to polyTHF formation.



Scheme 18. Alternate synthesis route to **18**

2.2.3 Incorporation of Acyl Ligand into Polymer End-Group

These *in-situ* NMR studies show that the Pd-acyl complex is the active initiator, and the role of CO is to generate this intermediate species **18**. Further evidence for the importance of **5** is found in the structure of the polyTHF product. The ^{1}H-NMR analysis of isolated polyTHF reveals a resonance at δ 2.01 (s) integrating to one methyl group per polymer chain.[6] This resonance becomes a doublet when ^{13}CO is employed in the polymerization. Both IR (ν_{CO} = 1739.9 cm^{-1}) and ^{13}C-NMR (δ 171.2) analysis show a carbonyl is also incorporated on the polymer. These spectral features correlate with a [CH_3CO] moeity on the polyTHF in the form of an ester-group (Figure 5).[7] The presence of this unit as a polymer end-group is determined by ^{13}C-decoupled ^{1}H-NMR experiment, which shows three bond coupling between the ^{13}C labeled carbonyl carbon and the terminal -OCH_2- hydrogens (δ 4.05) on the polyTHF ($^3J_{C\text{-}H}$ = 2.7 Hz), and two bond coupling to the CH_3- hydrogens ($^2J_{C\text{-}H}$ = 6.9 Hz). Considering the incorporation of ^{13}CO into this end-group, the ester moeity undoubtedly arises from coupling of the palladium acyl ligand with the polyTHF.

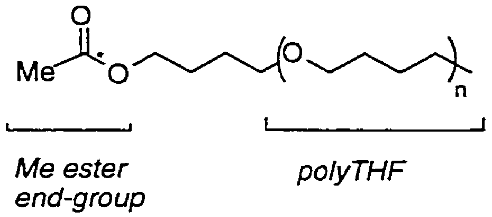
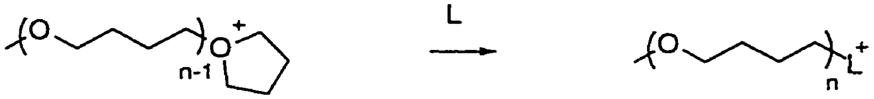


Figure 5. PolyTHF with methyl ester end-group

2.2.4 Participation of Ligand L in Termination

Molecular weight control is a key area of research in the development of many polymerization systems. In this regard, the synthesis of polymers with predictable molecular weights is intensely pursued, as it invariably provides control over fundamental polymer properties.[8] The influence of the dative ligand L in **14-17** towards THF polymerization is outlined in Table 2. The significant effect of L on molecular weight somewhat alludes to a Pd-mediated ring-opening system that conveniently operates beyond its regular function as initiator. In light of the *in situ* NMR studies, which show that L is dissociated from Pd during polymerization, its effect cannot be through changing the characteristics of the initiator. Instead, the ligand L on palladium is perceived to affect molecular weight by its participation in termination . The nucleophilic attack on the propagating onium ion by L will generate an L-terminated polyTHF (Equation 21).



(21)

A close examination of THF polymer generated with **15** reveals that there are additional ^{1}H-NMR peaks present: δ 2.38 (s, 3H), δ 4.45 (t, 2H), δ 7.3-7.8 (m, 9H), δ 9.34 (s, 1H). These spectral features correspond with the incorporation of PhN=C(H)Tol in the polymer as an immonium group, based on its spectral correlation to a model immonium compound, $CH_3(Ph)N{=}C(H)Tol^+$ OTf^- [^{1}H-NMR: δ 2.38 (s, 3H), δ 4.16 (s, 3H), δ 7.2-7.8 (m, 9H), δ 9.30 (s, 1H)]. When > 0.06 M PhN=C(H)Tol is added to the polymerization, the incorporation of this immonium moiety into the polymer is quantitative (Figure 6).[6] Similarly, the polymerization with **17** is observed to yield polyTHF containing the immonium fragment: $-CH_2(CH_3)N=C(H)Tol^+$ [^{1}H-NMR: δ 9.15 (s, 1H), δ 4.21 (t, 2H), δ 3.78 (s, 3H), δ 2.47 (s, 3H)].[9] However, no evidence for incorporation of ^{t}BuN=C(H)Tol or NCMe is noted with **14** and **16** respectively. Instead the N-alkylbipyridinium fragment: $-CH_2(bipy)^+$ OTf^- [^{1}H-NMR: δ 9.09 (d, 1H), δ 8.78 (d, 1H), δ 8.51 (t, 1H), δ 8.02 (m, 4H), δ 7.57 (m, 1H), δ 4.74 (t, 2H)] is observed in these larger molecular weight polymers.[10] COSY and TOCSY NMR experiments demonstrate that these immonium units are end-groups on the alkyl terminus of the polyTHF, as evident by the coupling of the $=NCH_2$- protons to the $-CH_2(CH_2)_2O$- protons (δ 1.92) on the end of the polymers.

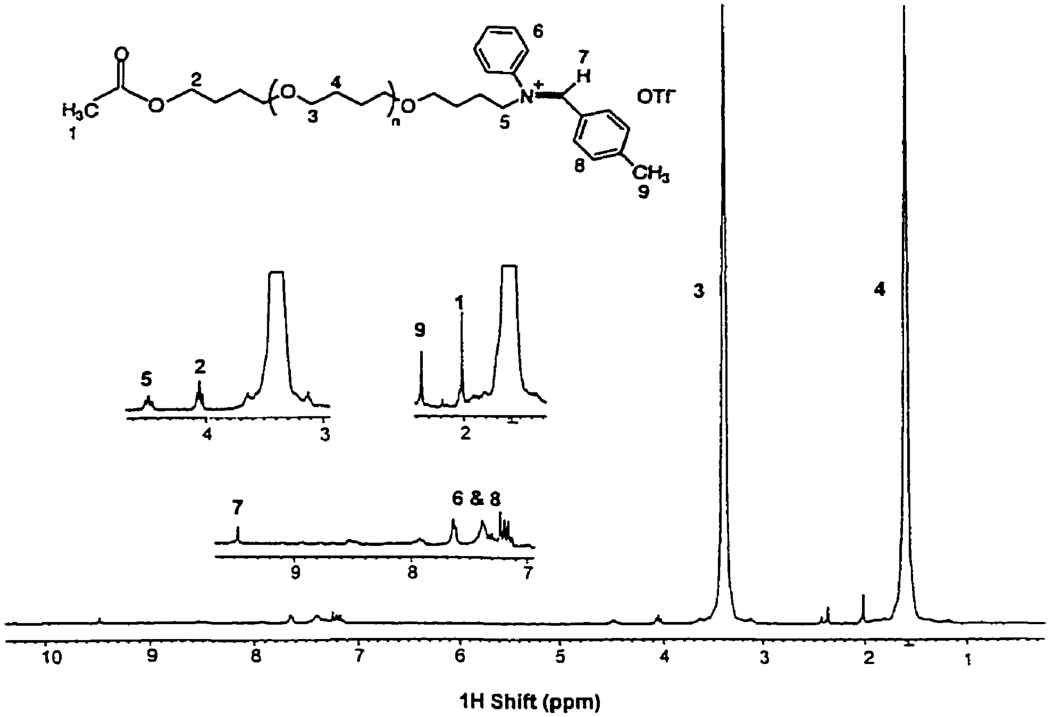


Figure 6. Immonium and methyl ester end-groups on polyTHF

The incorporation of imine into the polymer, and the lower polymer M_w observed with the more basic imines (PhN=C(H)Tol and MeN=C(H)Tol) on **15** and **17** suggest that ligand L is involved in termination of THF polymerization by nucleophilic attack on the growing polymer. This is further evident by the decreasing polymer M_w observed when increasing amounts of free PhN=C(H)Tol are added to polymerization with **14** (Table 3). This is consistent with a more rapid termination induced by a higher concentration of external ligand. The absence of NCMe or ^{t}BuN=C(H)Tol as end-groups in polymerization with **14** and **16** respectively can be attributed to a less basic or a highly bulky L, which cannot participate directly in termination via a nucleophilic attack on the propagating species. Instead, polymerization is terminated partially by the bipy ligand, which falls off Pd(0) center.

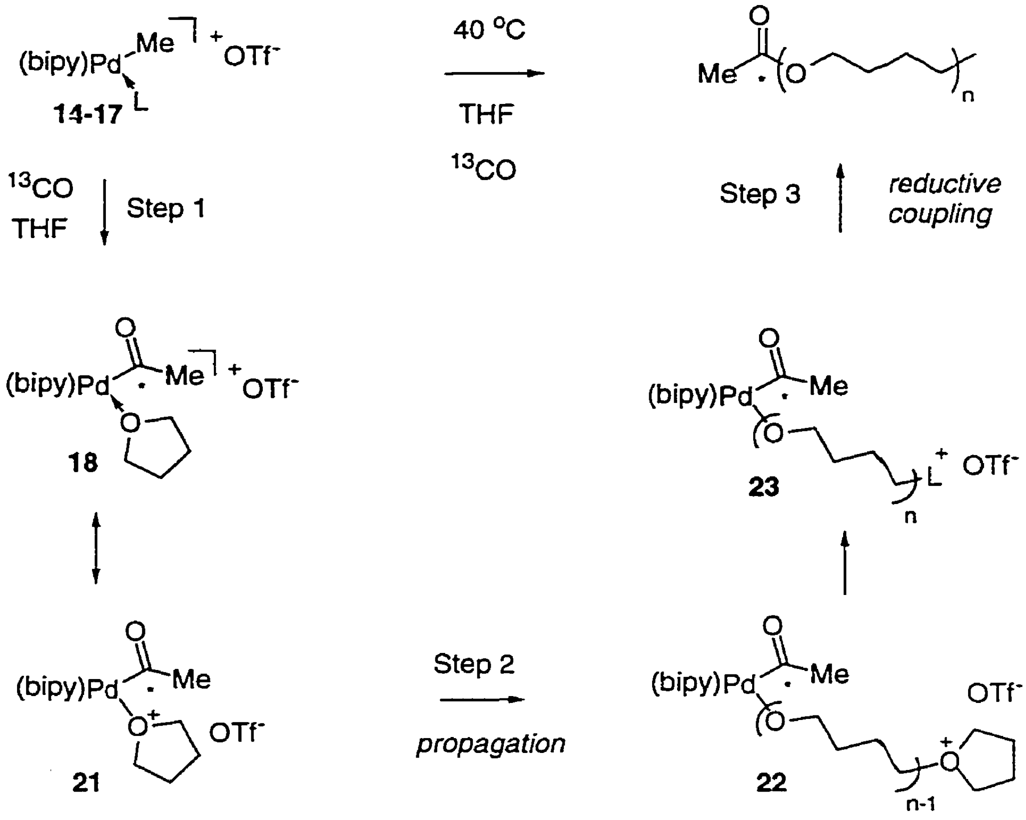
Table 3. Effect of external ligand on polymer yields and molecular weights

Catalyst	Amount of PhN=C(H)Tol (M)	Yield (g)	M_n (10^3)	M_w (10^3)
14	0.005	0.46	18.5	41.3
14	0.025	0.13	11.4	21.3
14	0.050	0.07	8.2	15.0

(reaction performed under 1 atm of CO at 70 °C for 24 hours with 10.0 g THF, 0.05 mmol of **15**, and the appropriate amount of PhN=C(H)Tol).

2.3 POSSIBLE MECHANISMS FOR RING-OPENING POLYMERIZATION WITH 14-17

Considering the above data, several plausible mechanisms for polyTHF formation with **14-17** can be envisaged. Perhaps the most straight forward of these is that which involves ring-opening on palladium, as shown in Scheme 19.



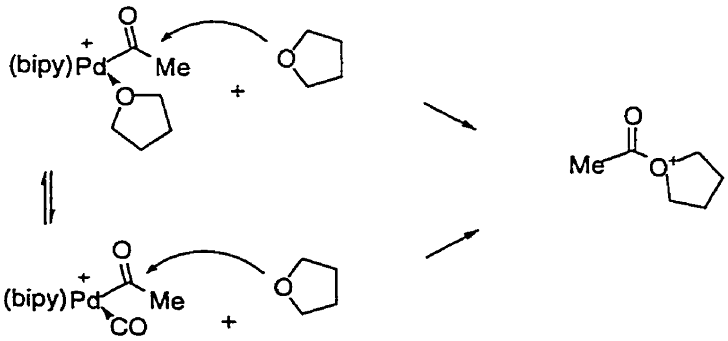
Scheme 19. Mechanism of Pd-mediated THF polymerization

In the initiating step 1, the addition of CO to **14-17** in THF yields the Pd-acyl complex **18** together with the quantitative formation of free ligand L as shown by NMR studies. The insertion of CO into the Pd-Me bond in **14-17** could be considered to generate a more electrophilic palladium, as electron density is withdrawn towards the electropositive acyl ligand.[11] This causes the coordinated THF substrate to bind tightly to palladium, and favors the resonance structure **21** with the positive charge on oxygen, similar to the formation of oxonium ion species initiated by Lewis acids (Scheme 11, Sect. 1.2.4). In step 2, surrounding THF molecules attack the electropositive α-carbon of the Pd-bound THF, resulting in a ring-opening with the re-generation of an onium ion to further propagate the polymerization process. The growing polyether chain (structure **22**) is eventually terminated through a nucleophilic attack by L. A reductive coupling of the Pd-bound polyether with the acyl ligand then produces the other end-group methyl ester observed.

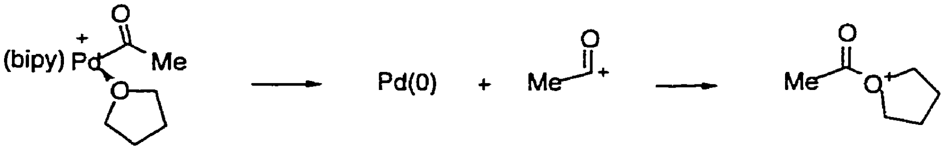
While the mechanism for polyTHF formation shown in Scheme 19 is consistent with our results, several alternative mechanisms for polyTHF formation also have precedent. For example, initiation of THF ring-opening polymerization could be achieved via direct acylation of the THF molecule. This acylation could occur via a number of mechanisms (Scheme 20).

(i) *Intramolecular*

(ii) *Intermolecular*

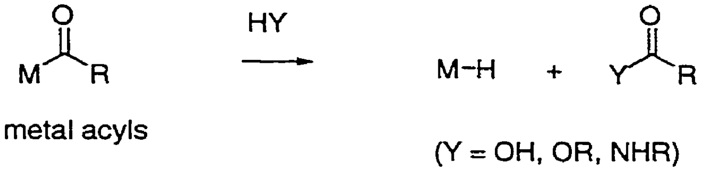


(iii) *Ionization*



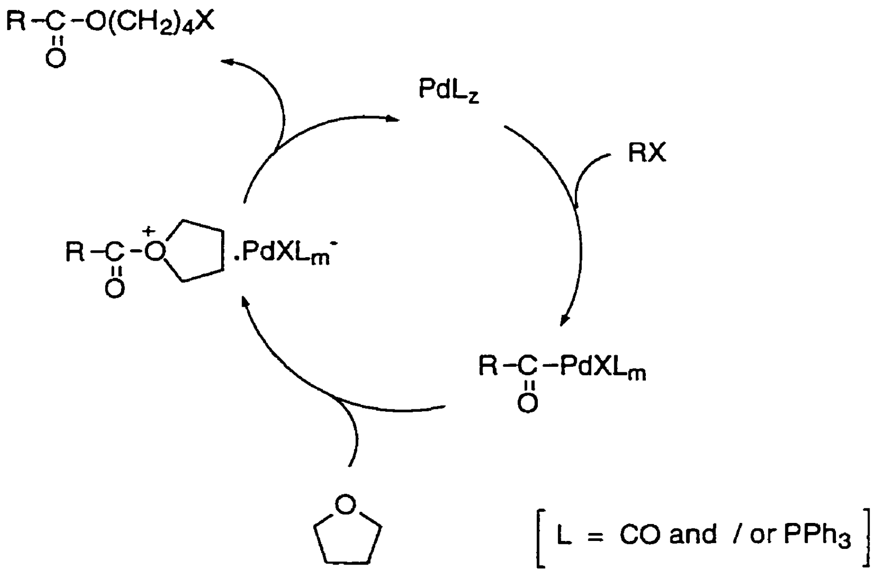
Scheme 20. Initiation via nucleophilic attack

Support for this mechanism of initiation can be found in the chemistry of metal acyl ligands, which have been shown to undergo direct nucleophilic attack at the acyl carbon with a number of nucleophiles (water, alcohols and amines) to generate acylated products (Equation 22).[13] Indeed, Tanaka and co-workers have proposed a similar mechanism for the Pd-catalyzed carbonylation of organic halides in the presence of cyclic ether (Scheme 21).[11] In this study, the ring-opening of the cyclic ethers is postulated to occur by a mechanism that involves the nucleophilic attack of the cyclic ether on the acyl fragment to form an acyloxnium ion intermediate. This key intermediate species was similarly invoked by Alper in an earlier work on the metal carbonyl ($M(CO)_6$, M = Cr, Mo and W) catalyzed reactions of ethers with acid halides.[14]



(22)

An acyloxonium ion formed in this manner is capable of propagating the continual ring-opening of the cyclic ethers present if a strongly coordinating anion (ie. a halide anion) is absent. Since the nucleophilic attack of THF on complex **18** produces hypothetically an acyloxonium ion associated with the weakly coordinating OTf⁻ anion (Scheme 20), successive ring-opening of THF can therefore be easily sustained to eventually yield a polyTHF with an attached *methyl ester* end-group.

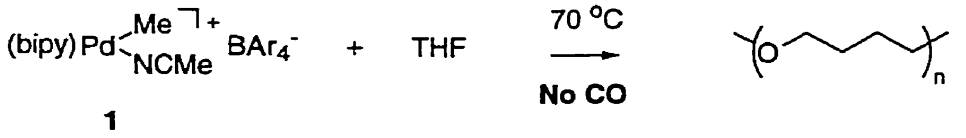


Scheme 21. Pd-catalyzed carbonylation of organic halides

Counter-Ion Effect

Neither the NMR studies nor the end-group analysis on polyTHF formation with **14-17** allow us to distinguish between a palladium-based (Scheme 19) or direct acylation-based (Scheme 20) mechanism for initiation. However, variations of the palladium initiator employed could provide insight into this step. Namely, if conditions could be achieved which block one mechanism but not the other, the result of reaction with THF could provide important information on the initiation step. This can be achieved by varying the counter-ion employed on the initiator. For example, the substitution of OTf$^-$ with a strongly coordinating Cl$^-$ anion has been shown to hinder ring-opening (Equation 17),[1] implying that an empty coordination site on the palladium center is essential.

Perhaps an even more compelling evidence can be found in replacing OTf$^-$ with a less coordinating anion BAr'$_4^-$ (Ar' = 3,5-$(CF_3)_2C_6H_3$). Unlike the reaction of **14**, warming of complex (bipy)Pd(Me)(NCMe)$^+$ BAr'$_4^-$ (**1**) (56 mg, 0.05 mmol) in THF (10 g) was found to lead to the formation of polyTHF (1.41 g, M_n = 3 700, M_w = 16 900) *without CO* (Equation 23). Since there is no acyl ligand generated in this reaction of **1**, the mechanisms in Scheme 20 are not possible, and Pd-based ring-opening is the only viable possibility.



(23)

A possible rationale for this observation may lie with the weaker interaction between the cationic Pd center and the bulky BAr'$_4^-$ anion present in complex **1** relative to the Pd$^+$ OTf$^-$ interaction in **14**. The OTf$^-$ anion is known to be more strongly coordinating than BAr'$_4^-$.[15] Hence a smaller extent of the charge on the metal is utilized for neutralizing the opposing charge on the BAr'$_4^-$ anion as compared to a OTf$^-$ anion, resulting in somewhat more Lewis acidic Pd center in **1** than in **14**. Thus, while the more cationic Pd center in **1** is sufficiently Lewis acidic to mediate THF ring-opening directly, complex **14** requires the insertion of CO to generate a slightly more backbonding acyl ligand, in order to induce ring-opening. To our knowledge, such fine control of the initiator electronics over heterocycle ring-opening has not been previously reported. Additionally, in the case of **14**, it provides a novel carbon monoxide "on switch" for THF polymerization.

The polymerization of THF by **1** clearly illustrates that initiation occurs directly at the metal center as postulated earlier (Scheme 19). Although this result does not conlusively support a particular mechanism for the polymerization of THF with **14-17** in the presence of CO, it provides a strong evidence for the mechanism involving initiation via THF coordination to the metal center.

2.4 CONCLUSIONS

The ring-opening polymerization of THF by the Pd complexes of the form (bipy)Pd(Me)(L)$^+$ OTf$^-$ (**14-17**) is clearly more elaborate than the corresponding polymerization initiated by (bipy)Pd(Me)(L)$^+$ BAr'$_4^-$ (**1**). The former can only be accomplished through the addition of CO to the reaction, and involves a series of metal-based reactions (ligand substitution and CO insertion) prior to polymerization. However the capricious pre-initiation steps also serve to infer a greater control on the ring-opening process, dictating its activation by a simple 'chemical switch' (CO). Such precise timing of the ring-opening process potentially allows further chemistry to be carried out on the metal center prior to ring-opening (*vide infra*).

The above reactions also illustrate the highly specific function and nature of the ligands and counter-ion in the Pd-based initiator. The intricate effect displayed by substitution of the OTf$^-$ with BAr'$_4^-$ counter-ion demonstrates a possible regulatory role dictated by the counter-ion. Meanwhile, variation of the labile ligand L provides a useful instrument for molecular weight control. Even the seemingly stagnant bidentate ligand can participate partially in termination of polymerization. Hence every aspect of the Pd complex (bipy)Pd(Me)(L)$^+$ OTf$^-$ is crucial in determining the activity of this metal initiator towards ring-opening polymerization. It will be interesting to study in greater depth the functions of these components on the palladium, particularly the effect on ring-opening upon substitution of bipy ligand with other nitrogen or phosphorus bidentate ligands. Additionally these components can be fine-tuned or manipulated to suit a particular ring-opening reaction, akin to catalyst design.

Finally, the defined end-groups on the polymer allude to a relatively well-behaved ring-opening system. The incorporation of CO (an insertion monomer) into the polymer in the form of an ester fragment via reductive coupling signifies the possibility of synthesizing ring-opened polymers, capped with various inserted elements, using these palladium complexes. The immonium end groups, generated via nucleophilic attack by L, can also be synthetically advantageous. They provide active sites for further modification to polymer ends in order to explore new chemistry.

2.5 REFERENCES

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3. This is analogous to the observed insertion of CO into **15-17** to form the corresponding acyl complexes (bipy)Pd(COMe)(L)$^+$ OTf$^-$ when the reactions are performed in CH_2Cl_2 instead of THF solvent. See Dghaym, R. D.; Yaccato, K. J.; Arndtsen, B. A. *Organomet.* **1998**, *17*, 4.

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6. End-group quantitation determined by comparison of M_n calculated from ^{1}H-NMR to M_n from GPC data.

7. Using ethyl acetate ($CH_3C(O)OCH_2CH_3$) as model compound: ^{1}H-NMR: δ 2.03 ($CH_3C(O)O$); ^{13}C-NMR: δ 170.9 (C(O)O); $\nu_{CO} = 1742$ cm^{-1}.

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9. Characterization based on spectral correlation to model imminium salt, $CH_3(CH_3)N{=}C(H)Tol^+$ OTf$^-$ [^{1}H-NMR: δ 2.47 (s, 3H), δ 3.79 (s, 3H), δ 3.95 (s, 3H), δ 7.80 (d, 2H), δ 7.39 (d, 2H), δ 9.16 (s, 1H)].

10. Characterization based on spectral correlation to the N-alkyl-2,2-bipyridinium ion, CH_3(bipy)$^+$ OTf$^-$ [^{1}H-NMR: δ 4.77 (t, 2H, $NC\mathit{H}_2$), δ 7.53 (m, 1H), δ 7.8-8.1 (m, 4H), δ 8.51 (t, 1H), δ 8.74 (d, 1H), δ 9.10 (d, 1H)].

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CHAPTER THREE.

THE COUPLING OF CO/OLEFIN INSERTION WITH THF RING-OPENING POLYMERIZATION

3.0 INTRODUCTION

In general, most commercial polymers we encounter are homopolymers.[1] However technological advancement has made it increasingly necessary to consider 'polymer hybrids' as a means to attain specific polymer properties not accessible with simple homopolymers.[2] Since block co-polymers provide perhaps the most effective method of combining the properties of two or more homopolymers in one material, substantial effort has thus been directed towards their synthesis. Block co-polymers are defined as macromolecules comprised of two or more homopolymer blocks joined together chemically.[3] They exhibit interesting properties due to incompability between the chemically dissimilar blocks,[2a,4] which are forced to co-exist together. Consequently *micro*phase separation arises, with the minor component block collapsing into discrete aggregates known as domains[2-4] (Figure 7), and the underlying morphological organization is altered.

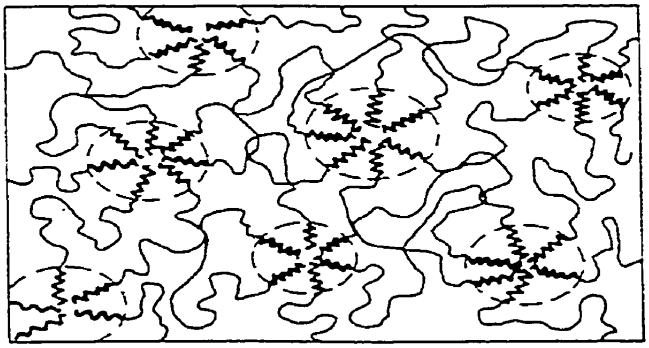


Figure 7. Schematic representation of a block co-polymer: discrete domains dispersed in matrix of the major component[3a]

The changes in the morphological structure are dependent to a certain degree upon the volume ratio of the component blocks.[2a] The minor block, present as discrete domains dispersed in the matrix of the major component block, can assume two forms: spherical shapes (at volume ratio of < 20%) or rod-like forms (at slightly higher volume ratio).[2a] However, when the two blocks are present in nearly equal volume ratio, they co-exist in continuous phases with lamellar structures (Figure 8). Obviously, these variations in the morphological structure will exert a major influence on the overall properties of block co-polymers. Hence, unique properties are often obtained.

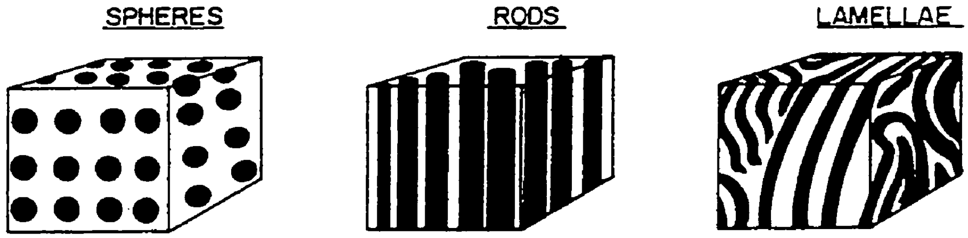


Figure 8. Various morphology of block co-polymers

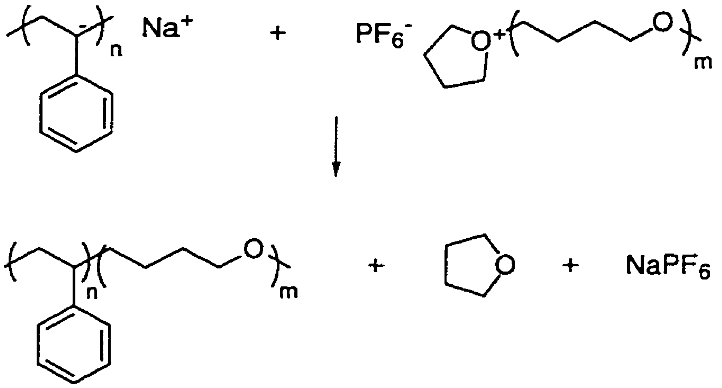
3.1 THERMOPLASTIC ELASTOMER

An interesting development illustrating the unique properties associated with block co-polymers is the thermoplastic elastomer. It combines the thermoplastic as well as elastomeric behaviors of polymers, which were previously thought to be mutually exclusive.[2a] The resulting material is rubbery despite the absence of chemical crosslinking, and yet the polymer is easily processed. An excellent example is the poly(butadiene-styrene) rubber (SBR),[2-3,5-6] which blends a soft, elastomeric poly(butadiene) to a hard, crystalline poly(styrene) thermoplastic. The resulting product is rubbery, and easily molded by heating above the T_g of the hard poly(styrene) block.[5] It can be commercially produced at low cost, and thus used extensively in footwear, injection-molded goods and as adhesives.[5-6]

Block co-polymers therefore provide one of the most useful means of forming 'polymer hybrids'. They are especially suited for highly incompatible polymer pairs, which do not mix well as an alloy.[3a] The microscale interactions between the component blocks can be further utilized to alter thermal, mechanical and chemical properties,[2a] effecting qualities such as processibility, solubility, surface activity, elasticity and impact resistance.[2] These properties are moreover adjustable by modification to the length and nature of the component blocks as well as the molecular weight distributions.[5,7] Occasionally, they may even display previously unanticipated behavior, in addition to combining the properties of the component blocks.[2a] They hence find extensive applications as materials, adhesives, additives, compatibilizers in polymer blends, polymeric amphiphiles and micelle forming species.[2b,3b]

3.2 BLOCK CO-POLYMER SYNTHESIS

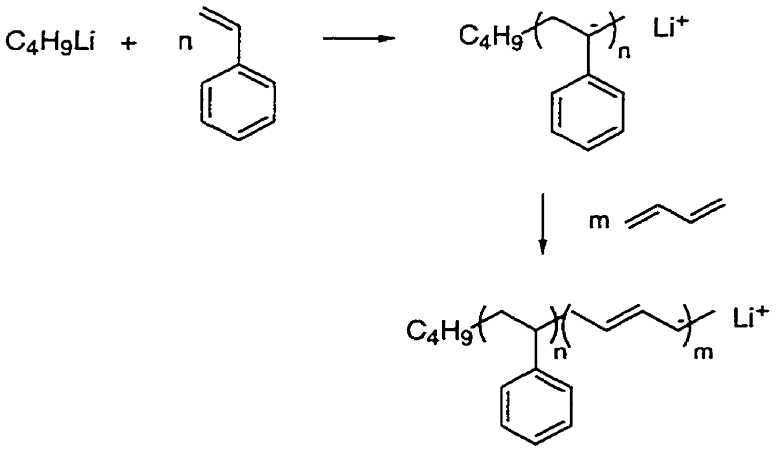
Despite the usefulness of block co-polymers, they are not easily prepared. Sophisticated synthetic techniques are often engaged to prepare such well-defined structures.[2a] Accurate knowledge and control of the polymerization processes are essential to obtain the appropriate sequential architecture.[2a] Certain parameters require strict conditions to ensure stability of active centers and absence of terminating steps or side reactions.[4] The simplest and most obvious approach of preparing block copolymers is by a *condensation or coupling* reaction. The component blocks are initially prepared separately, with certain functionalities affixed to each end. They are subsequently joined by a coupling reaction performed on their functionalized end groups.[3] For example, Richards and co-workers linked a living polystyrene block with an anionic end-group to a living polyTHF block, carrying a positively charged onium ion, by a simple ion exchange process (Equation 24).[8]



(24)

Although the above condensation reaction seems to provide an effective approach, it is a difficult process to realize for the synthesis of high molecular weight block co-polymers. In this case, the concentration of the end groups relative to the polymer is so small that the coupling reaction will be very slow and at times incomplete.[3b,9] This is especially true for a reaction consisting of two highly incompatible blocks, often resulting in a severe phase separation. The resulting heterogeneity further lowers the end-group reactivity, although initial block co-polymers formation may ease the phase separation partially by acting as compatibilizers.[3b]

A second, more common approach to block co-polymer synthesis is *living polymerization.* Living polymerization refers to a rare but highly desirable process in which the active center in a polymerization remains 'alive' after all the monomers have been consumed, due to the virtual absence of a terminating step.[3-4] The phenomenon is hence frequently applied to the synthesis of block co-polymers when a second polymerization is initiated through the fresh addition of monomers. This is shown by the synthesis of the poly(styrene-butadiene) rubber (Equation 25),[4] where both polymerization substrates (styrene and butadiene) are polymerized anionically by *sec*-butyllithium.



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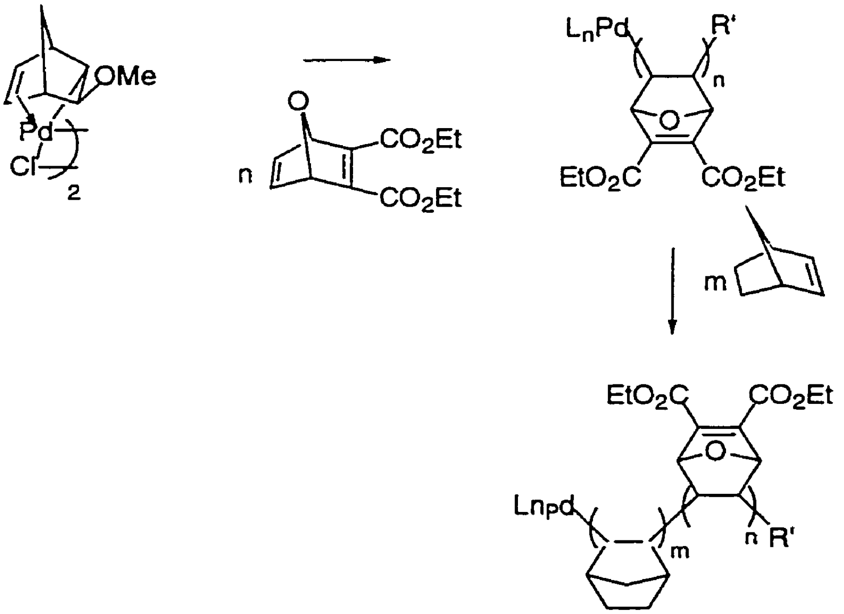
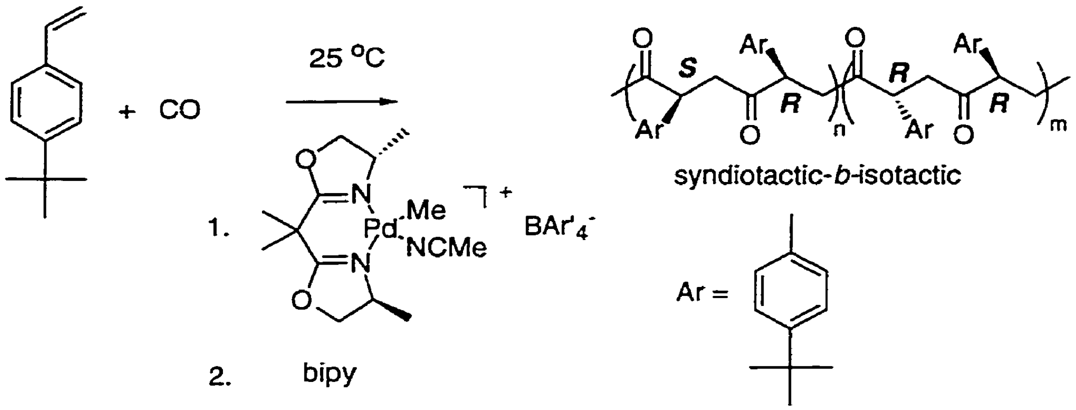
The living insertion polymerization of olefins catalyzed by palladium has also been applied to block co-polymers synthesis. Novak and co-worker carried out the co-polymerization of norbornene and diethyl 7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate with a series of Pd σ,π-alkyl complexes (Equation 26).[9] The polymerization of olefins with these Pd σ,π-alkyl complexes occurs quite efficiently. For example, it was found that diethyl 7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate could be quantitatively polymerized within 15 minutes using tetramethylurea as solvent. The resulting polymerization product is extremely stable such that it can be isolated and stored in air with the Pd still attached. This attests to the living nature of such a polymerization system, and allows the preparation of block co-polymers with higher architecture and pre-determined molecular weights. This is illustrated by the dissolution of the Pd terminated poly(diethyl 7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate) in a solution containing norbornene to yield the expected norbornene - diethyl 7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate block co-polymer (Equation 26).[9]



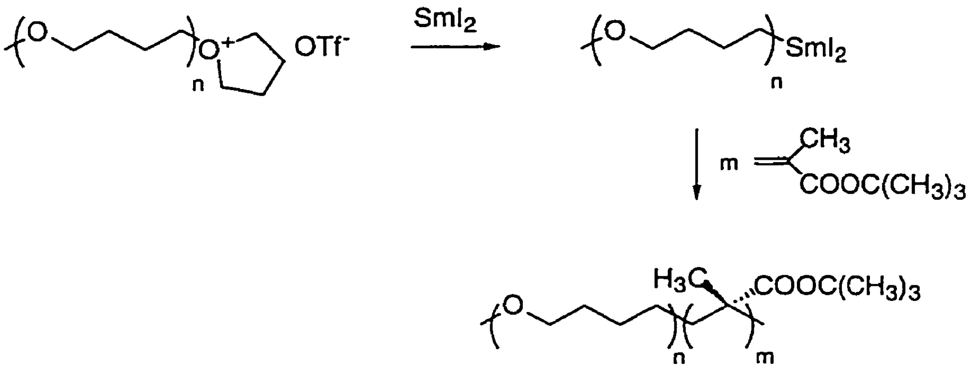
(26)

Brookhart and co-workers utilized a more unusual approach for the synthesis of ketone block co-polymers.[10] They varied the stereochemistry along the main chain of a polyketone chain by an *ancillary ligand exchange* process. An *isotactic* polyketone chain was initially synthesized through the living co-polymerization of CO (1 atm) and *tert*-butylstyrene (20 mL) with (bis-oxazoline)Pd(Me)(NCMe)$^+$ BAr'$_4^-$ complex (0.1 mmol) for a period of 23 hours (Equation 27). An equivalent amount of 2,2'-bipyridine ligand was subsequently added to displace the bis-oxazoline ligand from the Pd metal center. This initiates the synthesis of the second *syndiotactic* block, which was completed only after two hours of reaction time. A *stereoblock* polyketone was obtained.



(27)

The synthesis of stereoblock polyketone and the other examples discussed above clearly indicate that living polymerization is perhaps the most practical method available to synthesize block co-polymers. However, the technique is often limited in the monomers that can be employed, since it requires two or more monomers undergoing the same polymerization mechanism.[3] This limited utility of living polymerization can sometimes be resolved by a technique known as *active center transformation.*[3b,11] The method involves transformation of the active polymerization center to one which can undergo a second polymerization reaction with a completely distinct monomer type. The technique is relatively established and hence has the potential to diversify the scope of monomer types that can be assembled into block co-polymers. Many transformations have been developed to date to convert almost any kind of active center to suit a specified type of polymerization. An example is the reduction of the cationic propagating end of polyTHF to an anionic polymerization species by SmI_2.[12] This transformation converts the onium ion on the polyTHF chain to an organosamarium moiety, which can then initiate the anionic polymerization of *tert*-butyl methycrylate (Equation 28).

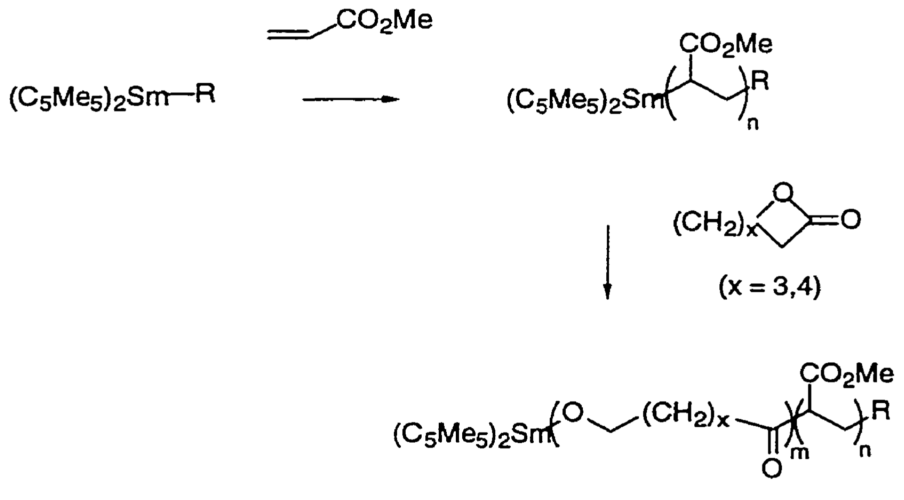


(28)

Rare Earth Metal Complexes

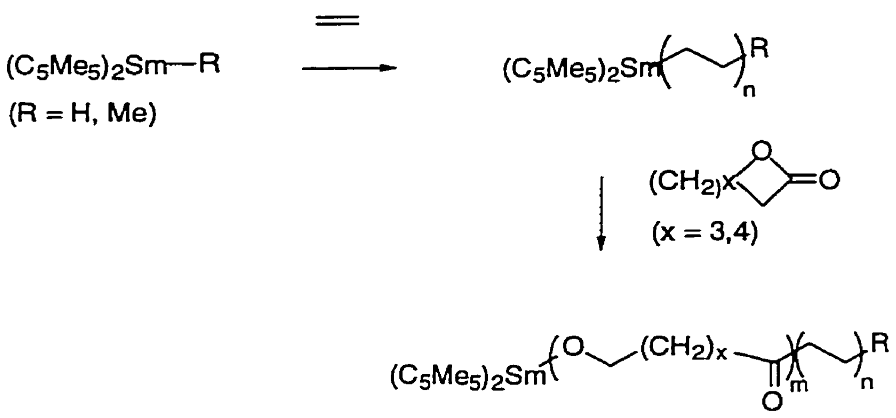
In contrast to active center transformation techniques, an ideal way to generate block co-polymers of monomers polymerized by distinct mechanisms will be to use a polymerization initiator (or catalyst) that could mediate both polymerization mechanisms and their coupling. However, to our knowledge, this process has only been noted in rare systems. Organolanthanide complexes are found to show surprising activity towards the polymerization of both polar and non-polar substrates, and can polymerize a diverse variety of monomers including ethylene, styrene, acetylene, alkyl acrylates, alkyl isocyanates, lactones, lactide, cyclic carbonates and oxiranes.[13] For example, $[SmH(C_5Me_5)_2]_2$ and $[LnMe(C_5Me_5)_2(THF)]$ (Ln = Sm, Y and Lu) are found to polymerize methyl methacrylate to give a high molecular weight syndiotactic polymer ($M_n > 500\ 000$, syndiotacticity > 95%).[13] These complexes can also polymerize δ-valerolactone and ε-caprolactone by $[SmMe(C_5Me_5)(THF)]$ and $SmH(C_5Me_5)_2]_2$ in a living fashion yielding poly(δ-valerolactone) and poly(ε-caprolactone) with molecular weight of up to 75 200 and 109 400 respectively.[14] The polydispersity index was extremely narrow (< 1.1) for both reactions.

This monomer diversity, combined with the living nature of the polymerization, provides an opportunity to incorporate two or more types of monomers in a single polymerization reaction. This was successfully achieved in the sequential polymerization of methyl methacrylate and lactone to yield a functionalized olefin-lactone block co-polymers (Equation 29).[15]



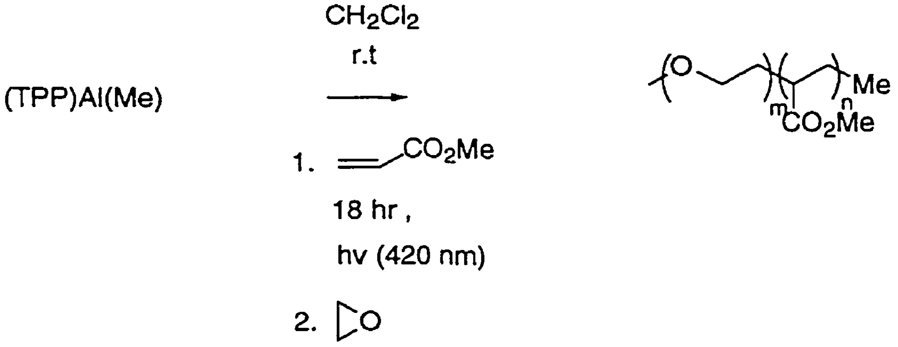
(29)

Block co-polymerization of ethylene and propylene with heterocycles have also been attained for the first time using these organolanthanide complexes, as shown by the synthesis of polyethylene-*b*-poly(δ-valerolactone) and polyethylene-*b*-poly(ε-caprolactone) below (Equation 30).[16] These block co-polymers are predicted to possess remarkable adhesive, dyeing and adsorbing properties. Their synthesis undoubtedly proves the extensive utility of rare earth metal complexes in assembling polymers of higher architecture.

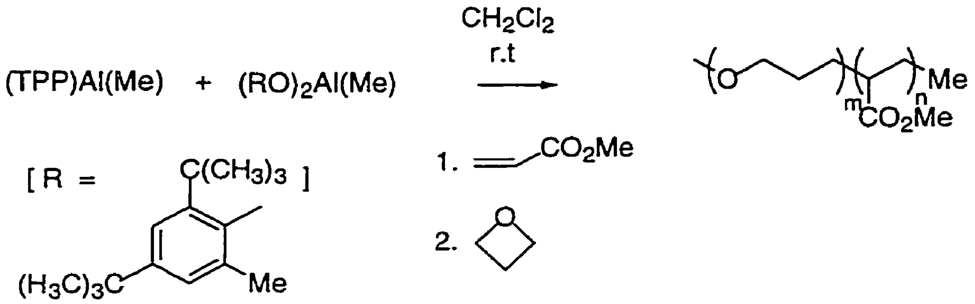


(30)

The success of rare earth metal complexes in combining two monomers of diverse nature is likewise reflected in polymerizations mediated by *metalloporphyrins*. They have been reported to similarly initiate a wide variety of monomers such as epoxides, lactones, lactide, cyclic carbonate, cyclic siloxanes, methacrylonitrile, methacrylic and acrylic esters.[17] Not surprisingly, a variety of tailored block co-polymers have thus been synthesized, such as methacrylate-epoxide[18] and methacrylate-oxetane[19] block co-polymers using (TPP)Al(Me) (TPP = 5,10,15,20-tetraphenylphosphinato) (Equation 31-32). No other initiators other than the aluminium porphyrin described have been known thus far to effect the polymerizations of epoxide and oxetane in a living manner.



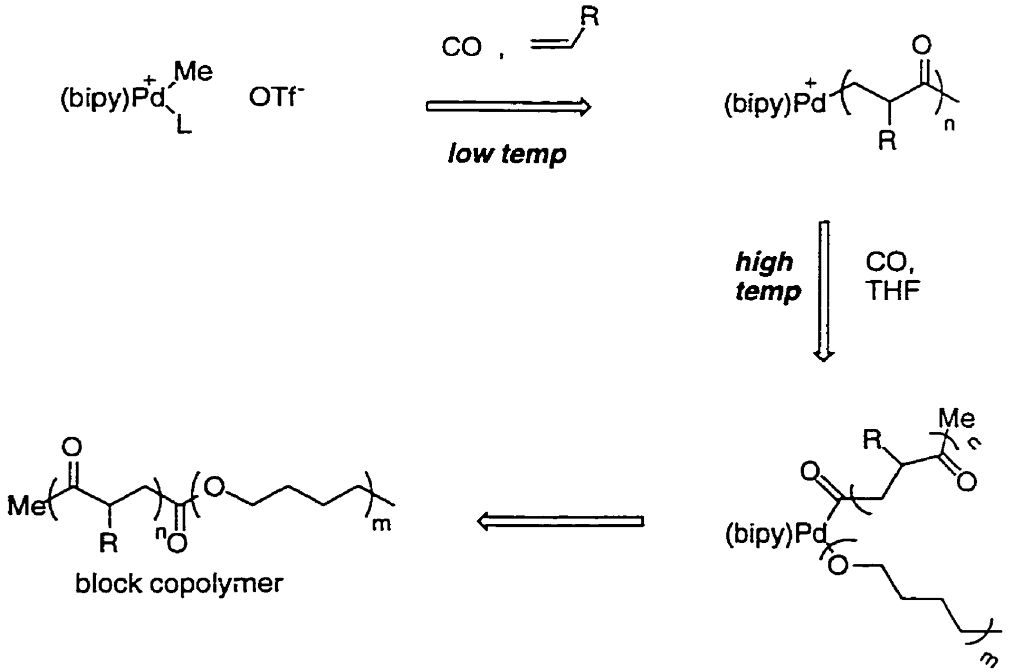
(31)



(32)

3.3 PROPOSED ROUTE FOR SYNTHESIS OF BLOCK CO-POLYMERS USING PALLADIUM(II) COMPLEXES

It can be seen that the coupling of various monomers is an important key to creating novel polymer materials. Despite the diversity of monomers available, there are however only very few methods that could be employed to combine these monomers in a controlled fashion. The rare earth metal complexes and metalloporphyrins are two such examples. However block co-polymerization of two contrasting monomers by these metal complexes was achieved via a *single polymerization mechanism*, namely insertion. On the other hand, palladium(II) complexes are known to catalyze the insertion polymerization of CO and olefin into polyketones,[20] as well as to initiate the ring-opening polymerization of heterocycles (Scheme 17, Section 1.3).[21] The earlier mechanistic study on THF ring-opening polymerization with (bipy)Pd(Me)(NCMe)$^+$ OTf$^-$ demonstrates that palladium(II) complexes can mediate the coupling of the insertion monomer CO with the ring-opened polymer yielding ester terminated polyTHF (Scheme 19, Sect. 2.3). The objective of the present study is to therefore examine the feasibility of combining these *distinct polymerizations* on Pd(II) complexes to develop a novel route to synthesize block co-polymers. The proposed route to couple CO/olefin insertion co-polymerization with ring-opening polymerization (of THF) using the palladium(II) complexes (bipy)Pd(Me)(L)$^+$ OTf$^-$ (L = NCMe, MeN=C(H)Tol, PhN=C(H)Tol, $(CH_3)_3CN$=C(H)Tol) is shown below (Scheme 22).



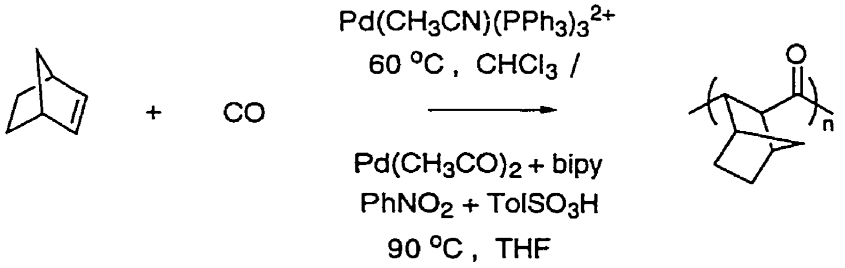
Scheme 22. Proposed combination of CO/olefin co-polymerization with ring-opening polymerization

Hypothetically the insertion and ring-opening processes will not interfere with each other since the former takes place at the Pd-Me bond while the latter ring-opening process has been shown to occur at the fourth coordination site. Additionally, the sequential insertion of CO and olefin to generate polyketone usually occurs at ambient temperature,[20] while the ring-opening polymerization of THF is favored at a higher temperature. Considering that the Pd-mediated ring-opening process requires the insertion of CO for initiation, CO can also be further utilized as an auxiliary tool to control the ring-opening process. It creates a more convenient block co-polymerization process as both insertion and ring-opening monomers can be introduced concurrently, which eliminates multiple additions of reagents. A single step process for the block co-polymerization is therefore possible.

3.4 THE CO-POLYMERIZATION OF CARBON MONOXIDE AND OLEFIN IN TETRAHYDROFURAN

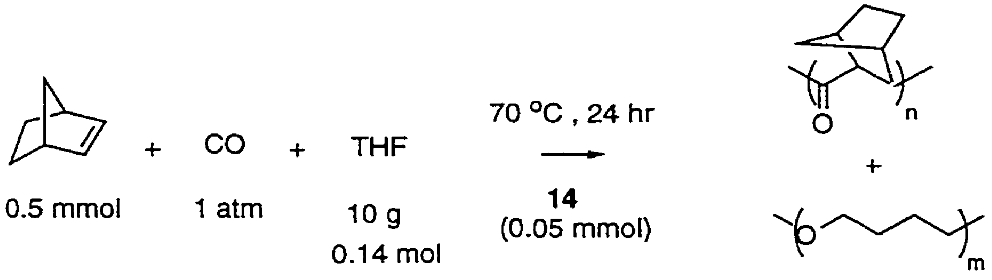
3.4.1 Co-Polymerization of Norbornene and CO in THF

In order to study the possibility of using $(bipy)Pd(Me)(L)^+$ OTf^- to mediate the coupling of insertion and ring-opening polymerization, the co-polymerization of CO and norbornene in THF with **14** was examined. The co-polymerization of CO and norbornene was first documented by Sen in 1982 using the catalyst $[Pd(MeCN)(PPh_3)_3](BF_4)_2$ (Equation 31).[22] The reaction, performed in $CHCl_3$ at 60 °C, yielded low molecular weight oligomers (M_n = 350) after 3 days. Liaw and co-workers subsequently repeated the reaction using $Pd(MeCOO)_2$/2,2'-bipyridine catalyst in combination with nitrobenzene and *p*-toluenesulfonic acid (Equation 31).[23] The co-polymerization, performed in *THF* at 90 °C with CO pressure of 2.3 MPa, yielded *only* polyketone (M_n = 6100) after two hours of reaction. No polymerization of THF was reported in the latter work.



(31)

In the present study, the co-polymerization of CO and norbornene in THF will be attempted with the Pd(II) complex (bipy)Pd(Me)(NCMe)$^+$ OTf$^-$ (**14**) (Equation 32). Upon mixing norbornene (5 mg, 0.5 mmol) and **14** (23 mg, 0.05 mmol) in THF (10 g) and adding 1 atm CO, the reaction mixture turned bright yellow, and solid Pd (black precipitate) was observed within 15 minutes. This is in stark contrast to the earlier polymerization of THF with **14** where no significant decomposition was observed until heating was applied (Chapter 2, Sect. 2.2). After heating the solution at 70 °C for 24 hours, filtration and removal of solvents yielded only 0.05 g of polymer product compared to 0.92 g obtained for the ring-opening polymerization of THF with **14**. Surprisingly ^{1}H-NMR analysis of the solid product indicated the presence of poly(norbornene-CO) and polyTHF in approximately a 4:1 ratio of norbornene/CO : THF units. However, GPC analysis showed that there were two components (M_n = 150 (97%) and 14 900 (3%)) in the product. Considering the work of Sen,[22] the low molecular weight component can be attributed to the polyketone, while the larger polymer is polyTHF.



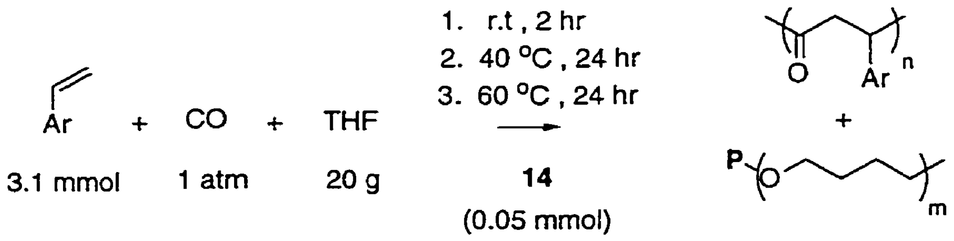
(32)

Both the multiple polymers obtained and the poor product yield (< 6% of the expected yield) suggest strongly that THF ring-opening polymerization did not occur in the expected mode. The rapid decomposition of the active catalyst to Pd(0) following CO addition presumably prevents a Pd-mediated ring-opening of THF to occur as anticipated. The reaction was thus repeated at a lower temperature (0 °C) but it failed to prevent the rapid decomposition mode.

3.4.2 Co-Polymerization of *tert*-Butylstyrene and CO in THF

The above reaction of norbornene/CO and THF yielded only relatively low molecular weight norbornene/CO co-polymers ($M_n < 150$), which indirectly alludes to a rapid termination associated with norbornene/CO co-polymerization. Since the ring-opening polymerization of THF is a much slower process than CO/olefin insertion, this system is thus unsuitable for the coupling of insertion and ring-opening polymerizations. Instead, the potential coupling of *tert*-butylstyrene/CO and THF was examined. Brookhart has shown that *tert*-butylstyrene/CO co-polymerization is living when performed under similar polymerization conditions (CO pressure = 40 psi, temperature = 25 °C) resulting in the formation of high molecular weight polyketones ($M_n > 10\ 000$).[24]

The initial co-polymerization of *tert*-butylstyrene and CO in THF was carried out at conditions shown in Equation 33. The reaction temperature was kept low (25 °C) at first to allow for the co-polymerization of CO and *tert*-butylstyrene to progress before it was gradually raised to 60 °C to initiate polymerization of THF. Unlike the previous co-polymerization of CO and norbornene, the Pd(II) species did not decompose immediately, but remained fairly stable for a prolonged period (reaction mixture only turned slightly grey after 1 hour). Significant decomposition was noted upon heating. At the completion of the reaction, the solution was grey and slightly viscous. Upon work-up, a white solid (0.43 g) was obtained. However ^{1}H-NMR showed predominantly *tert*-butylstyrene/CO co-polymer, and only traces of polyTHF. GPC analysis revealed two separate components ($M_p = 5\ 500$ (70 %), $M_p = 412\ 000$ (30%)). The major component of the polymer product was polyketone (as determined from ^{1}H-NMR integration). The identity of the minor component was less obvious. It can either be a THF polymer or a ketone-THF block co-polymer. Various reaction conditions (temperature, length of reaction, CO pressure and quantity of *tert*-butylstyrene) were systematically varied to optimize the yield of the high molecular weight fraction in order to assist characterization. However, no significant improvement in yield was gained from these endeavors. Attempts to chemically separate the minor component from the remaining product were also unsuccessful.



(33)

[**P** = t-butylstyrene/CO co-polymer]
or an unknown end-group

[Ar = $(CH_3)_3C_6H_5$]

While it is possible that a small amount of the complex **14** had directly initiated THF polymerization without first co-polymerizing CO and olefin to produce a high molecular weight polyTHF, the absence of methyl ester end-group in the ^{1}H-NMR spectrum makes this case less conceivable. The high molecular weight product might then consist of THF-ketone block co-polymer. However the ester linkage indicative of the connectivity between the polyketone and polyTHF blocks were obscured by the broad resonance of -C*H*(Ar)CO- proton (δ 4.05 - 4.15) in the CO/*tert*-butylstyrene co-polymer (Figure 9). This difficulty in determining the structure of the high molecular weight component conclusively compelled us to examine this coupling in a more controlled manner.

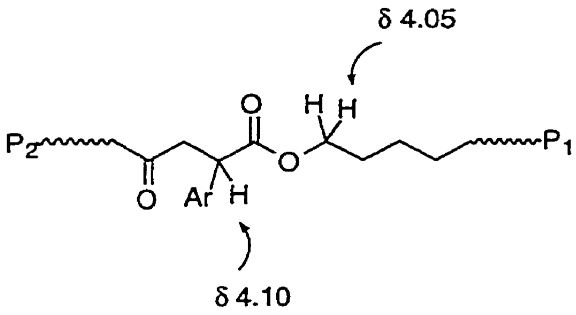
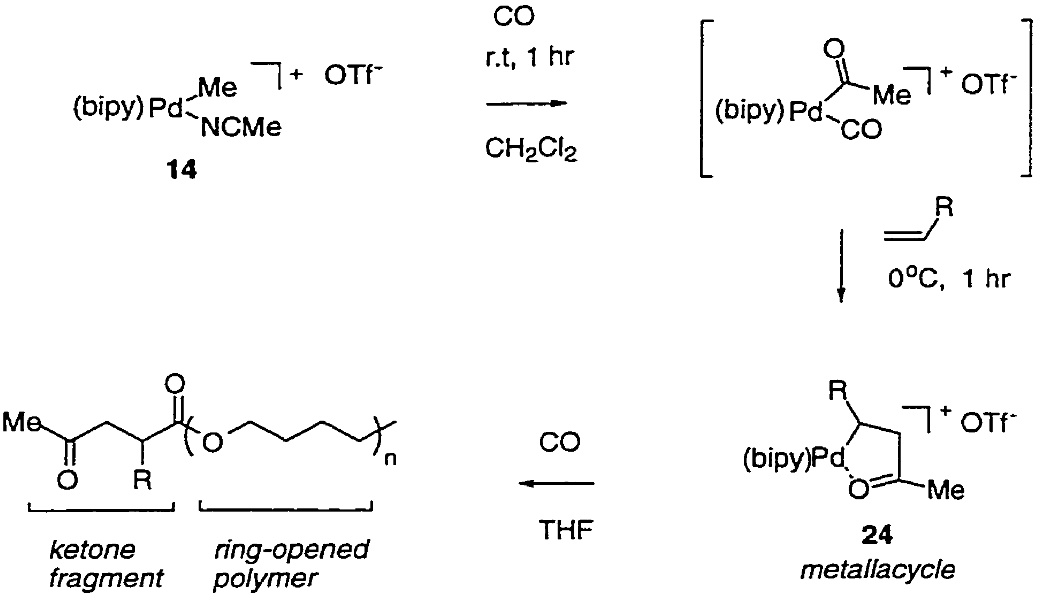


Figure 9. Expected ^{1}H-NMR chemical shifts of ester linkage

3.5 THF POLYMERIZATION WITH (Bipy)Pd(P)$^+$ OTf$^-$ (P = CO / OLEFIN CO-POLYMER)

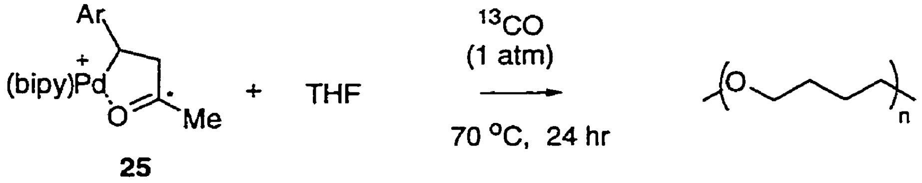
The second approach to investigate the Pd-mediated coupling of olefin/CO and THF entailed partitioning the reaction into two-separate synthetic steps: CO/olefin insertion followed by THF ring-opening. This was done to provide control over each separate polymerization reactions, as well as to facilitate product analysis. The general synthetic route involved the sequential insertion of CO and olefin into the Pd-Me bond of **14** to form the stable metallacycle **24**,[24] followed by addition of THF under CO atmosphere (Scheme 23). Thus, this small ketone unit represents a fragment of an actual CO/olefin co-polymer growing on the Pd metal center. This insertion product is subsequently used to initiate ring-opening polymerization of THF in the presence of CO, mimicking the analogous polymerization of THF by the Pd-alkyl complex **14** (Sect. 2.2).



Scheme 23. Mono-insertion of CO and olefin into **14**, followed by ring-opening

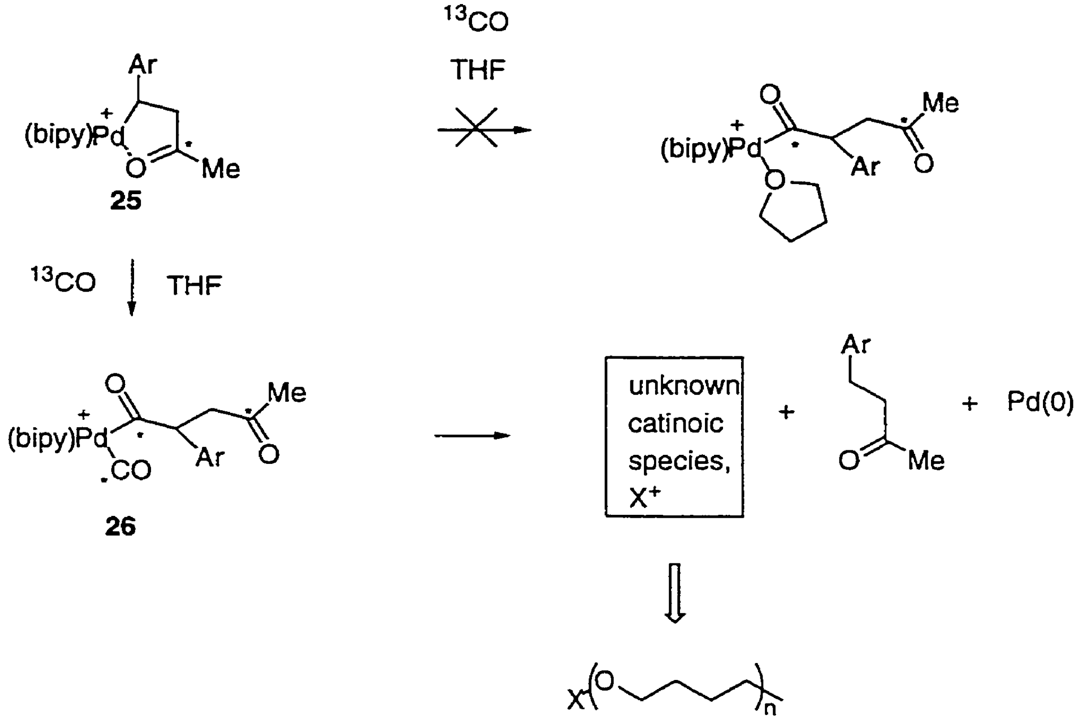
3.5.1 Reaction of CO/*tert*-Butylstyrene Mono-Insertion Product

The mono-insertion of ^{13}CO and *tert*-butylstyrene (**25**) can be prepared by a route similar to Scheme 23, as reported by Brookhart.[24] The addition of ^{13}CO (1 atm) to **25** (31 mg, 0.05 mmol) in THF (5 g) caused a rapid decomposition to Pd(0) within 15 minutes (Equation 34). After a 24-hour heating period, the solution was grey and viscous. Filtration through celite and removal of solvent yielded 0.35 g of polymer. Although GPC analysis showed only one product (M_n = 142 000), ^{13}C-NMR revealed *no ^{13}C labelled carbonyl signal* whatsoever in the polymer, demonstrating that the labelled ketone from **25** is not incorporated into the polyTHF. This puzzling result implies that THF ring-opening polymerization had occured in a completely different fashion than previously perceived.



(34)

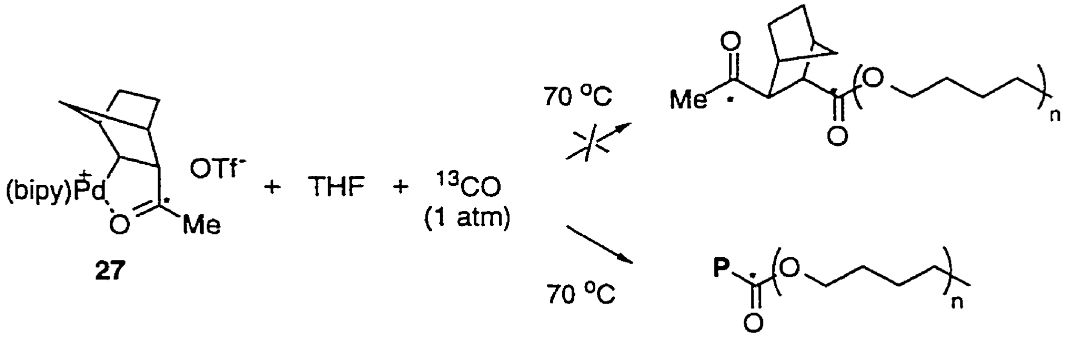
Monitoring this reaction of **25** with CO in d^8-THF by ^{1}H-NMR shows an immediate decomposition of the Pd-alkyl species to $CH_3C(O)CH_2CH_2(C_6H_4)C(CH_3)_3$ [^{1}H-NMR: δ 7.12 - 7.55 (m), δ 2.75 (m), δ 2.31 (m), δ 2.07 (s), δ 1.30 (s)] and solid Pd(0) over the course of 15 minutes, prior to initiating polyTHF formation. This decomposition likely occurs via protonation of the Pd-C bond. The formation of polyTHF is likely initiated by an unknown cationic species (Scheme 24).



Scheme 24. THF polymerization by **25** in presence of CO

3.5.2 Reaction of CO/Norbornene Mono-Insertion Product

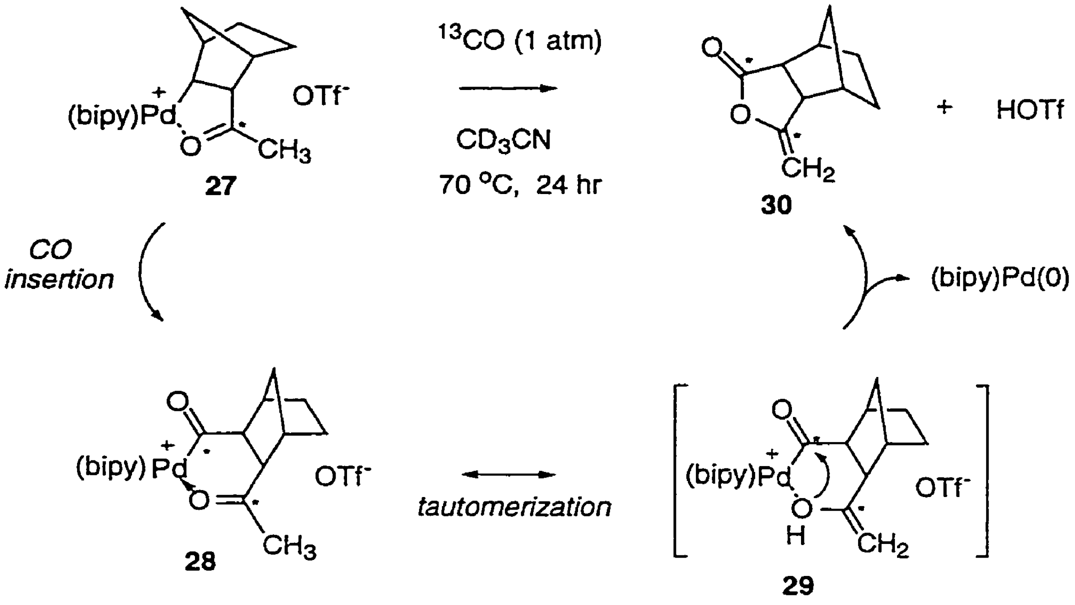
The mono-insertion of CO and norbornene into **14** was carried out according to literature procedure.[25] The resulting five-membered metallacycle (**27**) was examined for its activity towards ring-opening polymerization of THF (Equation 35). The reaction of **27** (28 mg, 0.05 mmol) with ^{13}CO in THF (10 g), followed by warming at 70 °C for 24 hours, yielded 0.21 g of polymer. ^1H-NMR of the product showed it to be polyTHF. However, unlike the preceding polymerization of THF with CO/*tert*-butylstyrene insertion product **25**, ^{13}C-NMR analysis detected several ^{13}C-labelled ester peaks (δ 178.3, δ 174.4, δ 173.8, δ 171.2) in addition to other unidentified peaks (δ 138.9, δ 138.8). The presence of ester resonances suggest the coupling of insertion substrates (^{13}CO and norbornene) with the ring-opened polyTHF proceeded as anticipated. Strangely, no resonance for the ketone were observed in the ^{13}C-NMR (no signal at 200 - 210 ppm), implying that the norbornene/^{13}CO fragment is joined to the polymer in a manner inconsistent with the original route postulated.



(35)

[P = unknown norbornyl]
derivative

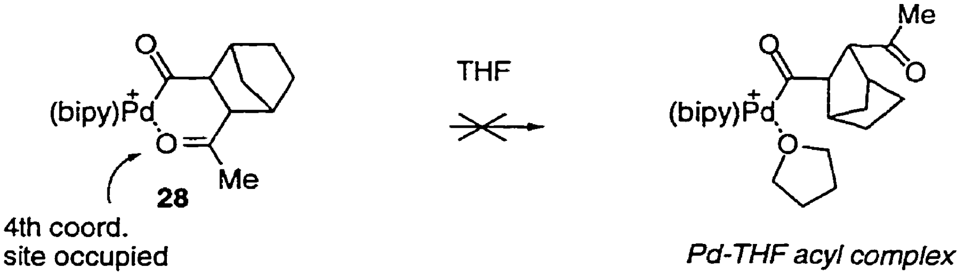
A possible rationale for this unusual incorporation of the norbornene/^{13}CO fragment into the polyTHF was found by examining the decomposition of **27** upon exposure to ^{13}CO. Warming **27** (10 mg, 0.02 mmol) to 70 °C in CD_3CN (1 mL) under 1 atm CO leads to the formation of an enol lactone **30** [^{1}H-NMR: δ 4.64 (m 1H), δ 4.34 (m, 1H), δ 2.95 (m, 1H), δ 2.65 (m 1H), δ 2.55 (s, 1H), δ 2.38 (s, 1H), δ 1.22 -1.57 (6 H); ^{13}C-NMR: δ 176.8, δ 160.9 (^{13}C-labelled signals)] and triflic acid [^{1}H-NMR: δ 14.02 (s)] (Scheme 25). This decomposition pathway is consistent with the observed unsaturated γ-lactone end-group reported by Roberto and co-workers in the co-polymerization of CO and norbornene catalyzed by $Pd(PPh_3)_4$ with bromostyrene.[26] The mechanism of incorporation of **30** into polymer will be discussed later.



Scheme 25. Decomposition of CO/norbornene insertion product in CO

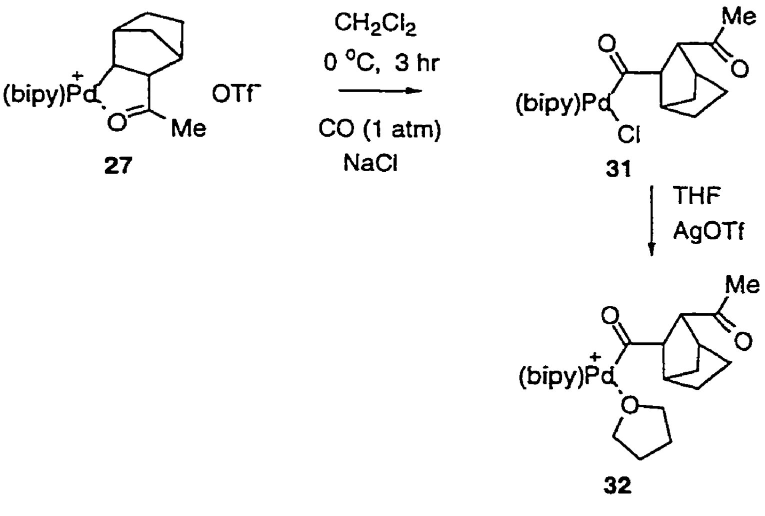
3.6 REACTION OF (Bipy)Pd(COC$_7$H$_{10}$COMe)Cl

The formation of multiple products upon reaction of **27** with CO in THF suggests Pd-mediated coupling is not proceeding as anticipated. A possible rationale for this observation is that the fourth coordination site on the Pd(II) center in the intermediate complex **28** is occupied by oxygen of a chelating carbonyl, making it less accessible to THF monomers (Equation 36). Therefore, initiation of THF polymerization on this site is impeded, which eventually undermines the intended coupling of insertion to ring-opening polymerization. A similar phenomenon was observed with (bipy)Pd(Me)(Cl), in which the vital coordination site for THF is blocked by the Cl^- anion (Equation 17, Sect. 2.0).



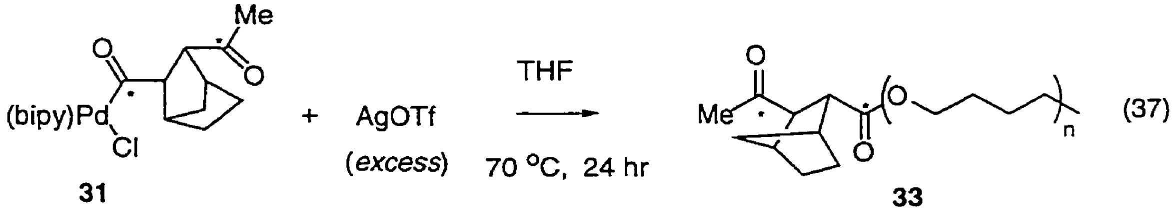
(36)

This problem could be resolved by introducing the required empty coordination site prior to initiation. A potential route to achieve this objective is outlined in Scheme 26, where a Cl^- ligand occupies the fourth coordination site to prevent the γ-carbonyl group from chelating to the metal center. CO insertion is carried out to yield the necessary Pd-acyl species **31**. Subsequent abstraction of the Cl^- ligand by AgOTf in THF is expected to lead to the solvated complex **32** prior to chelation of the carbonyl oxygen.



Scheme 26. Creating an empty coordination site for THF ligand

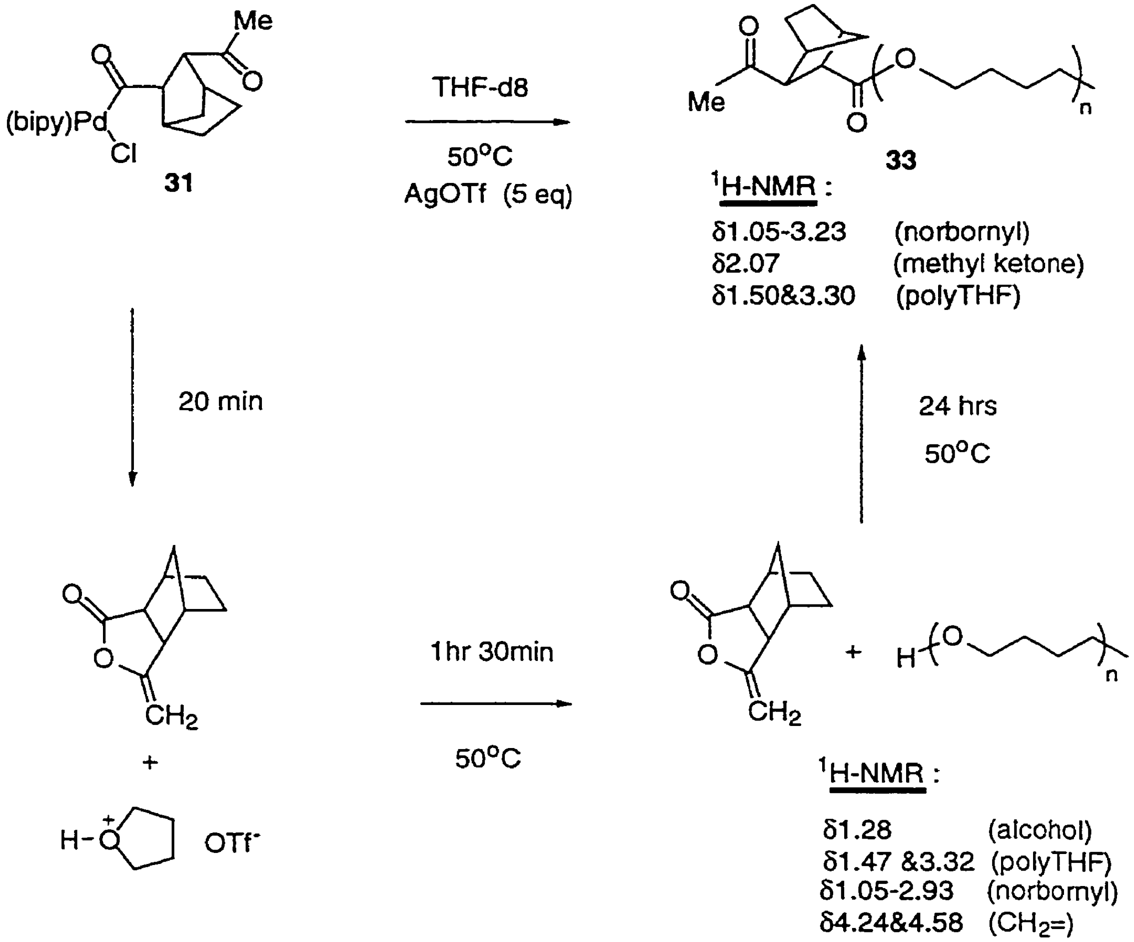
The complex (bipy)Pd($^{13}COC_7H_{10}{}^{13}COMe$)(Cl) (**31**) can be prepared from **27** by anion exchange in CO, as described by Markies and co-workers.[25] The reaction of **31** (23 mg, 0.05 mmol) with excess AgOTf (65 mg, 0.27 mmol) in THF solvent (10 g), followed by heating at 70 °C for 24 hours (Equation 37), yields 3.12 g of white polymer. GPC analysis of this material shows a monomodal distribution of a high molecular weight polymer (M_n = 156 300, M_w = 275 300). The most remarkable feature of this polymer however is found in the spectroscopic data. The ^{1}H-NMR shows the presence of $CH_3C(O)C_7H_{10}$, which integrates to one norbornyl unit per polymer chain.[27] In addition, the ^{13}C-NMR shows the presence of only two ^{13}C-labelled resonances (δ 207.7, δ 174. 9), consistent with the presence of one ketone and one ester ^{13}C-labelled carbon in the polymer. ^{13}C-decoupled ^{1}H-NMR subsequently showed a two bond coupling between the ^{13}C-labelled carbonyls to the norbornyl protons, and a three bond coupling of ^{13}C-labelled ester carbonyl to the terminal -OC*H*$_2$- hydrogens of polyTHF. These confirm the absolute connectivity of the norbornyl ketone fragment to the polymer chain as originally envisioned. The successful synthesis of the THF polymer with a terminal ketone unit affirms the possibility of coupling insertion with ring-opening polymerization on Pd(II) center and provides a novel method of attaching a ketone unit to a polyether chain.



(37)

Monitoring the Reaction of 31 with AgOTf in d^8-THF by ^{1}H-NMR

The mechanism of the coupling process was however radically disparate from the prevailing postulate. Monitoring the reaction of **31** (0.02 mmol) in d^8-THF (1 mL) upon the addition of excess AgOTf (0.09 mmol) revealed an unusual series of events. The initial displacement of the Cl$^-$ ligand by AgOTf did not lead to the Pd-THF acyl complex **32**, but instead the complex rapidly collapsed into a six-membered metallacycle with the terminal carbonyl substituent chelated to the Pd center (**28**) [^{1}H-NMR: δ 2.76 (s), 2.89 (m), 2.80 (m), 2.71 (d), 2.23 (s), 1.22-1.64 (m)] (Scheme 5). Complex **28** slowly decomposed over the course of 20 minutes to form the enol lactone **30** and solvated triflic acid (Scheme 27).[28] Heating this reaction mixture to 50 °C leads to the formation of polyTHF, which over the course of 24 hours, couples with **30** to generate polymer **33**.

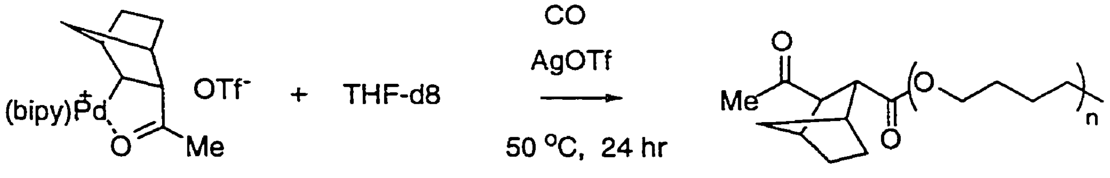


Scheme 27. Decomposition of **31** in the presence of AgOTf

The incorporation of the CO/norbornene fragment as MeCOC$_7$H$_{10}$CO- end-group on the polymer above differs completely to its more ambiguous incorporation in polyTHF for the earlier reaction of **27** with CO in THF (Equation 35). Although the intermediate **30** is observed in both instances, the two reactions do not yield the same product. Assuming the AgCl which is produced (Equation 37) is inert, the only difference between the two reactions is the presence of excess AgOTf in the latter. This suggests that AgOTf is somehow involved in the generation of **33**. This possibility is explored below.

3.7 REACTION OF CO/NORBORNENE MONO-INSERTION PRODUCT IN PRESENCE OF EXCESS AgOTf

The possible effect of AgOTf on the coupling of the norbornene/CO fragment to the polymer was examined by repeating the reaction of **27** with THF in the presence of excess AgOTf. Monitoring the reaction by ^{1}H-NMR, the solution of **27** (0.013 mmol) in d^8-THF (1 mL) with AgOTf (0.065 mmol) was observed to decompose within 15 minutes at 50 °C upon the addition of CO (1 atm), yielding enol lactone **30** (quantitative conversion by ^{1}H-NMR) (Equation 38). PolyTHF formation was perceived after 1 hr 30 min. All of the enol lactone generated was eventually coupled to the polyTHF to generate an identical polymer to that observed in Equation 16, after prolonged heating (24 hours).



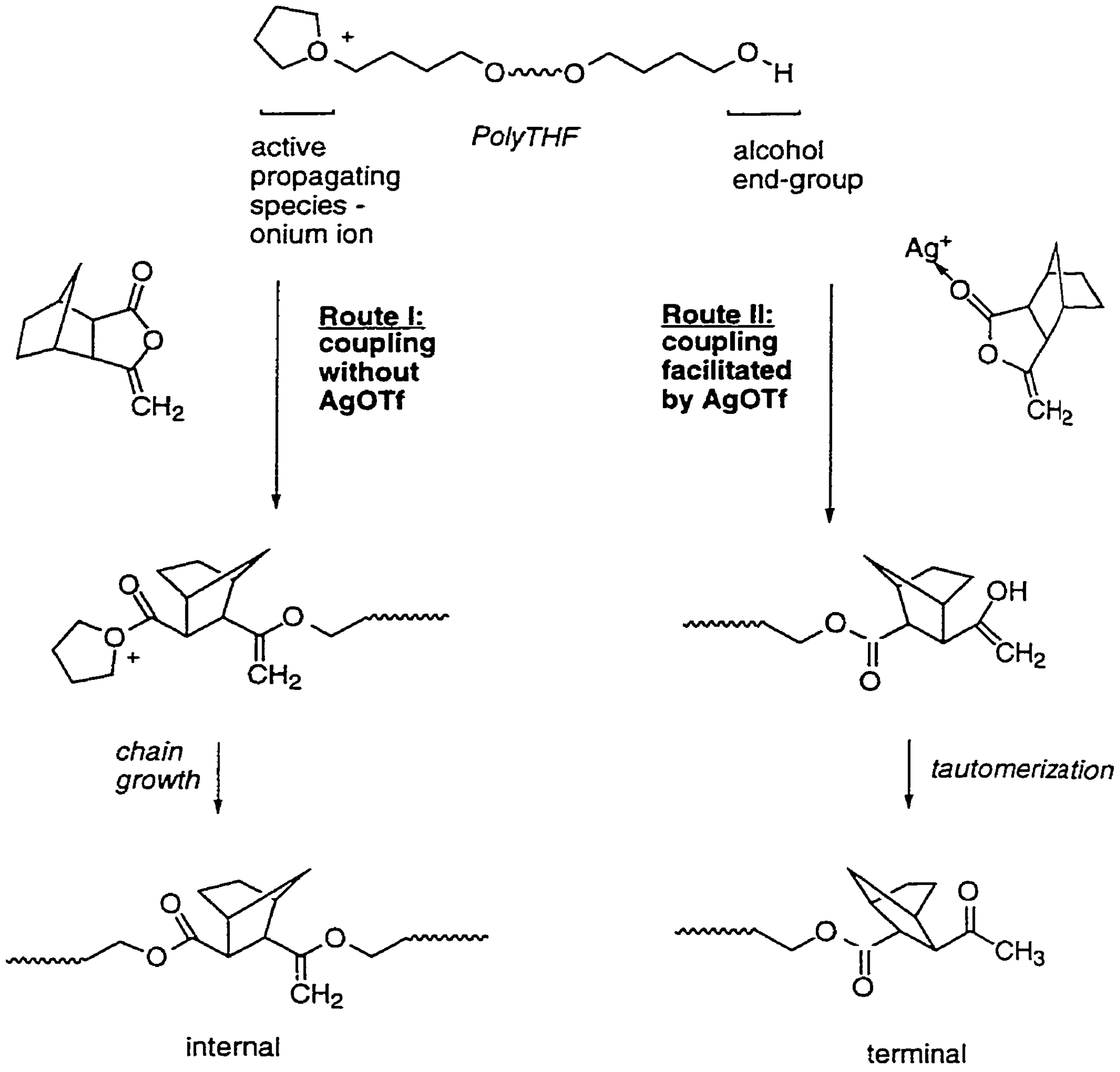
27 **33**

(38)

Possible Mechanism For Coupling of Enol Lactone (30) to PolyTHF

The results above demonstrate that the addition of AgOTf to reaction of **27** with CO in THF (Equation 38) indeed changes the mechanism of the coupling process. Although enol lactone and triflic acid are both produced from **28**, the presence of AgOTf influences the method by which the enol lactone is incorporated into the polymer. The exact role of AgOTf in this coupling process is of yet unclear. It is thought that this *weak Lewis acid* may activate the enol lactone towards a nucleophilic attack by the alcohol end-group of the THF polymer (Route II - Scheme 28). This can be envisaged by a possible weak coordination of the carbonyl or the ether oxygen on the enol lactone to AgOTf, making the carbonyl carbon more electrophilic and susceptible to a nucleophilic attack. Consistent with this postulate, other weak Lewis acid such as $Cu(OTf)_2$ have been found to similarly facilitate the selective coupling of the enol lactone to the polymer to yield **33**.

The mechanism of incorporation of this enol lactone into the polyTHF in the absence of AgOTf is less obvious. The observation of ^{13}C-NMR peaks at: δ 178.3, δ 174.4, δ 173.8, δ 171.2, δ 138.9 and δ 138.8 in reaction of **27** with ^{13}CO in THF (Equation 35) suggests that, upon incorporation into the polyTHF, enol lactone **30** rearranges to have ^{13}C-label in an ester and olefin carbon. A plausible mechanism involves enol lactone incorporation via a reaction with the propagating onium ion in the polymerization (Route I - Scheme 28). This could occur because **30** is not reactive enough to undergo coupling with the -OH end of the polymer by itself, and instead undergoes a secondary reaction with the onium ion located on the other end of the polymer chain, in a manner similar to that in the cationic ring-opening of lactones. The resulting polyTHF would not bear the CO/norbornyl fragment at its chain end as formerly predicted, but at *random* points along the chain. This random integration would result in the formation of an ester link, but the ketone functionality has been substituted with an olefin. Although this coupling of the CO/norbornene fragment to polyTHF occurs in an unanticipated sequence, the desired coupling effect is nevertheless obtained.



Scheme 28. Comparison of the coupling of enol lactone to polymer in the presence and absence of AgOTf

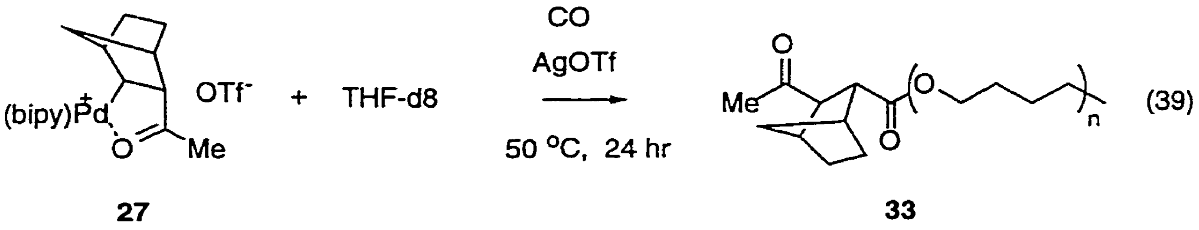
3.8 SINGLE-STEP COUPLING OF INSERTION MONOMERS TO RING-OPENED POLYMER

The initial aim of this project was to seek a novel route of coupling insertion and ring-opening polymerizations on Pd(II) center to generate block co-polymers. Although a single-step process was theoretically feasible, the direct co-polymerizations of CO and olefins (norbornene and *tert*-butylstyrene) and THF (Sect. 3.4.1 and 3.4.2) have failed to evince conclusively the expected coupling of insertion polymers (polyketone) to polyTHF. Instead, a multi-step approach was necessary to cleanly generate these products. This was demonstrated with the coupling of CO/norbornene mono-insertion product **27** to polyTHF in the presence of AgOTf (Sect. 3.7).

3.8.1 Coupling of Single CO/Norbornene Insertion With THF Polymerization

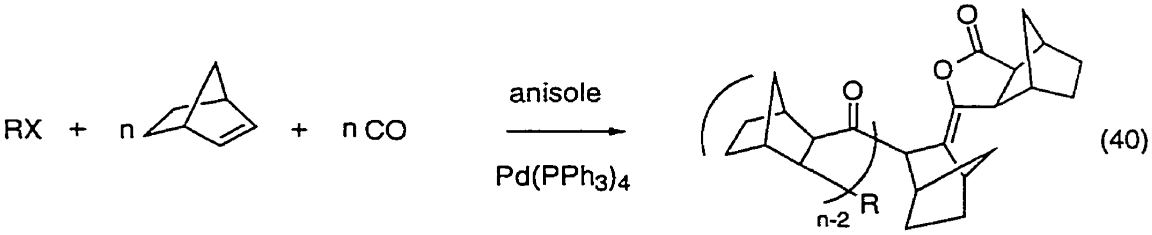
In the light of the favorable results obtained above with AgOTf, the initial objective of achieving the coupling process in a *single step* was re-examined. The insertion monomers (CO and norbornene) are hereby introduced directly to a solution of complex **14** in THF with AgOTf. The one-pot reaction of **14** (23 mg, 0.05 mmol) and norbornene (5 mg, 0.05 mmol) was performed in the presence of ^{13}CO (1 atm) and excess AgOTf (65 mg, 0.25 mmol) in THF solvent (10 g) (Equation 39). After heating at 70 °C for 24 hours, a white polymer (3.01 g) was isolated upon work-up, and it showed almost identical characteristics to the product obtained for the reaction of **31** with THF in CO (Equation 37). GPC analysis showed one product (M_n = 171,300, M_w = 267,400), while ^1H- and ^{13}C-NMR confirmed the $Me^{13}COC_7H_{10}{}^{13}COO$- end-group [$^1H$-NMR: δ 2.13 (d,

^{13}COMe), δ 1.17-3.22 (m, O^{13}COC$_7$H$_{10}$^{13}CO); ^{13}C-NMR: δ 207.7 (^{13}COMe), δ 174.9 (O^{13}COC$_7$H$_{10}$)]. These results have conclusively shown that the coupling process could be achieved in a single-step.



3.8.2 The Co-Polymerization of CO and Norbornene in Presence of AgOTf

The successful single-pot coupling of CO and norbornene to polyTHF with **14** in the presence of AgOTf prompted us to re-examine the possibility of combining the co-polymerization of CO and norbornene with THF polymerization, facilitated by AgOTf. Hypothetically, this undertaking appears reasonable particularly since Roberto and co-workers have demonstrated CO/norbornene co-polymers generated possess an unsaturated lactone end-group, which strongly resemble the structure of **30** (Equation 40).[26]



The reaction of norbornene (20 mg, 0.20 mmol), ^{13}CO (1 atm) and **14** (23 mg, 0.05 mmol) in THF (10 g) in the presence of AgOTf (0.5 mmol) at 70 °C for 24 hours yields 2.82 g of a white polymer (Equation 41). ^{1}H-NMR analysis of this product shows indisputably the incorporation of norbornene monomers into polyTHF, as evident by the characteristic broad norbornyl resonance at 0.8 to 2.4 ppm and those of polyTHF observed. However, the ^{13}C-NMR reveals only weak ester signals at δ 174.3 and δ 175.0. The absence of any ketone resonance reflects that there is no incorporation of the ^{13}CO monomers into the polymer as a ketone functionality. Considering the possibility of a direct insertion of norbornene into **14** instead of the anticipated co-polymerization of CO and norbornene, it is likely that the polymer product consists predominantly of a polynorbornene terminated polyTHF rather than the anticipated ketone-THF block co-polymer. This unanticipated coupling of polyolefins with polyTHF is explored in more detail in Chapter 4.

(41)

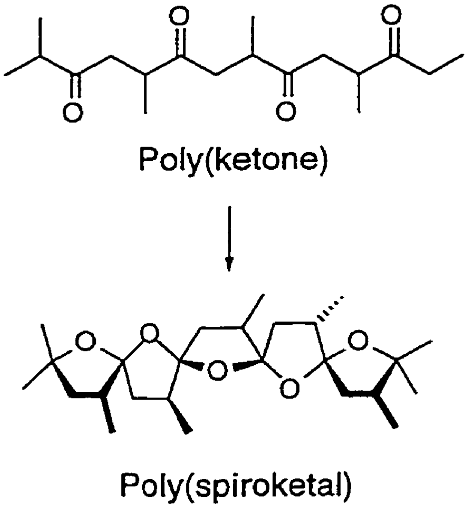
3.9 CONCLUSIONS

In conclusion, the Pd-mediated coupling of insertion and cationic ring-opening has been achieved, as demonstrated by the incorporation of a CO-norbornene unit to a ring-opened THF polymer. In the presence of a weak Lewis acid (AgOTf), this coupling process is found to occur *selectively* yielding a ketone-terminated polyTHF. However, the mechanism of coupling is not as anticipated, as revealed by NMR studies. Isomerization of the CO-norbornene fragment on palladium produces a novel enol lactone with the quantitative formation of triflic acid, which then initiates ring-opening polymerization of THF. Despite this unexpected sequence of side-reactions, the desired polymer product is obtained, demonstrating the potential utility of this palladium catalyst as an initiator for the preparation of ketone-THF block co-polymers.

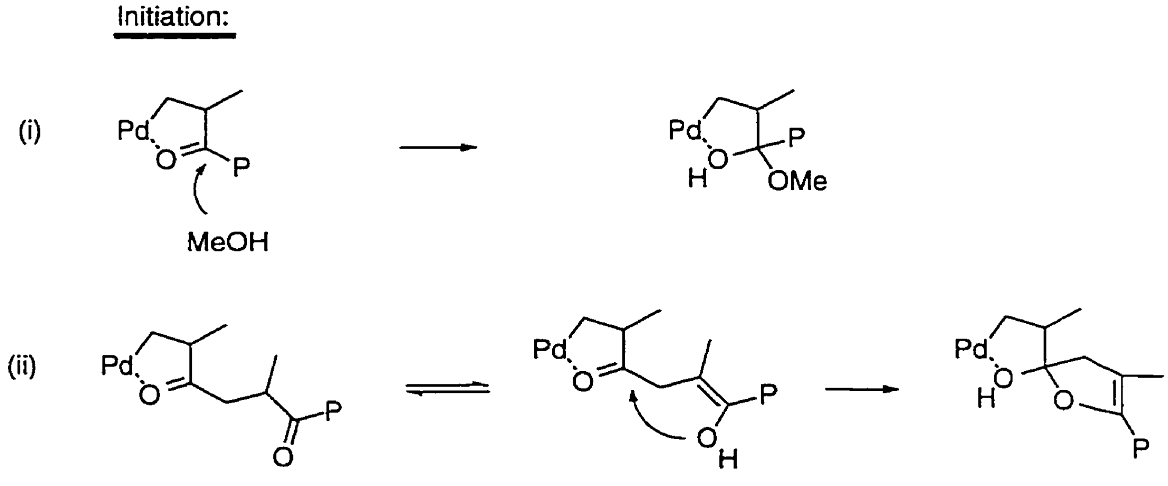
The co-polymerization of CO and norbornene with **14** in the presence of AgOTf does not lead to a ketone-THF block co-polymer. Instead, a direct insertion polymerization of norbornene into **14** is observed to generate polynorbornene. This competing insertion polymerization of olefin is examined in the next chapter to determine its potential application to the synthesis of olefin-THF block co-polymers.

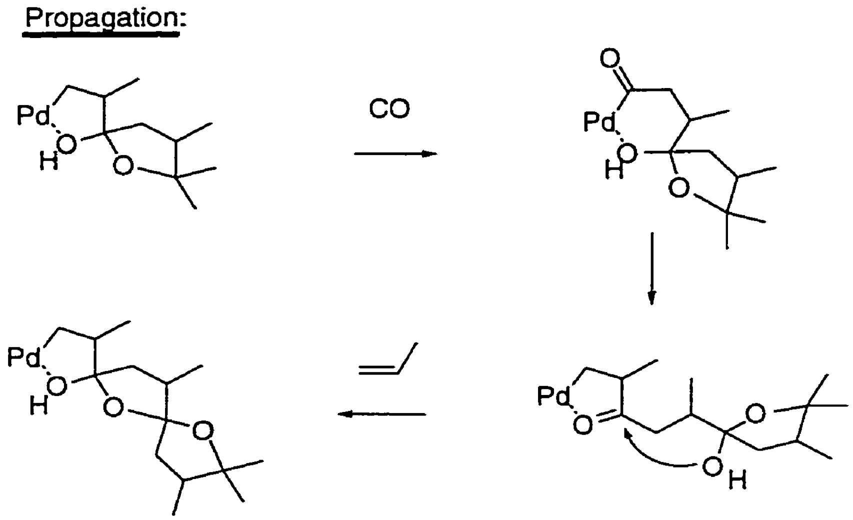
3.10 FUTURE DIRECTION

Interestingly, the cyclization of the CO/olefin insertion product is not unique to the CO/norbornyl system discussed above. Various research groups working on CO/olefin co-polymerization have observed that the ketone-based structure of the co-polymer can isomerize to a polyspiroketal through a series of cyclizations of the ketone repeating units.[29,30] The cyclization to produce spiroketal is particularly favored for α-olefins such as propene, as well as higher olefins such as but-1-ene, 4-methylpent-1-ene and allylbenzene.[31] The co-polymerization of CO and dicyclopentadiene, a cyclic olefin, has been documented to yield exclusively spiroketal structure.[32] Consiglio later confirmed that the increased substitutions at the C=C bond in these olefin systems serve to promote and stabilize the spiroketal structure due to the Thorpe-Ingold effect.[33]



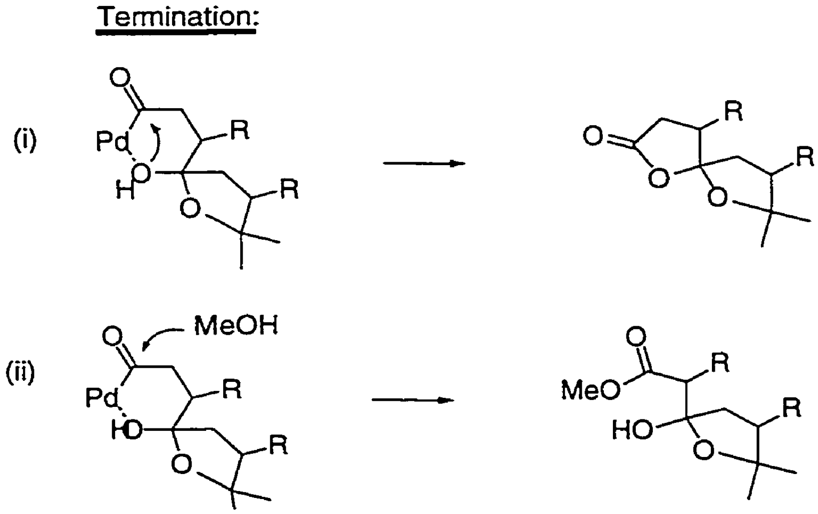
Although mechanistic details concerning the spiroketal formation is still lacking, Drent and co-workers has proposed an explanation for the cyclization process. It encompasses the initial addition of an enol or hydrate, formed by enolization of a ketone unit or through nucleophilic attack of an external methanol molecule, to a neighbouring ketone to form a spiroketal and a new hemiketal (Scheme 29a).[20a] The successive repetition of this process eventually yields a polyspiroketal.





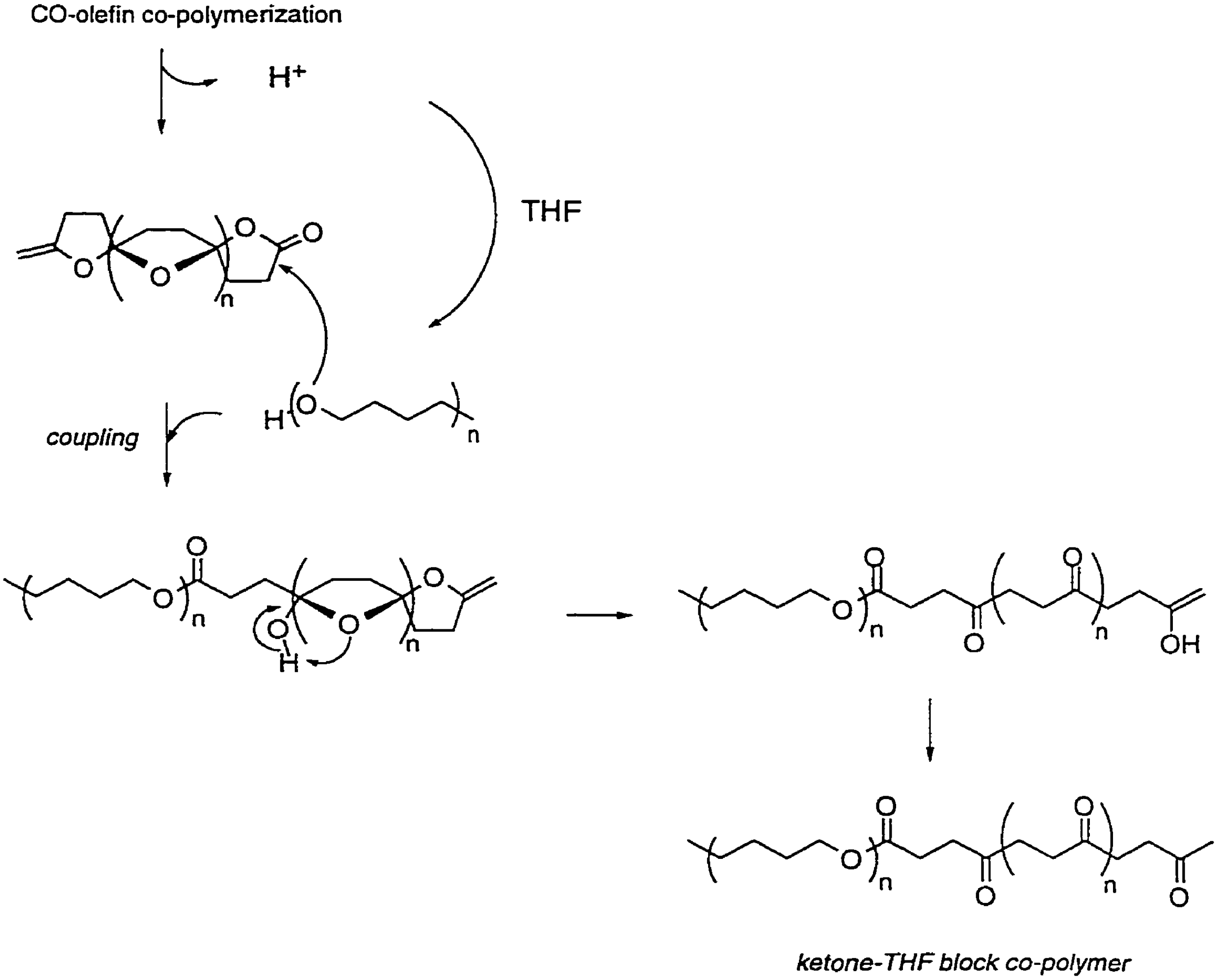
Scheme 29a. Spiroketal formation in CO/propylene co-polymer

Termination of the co-polymerization process can occur in the same way as that for a polyketone chain growth, that is by β-elimination or protonolysis of the alkyl ligand on the cationic Pd center.[20a] Alternatively, termination can also occur by oxidative carbonylation which yields either an ester or a lactone end-group for the polyspiroketal. (Scheme 29b).



Scheme 29b. Termination by oxidative carbonylation

The terminating route (i) is particularly exciting with respect to our work since it models the ideal co-polymerization system in which the resulting end-group on the polyketone will provide an opportunity for further manipulation through a coupling reaction to generate block co-polymers. This terminating route will also secure the quantitative production of an acid initiator, which is required for ring-opening polymerization. Thus, future research in this area could involve investigating the generation of polyTHF/polyketone block co-polymers with olefinic monomers known to lead to these spiroketal structures (Scheme 30).



Scheme 30. Proposed block co-polymer synthesis via coupling

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CHAPTER FOUR.

COUPLING OF OLEFIN POLYMERIZATION AND RING-OPENING POLYMERIZATION

4.0 OLEFIN POLYMERIZATION WITH LATE TRANSITION METAL COMPLEXES

Late transition metal (ie. Ni(II) and Pd(II)) complexes have recently been found to be excellent catalysts for the polymerization of ethylene, propylene, norbornene and a number of functionalized olefins.[1-3] The insertion polymerization of norbornene and its functionalized derivatives with these late metal catalysts have been particularly successful (Figure 10).[2-3] Termination of norbornene polymerization via β-hydride elimination, which is a common episode in late metal catalysis, is virtually unseen in these systems. At the same time, the metal-bound polymers are found to be exceptionally stable, with the metal-carbon bond often remaining intact even upon exposure to air and moisture.[3] The lack of decomposition is owed in part to the inaccessibility of the β-hydrogen atoms of an inserted norbornene substrate (Figure 10), which limits the formation of the unstable metal-hydride species often associated with rapid decomposition. The living nature of such polymerization system is an interesting area of study, as demonstrated by Goodall and co-workers at BFGoodrich, who were able to prepare extraordinarily *high molecular weight* polynorbornene ($M_n > 1\ 000\ 000$).[2]

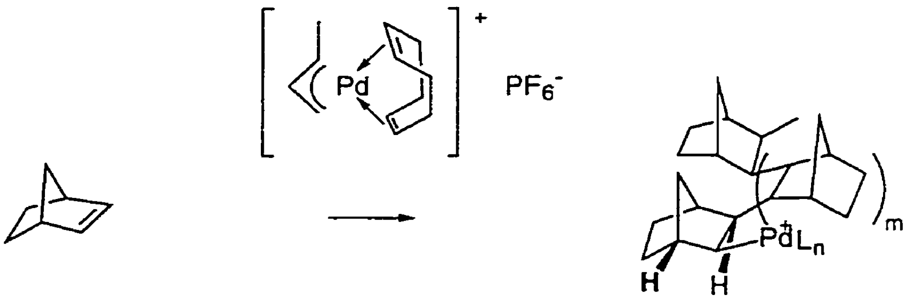
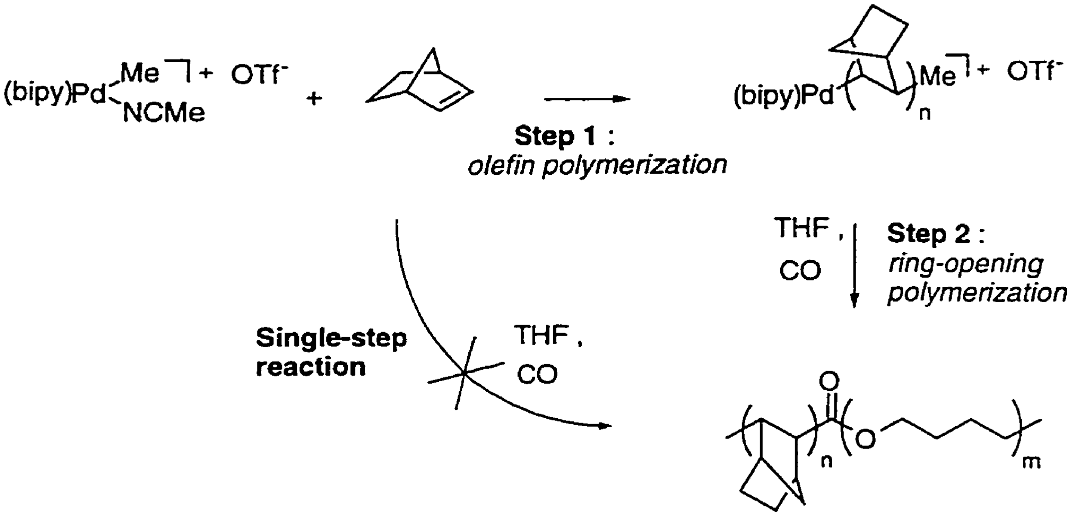


Figure 10. Norbornene polymerization with Pd(II) complex (β-protons are shielded from metal center)

As described in Chapter 3, the palladium(II) complex (bipy)Pd(Me)(NCMe)$^+$ OTf$^-$ (**14**) can also mediate the novel coupling of insertion monomers CO and norbornene into a ring-opened THF polymer. This coupling occurs via initial insertion of CO and norbornene into the Pd-Me bond, followed by a slower ring-opening reaction. A key feature to achieve coupling of insertion and ring-opening with **14** is that the product of insertion into the Pd-Me bond must remain sufficiently stable until the slower ring-opening occurs.

Since norbornene polymerization is known to occur in a living fashion with palladium(II) catalysts,[2,3] this monomer is thus selected for the coupling of olefin polymerization to THF ring-opening polymerization. If this coupling process is realized, it will provide a new route to the preparation of polyolefin-polyTHF block co-polymers. However, this coupling of olefin polymerization and ring-opening polymerization cannot be achieved in a single-step reaction (Scheme 31), as described earlier with the coupling of CO/olefin co-polymerization with THF ring-opening polymerization (Sect. 3.8.1). The introduction of CO into the reaction vessel will inevitably induce the olefin substrate to undergo co-polymerization with CO, and hence impede the formation of the poly(olefin). Thus, the coupling of polynorbornene with polyTHF must be performed in a two steps process, as shown in Scheme 31.

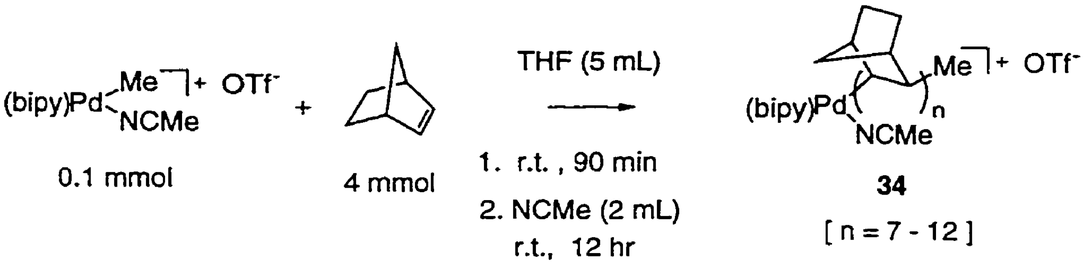


Scheme 31. Coupling of olefin and ring-opening polymerizations

4.1 COUPLING OF NORBORNENE INSERTION WITH THF RING-OPENING POLYMERIZATION

4.1.1 Norbornene Polymerization

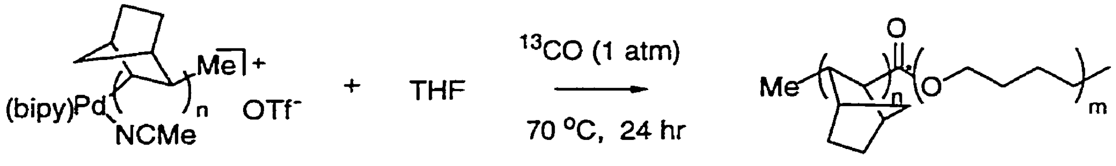
The *polymerization of norbornene* (0.36 g, 4 mmol) with **14** (45 mg, 0.1 mmol) in 10 mL THF at 25 °C yields a small polynorbornene block on the palladium complex (Equation 42). To favor the formation of this small, *soluble* polynorbornene, the polymerization of norbornene has to be terminated prior to completion by introducing MeCN to the reaction vessel (after 90 min).[4] The addition of MeCN also produces a more stable product, due to coordinating of MeCN to the fourth coordination site on palladium. The evaporation of solvent followed by washing with ether or pentane yields a pure norbornene polymer with the attached Pd(II) moiety as a grey solid (120 mg) (**34**). ^{1}H-NMR of **34** shows a broad norbornyl resonance from 0.8 to 2.4 ppm, a sharp doublet due to CH_3- at 0.85 ppm, and multiplets at 7.6 to 8.6 ppm due to the 2,2'-bipyridyl ligand on the attached Pd(II) complex. The integration on these two sets of peaks indicates an average of 8 norbornene units per palladium center. ^{13}C-NMR of **34** is consistent with this structure, showing multiple norbornyl peaks from 48.2 to 50.0 ppm, CH_3- (δ 19.69) and bipyridyl peaks (δ 122.9 to 156.9). This structural assignment is confirmed by LR-MS, which reveals a (bipy)Pd- and Me- end-capped norbornene polymer with mass ranging from 935 (n = 7) (Calculated for $(bipy)Pd(Me)(C_7H_{10})_7^+$: 935) to 1405 (n = 12) (Calculated for $(bipy)Pd(Me)(C_7H_{10})_{12}^+$: 1405). The series of peaks had a multiple mass of norbornene (94), with the highest intensity found at 935 (n = 7).



(42)

4.1.2 THF ring-opening polymerization

The reaction of the Pd-capped polynorbornene complex (**34**) (60 mg, 0.05 mmol) with THF (10 g) in the presence of ^{13}CO at 70 °C for 24 hours [conditions similar to polymerization of THF by **14** (Scheme 17, Sect. 1.3)], yields 0.72 g of a white polymer, which has been found to be a polyTHF terminated with a small polynorbornene block (**35**) (Equation 43). GPC analysis of **35** shows it to be monodispersed with M_w = 146 300 (P. I. = 3.56).



34 **35** (43)

The presence of polynorbornene in the THF polymer product is confirmed by ^{1}H-NMR. This shows a broad resonance between 0.8 to 2.5 ppm, previously assigned to the polynorbornene fragment in structure **34**, in addition to the broad polyTHF singlets at δ 1.57 and δ 3.38. Meanwhile, the ester linkage between the two polymer blocks is established by ^{13}C-NMR, which displays four labelled ester signals (δ 175.6, δ 175.4, δ 174.8, δ 174.5). The multiple ester resonances have been assigned to four possible triads on the polynorbornene block located adjacent to the ester group.[5] A triad represents the absolute configuration of a series of three repeating units within a polymer chain. The four triads in the polynorborenene block give rise to four stereoisomers, whose structures are shown below (Figure 10).

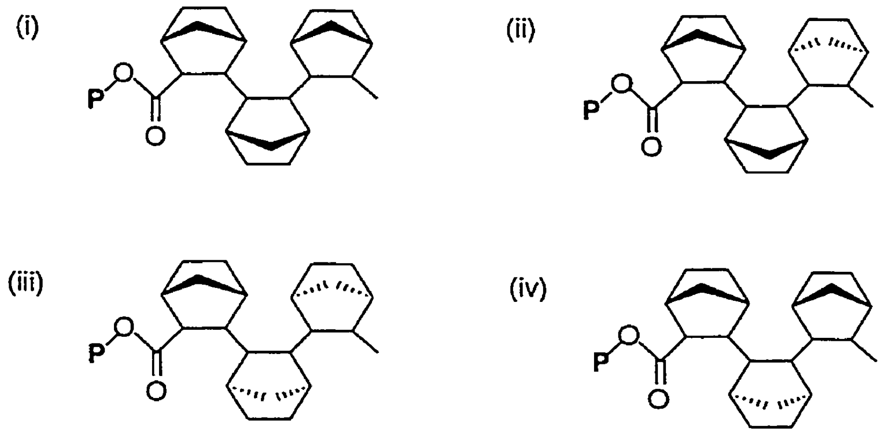
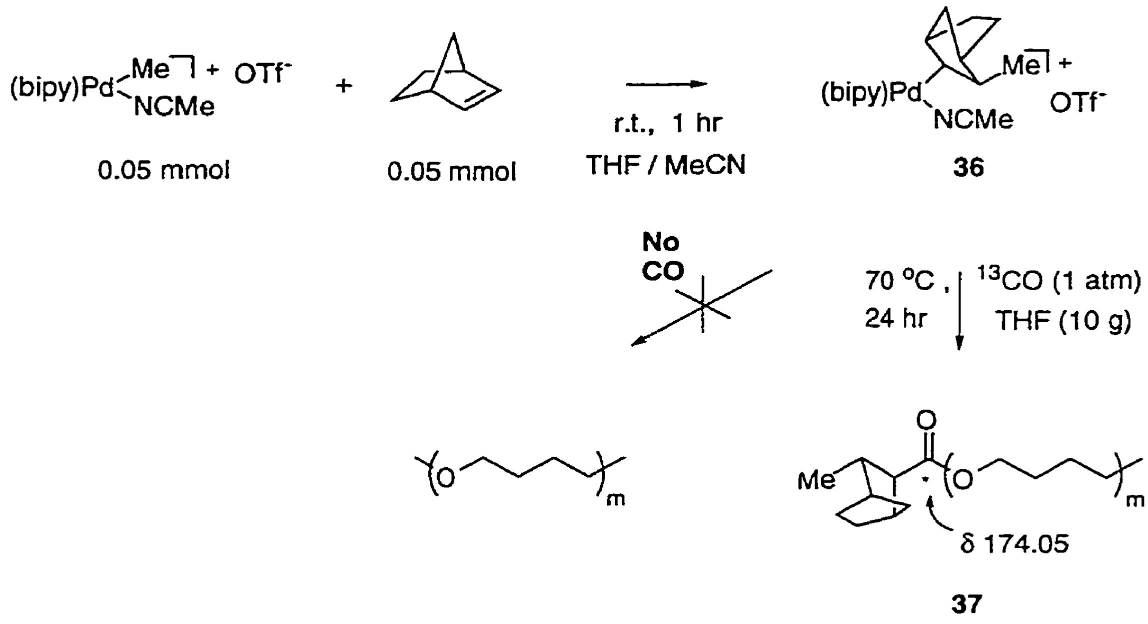


Figure 11. Stereoisomers of norbornene polymer (RRR, RRS, RSS, RSR) (**P** = polyTHF)

4.1.3 Single Insertion of Norbornene

Since the broad polynorbornene resonance overlaps into the resonance of polyTHF in the above ^{1}H-NMR spectrum of **35**, the absolute connectivity between the two polymer blocks could not be ascertained by ^{13}C-decoupled ^{1}H-NMR experiments. In order to confirm the connectivity of the norbornyl and polyTHF units, the reaction of the more easily characterized *single* norbornene insertion product (**36**) with THF was explored (Scheme 32). Complex **36** can be prepared by reaction of norbornene (30 mg, 0.3 mmol) with complex **14** (150 mg, 0.3 mmol) in a THF/acetonitrile mixture, followed by precipitation with ether. Complex **36** is characterized in a similar manner to the analogous polynorbornene-Pd complex **34**. Its ^{1}H- and ^{13}C-NMR (in CD_3CN) spectra reveal a simpler, more resolved norbornyl (^{1}H-NMR: δ 2.63 (d, 1H), δ 2.24 (d, 1H), δ 1.93 (m, 1H), δ 1.80 (m, 2H), δ 1.58 (m 1H), δ 1.36 (m, 2H), δ 1.19 (m 2H); ^{13}C-NMR: δ 56.88, δ 45.71, δ 45.24, δ 45.08, δ 34.79, δ 29.94, δ 28.98), bipyridyl resonances (^{1}H-NMR: δ 8.66 (d, 1H), δ 8.54 (d, 1H), δ 8.30 (m, 2H), δ 8.15 (m, 2H), δ 7.67 (m 2H); ^{13}C-NMR: δ 149.48, δ 148.48, δ 140.64, δ 140.30, δ 123.75, δ 122.96) and CH_3- resonance (^{1}H-NMR: δ 1.22 (d, 3H); ^{13}C-NMR: δ 21.49) (as compared to those of structure **34**), consistent with the expected structure shown in Scheme 32. This structure is verified by LS-MS analysis which shows a cation with a mass of 371, corresponding to $(bipy)Pd(C_7H_{10}Me)^+$.



Scheme 32. THF polymerization by single norbornene insertion product

The polymerization of THF (10 g) with **36** (28 mg, 0.05 mmol) in the presence of ^{13}CO (1 atm) is performed under the usual conditions (at 70 °C for 24 hours). Upon work-up, a white solid is obtained (0.81 g), which GPC analysis shows to be monodispersed polymer (P.I. = 2.0) with M_n = 27 200. As with **35**, the ^{1}H-NMR of **37** shows analysis shows broad polyTHF peaks (δ 1.53 and δ 3.33) and norbornyl resonance (δ 1.0 - 2.3). However, ^{13}C-NMR reveals only one ^{13}C-labelled resonance (δ 174.1), consistent with the fact there is only *one* norbornene unit in the polymer. The ^{13}C-decoupled ^{1}H-NMR establishes that the ^{13}C-labelled carbonyl moeity is positioned between a norbornyl fragment and the terminal -CH_2- unit on polyTHF (Figure 11), showing 3-bond coupling to H_a ($^3J_{C\text{-}H}$ = 3.0 Hz) and 2 bond coupling to H_b ($^2J_{c\text{-}H}$ = 8.0 Hz). The COSY spectrum demonstrates the correlation between the norbornyl fragment to the methyl end group, and the connectivity of the terminal -CH_2- unit (H_a) on polyTHF, to the rest of the polymer (Figure 11). These indisputable links therefore confirm the Pd-mediated coupling of inserted norbornyl fragment to ring-opened THF polymer.

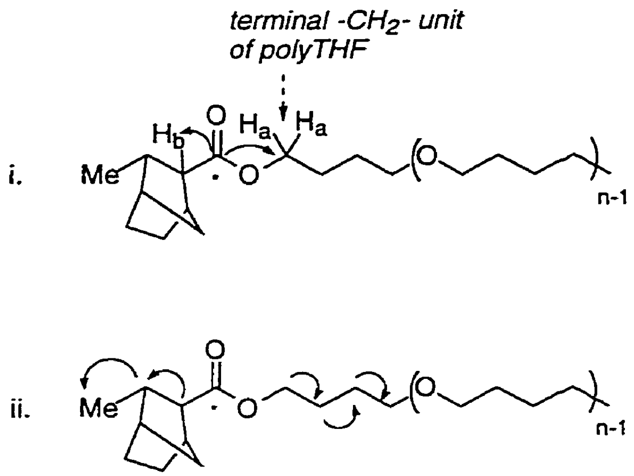


Figure 12. Connectivity of insertion monomer (norbornene) to polyTHF (i) by ^{13}C-decoupled ^{1}H-NMR and (ii) by COSY

4.2 CONCLUSION

In conclusion, the novel synthesis of norbornene-THF block co-polymers can be easily realized utilizing a multi-functional polymerization catalyst, (bipy)Pd(Me)(NCMe)$^+$ OTf$^-$ (**14**). This constitutes the first example of an insertion and ring-opening process occurring at a single metal center, followed by the coupling of the two polymers to generate a block co-polymer. Considering the diverse variety of monomers known to undergo insertion polymerization with Pd(II) complexes, this process has the potential to provide general access to new classes of block co-polymers. Future studies can focus on the use of these novel palladium catalysts to prepare complex block co-polymers as new polymeric materials.

4.3 GENERAL CONCLUSIONS

The Pd(II) complexes (bipy)Pd(Me)(L)$^+$ OTf$^-$ **14-17** have been shown to initiate two distinctly different classes of polymerization reactions. In addition to the well-known co-polymerization of CO and olefin to produce polyketones, complexes **14-17** can also initiate the ring-opening polymerization of heterocycles. Mechanistic studies with **14** revealed that the ring-opening process follows an unusual mechanism involving several metal-based reactions (substitution, insertion and reductive coupling). Interestingly, the process is controlled chemically through the insertion of CO. The labile ligand occupying the fourth coordination site also plays an important role, and provides a means of control over the molecular weight of the polymer product.

The most important aspect of these polymerization processes, however, involves the coupling of insertion and ring-opening monomers. As shown in Chapters 3 and 4, this coupling can be utilized to incorporate both CO/olefin and polyolefin insertion units onto polyTHF. While there have been other metal catalysts prepared that can mediate two distinct classes of polymerization (ie. insertion and ring-opening polymerizations), to our knowledge this is the first example which allows these two distinct processes to be coupled to form block co-polymers of substrates polymerized by distinct mechanisms. As such this system should provide facile access to a variety of block co-polymer materials not accessible by traditional methods.

4.4 REFERENCES

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3. (a) Mehler, C.; Risse, W. *Macromolecules* **1992**, *25*, 4226. (b) Safir, A. L.; Novak, B. M. *Macromolecules* **1995**, *28*, 5396.

4. Larger polynorbornene block ($M_n \sim 7000$) made by **14** is not soluble in THF. Hence the polymerization product cannot be utilized for the ring-opening process.

5. Norbornene insertion into M-C bond is known to occur in exo-fashion only (see ref. 2)

EXPERIMENTAL

4.5 GENERAL

^1H, ^{13}C, and ^{19}F NMR were recorded on JEOL-270 and Varian Unity-500 spectrometers. COSY, NOESY, TOCSY, HMQC, HMBC and ^{13}C-decoupled ^1H-NMR spectra were obtained on Varian Unity 500. Chemical shifts are reported in parts per million (δ) downfield from tetramethylsilane as an internal standard. Coupling constants (J values) are given in Hertz (Hz), and spin multiplicity are indicated as follow: s (singlet), d (doublet), t (triplet) and m (multiplet). MS was performed on a KRATOS MS 25RFA Mass Spectrometer in the direct inlet mode. Gel permeation chromatography was carried out using Waters 600E chromatograph equipped with Styragel HR 0.5, HR 2 and HR 4 columns in THF vs. polystyrene standards, and Waters 410 Differential Refractometer as detector.

Unless otherwise noted, all manipulations were carried out under an inert atmosphere in a Vacuum Atmosphere 553-2 drybox or by using standard Schlenk or vacuum line techniques. Diethyl ether, benzene, and THF were distilled from sodium benzophenone under nitrogen. Pentane, acetonitrile, chloroform and methylene chloride were distilled from CaH_2. Deuterated solvents were dried as their protonated analogues, but were vacuum-transferred from the drying agent and stored under nitrogen over 3Å molecular sieves.

Unless otherwise specified, all reagents were purchased from commercial suppliers and used without further purification. Liquids were freeze-pump-thawed three times to degas before use. UHP grade carbon monoxide was obtained from Matheson.

Imines were prepared by reaction of *p*-tolualdehyde and amine in toluene at room temperature for 1 day in the presence of 3Å molecular sieves as reported.[1] The Pd complexes: $(bipy)Pd(Me)(NCMe)^+ BAr'_4{}^-$ (**1**),[1] $(bipy)Pd(Me)(NCMe)^+$ OTf^- (**14**),[2] $(bipy)Pd(Me)(RN{=}C(H)Tol)^+$ OTf^- (R = Ph, ^{t}Bu and Me) (**15-17**),[3] $(bipy)Pd(CH(Ar)CH_2COMe)^+$ OTf^- (Ar = $(CH_3)_3C(C_6H_4)$) (**25**),[1] $(bipy)Pd(C_7H_{10}COMe)^+$ OTf^- (**27**),[4] and $(bipy)Pd(COC_7H_{10}COMe)(Cl)$ (**31**)[4] were prepared by literature methods.

4.6 SYNTHETIC PROCEDURES

Synthesis of $(bipy)Pd((C_7H_{10})_nCH_3)(NCCH_3)^+$ OTf^- (34)

Norbornene (376 mg, 4.0 mmole) was added to a slurry of $(bipy)Pd(Me)(NCMe)^+$ OTf^- (45 mg, 0.1 mmole) in THF (5 mL). The resulting pale yellow solution was stirred for one and the half hour at room temperature, forming a cloudy yellow solution. Acetonitrile (2mL) was added, and the solution further stirred for 1 day. A clear yellow solution was obtained, and subsequently concentrated to 1 mL under vacuum. Pentane (3 mL) and diethyl ether (3 mL) were added to precipitate the product. After decanting the layer of solvents, the yellow solid was dried under vacuum (120 mg). Spectroscopic data showed a mixture of (bipy)Pd((C_7H_{10})$_n$$CH_3$)($NCCH_3$)$^+$ OTf$^-$(n = 7 to 12).

^{1}H-NMR (CD_2Cl_2): δ 8.58 (d, 2H), δ 8.22 (m, 4H), δ 7.67 (m, 2H), δ 3.22 (d, 1H), δ 2.82 (d, 1H), δ 0.60 - 2.40 (m, broad, 83H), δ 0.34 (t, 1H). ^{13}C-NMR (CD_2Cl_2): δ 156.9, δ 152.1, δ 148.7, δ 148.6, δ 140.5, δ 140.2, δ 135.2, δ 127.7, δ 126.6, δ 124.0, δ 122.9, δ 58.9, δ 50.0, δ 49.5, δ 48.9, δ 48.2, δ 47.9, δ 47.8, δ 47.3, δ 46.8, δ 46.7, δ 46.0, δ 45.9, δ 44.7, δ 42.7, δ 41.8, δ 40.4, δ 39.3, δ 39.0, δ 38.7, δ 38.5, δ 38.2, δ 38.0, δ 37.9, δ 37.7, δ 37.6, δ 37.5, δ 37.1, δ 36.8, δ 36.6, δ 36.2, δ 35.6, δ 32.8, δ 32.5, δ 32.3, δ 31.9, δ 31.7, δ 31.6, δ 31.5, δ 31.0, δ 30.1, δ 29.8, δ 29.6, δ 29.3, δ 29.0, δ 28.2, δ 24.4, δ 19.7. LR-MS (FAB-NBA) m/e: 935 (42.7), 1029 (13.3), 1123 (36.7), 1218 (8.9), 1311 (9.3), 1405 (2.3).

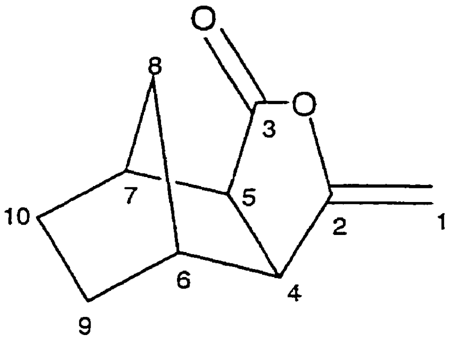
Synthesis of (bipy)Pd((C_7H_{10})CH_3)($NCCH_3$)$^+$ OTf$^-$ (36)

Norbornene (30 mg, 0.3 mmole) was added to a slurry of (bipy)Pd(Me)(NCMe)$^+$ OTf$^-$ (150 mg, 0.32 mmole) in a THF (15 mL) / acetonitrile (2 mL) mixture. After stirring for two hours, the clear yellow solution was concentrated to 3 mL under vacuum. Diethyl ether (8mL) was added, and the solution cooled to -40°C overnight. After decanting the solvents, a solid yellow product was collected and dried under vacuum (170 mg, 94% yield).

^{1}H-NMR (CD_3CN): δ 8.68 (d, 1H), δ 8.53 (d, 1H), δ 8.30 (m, 2H), δ 8.18 (m, 2H), δ 7.69 (m, 2H), δ 2.60 (d, 1H), δ 2.24 (d, 1H), δ 1.90 (d, 1H), δ 1.80 (m, 2H), δ 1.60 (m, 1H) δ 1.23 (d, 3H), δ 1.20 (m, 4H). ^{13}C-NMR (CD_3CN): δ 149.5, δ 148.5, δ 140.6, δ 140.3, δ 127.4, δ 123.8, δ 123.0, δ 56.9, δ 45.7, δ 45.2, δ 45.1, δ 34.8, δ 29.9, δ 29.0, δ 21.5. LR-MS (FAB-NBA) m/e: 371.

Synthesis of enol lactone (30)

(Bipy)Pd(C_7H_{10}COMe)$^+$ OTf$^-$ (0.51 g, 91 mmole) was dissolved in methylene chloride (10 mL) in a 100 mL reaction bomb. CO (850 torr) was added to the yellow solution, followed by stirring for 1 hour. The resulting grey solution was placed in heat bath (70°C) for twenty-four hours. After cooling, excess CO was removed by freeze-pump-thaw technique. LiOMe (1 g, 0.03 mole) was added to the solution. After shaking (ca. 5 minutes), the solution was filtered through silica to remove solid residue. The clear filtrate was concentrated to 1 mL under vacuum. The remaining liquid was distilled under vacuum (300 mtorr) to separate the product from other organic impurities. The distilled liquid (~ 60 mg) contained bipy impurities, which were removed by preparative TLC (using 1:1 pentane/ether mixture as eluent). A pale yellow liquid was obtained upon gradual evaporation of the solvent (15 mg, 0.1%).



^{x}C refers to carbon on position x as shown above

^{1}H-NMR ($CDCl_3$): δ 4.72, 4.29 (m, $^{1}CH_2$), δ 2.90 (d, ^{4}CH), δ 2.69 (s, ^{6}CH), δ 2.61 (d, ^{5}CH), δ 2.42 (s, ^{7}CH), δ 1.18 - 1.63 (m, br, $^{8\text{-}10}CH_2$). ^{13}C-NMR ($CDCl_3$): δ 176.8 (^{3}C), δ 159.9 (^{2}C), δ 88.3 (^{1}C), δ 48.0 (^{5}C), δ 46.0 (^{4}C), δ 44.3 (^{7}C), δ 40.5 (^{6}C), δ 33.6 (^{8}C), δ 27.7 (^{10}C), δ 26.7 (^{9}C).

The above assignments were made based on the following data from HMQC, HMBC and NOESY: HMQC (500 MHz, $CDCl_3$): δ 88.3 (δ 4.72, 4.28), δ 48.0 (δ 2.61), δ 46.0 (δ 2.88), δ 44.3 (δ 2.41), δ 40.5 (δ 2.69), δ 33.6 (δ 1.30, 1.25), δ 27.7 (δ 1.59, 1.30), δ 26.7 (δ 1.59, 1.30) {δ x (δ y) refers to the correlation of a carbon with chemical shift of x ppm to proton(s) with chemical shift of y ppm}. HMBC (500 MHz, $CDCl_3$): δ 4.72 (δ 159.9, 45.9), δ 4.28 (δ 177.7, 159.9, 46.1), δ 2.89 (δ 159.9, 88.2, 44.5, 40.8, 33.8, 26.7), δ 2.68 (δ 46.1, 26.9), δ 2.60 (δ 159.9, 44.5, 40.6, 33.6, 27.6), δ 2.42 (δ 160.1, 48.0, 40.5, 26.4), δ 1.64 (48.0, 40.5, 26.9), δ 1.62 (δ 48.0, 40.6, 26.9), δ 1.60 (159.9, 48.4, 44.3, 40.5, 30.0, 26.6), δ 1.29 (δ 48.2, 46.1, 40.5, 33.8), δ 1.26 (δ 46.1, 33.6, 28.0, 26.6), δ 1.22 (65.8, 48.2, 45.9) {δ x (δ y) refers to the correlation of a proton with chemical shift of x ppm to carbon(s) with chemical shift of y ppm}. NOESY (500 MHz, $CDCl_3$): δ 2.90 (δ 2.60) indicates that proton on ^{4}C is close in space to proton on ^{6}C (ie. they are cis to each other); δ 2.69 (δ 1.60, 1.29, 1.26) indicates that proton on ^{5}C is close in space to proton on ^{8}C and ^{10}C (ie. product has exo configuration) {δ x (δ y) refers to a strong correlation between a proton with chemical shift of x ppm to proton(s) with chemical shift of y ppm}.

Reaction of (bipy)Pd(^{13}COMe)(NCMe)$^{+}$OTf^{-} in d^{8}-THF

(Bipy)Pd(Me)(NCMe)]$^{+}$OTf (7 mg, 0.015mmol) was partially dissolved in d^{8}-THF (1mL) in a J-Young NMR tube. ^{13}CO (1 atm, 0.06mmol) was added to the slurry. After shaking, a clear yellow solution was obtained. ^{1}H- and ^{13}C-NMR shows the formation of free MeCN (δ 2.06), (bipy)Pd(^{13}COMe)(THF)$^+$ OTf$^-$, and the slow formation of poly-THF.

Spectral data for (bipy)Pd(^{13}COMe)(THF)$^+$ OTf$^-$:

^{1}H-NMR (d^8-THF): δ 8.57 (d, 2H), δ 8.48 (d, 2H), δ 8.19 (t, 2H), δ 7.70 (t, 2H), δ 2.82 (d, 3H, Pd^{13}C(O)C$\boldsymbol{H_3}$). ^{13}C-NMR (d^8-THF): δ 218.3 (Pd^{13}C(O)CH$_3$). ^{13}C-NMR (d^8-THF, 40°C): δ 218.3 (Pd^{13}C(O)CH$_3$), δ 177.0 (br, Pd^{13}CO).

Reaction of (bipy)Pd(^{13}COMe)(THF)]$^+$OTf$^-$ in d^8-THF

BipyPdMeCl (109 mg, 0.348 mmole) was partially dissolved in THF (10mL, chilled) in a 20 mL vial. A solution of AgOTf (98 mg, 0.381 mmole) in THF (5mL) was then added. Stirring for 45 minutes resulted in a clear yellow solution with a white precipitate (AgCl). This solution was then filtered through celite. Its clear yellow filtrate was subsequently concentrated by removing excess solvent under vacumn. Upon cooling to -40°C, a white precipitate was formed, which was isolated and dried in vacuo. A portion of this solid product (8 mg) was dissolved in d^8-THF (1mL) in a J-Young NMR tube. ^{13}CO (1 atm) was added, and the solution shaken for 10 min to promote CO insertion, yielding the complex (bipy)Pd(^{13}COMe)(THF)$^+$ OTf$^-$.

^{1}H-NMR (d^8-THF): δ 8.57 (d, 2H), δ 8.48 (d, 2H), δ 8.19 (t, 2H), δ 7.70 (t, 2H), δ 2.82 (d, 3H, Pd^{13}C(O)C$\boldsymbol{H_3}$). ^{13}C-NMR (d^8-THF): δ 218.3 (Pd^{13}C(O)CH$_3$).

Reaction of (bipy)Pd(C_7H_{10}^{13}COMe)$^+$ OTf$^-$ (27) with ^{13}CO in CD$_3$CN

^{13}CO (1 atm) was introduced to a solution of (bipy)Pd(C_7H_{10}^{13}COMe)$^+$ OTf$^-$ (10 mg, 0.02 mmole) in CD$_3$CN (1 mL) within a J-Young NMR tube. After shaking for 15 min, the yellow solution was placed in water bath (70 °C) for 24 hours. ^{1}H- and ^{13}C-NMR of the resulting grey solution showed the formation of enol lactone and triflic acid.

^{1}H-NMR (270 MHz, CD$_3$CN): δ 14.02 (s, 1 H, CF$_3$OSO$_2$$\boldsymbol{H}$); bipyridine: δ 8.84 (d, 2H), δ 8.46 (m, 4H), δ 7.88 (m 2H); enol lactone: δ 4.64 (m 1H), δ 4.34 (m, 1H), δ 2.95 (m, 1H), δ 2.65 (m, 1H), δ 2.55 (s, 1H), δ 2.38 (s, 1H), δ 1.22 -1.57 (m, 6H); ^{13}C-NMR (CD$_3$CN): δ 176.8 (O^{13}C(O)CH), 160.9 (CH^{13}CH$_2$O).

4.7 POLYMERIZATION PROCEDURES

Polymerization of THF with (bipy)Pd(Me)(NCMe)]$^+$OTf$^-$ (14) in ^{13}CO

Polymerization reaction was performed using (bipy)Pd(Me)(NCMe)]$^+$OTf$^-$ (23 mg, 0.05

mmol), 10.0 g of THF within a 25 mL reaction bomb. This was placed under 1 atm of $^{13}CO(g)$ prior to heating at 70°C over a period of twenty-four hours. After cooling, the viscous solution was diluted with CH_2Cl_2, filtered through celite to remove Pd(0) and solvent removed in vacuo. The polymer product was re-dissolved in minimum amount of CH_2Cl_2, and precipitated by adding CH_3CN. The resulting white solid was dried under vacuum overnight (yield = 0.92 g).

^{1}H-NMR ($CDCl_3$): δ 3.36 (s, 4H, $OC\boldsymbol{H}_2$), δ 1.54 (s, 4H, $OCH_2C\boldsymbol{H}_2$); Ester end-group: δ 2.01 (d, 3H, $CH_2O^{13}C(O)C\boldsymbol{H}_3$); Bipyridine end-group: δ 9.09 (d), δ 8.78 (d), δ 8.51 (t), δ 8.02 (m), δ 7.57 (m), δ 4.74 (t, $C\boldsymbol{H}_2C_{10}H_8N_2$). ^{13}C-NMR ($CDCl_3$): δ 70.7 ($OCH_2$), δ 26.6 ($OCH_2CH_2$), δ 171.2 ($O^{13}COCH_3$).

Ratio of bipyridine to ester end-group on ^{1}H-NMR: 0.35 / 1.

Polymer M_n calculated from ^{1}H-NMR of ester end-group: 3.3×10^4 ($\pm 1.4 \times 10^4$)

GPC analysis: M_n = 35 400, M_w = 78 400.

Polymerization of THF with (bipy)Pd(Me)(NCMe)]$^+$ BArf$_4^-$ (1)

Polymerization reaction was carried out using (bipy)Pd(Me)(NCMe)]$^+$ BArf$_4^-$ (56 mg, 0.05 mmol), 10.0 g of THF, within a 25 mL reaction bomb. After stirring for 1 hour, the pale yellowish brown solution was placed in heat bath maintained at 70°C over a period of twenty-four hours. After cooling, the viscous solution was diluted with CH_2Cl_2, filtered through celite and solvent removed in vacuo (yield = 1.41 g).

^{1}H-NMR ($CDCl_3$): δ 3.36 (s, 4H, $OC\boldsymbol{H}_2$), δ 1.54 (s, 4H, $OCH_2C\boldsymbol{H}_2$) (polymer end-groups could not be determined from spectrum). ^{13}C-NMR ($CDCl_3$): δ 70.7 (OCH_2), δ 26.6 (OCH_2CH_2). GPC: M_n = 3 700, M_w = 16 900.

General Polymerization Procedure With (bipy)Pd(Me)(RN=C(Tol)H)$^+$ OTf$^-$ (R = Ph, Me, *t*-butyl)

All polymerization reactions, unless otherwise specified, were performed using 0.05 mmol of catalyst, 10.0 g of THF within a 25 mL reaction bomb. This was placed under 1 atm of CO(g) prior to stirring for 1 hour at room temperature (to promote CO insertion). The reaction solution was subsequently placed in water bath maintained at 70°C over a period of twenty-four hours. The reaction solution was filtered through celite and solvent removed in vacuo. The polymer product was re-dissolved in diethyl ether, re-filtered through celite and the solvent removed. It was further washed with pentane to remove any excess imine, and dried under vacuum.

Poly(THF) generated from (bipy)Pd(Me)(PhN=C(Tol)H)$^+$ OTf$^-$ (15)

Yield = 0.44 g.

^{1}H-NMR (270 MHz, $CDCl_3$): δ 3.36 (s, br, $\mathrm{OC}\boldsymbol{H}_2$), δ 1.54 (s, br, $\mathrm{OCH_2C}\boldsymbol{H}_2$); Ester end-group: δ 2.01 (s, $\mathrm{CH_2OC(O)C}\boldsymbol{H}_3$); Immonium end-group: δ 9.34 (s, =C($\boldsymbol{H}$)), δ 7.3-7.8 (m, aryl), δ 4.45 (t, $\mathrm{CH_2C}\boldsymbol{H}_2\mathrm{N}$=), δ 2.38 (s, $\mathrm{C_6H_4C}\boldsymbol{H}_3$); Bipyridine end-group: δ 9.09 (d), δ 8.78 (d), δ 8.51 (t), δ 8.02 (m), δ 7.57 (m), δ 4.74 (t, $\mathrm{C}\boldsymbol{H}_2\mathrm{C_{10}H_8N_2}$). ^{13}C-NMR ($CDCl_3$): δ 70.7 ($\mathrm{O}\boldsymbol{C}\mathrm{H_2}$), δ 26.6 ($\mathrm{OCH_2}\boldsymbol{C}\mathrm{H_2}$).

Ratio of immonium to ester end-group from ^{1}H-NMR: 0.25 / 1.

Ratio of bipyridine to ester end-group from ^{1}H-NMR: 0.35 / 1.

GPC analysis: M_n = 23 900, M_w = 49 300.

Poly(THF) generated from (bipy)Pd(Me)(($CH_3)_3$CN=C(Tol)H)$^+$ OTf$^-$ (16)

Yield = 0.55 g.

^{1}H-NMR (270 MHz, $CDCl_3$): δ 3.38 (s, br, $\mathrm{OC}\boldsymbol{H}_2$), δ 1.63 (s, br, $\mathrm{OCH_2C}\boldsymbol{H}_2$); Ester end-group: δ 2.01 (s, $\mathrm{CH_2OC(O)C}\boldsymbol{H}_3$); Bipyridine end-group: δ 9.09 (d), δ 8.78 (d), δ 8.51 (t), δ 8.02 (m), δ 7.57 (m), δ 4.74 (t, $\mathrm{C}\boldsymbol{H}_2\mathrm{C_{10}H_8N_2}$). ^{13}C-NMR ($CDCl_3$): δ 70.7 ($\mathrm{O}\boldsymbol{C}\mathrm{H_2}$), δ 26.6 ($\mathrm{OCH_2}\boldsymbol{C}\mathrm{H_2}$).

Ratio of bipyridine to ester end-group from ^{1}H-NMR: 0.7 / 1.

GPC analysis: M_n = 32 700, M_w = 72 300.

Poly(THF) generated from (bipy)Pd(Me)(MeN=C(Tol)H)$^+$ OTf$^-$ (17)

Yield = 0.06 g.

^{1}H-NMR (270 MHz, $CDCl_3$): δ 3.38 (s, br, $\mathrm{OC}\boldsymbol{H}_2$), δ 1.63 (s, br, $\mathrm{OCH_2C}\boldsymbol{H}_2$); Ester end-group: δ 2.01 (s, $\mathrm{CH_2OC(O)C}\boldsymbol{H}_3$); Immonium end-group: δ 9.15 (s, =C($\boldsymbol{H}$)), δ 4.21 (t, $\mathrm{CH_2C}\boldsymbol{H}_2\mathrm{N}$=), δ 3.78 (s, $\mathrm{C}\boldsymbol{H}_3\mathrm{N}$=), δ 2.47 (s, $\mathrm{C_6H_4C}\boldsymbol{H}_3$); Bipyridine end-group: δ 9.09 (d), δ 8.78 (d), δ 8.51 (t), δ 8.02 (m), δ 7.57 (m), δ 4.74 (t, $\mathrm{C}\boldsymbol{H}_2\mathrm{C_{10}H_8N_2}$). ^{13}C-NMR ($CDCl_3$): δ 70.7 ($\mathrm{O}\boldsymbol{C}\mathrm{H_2}$), δ 26.6 ($\mathrm{OCH_2}\boldsymbol{C}\mathrm{H_2}$).

Ratio of immonium to ester end-group from ^{1}H-NMR: 0.50 / 1.

Ratio of bipyridine to ester end-group from ^{1}H-NMR: 0.25 / 1.

GPC analysis: M_n = 12 900, M_w = 18 500.

General Polymerization Procedure With (bipy)Pd(Me)(NCMe)$^+$ OTf$^-$ In Presence of Excess PhN=C(Tol)H

All polymerization reactions, unless otherwise specified, were performed using (bipy)Pd(Me)(NCMe)$^+$ OTf$^-$ (23mg, 0.05 mmol) and the appropriate amount of PhN=C(Tol)H dissolved in THF (10.0 g) within a 25 mL reaction bomb. This was placed under 1 atm of CO(g) and stirred for 1 hour at room temperature (to promote CO insertion). The reaction solution was subsequently placed in water bath maintained at 70°C over a period of twenty-four hours. After cooling, residual CO was removed under vacuum. The reaction solution was filtered through celite and solvent removed in vacuo. The polymer product was re-dissolved in diethyl ether, re-filtered through celite and the solvent removed. It was then further washed with pentane to remove any excess imine, and dried under vacuum.

Poly(THF) generated from (bipy)Pd(Me)(NCMe)$^+$ OTf$^-$ in CO with 0.005M PhN=C(Tol)H added

Yield = 0.46 g.

^{1}H-NMR ($CDCl_3$): δ 3.36 (s, br, $OC\boldsymbol{H}_2$), δ 1.54 (s, br, $OCH_2C\boldsymbol{H}_2$); Ester end-group: δ 2.01 (s, $CH_2OC(O)C\boldsymbol{H}_3$); Immonium end-group: δ 9.34 (s, =C($\boldsymbol{H}$)), δ 7.3-7.8 (m, aryl), δ 4.45 (t, $CH_2C\boldsymbol{H}_2N$=), δ 2.38 (s, $C_6H_4C\boldsymbol{H}_3$). ^{13}C-NMR ($CDCl_3$): δ 70.7 (OCH_2), δ 26.6 (OCH_2CH_2).
Ratio of immonium to ester end-group from ^{1}H-NMR: 0.25 / 1.
GPC analysis: M_n = 18 500, M_w = 41 300.

Poly(THF) generated from (bipy)Pd(Me)(NCMe)$^+$ OTf$^-$ in CO with 0.025M PhN=C(Tol)H added

Yield = 0.13 g.

^{1}H-NMR ($CDCl_3$): δ 3.36 (s, br, $OC\boldsymbol{H}_2$), δ 1.54 (s, br, $OCH_2C\boldsymbol{H}_2$); Ester end-group: δ 2.01 (s, $CH_2OC(O)C\boldsymbol{H}_3$); Immonium end-group: δ 9.34 (s, =C($\boldsymbol{H}$)), δ 7.3-7.8 (m, aryl), δ 4.45 (t, $CH_2C\boldsymbol{H}_2N$=), δ 2.38 (s, $C_6H_4C\boldsymbol{H}_3$). ^{13}C-NMR ($CDCl_3$): δ 70.7 (OCH_2), δ 26.6 (OCH_2CH_2).
Ratio of immonium to ester end-group from ^{1}H-NMR: 0.6 / 1.
GPC analysis: M_n = 11 400, M_w = 21 300.

Poly(THF) generated from (bipy)Pd(Me)(NCMe)$^+$ OTf$^-$ in CO with 0.05M PhN=C(Tol)H added

Yield = 0.07 g.

^{1}H-NMR ($CDCl_3$): δ 3.36 (s, br, $OC\boldsymbol{H}_2$), δ 1.54 (s, br, $OCH_2C\boldsymbol{H}_2$); Ester end-group: δ 2.01 (s, $CH_2O^{13}C(O)C\boldsymbol{H}_3$); Immonium end-group: δ 9.34 (s, =C($\boldsymbol{H}$)), δ 7.3-7.8 (m, aryl), δ 4.45 (t, $CH_2C\boldsymbol{H}_2N$=), δ 2.38 (s, $C_6H_4C\boldsymbol{H}_3$). ^{13}C-NMR ($CDCl_3$): δ 70.7 (OCH_2), δ 26.6 (OCH_2CH_2).
Ratio of immonium to ester end-group from ^{1}H-NMR: 1 : 1.
Polymer M_n calculated from ^{1}H-NMR of ester end-group: 5.3×10^3 ($\pm 1.2 \times 10^3$)
Polymer M_n calculated from ^{1}H-NMR of immonium end-group: 5.3×10^3 ($\pm 1.2 \times 10^3$)
GPC analysis: M_n = 8 200, M_w = 15 000.

Co-Polymerization of CO and Norbornene with $(bipy)Pd(Me)(NCMe)^+$ OTf^- (14) in THF

Norbornene (45 mg, 0.5 mmole) was added to a slurry of $(bipy)Pd(Me)(NCMe)^+$ OTf^- (23 mg, 0.05 mmole) in THF (10 g) within a 50 mL reaction bomb. CO (1 atm) was introduced, and the reaction solution stirred for 1 hour at room temperature. The resulting grey slurry was warmed at 70 °C for twenty-four hours. After cooling, the reaction solution was diluted with CH_2Cl_2, filtered through celite and solvent removed in vacuo. The polymer was re-dissolved in minimum amount of CH_2Cl_2, and precipitated by adding acetonitrile. The resulting white solid was dried under vacuum (yield = 0.05 g).

^{1}H-NMR ($CDCl_3$): δ 3.36 (s, br, $OC\boldsymbol{H}_2$), δ 1.54 (s, br, $OCH_2C\boldsymbol{H}_2$); δ 0.4 - 3.7 (m, br, $C(O)C_7\boldsymbol{H}_{10}C(O)$)). GPC analysis: 2 peaks with M_p = 150 (97%) and M_p = 14 900 (3%).

Co-Polymerization of CO and *t*-Butylstyrene with $(bipy)Pd(Me)(NCMe)^+$ OTf^- (14) in THF

t-Butylstyrene (0.5 g, 3.1 mmole) was added to a slurry of $(bipy)Pd(Me)(NCMe)^+$ OTf^- (23 mg, 0.05 mmole) in THF (20 g) within a 250 mL round bottom flask, capped with an air-free adapter. CO (850 torr) was then added, and the reaction solution stirred for 2 hours at room temperature. This was followed by heating at 40°C for twenty-four hours, and at 60°C for a further twenty-four hours. After cooling, the grey reaction solution was diluted with CH_2Cl_2, filtered through celite and solvent removed in vacuo. The polymer was re-dissolved in minimum amount of CH_2Cl_2, and precipitated by adding methanol. The resulting white solid was dried under vacuum (yield = 0.43 g).

^{1}H-NMR ($CDCl_3$): δ 3.36 (s, br, $OC\boldsymbol{H}_2$), δ 1.54 (s, br, $OCH_2C\boldsymbol{H}_2$); δ 7.01, 6.59 (d, $C(H)C_6\boldsymbol{H}_4C(CH_3)_3$), δ 4.11 (m, $C(\boldsymbol{H})C_6H_4C(CH_3)_3$), δ 3.00, 2.68 (dd, $C(O)C\boldsymbol{H}_2$), δ 2.17, 2.12 (s, $C(O)C\boldsymbol{H}_3$). GPC analysis: 2 peaks with M_p = 5 500 (70%) and M_p = 412 000 (30%).

Polymerization of THF with $(bipy)Pd(CH(Ar)CH_2{}^{13}COMe)^+$ OTf^- (25) in ^{13}CO

$(Bipy)Pd(CH(Ar)CH_2{}^{13}COMe)^+$ OTf^- (31 mg, 0.05 mmole) was dissolved in THF (5 g) in a 25 ml reaction bomb. ^{13}CO (1 atm) was introduced to the yellow solution, followed by stirring at room temperature for 1 hour. The resulting grey mixture was then placed in heat bath (70°C) for twenty-four hours. After cooling, the reaction solution was diluted with CH_2Cl_2, filtered through celite and solvent removed in vacuo. The polymer was re-dissolved in minimum amount of CH_2Cl_2, and precipitated by adding methanol. The resulting white solid was dried under vacuum overnight (yield = 0.35 g).

^{1}H-NMR ($CDCl_3$): δ 3.38 (s, $OC\boldsymbol{H}_2$), δ 1.59 (s, $OCH_2C\boldsymbol{H}_2$). ^{13}C-NMR ($CDCl_3$): δ 70.7

(OCH_2), δ 26.6 (OCH_2CH_2). GPC analysis: M_n = 142 000, M_w = 203 600.

Polymerization of THF with $(bipy)Pd(C_7H_{10}{}^{13}COMe)^+$ OTf^- in ^{13}CO

$(Bipy)Pd(C_7H_{10}{}^{13}COMe)^+$ OTf^- (28 mg, 0.05 mmole) was partially dissolved in THF (10.0 g) in a 25 ml reaction bomb. ^{13}CO (1 atm) was introduced to the slurry, followed by stirring at room temperature for 1 hour. The mixture was then placed in heat bath (70°C) for twenty-four hours. After cooling, the reaction solution was diluted with CH_2Cl_2, filtered through celite and solvent removed in vacuo. The polymer was re-dissolved in minimum amount of CH_2Cl_2, and precipitated by adding CH_3CN. The resulting white solid was dried under vacuum overnight (yield = 0.21 g).

^1H-NMR ($CDCl_3$): δ 3.38 (s, $OC\boldsymbol{H_2}$), δ 1.57 (s, $OCH_2C\boldsymbol{H_2}$), δ 0.76 - 2.55 (m, norbornyl). ^{13}C-NMR ($CDCl_3$): δ 178.3, 174.4, 173.8, 171.2 ($O^{13}\mathit{C}O$), δ 138.9, δ 138.8, δ 70.7 ($O\mathit{C}H_2$), δ 26.6 ($OCH_2\mathit{C}H_2$). GPC analysis: M_n = 93 600, M_w = 155 000.

Polymerization of THF with $(bipy)Pd(^{13}COC_7H_{10}{}^{13}COMe)(Cl)$ (31) in the presence of excess AgOTf

A solution of $(bipy)Pd(^{13}COC_7H_{10}{}^{13}COMe)(Cl)$ (23 mg, 0.05 mmole) in THF (10.0 g) was added to AgOTf (65 mg, 0.25 mmole) in a 25 ml reaction bomb. The bright yellow solution instantly turned pale yellow with the formation of white precipitate (AgCl). The slurry was immediately placed in heat bath (70°C) for twenty-four hours. After cooling, the viscous solution was diluted with CH_2Cl_2, filtered through celite and solvent removed in vacuo. The polymer was re-dissolved in minimum amount of CH_2Cl_2, and precipitated by adding CH_3CN. The resulting white solid was dried under vacuum overnight (yield = 3.12 g).

^1H-NMR (270 MHz, $CDCl_3$): δ 3.38 (s, $OC\boldsymbol{H_2}$), δ 1.57 (s, $OCH_2C\boldsymbol{H_2}$); Methyl-ketone end-group: δ 2.13 (d, $^2J_{C\text{-}H}$ = 5.9 Hz, $^{13}COC\boldsymbol{H_3}$); Norbornyl end-group: δ 1.17 - 3.22 (m, br, $O^{13}COC_7\boldsymbol{H_{10}}{}^{13}CO$). ^{13}C-NMR ($CDCl_3$): δ 70.7 ($O\mathit{C}H_2$), δ 26.6 ($OCH_2\mathit{C}H_2$); end-group: δ 207.7 ($^{13}\mathit{C}OCH_3$), δ 174.9 ($O^{13}\mathit{C}OC_7H_{10}$).

Polymer M_n calculated from ^1H-NMR of methyl ketone end-group: 2.0 x 10^5 (±0.7 x 10^5)

GPC analysis: M_n = 156 300, M_w = 275 300.

Polymerization of d^8-THF with $(bipy)Pd(^{13}COC_7H_{10}{}^{13}COMe)(Cl)$ (31) in the presence of excess AgOTf

A solution of $(bipy)Pd(^{13}COC_7H_{10}{}^{13}COMe)(Cl)$ (8 mg, 0.02 mmole) in THF-d8 (1 mL) was added to AgOTf (24 mg, 0.09 mmole) in a vial. The pale yellow slurry was then transferred to a J-Young NMR tube, and periodically monitored by ^1H-NMR as it was warmed at 50 °C for twenty-four hours.

Spectral data after 15 minutes of heating:

^{1}H-NMR (270 MHz, THF-d8, 50°C): δ 8.60 (m), δ 8.30 (m), δ 7.76 (m), δ 4.58 (d), δ 4.24 (d), δ 3.31 (s), 3.02 (s), 2.91 (s), 2.80 (d), δ 2.63 (m), δ 2.54 (s), δ 2.49 (d), δ 2.36 (s), δ 2.29 (s), δ 1.96 (d), δ 1.23 - 1.57 (m, br) corresponding to (bipy)Pd($C_7H_{10}COMe$)$^+$ OTf$^-$, (bipy)Pd($COC_7H_{10}COMe$)$^+$ OTf$^-$ and enol lactone.

Spectral data after 24 hours of heating:

^{1}H-NMR (270 MHz, THF-d8, 50°C): δ 3.31 (s, br), δ 3.23 (s, br), δ 2.83 (m), δ 2.67 (s, br), δ 2.49 (m), δ 2.07 (d), δ 1.51 (s, br), δ 1.08 -1.59 (m) corresponding poly(THF) with a norbornyl ketone end-group.

Polymerization of THF-d8 with (bipy)Pd($C_7H_{10}COMe$)$^+$ OTf$^-$ (27) and excess AgOTf in CO

(Bipy)Pd($C_7H_{10}COMe$)$^+$OTf$^-$ (7 mg, 0.015 mmol) and AgOTf (16 mg, 0.065 mmol) were partially dissolved in d^8-THF (1mL) in a J-Young NMR tube. CO (1 atm, 0.06mmol) was added to the slurry. After shaking, a clear yellow solution was obtained. ^{1}H-NMR shows the formation of (bipy)Pd($COC_7H_{10}COMe$)$^+$OTf$^-$ initially, which then re-arranged to produce the enol lactone. Upon heating (at 50°C), poly(THF) was observed to form slowly, and the enol lactone was converted to a ketone.

Spectral data before CO addition:

^{1}H-NMR (270 MHz, THF-d8): δ 8.60 (m, 4H), δ 8.30 (m, 2H), δ 7.76 (m, 2H), δ 3.03 (d, 1H), δ 2.84 (dd, 1H), δ 2.64 (d, 1H), δ 2.49 (s, 3H), δ 2.31 (m, 1H), δ 1.96 (d, 1H), δ 1.26 - 1.68 (m, 5H) corresponding to (bipy)Pd($C_7H_{10}COMe$)$^+$ OTf$^-$.

Spectral data after CO addition:

^{1}H-NMR (270 MHz, THF-d8): δ 7.75 - 9.02 (m), δ 4.58 (d), δ 4.24 (d), δ 3.49 (d), δ 2.28 - 3.03 (m), δ 2.77 (s), δ 2.49 (s), δ 1.22 - 1.96 (m) corresponding to (bipy)Pd($C_7H_{10}COMe$)$^+$ OTf$^-$, enol lactone and the intermediate (bipy)Pd($COC_7H_{10}COMe$)$^+$ OTf$^-$.

Spectral data after 15 minutes of heating:

^{1}H-NMR (270 MHz, THF-d8, 50°C): δ 4.58 (d, 1H), δ 4.23 (d, 1H), δ 2.90 (d, 1H), δ 2.58 (d, br, 2H), δ 2.36 (s, br, 1H), δ 1.56 (m, 2H), δ 1.28 (m, 5H) corresponding to enol lactone.

Spectral data after 1 hour and 30 minutes of heating:

^{1}H-NMR (270 MHz, THF-d8, 50°C): δ 4.58 (d), δ 4.23 (d), δ 3.32 (s), δ 2.90 (d), δ 2.58 (d), δ 2.36 (s), δ 1.58 (s), δ 1.56 (m), δ 1.28 (m) corresponding to enol lactone and poly(THF) with alcohol end-group.

Spectral data after 26 hours of heating:
^{1}H-NMR (270 MHz, THF-d8, 50°C): δ 3.30 (s, br), δ 3.23 (s, br), δ 2.82 (d), δ 2.68 (s, br), δ 2.57 (s), δ 2.48 (d), δ 2.07 (s), δ 1.51 (s, br), δ 1.08 -1.59 (m) corresponding poly(THF) with a norbornyl ketone end-group.

Polymerization of THF with (bipy)Pd(Me)(NCMe)$^+$ OTf$^-$ (14) in presence of norbornene, AgOTf and ^{13}CO

A slurry of (bipy)Pd(Me)(NCMe)$^+$ OTf$^-$ (23 mg, 0.05 mmole) in THF (10.0 g) was added to norbornene (5 mg, 0.05 mmole) and AgOTf (65 mg, 0.25 mmole) in a 25 ml reaction bomb. This was then placed under 1 atm of ^{13}CO(g), followed by stirring at room temperature for 1 hour. The mixture was subsequently placed in heat bath (70°C) for twenty four hours. After cooling, the reaction solution was diluted with CH_2Cl_2, filtered through celite and solvent removed in vacuo. The polymer product was re-dissolved in minimum amount of CH_2Cl_2, and precipitated by adding CH_3CN. The resulting white solid was dried under vacuum overnight (yield = 3.01 g).
^{1}H-NMR (270 MHz, $CDCl_3$): δ 3.38 (s, $OC\boldsymbol{H_2}$), δ 1.60 (s, $OCH_2C\boldsymbol{H_2}$); Methyl-ketone end-group: δ 2.13 (d, $^2J_{C\text{-}H}$ = 5.7 Hz, $^{13}COC\boldsymbol{H_3}$); Norbornyl end-group: δ 1.17 - 3.22 (m, br, $O^{13}COC_7\boldsymbol{H_{10}}{}^{13}CO$). ^{13}C-NMR ($CDCl_3$): δ 70.7 ($OCH_2$), δ 26.6 ($OCH_2CH_2$); End-group: δ 207.7 ($^{13}COCH_3$), δ 174.9 ($O^{13}COC_7H_{10}$). GPC analysis: M_n = 171 300, M_w = 267 400.

Co-polymerization of norbornene and ^{13}CO in THF with (bipy)Pd(Me)(NCMe)$^+$ OTf$^-$ (14) in presence AgOTf

A slurry of (bipy)Pd(Me)(NCMe)$^+$ OTf$^-$ (23 mg, 0.05 mmole) in THF (10.0 g) was added to norbornene (20 mg, 0.2 mmole) and AgOTf (130 mg, 0.50 mmole) in a 25 ml reaction bomb. This was then placed under 1 atm of ^{13}CO(g), followed by stirring at room temperature for 1 hour. The grey mixture was subsequently placed in heat bath (70°C) for twenty four hours. After cooling, the reaction solution was diluted with CH_2Cl_2, filtered through celite and solvent removed in vacuo. The polymer product was re-dissolved in minimum amount of CH_2Cl_2, and precipitated by adding CH_3CN. The resulting white solid was dried under vacuum overnight (yield = 2.82 g).
^{1}H-NMR (270 MHz, $CDCl_3$): δ 3.38 (s, $OC\boldsymbol{H_2}$), δ 1.60 (s, $OCH_2C\boldsymbol{H_2}$); δ 0.78 - 2.39 (m, norbornyl). ^{13}C-NMR ($CDCl_3$): δ 70.7 (OCH_2), δ 26.6 (OCH_2CH_2); Ester group: δ 174.3, δ 175.0 ($O^{13}CO$). GPC analysis: M_n = 171 300, M_w = 267 400.

Polymerization of THF with (bipy)Pd((C_7H_{10})$_n$Me)(NCMe)$^+$ OTf$^-$ (34) in ^{13}CO.

A solution of (bipy)Pd((C_7H_{10})$_n$Me)(NCMe)$^+$ OTf$^-$(n ~ 8) (60 mg, 0.05 mmole) in THF (10.0 g) was in a 25 ml reaction bomb was prepared in the box. The cloudy yellow solution was then placed under 1 atm of $^{13}CO(g)$, followed by stirring at room temperature for 1 hour. The mixture was subsequently placed in heat bath (70°C) for twenty four hours. After cooling, the reaction solution was diluted with CH_2Cl_2, filtered through celite and solvent removed in vacuo. The polymer product was re-dissolved in minimum amount of CH_2Cl_2, and precipitated by adding CH_3CN. The resulting white solid was dried under vacuum overnight (yield = 0.72 g).

^{1}H-NMR (270 MHz, $CDCl_3$): δ 3.38 (s, $OC\boldsymbol{H}_2$), δ 1.58 (s, $OCH_2C\boldsymbol{H}_2$); Norbornyl : δ 0.78 - 2.50 (m, $O^{13}CO(C_7\boldsymbol{H}_{10})_nC\boldsymbol{H}_3$). Ester end-group: δ 4.02, δ 3.96 (m, $C\boldsymbol{H}_2O^{13}CO(C_7H_{10})_nCH_3$); ^{13}C-NMR ($CDCl_3$): δ 70.7 ($OCH_2$), δ 26.6 ($OCH_2CH_2$); Ester end-group: δ 175.6, δ 175.4, δ 174.8, δ 174.5 (4 isomers, $CH_2O^{13}CO(C_7H_{10})_n$). GPC analysis: M_n = 41 000, M_w = 146 300.

Polymerization of THF with $(bipy)Pd((C_7H_{10})Me)(NCMe)^+ OTf^-$ (36) in ^{13}CO

A slurry of $(bipy)Pd((C_7H_{10})Me)(NCMe)^+ OTf^-$ (28 mg, 0.05 mmole) in THF (10.0 g) in a 25 ml reaction bomb was prepared in the box. The resulting cloudy yellow solution was then placed under 1 atm of $^{13}CO(g)$, followed by stirring at room temperature for 1 hour. The dark grey mixture was subsequently placed in heat bath (70°C) for twenty four hours. After cooling, the reaction solution was diluted with CH_2Cl_2, filtered through celite and solvent removed in vacuo. The polymer was re-dissolved in minimum amount of CH_2Cl_2, and precipitated by adding CH_3CN. The resulting white solid was dried under vacuum overnight (yield = 0.81 g).

^{1}H-NMR (270 MHz, $CDCl_3$): δ 3.33 (s, $OC\boldsymbol{H}_2$), δ 1.53 (s, $OCH_2C\boldsymbol{H}_2$); Norbornyl end-group: δ 0.75 - 2.33 (m, $O^{13}COC_7\boldsymbol{H}_{10}C\boldsymbol{H}_3$); Ester end-group: δ 3.96 (m, $C\boldsymbol{H}_2O^{13}COC_7H_{10}CH_3$); ^{13}C-NMR ($CDCl_3$): δ 70.4 ($OCH_2$), δ 26.3 ($OCH_2CH_2$); Ester end-group: δ 174.1 ($CH_2O^{13}COC_7H_{10}$).

Polymer M_n calculated from ^{1}H-NMR of norbornyl end-group: 2.4 x 10^4 (±0.6 x 10^4)

GPC analysis: M_n = 27 200, M_w = 55 600

4.8 REFERENCES

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