Polymerization of Norbornene and Methyl Acrylate by a Bimetallic Palladium(II) Allyl Complex

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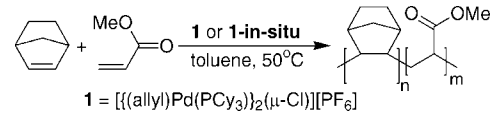
The sequential reaction of $\{(allyl)Pd(\mu\text{-}Cl)\}_2$ (**2**) with $AgPF_6$ and PCy_3 in CH_2Cl_2 generates a mixture (**1-in situ**) of $[\{(allyl)Pd(PCy_3)\}_2(\mu\text{-}Cl)][PF_6]$ (**1**), **2**, $[(allyl)Pd(PCy_3)_2][PF_6]$ (**3**), and $(allyl)PdCl(PCy_3)$ (**4**), which evolves to form pure **1** after 20 h at 23 °C. Complex **1** reacts with PCy_3 to generate **3** and **4** and undergoes facile exchange of Pd units with **4**. Both **1** and **1-in situ** polymerize mixtures of norbornene (NB) and methyl acrylate (MA) to a mixture of poly(NB) and poly(MA) via competing NB insertion polymerization and MA radical polymerization.

Introduction

Metal-catalyzed copolymerization of nonpolar and functionalized olefins by insertion chemistry could provide new materials with controlled composition and structure and new properties. Designing metal catalysts for this purpose is a challenging task.[1] The copolymerization of ethylene and acrylate monomers has been achieved with Pd,[2] Ni,[3] and Cu catalysts,[1g,4] but general strategies for designing catalysts with high functional group tolerance are lacking.

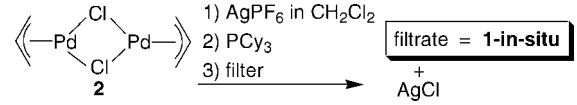
Sen reported the copolymerization of norbornene (NB) and methyl acrylate (MA) by $\{Me(L)PdCl\}_2$ complexes (L = PPh_3, PCy_3, PMe_3, pyridine) to give MA-rich polymers and proposed that this reaction proceeds by an insertion mechanism.[5] However, Novak showed that (N^N)PdMe(L) (N^N = pyrrolide-imine ligand; L = PPh_3, PMe_3, pyridine) catalysts make MA-rich NB/MA copolymers by a radical mechanism.[6] Recently, Sen reported the synthesis of NB/MA copolymers by Cu-mediated atom transfer radical polymerization.[7]

Goodall and co-workers disclosed that the bimetallic "cationic metal pair complex" $[\{(allyl)Pd(PCy_3)\}_2(\mu\text{-}Cl)][PF_6]$ (**1**), either in isolated form or generated in situ (**1-in situ**), and analogous $B(C_6F_5)_4^-$ and SbF_6^- salts copolymerize NB and MA to materials with a wide range of compositions (NB/MA mole ratio = 19/81 to 85/15), as shown in eq 1.[8] The polymers were proposed to be copolymers based on the observation of narrow unimodal molecular weight distributions (MWDs) by GPC (M_w/M_n = 1.3–1.9). Similar copolymerizations with methyl methacrylate and *tert*-butyl acrylate were also disclosed.



(1)

Goodall and co-workers generated **1-in situ** by sequential treatment of a dichloromethane solution of $\{(allyl)PdCl\}_2$ (**2**) with $AgPF_6$ and PCy_3 followed by filtration to remove AgCl, giving a filtrate containing the active catalyst (**1-in situ**, eq 2).[9] Complex **1** was isolated by crystallization by slow diffusion of pentane into the CH_2Cl_2 filtrate and characterized by ^1H and ^{31}P NMR. It was proposed that the bimetallic structure of **1** is important for copolymerization.



(2)

Recent work suggests that binuclear catalysts can exhibit unique behavior in olefin polymerization catalysis and other

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(9) (a) See example 10 in ref 8. (b) Other catalyst generation methods in ref 8 include (i) successive treatment of **2** with 2 equiv of $Li[B(C_6F_5)_4]$ and 2 equiv of PCy_3, and treatment of $(allyl)Pd(PCy_3)Cl$ with 0.5 equiv of $AgPF_6$.

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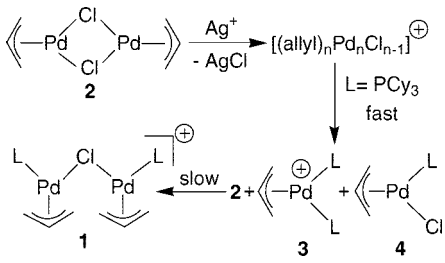
Scheme 1



reactions.[10] In view of these results, we have studied the Goodall catalyst in more detail to (i) characterize the solution behavior of **1**, (ii) establish the composition and structure of the NB/MA materials, with particular emphasis on the question of whether these materials are copolymers or mixtures of homopolymers, and (iii) understand the mechanism of the reaction of **1** with NB and MA.

Results and Discussion

Synthesis of 1 and Composition of 1-in situ. We first studied the synthesis of **1** by eq 2 to characterize the Pd species that are present at each stage of the reaction and in **1-in situ**. The results are shown in Scheme 1. The reaction of **2** with $AgPF_6$ in CH_2Cl_2 at 23 °C results in the rapid precipitation of AgCl and insoluble Pd species (85–90% of the total Pd). ESI-MS analysis of the acetone-soluble portion of the precipitate revealed that higher-order Pd cations, $[(allyl)_3Pd_3Cl_2]^+$, $[(allyl)_4Pd_4Cl_3]^+$, and solvent adducts of these species, were present. Addition of PCy_3 followed by filtration generates a solution containing an approximately equimolar mixture of **1**, **2**, $[(allyl)Pd(PCy_3)_2][PF_6]$ (**3**), and $(allyl)PdCl(PCy_3)$ (**4**).[11] Complexes **3** and **4** were identified by NMR and independent synthesis. This mixture converts almost completely to **1** over 20 h at 23 °C or 1 h at 50 °C. Layering the filtrate with pentane for 12 h at 23 °C gives crystals of **1** (70%).

These observations show that (i) the formation of **1** occurs by chloride abstraction followed by a series of ligand exchange reactions, (ii) the PCy_3 must be added before filtering off the AgCl to avoid loss of Pd in the form of the higher order cations, and (iii) the **1-in situ** catalyst is a mixture of Pd species whose concentrations vary with aging.

Streamlined Synthesis of 1. The conversion of the initially formed mixture of **2**, **3** and **4** (i.e., **1-in situ**) to **1** in Scheme 1 requires cleavage of a chloride bridge of **2** and ligand exchange steps. While the details of these reactions are unknown, it is reasonable to expect that this process may be promoted by coordinating solvents. Indeed, successive reaction of **2** in acetone with $AgPF_6$ (1 equiv, 15 min) and PCy_3 (2 equiv, 2 h), followed by filtration, concentration, and cooling (0 °C, 1 h), results in crystallization of **1** (77%).

Molecular Structure of 1. The solid state structure of **1** was confirmed by X-ray crystallography (Figure 1). The cation contains two $Pd(PCy_3)(\pi\text{-allyl})$ units linked by a bridging chloride. The allyl ligands are disordered over two positions with refined site occupancies of 80/20 and 64/36.

Solution Behavior of 1. The ^1H NMR spectra of **1** in low-polarity solvents such as toluene-d_8 or toluene-d_8/CD_2Cl_2 mixtures contain two sets of allyl resonances (Figure 2a,b),[12] which, based on data for **4** and $^1H-^1H$ COSY data for **1**, were assigned to two inequivalent, unsymmetrical allyl groups. The ^{31}P NMR spectrum of **1** contains one signal in toluene-d_8/CD_2Cl_2. The different allyl environments may be associated with different conformers of **1**.

Several observations revealed that the solution behavior of **1** is complex. First, when a solution of **1** in toluene-d_8/CD_2Cl_2 (1/1 by volume) was heated to 50 °C, the H^{3A}/H^{3B} and H^{5A}/H^{5B} pairs of resonances each collapsed to a single resonance at the average chemical shifts of the original peaks. After cooling the sample to 23 °C, these resonances each split back to two

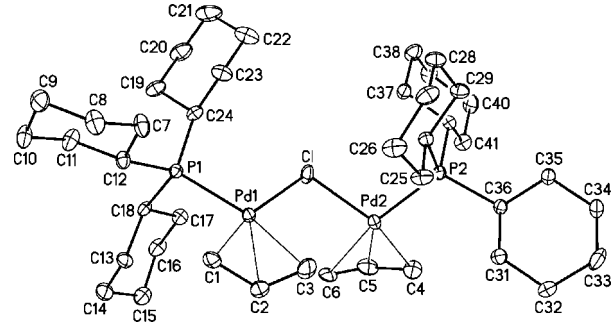


Figure 1. Molecular structure of the cation of $[\{(allyl)Pd(PCy_3)\}_2(\mu\text{-}Cl)][PF_6]$ (**1**). The major allyl environments are shown. Hydrogen atoms are omitted. Key bond distances (Å) and angles (deg): Pd(1)−C(1) 2.095(6), Pd(1)−C(2) 2.157(5), Pd(1)−C(3) 2.239(6), Pd(1)−P(1) 2.313(1), Pd(1)−Cl 2.386(1), Pd(2)−C(4) 2.115 (9), Pd(2)−C(5) 2.139(8), Pd(2)−C(6) 2.235(9), Pd(2)−P(2) 2.321(1), Pd(2)−Cl 2.410(1), C(1)−C(2) 1.440(1), C(2)−C(3) 1.325(9), C(4)−C(5) 1.36(2), C(5)−C(6) 1.31(2), P(1)−Pd(1)−Cl 97.63(4), Pd(1)−Cl−Pd(2) 117.71(5), P(2)−Pd(2)−Cl 97.07(4).

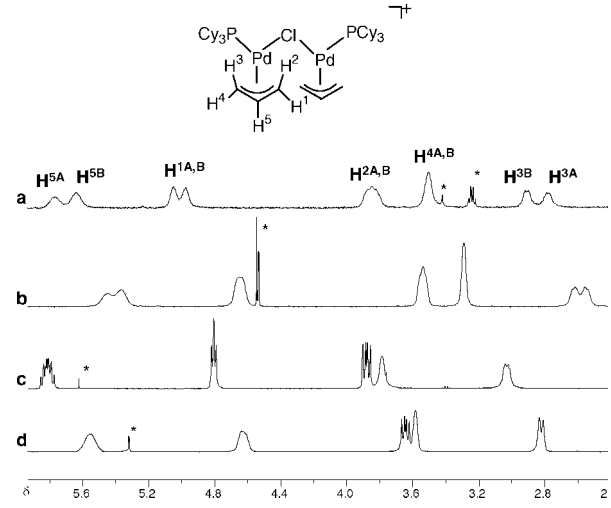


Figure 2. ^1H NMR spectra of **1** at 23 °C in (a) toluene-d_8 (b) toluene-d_8/CD_2Cl_2 (ca. 1/1), (c) acetone-d_6, and (d) CD_2Cl_2 solution. The allyl region is shown. * indicates residual solvent and impurity peaks.

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(12) At NMR concentrations, **1** precipitates from toluene in a few minutes at room temperature.

Table 1. Polymerization of NB/MA Mixtures[a]

run	catalyst	[Pd] (mM)	time (h)	NB/MA ratio in polymer[b]	NB conv (%)[c]	MA conv (%)[c]	M_w[d] (10^3)	M_w/M_n[e]
1	**1**	1.44	5	72/28	99	38	84.5	1.1
2	**1**	1.44	1	91/9	93	9	64.8	1.7
3	**1-in situ**[f]	1.44	5	71/29	100	42	66.1	1.3
4	**3**	0.72	5	85/15	98	17	197	1.9

[a] Conditions: toluene/CH_2Cl_2 (91/9 v/v), 50 °C, [NB] = [MA] = 0.87 M. [b] Determined by ^{1}H NMR by integration of δ 3.64 and 0.8–2.5 resonances. [c] Based on polymer yield, amounts of NB and MA in the feed and NB/MA mole ratio in the polymer. [d] Weight average molecular weight determined by GPC vs polystyrene standards using RI detection. [e] Polydispersity determined by GPC vs polystyrene standards using RI detection. [f] Solution of **1** in CH_2Cl_2 generated in situ by eq 2.

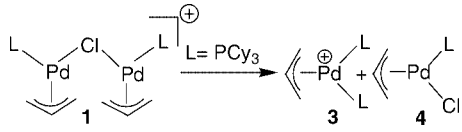
Table 2. NB and MA Homopolymerization by 1-in situ[a]

run	catalyst	[NB] (M)	[MA] (M)	time (h)	NB conv (%)[b]	MA conv (%)[b]	M_w[c] (10^3)	M_w/M_n[d]
5	**1-in situ**[e]	0.87		5	100		88.4	1.6
6	**1-in situ**[e]	0.87		1	91		104.6	1.4
7	**1-in situ**[e]		0.87	5		42	37.3	1.9
8	**1-in situ**[e]		0.87	1		10		

[a] Conditions: toluene/CH_2Cl_2 (91/9 v/v), 50 °C, [Pd] = 1.44 mM. [b] Monomer conversion (%) = (weight of polymer/weight of monomer in the feed) x 100. [c] Weight average molecular weight determined by GPC vs polystyrene standards using RI detection. [d] Polydispersity determined by GPC vs polystyrene standards using RI detection. [e] Solution of **1** in CH_2Cl_2 generated in situ by eq 2.

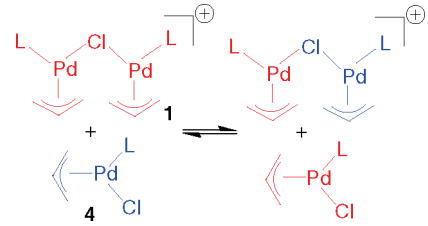
peaks, but the signals were broader than they were before heating. Second, when a solution of **1** in toluene-d_8/CD_2Cl_2 (2/1.5) was maintained at 23 °C for one week, the pairs of H^{3A}/H^{3B} and H^{5A}/H^{5B} resonances collapsed to single resonances. Finally, ^{1}H NMR spectra of **1** in acetone-d_6 and CD_2Cl_2 contain only one set of unsymmetrical allyl resonances at 23 °C, even immediately after dissolution (Figure 2c,d).

These observations suggest that exchange of the two allyl environments in **1** is catalyzed by a minor species that is generated from **1** in situ, either thermally or in the presence of polar/coordinating solvents. To test the possibility that PCy_3 catalyzes the exchange of allyl environments of **1**, the reaction of these species was investigated. The ^{1}H and ^{31}P NMR spectra taken immediately after addition of 20 mol % PCy_3 to **1** in toluene-d_8/CD_2Cl_2 (2/1.5) solution reveal formation of **3** (20%; ^{31}P NMR: δ 36.4). Complex **3** forms by displacement of **4** from **1** by PCy_3 (eq 3). However, **4** is not directly observed because it exchanges rapidly with **1** (eq 4), which was confirmed by NMR studies of mixtures of these species.[13] Thus, the ^{1}H NMR spectrum of the **1**/PCy_3 mixture contains, in addition to the resonances for **3**, only one set of unsymmetrical allyl resonances for **1** and **4**. The ^{31}P NMR spectrum contains, in addition to the resonance for **3**, one resonance at δ 41.4, close to the expected weighted average position (δ 41.3) of the resonances of **1** (41.2) and **4** (δ 42.1).[14]



(3)

These results provide an explanation for the effects of heating, aging, and coordinating/polar solvents on the NMR spectra of **1**. Free PCy_3, generated in situ from **1**, reacts with **1** to form **4**. Fast chemical exchange of **1** and **4** exchanges the inequivalent



(4)

(5)

allyl environments of **1**. Polar/coordinating solvents may facilitate the release of PCy_3 from **1** or may react with **1** to form **4** (eq 5).

Active Catalysts for Polymerization of NB/MA Mixtures. We tested several catalysts for NB/MA copolymerization under conditions similar to those used by Goodall and co-workers,[8] and representative results are shown in Table 1. Complexes **1** and **3** and **1-in situ** are active catalysts under these conditions. Comparison of runs 1 and 2 shows that NB is consumed faster than MA. The polymers exhibit narrow unimodal MWDs by GPC (RI detection). Complexes **2** and **4**, $AgPF_6$, PCy_3, and a 1/1 mixture of $AgPF_6$ and PCy_3 showed no catalytic activity.

NB and MA Homopolymerization. We investigated NB and MA homopolymerization by **1-in situ** under the same conditions used in the NB/MA reactions in Table 1. Representative results are shown in Table 2. NB homopolymerization proceeded with high conversion similar to that observed in Table 1. The M_w of the poly(norbornene) (PNB) was similar to that of the NB/MA material made by **1-in situ**. MA homopolymerization by **1-in situ** proceeded without an induction period, and the MA conversion was similar to that observed in the NB/MA reactions in Table 1. The M_w of the poly(methyl acrylate) (PMA) was lower than that of the NB/MA material made by **1-in situ**.

Copolymer versus Mixture of Homopolymers. The ^{1}H and ^{13}C NMR spectra of the NB/MA materials produced in the

(13) The ^{1}H NMR spectrum of a solution of **1** and **4** (30 mol %) in toluene-d_8/CD_2Cl_2 (2/1.5) taken immediately after mixing contains only one set of allyl resonances. The ^{31}P spectrum taken immediately after mixing contains one resonance at δ 41.5, close to the weighted average position (δ 41.3) of **1** and **4**. Similar results were obtained by addition of different amounts of **4** to **1**.

(14) Similar results were obtained when different amounts of PCy_3 were added to **1**.

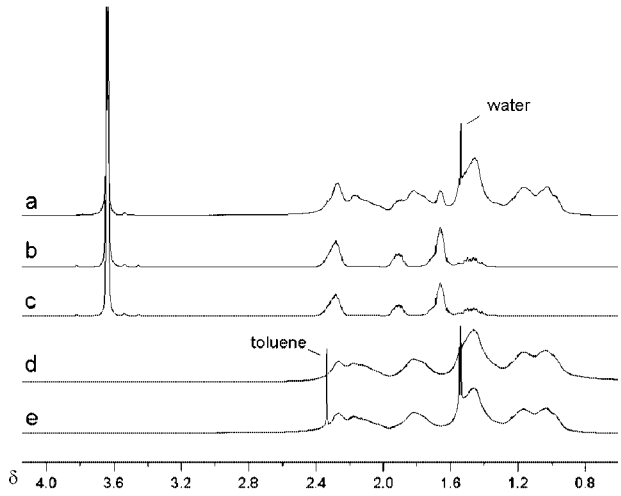


Figure 3. ^{1}H NMR spectra ($CDCl_3$, 23 °C) of NB and MA polymers. (a) NB/MA material (Table 1, run 3); (b) PMA fraction of the NB/MA material in (a); (c) PMA from homopolymerization of MA (Table 2, run 7); (d) PNB fraction of the NB/MA material in (a); (e) PNB from homopolymerization of NB (Table 2, run 5).

reactions in Table 1 correspond closely to the simple superposition of the spectra of the PNB and PMA homopolymers produced under identical conditions in Table 2. Representative ^{1}H NMR spectra are shown in Figure 3. This result suggests that the NB/MA materials are mixtures of the component homopolymers. To test this possibility, we conducted fractionation experiments.

The PNB and PMA produced by **1-in situ** (Table 2) are both soluble in $CHCl_3$; however, the PNB is completely insoluble in acetone, while the PMA is soluble in acetone. Accordingly, the NB/MA materials from Table 1 were fractionated by (i) dissolution of the NB/MA material in $CHCl_3$, (ii) slow diffusion of acetone by layering onto the $CHCl_3$ solution, (iii) filtration to give a filtrate that contained pure PMA and a solid that was an NB/MA material with decreased MA content, and (iv) recycling of the solid. Subjection of the NB/MA materials produced by **1** and **1-in situ** in Table 1 (runs 1 and 3) to four fractionation cycles resulted in separation into pure PNB and PMA with >95% mass balance. ^{1}H and ^{13}C NMR analysis showed that the fractions are pure homopolymers (Figure 3 and Supporting Information). These results show that **1** and **1-in situ** do not copolymerize NB and MA, but rather these catalysts catalyze or initiate competing homopolymerizations of the two monomers.

GPC Analysis of NB/MA Materials and the Corresponding PNB and PMA Fractions. It is surprising that the MWDs of the NB/MA materials in Table 1 are narrow even though these materials are mixtures of PNB and PMA. However, it should be noted that PNB and PMA give signals with opposite signs in GPC using RI detection in 1,2,4-trichlorobenzene solvent. The GPC traces for an NB/MA material made by **1-in situ** and the PNB and PMA components obtained by fractionation of this material are shown in Figure 4. This comparison clearly shows that the PNB and PMA fractions have significantly different molecular weights. The NB/MA material produces an apparent unimodal MWD as a result of signal cancelation due to the opposite signs of the signals of the PNB and PMA components.

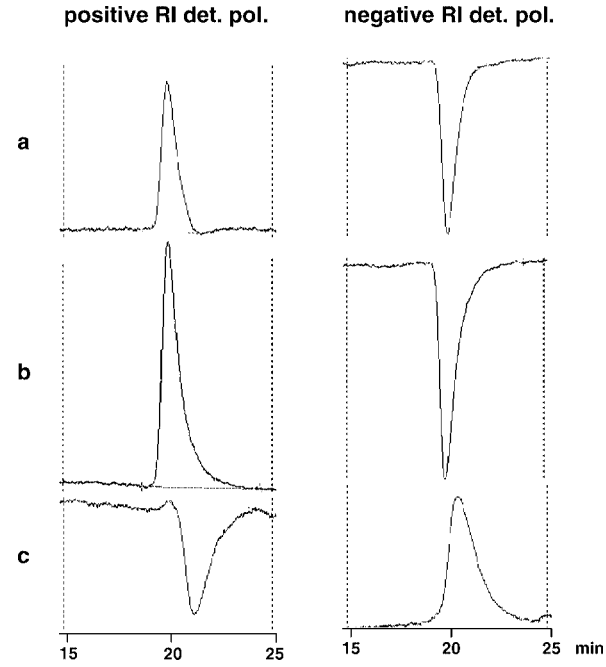


Figure 4. GPC traces (1,2,4-trichlorobenzene, 150 °C) for a NB/MA material and its component PNB and PMA fractions run with positive and negative RI detector polarity (det. pol.) settings. (a) NB/MA material from Table 1, run 3; apparent M_w = 66 100, apparent M_w/M_n = 1.3. (b) The PNB fraction of the material in (a); M_w = 60 000, M_w/M_n = 1.7. (c) PMA fraction of the material in (a); M_w = 39 000, M_w/M_n = 1.9. M_w values are relative to polystyrene.

Mechanism of NB Polymerization.[15] The lack of olefin signals in the NMR spectra of the PNB produced by **1** and **1-in situ** rules out a ring-opening metathesis polymerization mechanism.[16] Both discrete **1** and **1-in situ** produce high yields of PNB with high molecular weights, which is inconsistent with radical and cationic mechanisms, which generally give low yields and molecular weights.[17] A radical mechanism is further ruled out by the following experiments: (i) attempted polymerization of NB by 2,2′-azo-bis(isobutyronitrile) (AIBN) under the conditions used in Tables 1 and 2 did not yield polymer, and (ii) NB polymerization by **1-in situ** is not affected by oxygen, a potent radical inhibitor. Therefore, it is clear that NB polymerization by **1** and **1-in situ** occurs by an insertion

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Table 3. Polymerization of MA, *Z*-MA-d_1, and NB/*Z*-MA-d_1 by AIBN and 1-in situ[a]

run	initiator or catalyst	[NB] (M)	[MA] (M)	[*Z*-MA-d_1] (M)	time (h)	NB conv (%)[c]	MA conv (%)[c]	M_w[d] (10^3)	M_w/M_n[e]
9	AIBN		0.87		5		10	35.3	2.0
10	AIBN			0.87	5		13	35.1	2.1
11	**1-in situ**[f]			0.87	10		42	25.9	2.2
12	**1-in situ**[f]	0.87		0.87	5	92[b]	47[b]	75.0[g]	1.2[g]

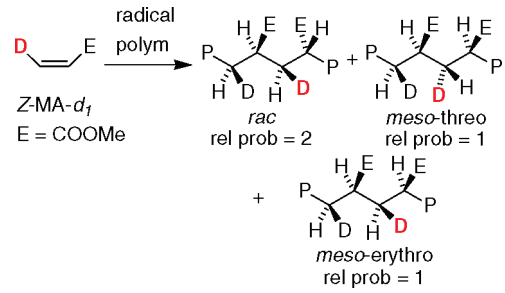
[a] Conditions: toluene/CH_2Cl_2 (91/9 v/v), 50 °C. Runs 9, 10: [AIBN] = 4.33 mM; runs 11, 12: [Pd] = 1.44 mM. [b] The NB/*Z*-MA-d_1 mole ratio in the polymer product is 66/34 as determined by ^{1}H NMR by integration of the δ 3.64 and 0.8–2.5 resonances. [c] Based on polymer yield, amounts of monomers in the feed, and monomer mole ratio in the polymer. [d] Weight average molecular weight determined by GPC vs polystyrene standards using RI detection. [e] Polydispersity determined by GPC vs polystyrene standards using RI detection. [f] Solution of **1** in CH_2Cl_2 generated in situ by eq 2. [g] These data refer to the unfractionated NB/*Z*-MA-d_1 material.

mechanism, as observed for other Pd and Ni catalysts.[18] The ^{13}C NMR spectrum of PNB made by **1** and **1-in situ** is similar to that observed for PNB produced by Ni(C_6F_5)$_2$(PPh$_2$ CH_2C(O)Ph) and related Ni catalysts, which was assigned a microstructure of low diisotacticity containing only *rr* and *mr* triads, based on data for model compounds.[19] No ^{13}C NMR resonances are present in the δ 20–24 range, which suggests *exo* rather than *endo* enchainment of the NB units.[20] The active species in NB polymerization by **1** and **1-in situ** is unknown. However, the ^{1}H and ^{13}C NMR spectra of PNB produced by **1**, **1-in situ**, and **3** are identical (see Supporting Information), which strongly suggests that Pd(PCy_3)R^+ species are active in all three systems.[18b]

Mechanism of MA Polymerization. Anionic and radical polymerizations of MA are known.[21] Alkyl acrylate polymerization via mechanisms involving Michael addition of an O-bound metal enolate to an O-bound acrylate catalyzed by early metal or lanthanide species is also known.[22] However, metal-catalyzed insertion homopolymerization of MA is unknown. The yield of PMA in MA homopolymerization by **1-in situ** is not affected by the presence of MeOH (125 equiv per Pd), which is inconsistent with anionic or metal O-enolate mechanisms.[23]

The PMA from **1-in situ** homopolymerization (Table 2, run 7) and the PMA fractions from the reaction of **1** and **1-in situ** with NB/MA mixtures (Table 1, runs 1 and 3) are atactic (*rac*/*meso* = 1 by ^{1}H NMR). PMA produced by AIBN-initiated radical polymerization under the same conditions (Table 3, run 9) is also atactic. Additionally, attempted homopolymerization of MA by **1-in situ** in air gave no polymer, and polymerization of an NB/MA mixture by **1-in situ** in air gave only PNB (100% NB conversion). The inhibition of MA polymerization in the presence of air is attributed to oxygen, which is a potent inhibitor of free radical polymerizations and also may inhibit insertion polymerization. These results are consistent with a radical mechanism but do not rule out a nonstereoselective insertion mechanism.

Scheme 2



Polymerization of *Z*-MA-d_1. To distinguish between radical and insertion mechanisms for MA homopolymerization by **1-in situ**, we investigated the polymerization of the selectively deuterated monomer *Z*-MA-d_1. Free radical MA polymerization is nonstereoselective with respect to cis/trans addition due to fast C−C bond rotation in the propagating radical, which results in the loss of C=C bond stereochemistry.[21b] The expected outcome of radical polymerization of *Z*-MA-d_1 is shown in Scheme 2. The ^{2}H NMR spectrum of the polymer will contain *rac*, *meso*-threo, and *meso*-erythro signals in a 2/1/1 ratio. In contrast, insertion polymerization of MA should proceed by cis-addition (Scheme 3), and the ^{2}H NMR spectrum of poly(*Z*-MA-d_1) produced by this mechanism should contain only *rac* and *meso*-threo signals.

Z-MA-d_1 was polymerized by AIBN and by **1-in situ**, and a 1/1 NB/*Z*-MA-d_1 mixture was polymerized by **1-in situ**. The results are summarized in Table 3. The ^{2}H{^{1}H} NMR spectra of the poly(*Z*-MA-d_1) generated by AIBN and by **1-in situ** and the poly(*Z*-MA-d_1) fraction of the PNB/poly(*Z*-MA-d_1) mixture generated by **1-in situ** are shown in Figure 5.[24] Each spectrum contains *rac* (δ 1.68), *meso*-threo (δ 1.49), and *meso*-erythro (δ 1.94) signals in a ca. 2/1/1 ratio, consistent with a radical polymerization mechanism in each case. These results show that catalyst **1-in situ** polymerizes MA by a radical mechanism, both in MA homopolymerization reactions and in the presence of competing NB insertion polymerization. The mechanism of initiation in these reactions is unknown. However, as noted above, it is well established that Pd catalysts can initiate radical polymerization of vinyl monomers.[6,23,25]

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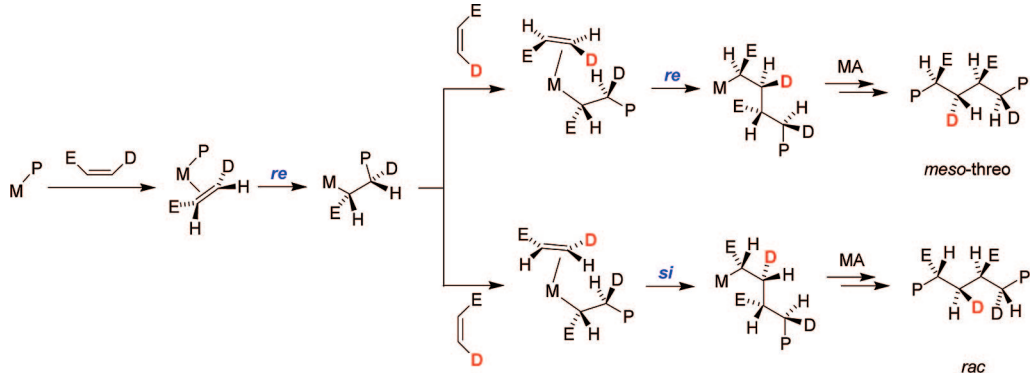
Scheme 3



Conclusion

The sequential reaction of {(allyl)Pd(μ-Cl)}$_2$ (**2**) with $AgPF_6$ and PCy_3 in CH_2Cl_2 generates a mixture (**1-in situ**) of [{(allyl)Pd(PCy_3)}$_2$(μ-Cl)][PF_6] (**1**), **2**, [(allyl)Pd(PCy_3)$_2$][PF_6] (**3**), and (allyl)PdCl(PCy_3) (**4**), which evolves to form pure **1** after 20 h at 23 °C. Complex **1** reacts with PCy_3 to generate **3** and **4** and undergoes facile exchange of Pd units with **4**. Both **1** and **1-in situ** polymerize mixtures of NB and MA to a mixture of pure PNB and PMA via competing NB insertion polymerization and MA radical polymerization.

Experimental Section

General Procedures. All experiments were performed using drybox or Schlenk techniques under a nitrogen atmosphere unless indicated otherwise. Nitrogen was purified by passage through columns containing activated molecular sieves and Q-5 oxygen scavenger.

CH_2Cl_2 and $CHCl_3$ were distilled from CaH_2. Pentane and toluene were purified by passage through columns of activated alumina and BASF R3-11 oxygen scavenger. CD_2Cl_2 and $CDCl_3$ were distilled from P_2O_5. THF and toluene-d_8 were distilled from sodium benzophenone ketyl. Acetone and acetone-d_6 were distilled from activated molecular sieves (4 Å). (allyl)Pd(Cl)(PCy_3) (**4**) was prepared by the literature procedure.[26] *Z*-MA-d_1 was prepared by a modification of the literature procedure (see Supporting Information).[27] {(allyl)PdCl}$_2$ (**2**) and PCy_3 were purchased from Strem and used as received. Methyl acrylate (MA) and norbornene (NB) (Aldrich) were purified by the methods of Goodall and co-workers, as follows.[8] MA was passed through columns of hydroquinone monomethyl ether (MEHQ) and activated molecular sieves (4 Å) and purged with nitrogen for 30 min. NB was dissolved in a small amount of toluene, passed through a column of activated molecular sieves (4 Å), and purged with nitrogen for 30 min. The NB concentration was determined by NMR. All other chemicals were purchased from Aldrich and used as received. Elemental analysis was performed by Midwest Microlab.

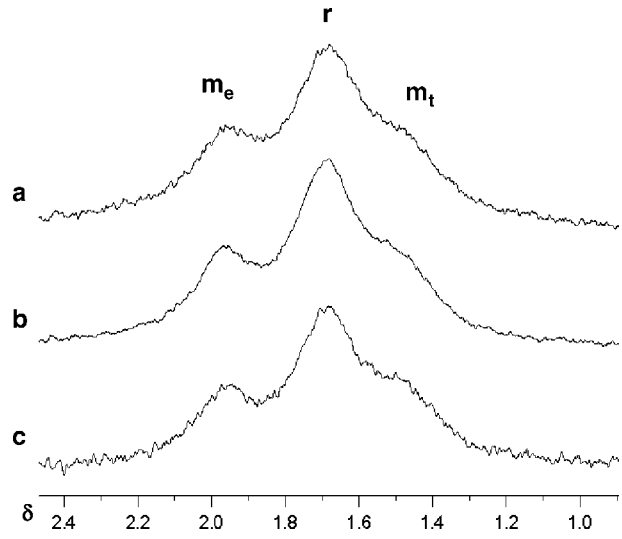


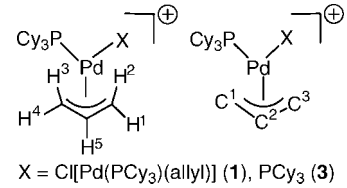
Figure 5. $^2H\{^1H\}$ NMR spectra (1,2-dichlorobenzene, 135 °C) of MA-d_1 polymers. (a) P(*Z*-MA-d_1) fraction of NB/*Z*-MA-d_1 polymer produced by **1-in situ** (Table 3, run 12). (b) P(*Z*-MA-d_1) produced by **1-in situ** (Table 3, run 11). (c) P(*Z*-MA-d_1) produced by AIBN (Table 3, run 10). Peak assignments are as follows m_e = *meso*-erythro (δ 1.94); r = *rac* (δ 1.68); m_t = *meso*-threo (δ 1.49) signals.

Electrospray mass spectra (ESI-MS) were recorded on freshly prepared samples (ca. 1 mg/mL in acetone) using an Agilent 1100 LC-MSD spectrometer incorporating a quadrupole mass filter with a *m*/*z* range of 0–3000. In cases where assignments are given, the observed isotope patterns closely matched calculated isotope patterns. The listed *m*/*z* value corresponds to the most intense peak in the isotope pattern.

NMR spectra were recorded on Bruker DMX-500 or DRX-400 spectrometers in Teflon-valved tubes at ambient temperature unless otherwise indicated. ^1H and ^{13}C chemical shifts are reported relative to $SiMe_4$ and were determined by reference to the residual ^1H and ^{13}C solvent resonances. ^{31}P chemical shifts are reported relative to H_3PO_4. Coupling constants are given in Hz. $^2H\{^1H\}$ NMR spectra of poly(*Z*-MA-d_1) were recorded on a DRX-400 spectrometer in Teflon-valved tubes in 1,2-dichlorobenzene at 135 °C. ^2H chemical shifts were determined by reference to external $CDCl_3$.

GPC analyses were performed on a Polymer Laboratories PL-GPC 220 instrument using 1,2,4-trichlorobenzene solvent (stabilized with 125 ppm BHT) at 150 °C. A set of three PLgel 10 μm Mixed-B LS columns was used. Samples were prepared at 160 °C. Polymer molecular weights were determined versus polystyrene standards.

The labeling system used in NMR assignments is:



X = Cl[Pd(PCy_3)(allyl)] (**1**), PCy_3 (**3**)

[{(allyl)Pd(PCy_3)}$_2$(μ-Cl)][PF_6] (1). This method follows the literature procedure except that acetone is used as the solvent.[8] A solution of {(allyl)PdCl}$_2$ (**2**) (60.0 mg, 0.164 mmol) in acetone (1 mL) was prepared and a solution of $AgPF_6$ (41.4 mg, 0.164 mmol) in acetone (0.8 mL) was added. The resulting suspension was stirred

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Table 4. Summary of X-Ray Diffraction Data for [{(allyl)Pd(PCy$_3$)}$_2$(μ-Cl)][PF$_6$] (1)

formula	$C_{42}H_{76}ClF_6P_3Pd_2$
fw	1036.19
cryst syst	orthorhombic
space group	*Pbca*
a (Å)	17.332(2)
b (Å)	19.320(2)
c (Å)	27.697(4)
V (Å^3)	9274(2)
Z	8
T (K)	150(2)
cryst color, habit	yellow, block
GOF on F^2	1.024
R indices ($I > 2\sigma(I)$)[a]	R1 = 0.0493 wR2 = 0.1114
R indices (all data)[a]	R1 = 0.0782 wR2 = 0.1256

[a] $R1 = \Sigma\Delta F_o| - |F_c\Delta/\Sigma|F_o| = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2]^{1/2}$, where $w = q[119^2(F_o^2) + (aP)^2 + bP]^{-1}$.

for 15 min at room temperature. A solution of PCy_3 (92 mg, 0.328 mmol) in CH_2Cl_2 (0.5 mL) was added to the mixture. (*Note*: PCy_3 is not soluble in acetone.) The color of the suspension turned to grayish yellow. The mixture was stirred for 2 h and filtered through Celite to give a clear yellow filtrate. The filtrate was concentrated to 0.3 mL and cooled to 0 °C for 1 h, resulting in the formation of yellow crystals, which were isolated by filtration, washed with pentane, and dried under vacuum to give **1** (131 mg, 77%). Data for **1**: ^{1}H and ^{13}C NMR assignments are based on COSY NMR and reported data for (allyl)PdCl(PCy$_3$).[11] ^{1}H NMR (acetone-d_6, 23 °C): δ 5.81 (m, 2H, H^5), 4.81 (br t, J_{HH} = 6.9, 2H, H^1), 3.88 (dd, J_{HH} = 8.7, 14.2 Hz; 2H, H^2), 3.79 (br s, 2H, H^4), 3.03 (br s, 2H, H^3), 2.28–1.30 (m, 66H, Cy). ^{13}C{^{1}H} NMR (CH_2Cl_2, 23 °C): δ 118.0 (d, J_{CP} = 4.7, C^2), 83.7 (d, J_{CP} = 25.6, C^3), 52.4 (br s, C^1), 34.5–26.5 (PCy$_3$). ^{31}P{^{1}H} (acetone-d_6, 23 °C): δ 42.5 (s, PCy$_3$), −142.6 (septet, J_{PF} = 706, PF_6^-). Anal. Calcd for $C_{42}H_{76}ClF_6P_3Pd_2$: C, 48.68; H, 7.39. Found: C, 48.63; H, 7.15. ESI-MS: [{(allyl)Pd(PCy$_3$)}$_2$(μ-Cl)]$^+$: calcd *m*/*z* = 891.3, found 891.3.

X-Ray Crystallographic Analysis of [{(allyl)Pd(PCy$_3$)}$_2$(μ-Cl)][PF$_6$] (1). Crystallographic data are summarized in Table 4. Data were collected on a Brüker-AXS APEX diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The structure was solved using direct methods and refined with full-matrix, least-squares procedures on F^2. The allyl ligands were located disordered over two positions with refined site occupancies of 80/20 and 64/36. Chemically equivalent atoms in the disordered contributions were treated with equal atomic displacement parameters and refined with equal distance restraints to adjacent equivalent atoms. Antibumping restraints were applied between the anion, 20% disordered allyl ligand contributor, and cyclohexyl moieties. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions.

Generation of 1-in situ. A solution of {(allyl)PdCl}$_2$ (**2**) (11 mg, 30 μmol) in CH_2Cl_2 (1 mL) was prepared. A solution of $AgPF_6$ (7.6 mg, 30 μmol) in CH_2Cl_2 (1 mL) was added, and the resulting suspension was shaken for 1 min. A solution of PCy_3 (16.8 mg, 60 μmol) in CH_2Cl_2 (1 mL) was added, yielding a grayish-yellow suspension. The mixture was shaken for 1 min and filtered through Celite to give a clear yellow filtrate containing **1-in situ**.

[(allyl)Pd(PCy$_3$)$_2$][PF$_6$] (3). This compound was prepared by the method published for the corresponding BF_4^- salt.[28] A solution of {(allyl)PdCl}$_2$ (**2**) (73.2 mg, 0.2 mmol) in CH_2Cl_2 (1 mL) was prepared. A solution of $AgPF_6$ (101.1 mg, 0.4 mmol) in CH_2Cl_2 (1 mL) was added, and the mixture was stirred for 30 min at 23 °C. A solution of PCy_3 (224.3 mg, 0.8 mmol) in CH_2Cl_2 (2 mL) was added, and the mixture was stirred for 1 h. The mixture was filtered, and filtrate was taken to dryness under vacuum. The product was washed with pentane to give pure **3** (323.9 mg, 95%). ^{1}H NMR (CD_2Cl_2): δ 5.41 (m, 1H, H^5), 4.53 (m, 2H, H^1 and H^4), 2.99 (m, 2H, H^2 and H^3), 2.50–1.16 (m, 66H, PCy$_3$). ^{31}P{^{1}H} (CD_2Cl_2, 23 °C): δ 36.5 (s, PCy$_3$), −144.2 (septet, J_{PF} = 710, PF_6^-).

Polymerization of NB/MA Mixtures. A 20 mL vial was charged with norbornene (565 mg, 6 mmol, 2.05 mL of a 2.92 M stock solution in toluene), methyl acrylate (516 mg, 6 mmol, 0.54 mL), toluene (3.83 mL), and (a) catalyst **1** (5.2 mg, 0.5 mL of a 0.01 M stock solution in CH_2Cl_2, 5 μmol of **1**, 10 μmol Pd) *or* (b) freshly generated **1-in situ** in CH_2Cl_2 (0.5 mL, 10 μmol Pd) *or* (c) complex **3** (4.3 mg, 5 μmol Pd, in 0.5 mL of CH_2Cl_2) in the drybox. The vial was closed with a cap equipped with a rubber septum and taken out of the drybox. The mixture was heated to 50 °C in an oil bath and stirred for 5 h. The mixture was poured into MeOH (80 mL) and filtered, and the pale yellow solid was dried under vacuum at 50 °C overnight ((a) 763 mg, NB/MA = 72/28 (Table 1, run 1), (b) 780 mg, NB/MA = 71/29 (Table 1, run 3), and (c) 643 mg, NB/MA = 85/15 (Table 1, run 4)).

Homopolymerization of NB by 1-in situ. A 10 mL vial was charged with norbornene (282 mg, 3 mmol, 0.39 mL of a 7.69 M stock solution in toluene), toluene (2.82 mL), and freshly generated **1-in situ** in CH_2Cl_2 (0.25 mL, 5 μmol Pd) in the drybox. The vial was closed with a cap equipped with a rubber septum and taken out of the drybox. The mixture was heated to 50 °C in an oil bath and stirred for 5 h. The mixture was poured into MeOH (80 mL) and filtered, and the pale yellow solid was dried under vacuum at 50 °C overnight (282 mg, 100%) (Table 2, run 5).

Homopolymerization of MA. Polymerization by 1-in situ: A 10 mL vial was charged with methyl acrylate (258 mg, 3 mmol, 0.27 mL), toluene (2.94 mL), and freshly generated **1-in situ** in CH_2Cl_2 (0.25 mL, 5 μmol Pd) in the drybox. The vial was closed with a cap equipped with a rubber septum and taken out of the drybox. The mixture was heated to 50 °C in an oil bath and stirred for 5 h. The product was precipitated from MeOH (80 mL), filtered, and dried under vacuum at 50 °C overnight to give a transparent film (108 mg, 42%) (Table 2, run 7). **Polymerization by AIBN:** The same procedure was used except that AIBN (2.46 mg, 15 μmol) and CH_2Cl_2 (0.25 mL) were used instead of **1-in situ**/CH_2Cl_2. Yield: 25.8 mg 10% (Table 3, run 9).

Polymerization of *Z*-MA-d_1. The polymerization of a *Z*-MA-d_1/NB (1/1) mixture by **1-in situ**, polymerization of *Z*-MA-d_1 by **1-in situ,** and polymerization of *Z*-MA-d_1 by AIBN were performed using the procedures described above for nondeuterated MA. The results are given in Table 3 (runs 10–12).

Fractionation Procedure. The product from the polymerization of an NB/MA mixture by **1-in situ** (Table 1, run 3; 30 mg, NB/MA = 71/29) was dissolved in $CHCl_3$ (0.8 mL) and layered with acetone (3.5 mL) at room temperature. Acetone diffused into the $CHCl_3$ solution over 12 h, giving a solid and a liquid phase. Most of the solids settled, but the liquid phase also contained suspended fine particles. Filtration through a 0.45 μm syringe filter gave a clear liquid phase and yellow solids. The particles trapped in the filter were removed by dissolution in chloroform and mixed with the rest of the solids. The filtrate was stripped under vacuum, leaving a colorless film that was identified as pure PMA by ^{1}H NMR. The yellow solid fraction was found to be an NB/MA material with a significantly decreased MA content (6 mol %). This solid was recycled through the fractionation procedure three more times; after the last cycle the solid fraction was pure PNB (21.0 mg). The PMA fractions of all the fractionation cycles were combined (total 7.6 mg). The calculated weights of the PNB and PMA fractions of the starting polymer based on the monomer composition are 21.9 mg PNB and 8.1 mg PMA. The polymer product from Table 1, run 1, was fractionated into pure PNB and PMA fractions using the same procedure with >95% mass balance.

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Supporting Information Available: Additional experimental details and NMR data. This material is available free of charge via the Internet at http://pubs.acs.org.

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