

# Perspective on metal-mediated polar monomer/alkene copolymerization

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## Abstract

A major unsolved problem in polymer synthesis is the design of efficient metal-mediated systems for the copolymerization of alkenes with polar vinyl monomers, such as acrylates and methacrylates. There are several reasons for the absence of efficient transition metal-based insertion copolymerization catalysts. First, following insertion, the ester group of the acrylate coordinates to the metal thereby hindering subsequent monomer coordination. A second reason stems from the preferred 2,1-insertion of acrylates into metal–carbon bonds resulting in the placement of the ester group on the  $\alpha$ -carbon. This makes the metal–alkyl species particularly prone to homolysis because of the enhanced stability of the resultant alkyl radical, one that is essentially the same as the propagating species in radical-initiated acrylate polymerization. In this perspective we focus on this issue of facile metal–carbon bond homolysis, especially following acrylate insertion, using examples from our own work. We suggest ways to circumvent these issues, for example forcing 1,2-insertion by imposing steric crowding at the metal. Finally, we discuss the danger of relying on radical traps as probes for polymerization mechanism. Radical traps can react with metal-hydrides and attenuate metal-centered nonradical reactions. However, even when radical traps fail to stop an observed polymerization, it may be wrong to conclude that a nonradical mechanism is at work since the traps can be destroyed under certain reaction conditions.

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## 1. Introduction

A major unsolved problem in polymer synthesis is the design of efficient metal-mediated systems for the copolymerization of alkenes with polar vinyl monomers, such as acrylates and methacrylates. A successful outcome will realize a key milestone of the Council for Chemical Research's "Vision 2020 Catalysis" and thus represent a true Change-Maker Technology [1].

Initially, both polyacrylates and polyalkenes (ethene and 1-alkenes) were made using free radical chemistry by batch processes and, 70 years later, acrylate polymers are still made in this way. Alkene polymerization, on the other hand, has enjoyed a number of breakthroughs so that today the vast majority of polyalkenes (>80%) are pro-

duced by continuous processes using transition metal catalysts. The use of catalysts has significantly improved the economics (low energy and low pressure processes), greatly improved the product properties, and enabled new polymer products (e.g., engineering plastics, elastomers, and medical packaging) by virtue of molecular level control of the polymer architecture.

Traditionally in the "Acrylics World", where free radical methods give little or no architectural control of the polymer formed, product performance is controlled by incorporating more or less, "hard" (styrene or methyl methacrylate) or "soft" (butyl acrylate) monomers. Traditionally in the "Polyalkenes World", where Ziegler–Natta and metallocene catalysts only allow the use of hydrocarbon monomers, this is done by controlling tacticity (e.g., atactic polypropene (PP) has been used in chewing gum, while isotactic PP melts >160 °C, free radical polystyrene (PS) has a  $T_g$  of around 100 °C whereas syndiotactic PS melts at ~270 °C).

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Of the many permutations available for modifying the properties of a polymer, the incorporation of functional groups into an otherwise nonpolar material is of particular commercial interest [2,3]. Polar groups exercise control over important properties, such as toughness, adhesion, barrier properties, surface properties (paintability, printability, gloss, hardness, and mar resistance), solvent resistance (or its inverse), miscibility with other polymers, and rheological properties. By incorporating polar groups into hydrocarbon polymers, such as polyethene and polypropene, not only would the important properties related to crystallinity be maintained (modulus, strength, and solvent resistance), but new properties would also be expressed.

## 2. State of the art

Early transition metal Ziegler–Natta and metallocene-type complexes are used extensively for the insertion polymerization of ethene, propene, and other 1-alkenes. The high oxophilicity of these titanium-, zirconium-, and chromium-based catalysts causes them to be poisoned by most functionalized polar vinyl monomers, particularly the commercially available polar monomers, such as acrylates, methacrylates, and vinyl acetate [3]. However, there are examples of copolymerizations with special (protected in one way or another) substrates [4] or with very high levels of a Lewis acid incorporated into the polymerization system to protect the polar functionality through complexation [5].

Currently, commercial procedure for the copolymerization of ethene with polar monomers such as acrylates, methacrylates, and vinyl acetate employ free radical processes [6] similar to those used for LDPE (low density polyethene) production [7]. Incorporation of the polar functionality is relatively random. These free radical processes require extreme pressures resulting in high capital investment and manufacturing costs. Very recently, we have described the free radical-initiated random copolymerization of polar vinyl monomers (such as acrylates and vinyl acetate) with ethene and 1-alkenes under mild conditions [8]. In the presence of a Lewis acid capable of coordinating to the ester carbonyl group of the acrylate, the reactivity and electrophilicity of the radical derived there from is enhanced, making it more likely to add to an electron-rich alkene (polar effect). Thus, when the copolymerizations are carried out in the presence of catalytic amounts of Lewis acids, the incorporation of the alkene approaches 50 mol% and alternating copolymers are formed [9]. Unfortunately, since the composition of the materials is governed by the radical reactivity ratios of the respective monomers, good yields of copolymers with >50 mol% incorporation of alkene appear unattainable in this way.

In recent years, late transition metal catalysts have attracted attention not only for the polymerization of ethene and 1-alkenes, but more importantly for the copolymerization of hydrocarbon monomers with readily available polar monomers such as acrylates [10]. Brookhart

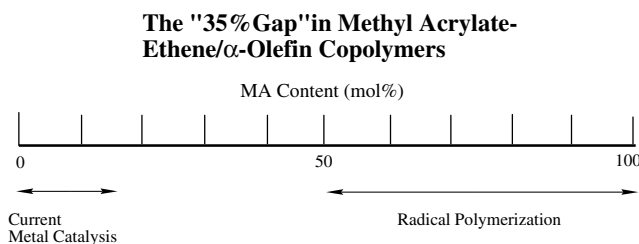


Fig. 1. The “35% gap” in methyl acrylate-ethene/1-alkene copolymers.

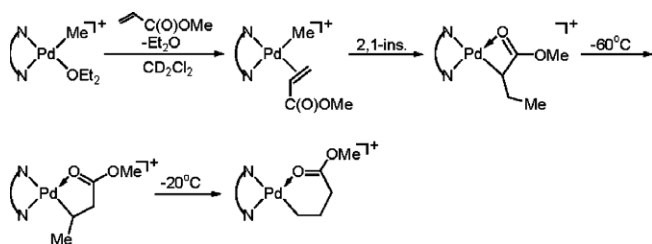
was the first to demonstrate the insertion copolymerization of methyl acrylate (MA) with ethene using a well-defined catalyst [11]. However, because of “chain-walking” by the metal, the resultant polymer is branched with the acrylate units constituting the branch ends. More recently, the incorporation of acrylate monomers into *linear* polyethene was reported by Drent and co-workers who described the use of a neutral palladium catalyst with a chelating P–O ligand to generate linear copolymers with random incorporation of acrylate monomers (2–17 mol%) albeit at relatively low molecular weight ( $M_n = 2000–20,000$ ) [12].

The other new development is from the DuPont group, which reported that by increasing the ethene pressure to 1000 psi, and adding large excesses (200–300×) of the expensive Lewis acid, tris(pentafluorophenyl)borane to nickel catalysts bearing hindered diamine ligands, it is possible to make linear copolymers of ethene and acrylates [13]. However, yields are poor and acrylate incorporation (<6 mol%) and molecular weights ( $M_w < 18,000$ ) are low. Furthermore, it represents only an incremental advance over work more than 30 years old in which 2 mol% acrylic acid was incorporated into isotactic polypropene by protecting it with an inexpensive Lewis acid (diethylaluminum chloride) [14].

Thus, there is a significant composition gap in acrylate/alkene copolymers that are available through either radical or existing metal-catalyzed copolymerizations (see Fig. 1). Clearly, a need exists for new systems capable of copolymerizing alkenes and polar monomers under mild conditions in a more controlled fashion and with a wider range of compositions.

## 3. Scientific challenge

There appears to be *three* fundamental reasons for the absence of efficient transition metal-based insertion polymerization catalysts for the copolymerization of acrylate monomers with alkenes. First, following insertion, the ester group of the acrylate coordinates to the metal as shown by Brookhart for the copolymerization of ethene with methyl acrylate catalyzed by cationic bisimine–Pd(II) complexes (see Scheme 1) [11]. Since in Pd(II) complexes migratory insertions occur through a four-coordinate intermediate, this has the effect of attenuating polymerization activity because the next incoming monomer has to coordinate by breaking the metal–oxygen bond.



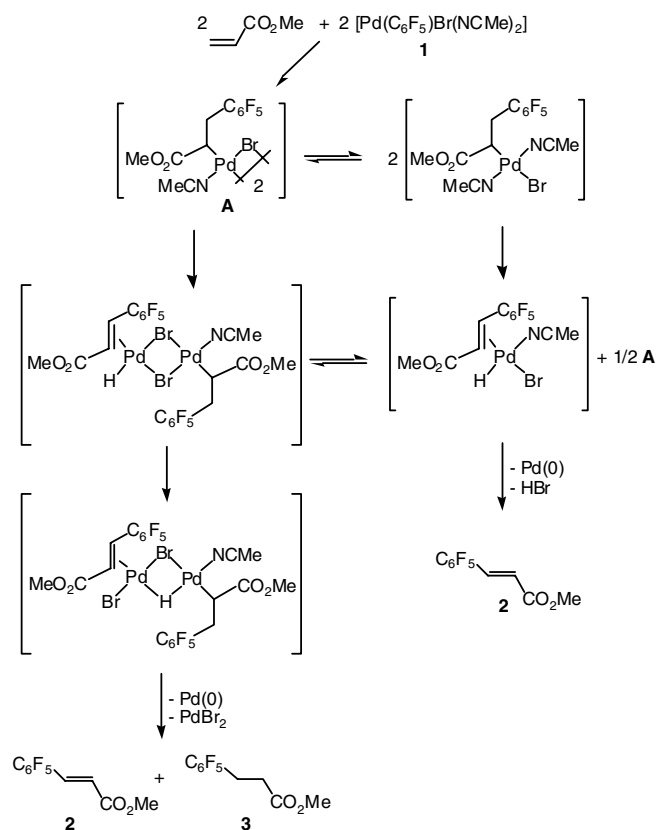
Scheme 1. Ester coordination following acrylate insertion into Pd–methyl bond [11].

A second, possibly less-appreciated, reason for the low activity of metal-based acrylate copolymerization systems involves the actual insertion step. For electronic reasons, acrylates have a strong preference for 2,1-insertion into metal–carbon bonds [15,16]. The resultant species has an electron-withdrawing ester group on the  $\alpha$ -carbon. Since the insertion of an alkene into the metal–carbon bond is viewed as an intramolecular nucleophilic attack by the alkyl group on the coordinated alkene, it is possible that this step may be retarded if the alkyl group is less nucleophilic.

Finally, the formation of a species with an ester group on the  $\alpha$ -carbon due to 2,1-insertion of acrylate monomer also makes the metal–alkyl species particularly prone to homolysis because of the enhanced stability of the resultant alkyl radical, one that is essentially the same as the propagating species in radical-initiated acrylate polymerization [17].

#### 4. Metal–carbon bond homolysis

In this perspective we focus on this issue of facile metal–carbon bond homolysis, especially following acrylate insertion. While several groups have published on the subject [18], the illustrative examples are drawn primarily from our own work. The addition of 1 equiv. of methyl acrylate to the known Pd(II) compound,  $[\text{Pd}(\text{C}_6\text{F}_5)\text{Br}(\text{NCMe})_2]$  (**1**), resulted in the formation of two products  $\text{CH}(\text{CO}_2\text{Me})=\text{CHC}_6\text{F}_5$  (**2**) and  $\text{CH}_2(\text{CO}_2\text{Me})\text{CH}_2\text{C}_6\text{F}_5$  (**3**), in approximately 2:1 ratio. Additionally, the precipitation of metallic palladium was observed. The overall mechanism is outlined in Scheme 2 [17b]. In solution **1** exists in equilibrium with the dimer  $[\text{Pd}_2(\mu\text{-Br})_2(\text{C}_6\text{F}_5)_2(\text{NCMe})_2]$  plus free MeCN. The alkene **2** is then formed by insertion of the monomer into the Pd– $\text{C}_6\text{F}_5$  bond followed by subsequent  $\beta$ -hydrogen abstraction, whereas the saturated product, **3**, is formed via an eventual hydride transfer and subsequent reductive elimination. The formation of a similar mixture of saturated and unsaturated products by reaction of **1** with styrene has been previously studied in detail [19]. The 3:2 ratio increases with the percentage of H-atom transfer via a binuclear compound. The formation of **3** is reduced or eliminated in the presence of additional ligands that preclude the formation of the bridged species.



Scheme 2. Formation of compounds **2** and **3** by acrylate insertion [17b].

The reaction of methyl methacrylate (MMA) with **1** proceeded in an analogous manner forming a 1:1 mixture of the unsaturated and saturated products,  $\text{CH}_2=\text{C}(\text{CO}_2\text{Me})\text{CH}_2\text{C}_6\text{F}_5$ , and  $\text{MeCH}(\text{CO}_2\text{Me})\text{CH}_2\text{C}_6\text{F}_5$  [17b]. Note that the  $\beta$ -hydrogen abstraction occurs from the methyl group following 2,1-insertion of the alkene. A competition experiment involving the simultaneous addition of both methyl acrylate and methyl methacrylate to **1** revealed that the reaction of **1** with methyl acrylate proceeded ca. 1.25 times faster than the corresponding reaction with methyl methacrylate. Since the coordination of the bulkier methyl methacrylate is likely to be disfavored compared to methyl acrylate, this result suggests that  $\beta$ -hydrogen abstraction from the  $\text{CH}_3$  group in the inserted methyl methacrylate is much faster than that from the  $\text{CH}_2\text{C}_6\text{F}_5$  group in either inserted acrylate or methacrylate. Indeed, in the reaction with methyl methacrylate, the possible competing  $\beta$ -hydrogen abstraction product  $\text{MeC}(\text{CO}_2\text{Me})=\text{CHC}_6\text{F}_5$  was not observed by NMR, which suggests that the rates of  $\beta$ -hydrogen elimination from the two possible sites differ by at least two orders of magnitude, in favor of  $\text{CH}_3$  (Fig. 2).

When 1 equiv. of a monodentate phosphine or pyridine was added to **1** along with excess methyl acrylate, there was no precipitation of metallic palladium and the formation of poly(methyl acrylate) occurred. In the absence of added ligand even reactions attempted in neat methyl acrylate led to catalyst decomposition. Methyl methacrylate was not polymerized and, furthermore, its addition stopped

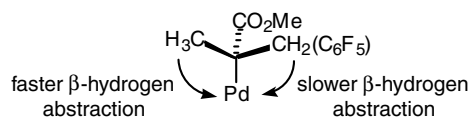


Fig. 2. Relative rates of  $\beta$ -hydrogen abstraction in the insertion product of MMA [17b].

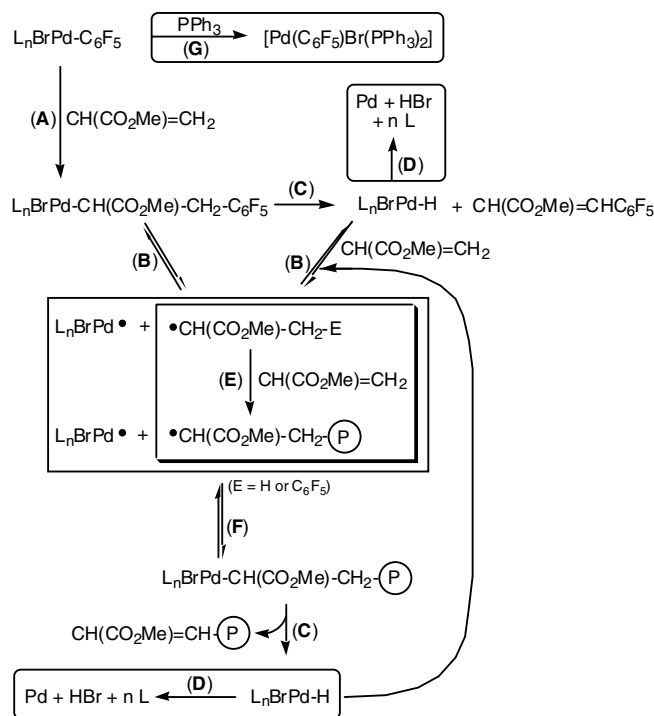
the progress of independently initiated methyl acrylate polymerization in the phosphine-based system. Addition of ethene also inhibited the polymerization of methyl acrylate. However, over 10 mol% incorporation of 1-hexene in the polymer was achieved when the latter was added together with methyl acrylate. The copolymers with 1-alkenes are invariably much richer in acrylate.

Observations that are consistent with a radical mechanism are as follows. Control experiments involving the polymerization of methyl acrylate in the presence of 1-hexene using AIBN as a free radical initiator resulted in the incorporation of 1-hexene in poly(methyl acrylate) at levels comparable to that observed with our systems. The tacticity of the poly(methyl acrylate) formed matched with those calculated using Bernoullian statistics suggesting an atactic polymer [20]. Furthermore, the values were also in agreement with those for a polymer made using AIBN as the initiator.

Under standard reaction conditions, the addition of 5 equiv. (per palladium) of 2,6-*tert*-butyl-4-methylphenol, a free radical inhibitor, did not slow down the polymerization of methyl acrylate, but it has been suggested that 2,6-*tert*-butyl-4-methylphenol is not an efficient inhibitor for free radical polymerization of acrylates [21]. More potent inhibitors are 2,2,6,6-tetra-methyl-1-piperidinyloxy (TEMPO) and galvinoxyl. The addition of a few equivalents of these inhibitors effectively halted the polymerization.

All the evidence taken together appears to favor a radical pathway for the polymerizations. Nevertheless, it is clear that a *classical* free radical mechanism is not being followed; rather, it occurs in conjunction with insertion and  $\beta$ -hydrogen elimination steps. This is evident from several observations including (a) the pronounced effect of added ligands, (b) the failure of monomers, such as styrene and methyl methacrylate to undergo polymerization, and (c) the ability of methyl methacrylate to suppress polymerization when added together with methyl acrylate and to inhibit further polymerization of methyl acrylate when added after the polymerization has been initiated in the phosphine-based system.

A proposed mechanism that reconciles our observations is shown in Scheme 3 [17b,17c]. The first step involves the insertion of acrylate into the Pd–C<sub>6</sub>F<sub>5</sub> bond (step A). In the absence of added ligand, this is quickly followed by  $\beta$ -hydrogen abstraction (step C) and the decomposition of the resultant palladium-hydride (step D). In the presence of coordinating ligands, steps C and D are retarded, thereby allowing the competing palladium–carbon bond



Scheme 3. Mechanism of acrylate polymerization by  $[\text{Pd}(\text{C}_6\text{F}_5)\text{Br}(\text{NCMe})_2]$  + ligand [17b].

homolysis and/or the insertion of acrylate into the Pd–H bond to occur. The bond homolysis step is reversible and at any given time the concentration of radicals is low. This explains our inability to detect the radical by ESR while a signal was observed in the classical radical polymerization initiated by AIBN. Similar pathways for radical generation have been observed in stable free radical polymerizations (SFRP) [18b] and in cobalt-mediated radical polymerizations [22].

The actual polymerization occurs by successive addition of acrylate monomer to the alkyl radical (Scheme 3, step E). The growing radical chain is in equilibrium with the corresponding palladium-bound polymeric alkyl (steps B and F). Chain termination by  $\beta$ -hydrogen abstraction can occur from the latter (step C). As our experiments suggest, the latter step will be significantly faster if the last added monomer is methyl methacrylate or 1-hexene rather than methyl acrylate. Indeed, if methyl methacrylate is present from the outset, no polymerization occurs because of facile  $\beta$ -hydrogen abstraction. If it is added after acrylate polymerization has started, rapid termination of the growing chains occurs. Because of the relatively high molecular weight of the polymers obtained even at low conversions, it has not been possible to identify the end-groups.

The deactivation of the catalyst is associated with  $\beta$ -hydrogen abstraction (step C) and irreversible decomposition of the resulting hydride (step D). Since irreversible decomposition competes with insertion and reentry into the polymerization system, the actual behavior depends on the last alkene added to the growing chain, and on



the ancillary ligands on palladium. Methyl methacrylate and 1-hexene facilitate the formation of palladium hydride by  $\beta$ -hydrogen elimination compared to methyl acrylate, and the decomposition rate of the catalyst increases.

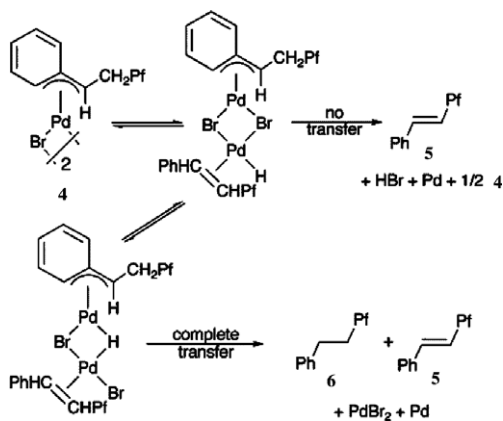
### 5. Relevance of radical traps

The deactivating effect of galvinoxyl or TEMPO is two-fold. First, they react with the growing chains in the radical polymerization process. Additionally, they can react with the Pd-hydride formed by  $\beta$ -hydrogen abstraction [23], preventing its reentrance to initiate new chain growth. To check the reactivity of palladium-hydrides with radical traps, we have also studied their effect on the intramolecular hydride transfer in a dimer generated by  $\beta$ -H elimination from a palladium benzylic derivative **4** (Scheme 4) [23]. The H-transfer and subsequent reductive elimination produces the alkane **6**, and the efficiency of the transfer is measured by the ratio **6/5**. This ratio should be 1 if all of the Pd–H formed (the same molar amount as **5**) leads to **6**, and should drop to 0 if, on the contrary, all of the hydride formed was trapped by the radical trap. The results obtained in the presence of different radical traps are collected in Table 1. Compound **4** is also an effective catalyst for alkene isomerization. The accepted mechanism involves the insertion of the C=C bond into the M–H bond and subsequent  $\beta$ -H elimination. Consistent with the destruc-

tion of the palladium-hydride by reactive radical traps, we observed that the isomerization of alkenes catalyzed by **4** is sharply inhibited by the addition of either galvinoxyl or 2,2-di(4-*tert*-octyl phenyl)-1-picrylhydrazyl (DPPH). The experiments clearly demonstrate that radical traps can react with some palladium hydrides, halting reactions that follow an insertion mechanism involving Pd–H bonds. Thus, the suppression of polymerization by the addition of highly reactive radical traps cannot be relied upon as an infallible diagnostic test for radical polymerization in metal-based polymerization systems, since radical traps can also interrupt insertion-based reactions.

The results described above clearly show that radical traps can react with metal-hydrides and halt or slow down metal-centered nonradical reactions. However, even when radical traps such as galvinoxyl, DPPH, and TEMPO fail to stop an observed polymerization reaction it may be wrong to conclude that a nonradical mechanism is at work. Recently, several reports have appeared claiming insertion polymerization of acrylates by late transition metal-based systems [24]. The common feature of these systems is that they employ methylaluminoxane (MAO) as the activator. The primary evidence cited against an alternative radical mechanism has been the failure of radical traps to halt the polymerization. While the reliability of phenolic radical traps, such as di-*tert*-butyl phenol has been questioned [21], stable radicals such as galvinoxyl, DPPH, and TEMPO have been used as benchmark traps for probing the intermediacy of radicals in polymerizations. The test is based on the hypotheses that the radical trap reacts only with radical species in the medium and is not affected by other species. The fallacy of this hypothesis can be illustrated by our work on methyl methacrylate polymerization in the presence of copper–DMOX complex (DMOX = 1,2-bis(4,4-dimethyl-2-oxazolin-2-yl)ethane) (Table 2) [25].

Polymerizations were carried out at various temperatures from ambient to 80 °C with good monomer conversions. A comparison with the polymers obtained using either the radical initiator AIBN or a combination of AIBN and MAO showed that the polymers formed by the copper-based system were slightly more syndiotactic (e.g., rr dyad was 5–8% higher) for all three temperatures examined (60, 70, and 80 °C) (see Table 2). The system is also effective for the homopolymerization of methyl acrylate and its copolymerization with ethene and propene. However, the poly(methyl acrylate) obtained is atactic. The introduction of ethene or propene into the MA homopolymerization system resulted in the formation of acrylate-rich copolymers in greatly reduced yields. Additionally, the level of alkene incorporation in the copolymers was similar to that observed by us and others for well-documented radical polymerization systems [8,17b,17d]. Cu(OAc)<sub>2</sub> was tested with our system and yielded PMMA with significantly lower yield and syndiotacticity than that observed with Cu(DMOX)Cl<sub>2</sub> (see Table 2), thereby demonstrating the importance of the ligand.



Scheme 4. Decomposition of Complex **4** [23].

Table 1  
Decomposition of complex **4** in the presence of radical traps<sup>a</sup>

Entry	Additive <sup>b</sup>	<b>6/5</b>
1	None	0.74
2	None, in air <sup>c</sup>	0.76
3	Di- <i>tert</i> -butyl phenol (TBP)	0.73
4	Galvinoxyl	0.33
5	DPPH	0.18
6	TEMPO	0.11

<sup>a</sup> Samples of **4** in CDCl<sub>3</sub> in a N<sub>2</sub> atmosphere were left to decompose for 10 days.

<sup>b</sup> Molar ratio **4**:additive = 1:2.

<sup>c</sup> Oxygen can affect radical reactions.

Table 2  
Methyl methacrylate homopolymerization<sup>a</sup>

Entry	Initiator/Catalyst	Cocat <sup>b</sup>	Inhibitor <sup>c</sup>	Temperature (°C)	Yield (%)	$M_w^d \times 10^{-3}$	$M_w/M_n^d$	Tacticity <sup>e</sup> (%)		
								mm	mr	rr
1	Cu(DMOX)Cl <sub>2</sub>	MAO		50	55	316	4.3	5.3	26.6	68.1
2	Cu(DMOX)Cl <sub>2</sub>	MAO		60	60	278	3.8	4.6	29.9	65.5
3	Cu(DMOX)Cl <sub>2</sub>	MAO		70	48	389	4.4	5.3	30.6	64.1
4	Cu(DMOX)Cl <sub>2</sub>	MAO		80	42	257	3.7	5.9	31.6	62.5
5	Cu(DMOX)Cl <sub>2</sub>			40	N.R.					
6	Cu(DMOX)Cl <sub>2</sub>	MAO	Galvinoxyl	40	41	131	4.2	5.4	30.6	63.9
7	AIBN		Galvinoxyl	60	N.R.					
8	AIBN			60	77	73	1.9	5.3	34.4	60.4
9	AIBN			70	77	62	1.5	7.0	34.5	58.2
10	AIBN			80	81	32	1.5	6.3	36.4	57.3
11	AIBN	MAO		60	72	114	1.3	4.9	33.9	61.2
12	Cu(OAc) <sub>2</sub>	MAO		60	25	170	3.9	5.9	37.9	56.2

<sup>a</sup> Conditions: Either AIBN (0.030 mmol) or Cu compound (0.022 mmol); PhCl, 5 mL; MMA, 0.01 mol; 21 h in dry box.

<sup>b</sup> 80 mg of 30% MAO solution (0.42 mmol).

<sup>c</sup> 1 equiv. galvinoxyl.

<sup>d</sup> Determined by GPC against polystyrene standards using refractive index detector.

<sup>e</sup> Calculated from <sup>1</sup>H NMR integration of  $\alpha$ -methyl resonances.

In order to examine whether free radicals were involved in the polymerization process, 1 equiv. of galvinoxyl per Cu was added to the reaction mixture. As shown in Table 2, a similar yield of PMMA was obtained. In contrast, an equivalent amount of galvinoxyl totally quenched the polymerization activity of AIBN. The above results with galvinoxyl posed a dilemma. The polymerization profile, specifically the failure to homopolymerize unactivated alkenes (e.g., ethene or 1-alkenes) or to incorporate them in significant amounts in copolymerizations, clearly suggested a radical mechanism. In contrast, the strongest (and the most widely accepted) evidence against a radical mechanism was the failure to stop or slow the MMA homopolymerization by adding galvinoxyl. However, we observed the disappearance, at ambient temperature, of the EPR signal of galvinoxyl when a solution of it in chlorobenzene was added to a solution prepared by dissolving Cu(DMOX)Cl<sub>2</sub> and MMA in chlorobenzene followed by the addition of a MAO solution. In order to probe the generality of the deactivation of galvinoxyl by the combination of a metal species and MAO, Cu(OAc)<sub>2</sub>, Ni(acac)<sub>2</sub>, Co(acac)<sub>2</sub>, and Fe(OAc)<sub>2</sub> were also employed under similar reaction conditions. In every case the EPR signal of galvinoxyl disappeared and polymer (PMMA) formation was observed.

The above experiments led us to suspect that MAO was responsible for the deactivation of galvinoxyl through reduction. Indeed, EPR experiments demonstrated that the radical signal of galvinoxyl, as well as two other commonly employed radical traps DPPH and TEMPO, disappeared upon the addition of excess MAO. Additionally, we observed that AIBN-initiated homopolymerization of MMA was completely halted when any one of the above radical traps was added but polymer was obtained when MAO was also present in the reaction mixture (Table 2).

Finally, in order to ascertain the fate of galvinoxyl in its reaction with MAO, galvinoxyl was mixed with excess MAO in chlorobenzene. After stirring at ambient temperature, the mixture was added to an excess of aq. HCl, and the resultant diamagnetic organic product was isolated. Mass spectral analysis suggested a phenol derived from galvinoxyl, formed by the reduction of the latter to the anion by MAO, a strong reducing agent.

It is clear from the above experiments that radical traps may fail to intercept even radical reactions that proceed in the presence of MAO. Clearly, it is necessary to rely on several independent lines of evidence before coming to a firm mechanistic conclusion. For example, the formation of copolymers whose compositions vary significantly from that predicted from the radical reactivity ratios must be demonstrated before a nonradical mechanism can be invoked.

## 6. Steric and electronic effects

Returning to the issue of catalyst poisoning by polar monomers, one possible way to prevent the coordination of the oxygen functionality of the acrylate to the metal center (see Scheme 1) is by decreasing electrophilicity of the metal center, i.e. by moving from a cationic to a neutral metal species. What about the coordination of the monomer itself? Significant incorporation of acrylate units in the polymer requires that the acrylate monomer compete effectively with alkenes for coordination to the metal (*the actual insertion of acrylate into a late transition metal-carbon bond proceeds faster than the corresponding insertion of ethene and 1-alkenes*) [11,26]. In a recent theory paper, Ziegler has shown that the interaction of the ester group of acrylate with the metal center is weaker in neutral complexes when compared with the corresponding cationic species [27]. On the other hand, the bonding of the vinylic

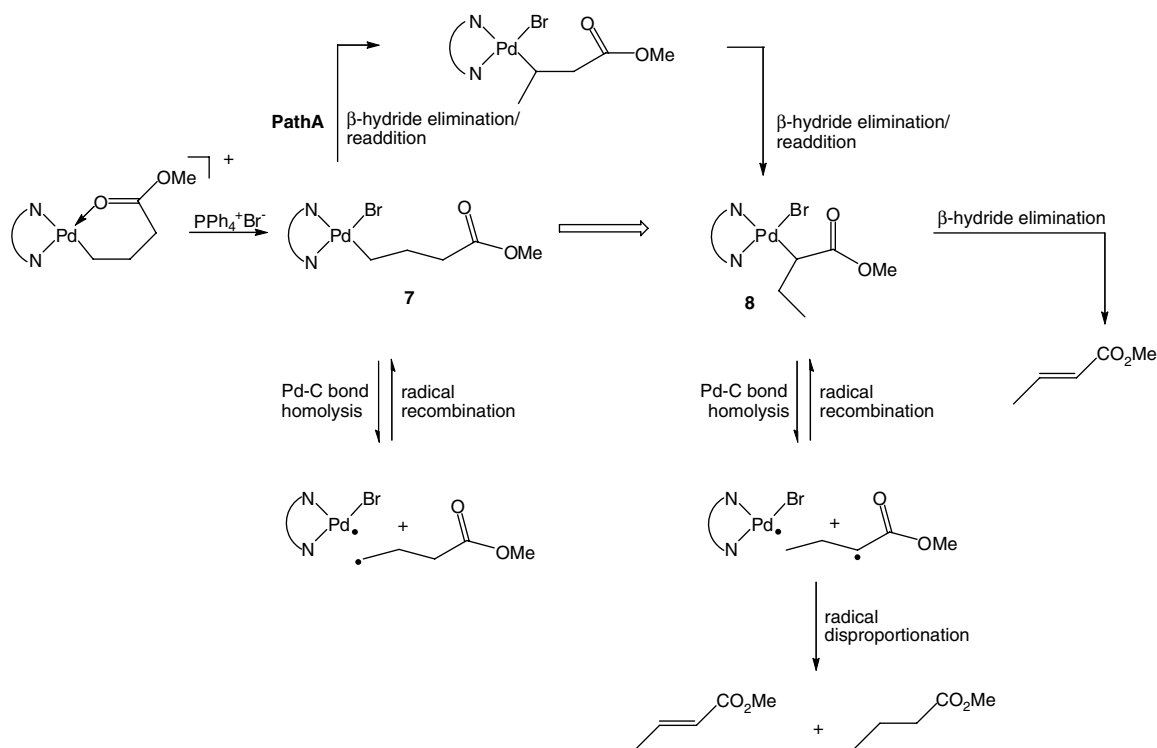
functionality is not significantly affected because the weaker alkene to metal charge transfer in the neutral complex is compensated by stronger metal to alkene back-bonding. Grubbs and we have recently reported on neutral nickel-based polymerization systems that tolerate functionalities present on norbornene monomers [28]. However, they are ineffective for acrylates, presumably because the coordination of the ester group is stronger with “harder” nickel(II) than palladium(II) [27].

Unfortunately, as discussed below, increasing the electron density on the metal center by moving from a cationic to a neutral species makes the corresponding metal–carbon bond *more* prone to homolysis. One of the very few systems that copolymerize acrylates through an insertion mechanism is by Brookhart and involves cationic Pd(II)-based complexes of the general type,  $[(\tilde{N}N)Pd(Me)(L)][B(Ar_f)_4]$  ( $(\tilde{N}N) = 2,3$ -bis(2,6-di-isopropylphenylimino)butane,  $Ar_f = 3,5$ -( $CF_3$ ) $_2C_6H_3$ ,  $L = Et_2O$ ) [11]. This system is able to incorporate up to 15 mol% acrylate in copolymerizations with ethene and 1-alkenes. A novel feature of this system is the rearrangement that follows acrylate insertion resulting in the removal of the ester functionality from the  $\alpha$  position to the metal, eventually forming a six-membered chelate (Scheme 1). This unique feature of the system prompted us to examine the stability of the complex upon opening of the six-membered chelate by forming a neutral species [17a].

When 1 equiv. of tetraphenylphosphonium bromide was added to the cationic six-membered chelate shown in Scheme 1, a complete and rapid conversion to **7** was

observed (Scheme 5). Compound **7** is not stable at room temperature and rearranges to **8** within minutes. The driving force for this rearrangement is presumably the same as that for the 2,1-insertion of acrylates into Pd–C bonds; in the cationic Brookhart system the isomerization proceeds in the opposite direction because of the enhanced stability of the six-membered chelate over the smaller chelate rings. Finally, **8** was found to decompose on further standing at room temperature to yield methyl crotonate (68% overall yield), together with methyl butyrate (6% overall yield) and a trace amount of the diester, dimethyl suberate. While the transformations, **7**–**8** and **8** to methyl crotonate, can be explained by invoking the usual  $\beta$ -hydrogen abstraction/readdition mechanism, the formation of methyl butyrate suggested the possibility that the methyl butyrate and at least some of the methyl crotonate arose through Pd–carbon bond homolysis in **8** followed by the well-known disproportionation of the resultant radical. Likewise, the fragmentation of the palladium–alkyl bond in **7** followed by radical–radical combination would lead to the formation of dimethyl suberate. Further support for the intermediate formation of radicals came from the observation that when the bromide salt was added to the initial cationic six-membered chelate in the presence of excess methyl acrylate (MA), the homopolymerization of MA ensued.

To provide more convincing evidence for the presence of radicals, one equivalent of  $CBr_4$  was added to initial cationic six-membered chelate and  $PPh_4^+Br^-$ . After several hours, the reaction mixture contained methyl 2-bromobutyrate (20% overall yield), the trapped product from



Scheme 5. Proposed reaction pathways following disruption of the six-membered chelate [17a].

homolytic cleavage of the palladium–alkyl bond in **8**. A second species, methyl 4-bromobutyrate, was also observed in a much greater concentration (38% overall yield).

There is a possibility that the observed alkyl bromides arise, not from radical trapping with  $\text{CBr}_4$ , but through reductive elimination from the corresponding  $\text{Pd}(\text{alkyl})(\text{Br})$  species, **7** and **8**. To further clarify the origin of the alkyl bromides,  $\text{NEt}_4^+\text{Cl}^-$  was used to disrupt the chelate and  $\text{CBr}_4$  was used as the radical trapping agent. In this case, alkyl radicals trapped by  $\text{CBr}_4$  would generate bromides while reductive elimination would lead to the formation of chlorides. Only alkyl bromides were observed, the yields being similar to those observed previously. As a final control experiment, we verified that  $\text{CBr}_4$  by itself did not react with initial cationic six-membered chelate. Our observations clearly suggest that the palladium–alkyl species present in the system readily undergo bond homolysis to generate alkyl radicals.

The results are most consistent with the pathways shown in Scheme 5 [17a]. The rearrangement of **7**–**8** appears to proceed via the traditional  $\beta$ -hydrogen elimination/readdition pathway (path A). On the other hand, both **7** and **8** appear to readily undergo (reversible) Pd–C bond homolysis and the resultant radicals get trapped as bromides in the presence of  $\text{CBr}_4$ . Methyl crotonate can form via either radical disproportionation or  $\beta$ -hydrogen elimination whereas methyl butyrate can only arise by radical disproportionation. Consequently, the low observed ratio of methyl butyrate to methyl crotonate suggests that Pd–C bond homolysis is reversible and that the predominant route to methyl crotonate is by traditional  $\beta$ -hydrogen abstraction from **8** rather than Pd–C bond homolysis. Nevertheless, sufficient alkyl radicals can and do escape the solvent cage and are capable of initiating traditional radical polymerization of polar vinyl monomers. This possibility needs to be taken into account before mechanistic claims can be made with respect to metal-mediated polymerization of these monomers.

In conclusion, our findings illustrate the propensity of late transition metal–alkyl species to undergo M–C bond homolysis. In the present instance, the blocking of one of the coordination sites on palladium by the halide ligand, a possible strategy to prevent coordination of the acrylate ester group, favors this pathway. Thus, simply preventing the coordination of the functionality present on the polar vinyl monomer may not necessarily result in a viable system for insertion polymerization. Indeed, it appears that the success of the Brookhart system in copolymerizing acrylates is due to stable six-membered chelate formation following acrylate insertion; when the chelate is forced to open by forming a neutral halide-coordinated complex, homolysis of the Pd–C bond is observed. The price paid for chelate formation in the Brookhart system is slow polymerization and the placement of the functionality predominantly at the branch ends.

One possible solution to the issues discussed above is to impose steric crowding at the metal center by the use of

bulky ligands. The crowding of the metal center is likely to produce two beneficial effects. First, the binding of the ester functionality will be prevented or decreased. In addition, with sufficient steric crowding, it may be possible to override the electronic preference for 2,1-insertion of acrylates, resulting in less sterically demanding 1,2-insertion. The ensuing alkyl will no longer have an ester functionality on the  $\alpha$ -carbon, making it (a) more nucleophilic, thereby facilitating the next insertion step, and (b) less prone to undergo metal–carbon bond homolysis due to lower stability of the resultant radical. Another huge potential bonus of tuning the catalysts to undergo 1,2-insertion of acrylate monomers is to be found in the case of methyl methacrylate. When MMA inserts in a 2,1 fashion the ensuing alkyl bears both an ester functionality and a methyl group on the  $\alpha$ -carbon resulting in extreme steric congestion. This greatly disfavors further monomer insertion (chain growth) but offers five  $\beta$ -hydrogens resulting in facile elimination of the growing polymer chain with an MMA-derived end group (see Fig. 2) [17b,29,30]. On the other hand, incorporation of MMA in a 1,2 fashion would make it a good comonomer for copolymerization with ethene and 1-alkenes: the ensuing alkyl would have no substituents on the  $\alpha$ -carbon and would contain *no*  $\beta$ -hydrogens.

Our optimism with regard to the switch in regioselectivity of acrylate insertion is supported by recent calculations by Ziegler of barriers for the 1,2- and 2,1-insertion of methyl acrylate into the Pd–carbon bond in Brookhart-type diimine complexes [16]. The results clearly show that for sterically unencumbered catalyst the 2,1-insertion is strongly preferred: the transition state for the 2,1-insertion has a lower energy by 4.5 kcal/mol than the corresponding 1,2-insertion transition state structure. For the “real” system with bulky ligands, the 2,1-insertion barrier is lower by only 0.5 kcal/mol compared to 1,2-insertion. It should be noted that for sterically unencumbered catalyst, a similar preference for the 2,1-insertion path has been found for propene with a much smaller energy difference (2 kcal/mol)

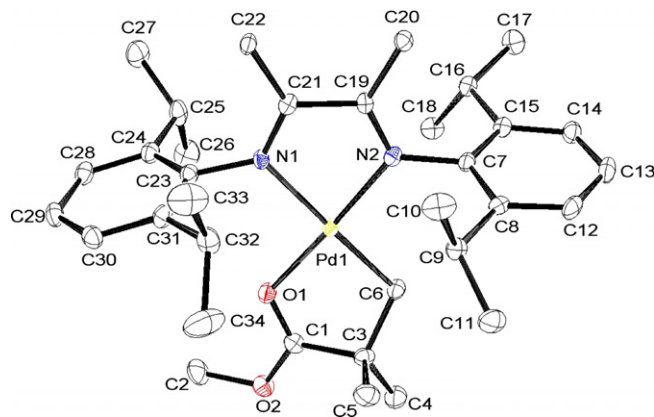


Fig. 3. X-ray crystal structure of product formed by 1,2-insertion of methyl methacrylate into the Pd–Me bond in  $[(2,3\text{-bis}(2,6\text{-diisopropylphenylimino)butane})\text{Pd}(\text{Me})(\text{Et}_2\text{O})][\text{B}(\text{Ar}'_f)_4]$ . The hydrogens and  $[\text{B}(\text{Ar}'_f)_4]$  are omitted for clarity.



between the two transition states; in the “real” systems, this preference becomes *inverted*: the 1,2-propene insertion barrier is lower by ca. 0.5 kcal/mol compared to 2,1-insertion. As in the case of propene, in the “real” systems the 2,1-acrylate insertion transition state is destabilized due to the steric repulsion between the bulky substituents on the ligand and the alkene substituent. The 1,2-insertion transition state is practically not affected by the steric effects. As a result, the insertion preference is decreased and may actually reverse with appropriately bulky ligands.

In line with the above analysis, we have very recently observed that methyl methacrylate undergoes *1,2-insertion* into the Pd–Me bond in the Brookhart system (see Fig. 3) [31], a regioselectivity that is the reverse of that observed by Brookhart for the less sterically encumbered methyl acrylate. Unfortunately, this does not lead to facile catalysis of MMA/alkene copolymerizations since the methacrylate insertion rate is too slow to compete with the insertion of alkenes.

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