Palladium-Based System for the Polymerization of Acrylates. Scope and Mechanism

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The neutral palladium complex $[Pd(C_6F_5)Br(NCMe)_2]$ (**1**) was found to effect the polymerization of acrylates upon addition of 1 equiv of a monodentate phosphine or pyridine or an excess of halide. Methyl methacrylate was not polymerized, and furthermore, its addition stopped 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 polymerizaion mechanism is discussed.

Introduction

Since the advent of Ziegler−Natta catalysts nearly 40 years ago, innumerable transition-metal complexes have been developed for the successful polymerization of simple alkenes through a mechanism involving successive insertions of the monomer into a preformed metal−carbon bond.[1,2] However, very few of the currently known transition-metal-based insertion polymerization systems tolerate the presence of heteroatoms in the monomer, and none have been able to homopolymerize alkenes bearing oxygen functionalities directly adjacent to the C=C bond, such as acrylates.[3] As a result, the nearly 2 000 000 000 lb of methacrylic and acrylic ester based polymers manufactured each year are exclusively produced by radical and anionic routes.[4] The group-transfer polymerization of acrylates and polymerization through an enolate mechanism by early-transition-metal and lanthanide complexes are also known.[4b,5]

In 1975, Yamamoto reported the polymerization of methyl acrylate by a ruthenium compound.[6] On the basis of monomer reactivity ratios observed in copolymerization reactions, an insertion mechanism was inferred. More recently, Brookhart and Drent have reported the catalytic copolymerization of ethene and acrylates with cationic palladium compounds where an insertion mechanism is operative.[7] However, a maximum incorporation of ∼15% methyl acrylate in the copolymer was achieved. Grubbs has also reported a somewhat related system based on neutral nickel compounds that is able to polymerize functionalized alkenes.[8] However, this system is ineffective for acrylates.

We have presented a preliminary report on the activity of palladium−pentafluorophenyl-based systems for the polymerization of acrylates and have been studying their mechanism and scope.[9] Very recently, Novak has also reported on acrylate polymerization by palladium compounds where a radical mechanism was invoked.[10] Prompted in part by the Novak report, we

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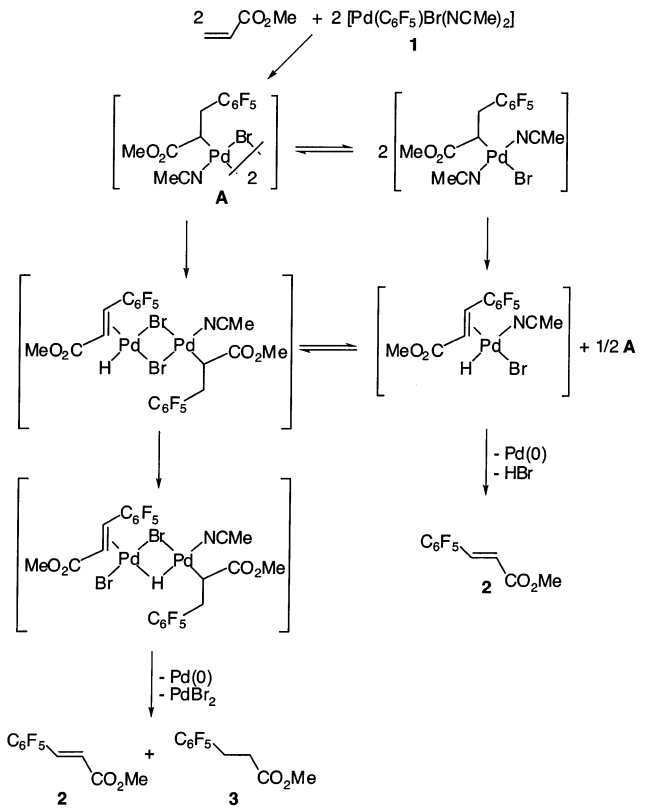
Scheme 1



describe herein details of our palladium-based systems which polymerize acrylates and present some rather intriguing features.

Results and Discussion

A. Single-Insertion Reactions. The addition of 1 equiv of methyl acrylate to the known palladium(II) compound $[Pd(C_6F_5)Br(NCMe)_2]$ (**1**)[11] resulted in the formation of two products, $CH(CO_2Me)=CHC_6F_5$ (**2**) and $CH_2(CO_2Me)CH_2C_6F_5$ (**3**), in an approximately 2:1 ratio. Additionally, the precipitation of metallic palladium was observed. The overall mechanism is outlined in Scheme 1. In solution **1** exists in equilibrium with the dimer $[Pd_2(\mu\text{-}Br)_2(C_6F_5)_2(NCMe)_2]$ plus free MeCN.[11] The alkene **2** is then formed by insertion of the monomer into the $Pd-C_6F_5$ bond followed by subsequent β-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.[12] 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.

The reaction of methyl methacrylate with **1** proceeded in an analogous manner, forming a 1:1 mixture of the unsaturated and saturated products $CH_2=C(CO_2Me)$-$CH_2C_6F_5$ (**4**) and $MeCH(CO_2Me)CH_2C_6F_5$ (**5**). Note that the β-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 *β-hydrogen abstraction from the CH_3 group in the inserted methyl methacrylate is much faster than that from the $CH_2C_6F_5$ group in either inserted acrylate or methacrylate.* Indeed, in the reaction with methyl methacrylate, the possible competing β-hydrogen abstraction product $MeC(CO_2Me)=CHC_6F_5$ was not observed by NMR, which suggests that the rates of β-hydrogen elimination from the two possible sites differ by at least 2 orders of magnitude, in favor of CH_3 (Chart 1).

Chart 1. Relative Rates of β-Hydrogen Abstraction in the Insertion Product of Methyl Methacrylate

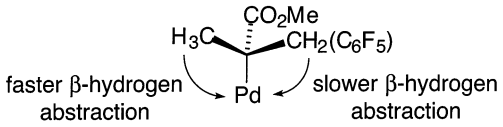


Table 1. Polymerization of Methyl Acrylate (MA) with $[Pd(C_6F_5)Br(NCMe)_2]$ (1) + Ligand[a]

amt of **1** (mmol)	ligand	solvent	amt of MA (mmol)	poly(MA) (% yield)	M_w[b]	M_w/M_n[b]
0.012			41.0	trace		
0.012	PPh_3		51.5	63.0	8.4×10^5	2.4
0.014	PPh_3	$CHCl_3$	24.7	74.3	1.5×10^6	3.9
0.012	PPh_3	PhCl	23.9	91.4	1.2×10^6	1.9
0.005[c]	PPh_3	Me_2CO	11.1	78	3.4×10^5	6.8
0.025	PMe_3[d]	$CHCl_3$	12.4	41.1	7.5×10^5	1.5
0.021	pyridine	$CHCl_3$	14.3	64.2	7.4×10^5	1.7

[a] Conditions: 1 equiv of ligand per palladium; solvent, 4 mL; ambient temperature. [b] Determined by SEC relative to polystyrene standards. [c] Conditions: solvent, 2 mL. [d] As a 1 M solution in THF.

B. Polymerization in the Presence of Phosphine or Pyridine. 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. Table 1 shows selected polymerization results for methyl acrylate. It must be noted that, as the polymerizations proceeded, the reaction mixtures became extremely viscous and stirring was completely halted. Consequently, mass transfer problems may be one factor that limits monomer conversion (and increases polydispersity). The best yields were observed with 1 equiv of PPh_3 or pyridine. The use of PMe_3 and $AsPh_3$ resulted in decreased yields, as well as some catalyst decomposition. The very bulky phosphines P^tBu_3 and P^tBu_2(biphenyl) led to decomposition to metallic palladium and no polymer formation. The addition of 2 equiv of ligand per palladium resulted in the formation of a stable inactive complex, *trans*-

(11) Albéniz, A. C.; Espinet, P.; Foces-Foces, C.; Cano, F. H. *Organometallics* **1990**, *9*, 1079−1085. ^{19}F NMR (282 MHz, $CDCl_3$, 293 K): δ −164.5 (m, $2F_{meta}$), −160.5 (t, $1F_{para}$), −121.0 (m, $2F_{ortho}$).

(12) Albéniz, A. C.; Espinet, P.; Lin, Y.-S. *Organometallics* **1997**, *16*, 4030−4032.

$[Pd(C_6F_5)Br(PPh_3)_2]$.[13] As shown in Table 1, the polymerization of methyl acrylate can proceed in a variety of solvents and without solvent.

Preliminary investigations into the active species resulted in some interesting observations. In a stoichiometric experiment the addition of 1 equiv of PPh_3 to **1** was followed by ^{19}F and ^{31}P NMR spectroscopy. Upon initial addition of PPh_3 to **1** in $CDCl_3$ several species were observed in solution, including **1**, the inactive bis(phosphine) complex *trans*-$[Pd(C_6F_5)Br(PPh_3)_2]$, and the dimer $[Pd_2(\mu\text{-}Br)_2(C_6F_5)_2(PPh_3)_2]$ (**6**) (eq 1). Over time the only $Pd(C_6F_5)$ species in solution was the dimer **6**.

$$[Pd(C_6F_5)Br(NCMe)_2] \xrightarrow[-CH_3CN]{PPh_3} [Pd(C_6F_5)Br(PPh_3)_2] + [Pd_2(\mu\text{-}Br)_2(C_6F_5)_2(PPh_3)_2] \quad (1)$$

Very interestingly, the isolated dimer did not catalyze the polymerization of acrylates, and no insertion of acrylate into the $Pd-C_6F_5$ bond was *observed*. However, as stated above, the formation of polymer did take place when methyl acrylate and 1 equiv of PPh_3 were simultaneously added to **1**. At the same time, the ^{19}F NMR spectrum of the reaction mixture revealed that insertion of the monomer into the $Pd-C_6F_5$ bond had occurred, as evidenced by the typical shift of the ortho fluorines of the C_6F_5 group (a C_6F_5 group attached to Pd shows a chemical shift of approximately -118 ppm for the ortho fluorines,[11,13] compared to approximately -140 ppm for the ortho fluorines for a C_6F_5 fragment bonded to carbon;[11,12] thus, the large shift of the ortho fluorine resonances in the ^{19}F NMR spectra is a simple indicator of monomer insertion into the $Pd-C_6F_5$ bond). ^{19}F and ^{31}P NMR monitoring of a solution in which polymerization was occurring revealed the presence of the inactive dimer **6**, whose concentration increased with time at the early stages of the reaction. This means that part of the catalyst was being lost by transformation into the inactive dimer. Also present were **1**, the inactive bis(phosphine) complex *trans*-$[Pd(C_6F_5)Br(PPh_3)_2]$, and other unidentified species. It is clear from these experiments that the active species is formed through the reaction of **1** with 1 equiv of PPh_3 in the presence of methyl acrylate, but it is *not* the dimer **6**. This strongly suggests that the polymerization must begin with the species $[Pd(C_6F_5)Br(PPh_3)(L)]$ (L = MeCN, methyl acrylate) before it converts to the inactive dimer **6**. Obviously, the concentration of the active species must be significantly lower than the concentration of **1** initially added to the reaction mixture.

Apart from methyl acrylate, other acrylates that were either homopolymerized or copolymerized with methyl acrylate were ethyl and *n*-butyl acrylate. Interestingly, methyl methacrylate was not homopolymerized (see below).

The addition of ethene to the methyl acrylate polymerization system completely inhibited the formation of poly(methyl acrylate). The formation of $C_6F_5CH{=}CH_2$ was observed instead, suggesting the preferential insertion of ethene into the $Pd-C_6F_5$ bond followed by β-hydrogen abstraction. The identity of $C_6F_5CH{=}CH_2$ was confirmed by its formation when ethene was added to a mixture of **1** and 1 equiv of PPh_3 and by comparison with a commercial sample. Because of sterics, 1-hexene would be expected to insert more slowly than ethene into the $Pd-C_6F_5$ bond. Accordingly, the polymerization of methyl acrylate was carried out in the presence of varying amounts of 1-hexene. As shown in Table 2, there was a decrease in the yield and molecular weight of the polymer obtained with increasing amounts of added 1-hexene. ^1H and ^{13}C NMR spectra of the polymers revealed up to 10% incorporation of 1-hexene. No polymer was obtained if a large excess of 1-hexene was employed.

Table 2. Effect of Added 1-Hexene on the Polymerization of Methyl Acrylate[a]

amt of 1-hexene (mmol)	amt of MA (mmol)	amt of polymer (g)	amt of 1-hexene incorporated (mol %)[b]	M_w[c]	M_w/M_n[c]
0.6	22.7	1.48	trace	13.6×10^5	5.3
2.5	21.0	1.00	0.3	7.7×10^5	2.5
6.7	16.8	0.42	3.8	2.4×10^5	3.8
13.3[d]	10.0	0.16	9.4	1.8×10^5	2.0

[a] Conditions: $[Pd(C_6F_5)Br(NCMe)_2]$, 0.009 mmol; 1 equiv of PPh_3; PhCl, 4 mL; total monomer (methyl acrylate + 1-hexene), 2 g; ambient temperature. [b] Determined by integration of ^1H NMR. [c] Determined by SEC relative to polystyrene standards. [d] Conditions: $[Pd(C_6F_5)Br(NCMe)_2]$, 0.011 mmol.

The experiments described above involving methyl acrylate and 1-hexene suggest that rapid chain termination (or transfer) occurs via β-hydrogen abstraction upon the addition of these monomers to the growing polymer chain. Support for the importance of β-hydrogen abstraction comes from the following set of experiments. A dichloromethane solution containing **1** (0.025 mmol), PPh_3, and methyl acrylate (molar ratio 1:1:2000) was separated into three equal samples. After 25 min the samples were treated as follows. Sample 1 was quenched by adding it to a large excess of methanol, resulting in the precipitation of 0.15 g of polymer. Methyl methacrylate (635 molar equiv) was added to sample 2 and the reaction was allowed to continue for 17 h; at the end of this time, quenching with methanol gave 0.29 g of copolymer (methyl acrylate:methyl methacrylate ratio in polymer 1:3). For sample 3, a volume of dichloromethane equal to the volume of methyl methacrylate used in sample 2 was added to avoid a concentration change; quenching after 17 h yielded 1.27 g of polymer. The above experiment indicates that the addition of methyl methacrylate produces only a small amount of the copolymer and inhibits further polymerization of methyl acrylate even after it has been initiated. This reactivity pattern is inconsistent with a *classical* radical polymerization pathway but consistent with a termination step initiated by fast β-H abstraction from an alkyl chain which is linked to Pd by the last inserted methyl methacrylate moiety, followed by decomposition of the resulting hydride complex.

C. Polymerization in the Presence of Excess Halide. The addition of an excess of halide to **1** also resulted in a system capable of polymerizing acrylates. Some of the results are summarized in Table 3. The efficacy of added halide was found to decrease in the order $Br^- > Cl^- > I^-$. On the other hand, the addition

(13) Usón, R.; Forniés, J.; Nalda, J. A.; Lozano, M. J.; Espinet, P. Albéniz, A. C. *Inorg. Chim. Acta* **1989**, *156*, 251−256. ^{19}F NMR (282 MHz, $CDCl_3$, 293 K): δ −162.9 (m, $2F_{meta}$), −162.8 (t, $1F_{para}$), −117.7(m, $2F_{ortho}$). ^{31}P NMR (121.4 MHz, $CDCl_3$, 293 K): δ 24.6.

Table 3. Homopolymerization of Methyl Acrylate in the Presence of Added Halide Ligand[a]

amt of **1** (mmol)	halide	solvent	amt of MA (mmol)	poly(MA) (%)	M_w[b]	M_w/M_n[b]
0.012			41.0	trace		
0.0092	NBu_4Cl		44.4	trace		
0.0069	NBu_4Cl	PhCl	23.3	53.0	8.5×10^5	5.3
0.0075	NBu_4Br	PhCl	23.2	75.0	3.7×10^5	3.4
0.0073	NBu_4I	PhCl	23.3	31.6	14.5×10^5	9.7
0.011	NH_4BPh_4	PhCl	23.6	trace		
0.0069	NBu_4BF_4	PhCl	23.5	trace		
0.0092	NBu_4Cl	acetone	22.2	trace		

[a] Conditions: 10 equiv of ligand/Pd; solvent, 4 mL; 24 h; room temperature. [b] Determined by SEC relative to poly(styrene) standards.

Table 4. Effect of Reaction Time on the Polymerization of Methyl Acrylate (MA)[a]

reacn time (h)	amt of MA (mmol)	poly(MA) (%)	M_w[b]	M_w/M_n[b]
0.17	23.3	4.0	10.6×10^5	3.2
1	23.3	11.1	8.0×10^5	4.2
4	23.2	24.4	7.0×10^5	3.9
12	23.2	71.0	4.7×10^5	2.6

[a] Conditions: $Pd(C_6F_5)Br(NCCH_3)_2$, 0.007 mmol; NBu_4Br, 10 equiv/Pd; PhCl, 4 mL; room temperature. [b] Determined by SEC relative to poly(styrene) standards.

Table 5. Effect of Monomer Feed Ratio on the Polymerization of Methyl Acrylate (MA) and Methyl Methacrylate (MMA)[a]

amt of MA (mmol)	amt of MMA (mmol)	amt of polymer (g)	polymer composition (MA:MMA)[b]	M_w[c]	M_w/M_n[c]
15.7	6.5	0.66	1:0.8	8.4×10^5	8.6
11.2	10.4	0.48	1:1.9	7.0×10^5	7.8
7.9	13.0	0.35	1:3.7	4.7×10^5	4.8
12.3[d]	11.3				

[a] Conditions: $Pd(C_6F_5)Br(NCCH_3)_2$, 0.0092 mmol; NBu_4I, 10 equiv/Pd; PhCl, 4 mL; total monomer (MA and MMA), 2.0 g; 25 h, room temperature. [b] Determined by integration of ^1H NMR. [c] Determined by SEC relative to poly(styrene) standards. [d] Conditions: $Pd(C_6F_5)Br(NCCH_3)_2$, 0.014 mmol; PPh_3, 1 equiv/Pd; 17 h.

of noncoordinating anions such as ammonium tetraphenylborate (NH_4BPh_4) and tetrabutylammonium tetrafluoroborate (NBu_4BF_4) resulted in catalyst decomposition and no polymer formation. This suggests that (a) a coordinating anion is required and (b) the ammonium cation has no effect on the system. By using varying amounts of NBu_4Br, it was determined that the optimal polymerization yield was obtained when 10 equiv of Br^- was added. Table 4 shows selected data for the polymerization of methyl acrylate in the presence of 10 equiv of NBu_4Br per palladium for reaction times varying from 10 min to 12 h. While higher yields of poly(methyl acrylate) were achieved as the reaction time was increased, the polymer molecular weight remained relatively unchanged.

While the homopolymerization of methyl methacrylate in the presence of halide afforded very low yields of polymer (<10%), the copolymerization with methyl acrylate was more successful. The composition of the methyl acrylate−methyl methacrylate copolymers was controlled by varying the monomer feed ratio, as presented in Table 5. As the ratio of methyl acrylate to methyl methacrylate in the feed decreased (Table 5, entries 1−3), the incorporation of methyl methacrylate into the polymer increased, as determined by ^1H NMR integration. At the same time, there was a drop in the molecular weight and, especially, the yield of the polymer, reminiscent of the copolymerization reactions of 1-hexene.

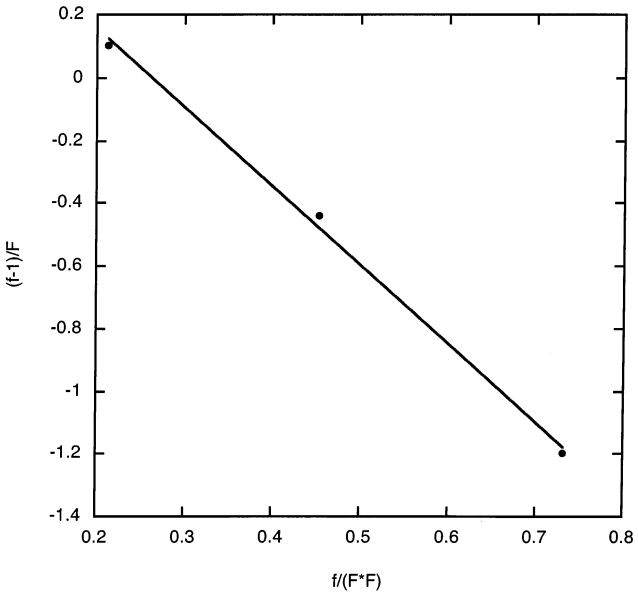


Figure 1. Plot of $(f - 1)/F$ vs f/F^2 for the copolymerization of methyl acrylate and methyl methacrylate ($F = M_1/M_2$, $f = m_1/m_2$, M = monomer composition, m = polymer composition, r_1 and r_2 = reactivity ratios for monomers 1 and 2, respectively).

The polymers formed in the copolymerization of methyl acrylate and methyl methacrylate were analyzed by size exclusion chromatography (SEC) and NMR spectroscopy. SEC showed unimodal distributions, suggesting that the formed polymers are copolymers and not mixtures of homopolymers. The random nature of the copolymers formed was verified by ^1H and ^{13}C NMR spectroscopy. The NMR investigation was aided by synthesizing copolymers using methyl methacrylate-d_8.

The data from Table 5 were used to determine the reactivity ratio of the two monomers by the Fineman−Ross method[14] (see Figure 1) and yielded the following values: $r(MA) = 0.66$, $r(MMA) = 2.53$. These are in good agreement with those reported in the literature for radical copolymerization of the two monomers.[15]

The copolymerization of methyl acrylate with 1-hexene in the presence of halide was also studied. These reactions afforded copolymers with a maximum of 13% 1-hexene incorporated into the polymer, as determined by integration of the ^1H NMR spectra. Like the copolymerizations carried out in the presence of 1 equiv of phosphine, as the amount of added 1-hexene in the monomer feed increased, the incorporation of 1-hexene into the polymer increased while the copolymer yield and molecular weight decreased. SEC analysis showed unimodal distributions, implying the formation of copolymers. NMR spectroscopy showed the random nature of the copolymers. Figure 2 shows a ^{13}C NMR spectrum of a methyl acrylate−hexene copolymer with resonances at 175.1 (−*C*(O)O), 52.1 (−O*C*H_3), 41.5 (−*C*H−), and

(14) Fineman, M.; Ross, S. D. *J. Polym. Sci.* **1950**, *5*, 256.
(15) Greenley, R. Z. In *Polymer Handbook*; Brandrup, J., Immergut, E. H., Grulke, E. A., Eds.; Wiley: New York, 1999; p II/181.

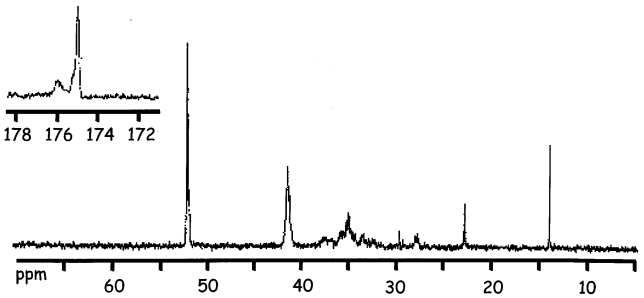


Figure 2. ^{13}C NMR spectrum of a copolymer of methyl acrylate and 1-hexene in $CDCl_3$.

35.0 ppm ($-CH_2-$) resulting from consecutive methyl acrylate units. In addition, peaks at 175.9, 37.5−32.4, 27.9, 23.0, and 14.2 ppm were observed for the methyl acrylate−hexene sequence. The absence of a resonance at 43.4 ppm implies that consecutive hexene units such as HHH, HHA, and HAH, where H = 1-hexene and A = methyl acrylate, are not present.

D. Mechanistic Studies. The three possible mechanisms for the palladium-mediated polymerization of acrylates are anionic, radical, and insertion. The first can be discounted on the basis of the fact that the addition of the anionic polymerization terminating agent methanol (139 equiv per palladium) had no effect on either the yield or the molecular weight of the poly(methyl acrylate) formed.

Distinguishing between the other two mechanisms is, however, more difficult and the mechanistic results that we have obtained display facets that can fit either mechanism. For example, the observation under stoichiometric conditions of products derived from the insertion of the monomer into the $Pd-C_6F_5$ bond and the decrease in polymer molecular weight upon the addition of 1-hexene are consistent with the initiation and termination steps, respectively, of an insertion mechanism. Other observations not fitting into a classical radical mechanism are as follows. Neither styrene nor methyl methacrylate, which readily undergo free radical or metal based ATRP polymerization,[16] were efficiently polymerized by either the phosphine- or halide-based systems. Moreover, in the phosphine-based system, the polymerization of methyl acrylate was quickly halted when methyl methacrylate was added to the reaction mixture (see section B), as discussed before. This is in sharp contrast with typical radical-initiated polymerizations (e.g., by AIBN), which readily convert a mixture of methyl acrylate and methyl methacrylate to the corresponding copolymer. Indeed, the copolymer in the latter case is richer in methyl methacrylate because of its higher reactivity compared to methyl acrylate.[15]

In two parallel polymerizations of methyl acrylate, one initiated by AIBN and the other catalyzed by 1 + PPh_3, the radical $^{\bullet}CH(CO_2Me)CH_2R$[17] could be detected by ESR in the first (Figure 3) but not in the second experiment.

On the other hand, observations that may be more consistent with a radical mechanism are as follows.

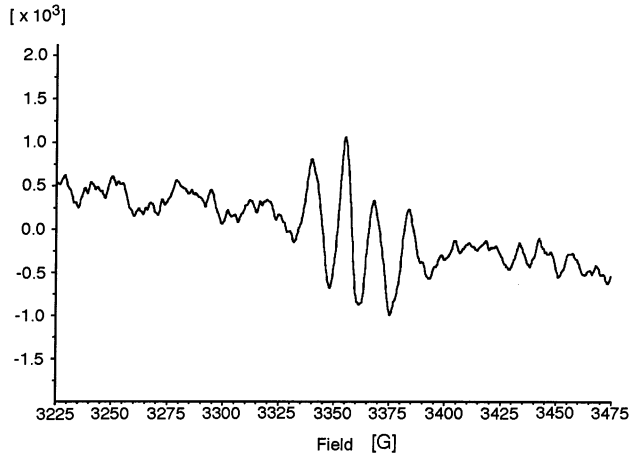


Figure 3. ESR spectrum, at 70 °C, of the poly(methyl acrylate) radical species detected during the AIBN-initiated polymerization of methyl acrylate.

Control experiments involving the polymerization of methyl acrylate in the presence of 1-hexene using AIBN as a free radical initiator reveal the incorporation of 1-hexene in poly(methyl acrylate) at levels comparable to those observed with our systems.

The tacticity of the poly(methyl acrylate) formed by the phosphine and halide-based systems was ascertained from analysis of the methine-coupled and -decoupled ^1H NMR spectra, which provided information concerning the dyad (m, r), triad (mm, mr, rr), and tetrad (mmm, mmr + rmm, rmr) sequences (m = meso, r = racemic) in the polymer chain.[18] The observed values matched those calculated using Bernoullian statistics, suggesting an atactic polymer.[19] Furthermore, the values were also in agreement with those for a polymer made using AIBN as the initiator. Finally, the copolymer of methyl acrylate and methyl methacrylate produced by the halide-based system is richer in methyl methacrylate, in good agreement with the data reported in the literature for radical polymerization of the two monomers.[15]

Finally, 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 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.[20] More potent inhibitors are TEMPO and galvinoxyl. The addition of a few equivalents of these inhibitors to either the phosphine- or halide-based system effectively halted the polymerization.

The inhibition of polymerization by TEMPO or galvinoxyl has been widely used as a diagnostic test for radical polymerizations. Unfortunately, there is always the possibility that, because of their high reactivity, these radical scavengers can react and deactivate metal-based catalysts that effect polymerization through an insertion mechanism. To examine this possibility, we

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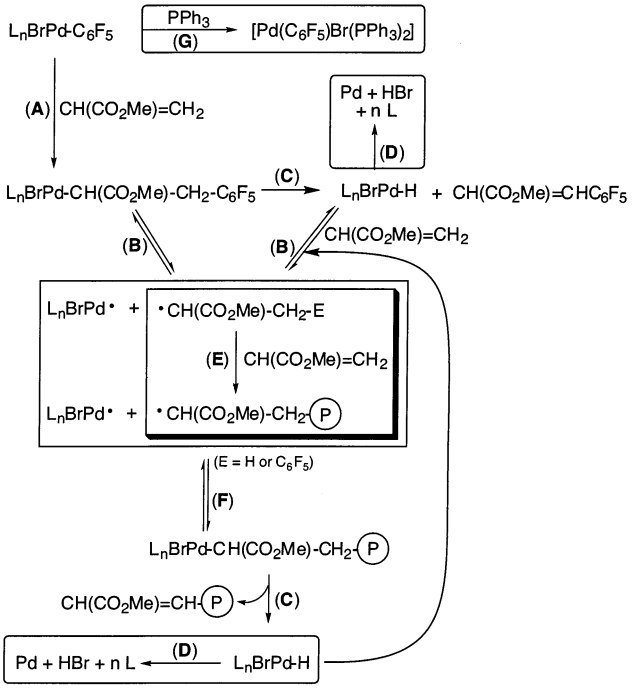
have investigated the reaction with galvinoxyl. The addition of 1 equiv of galvinoxyl to **1** in $CDCl_3$ at room temperature did not result in any discernible reaction. When the reaction was repeated in the presence of 1 equiv of methyl acrylate, the rapid formation of $CH(CO_2Me)=CHC_6F_5$ (**2**) was observed (86% yield in 30 min). Curiously, unlike the reaction of **1** with methyl acrylate in the *absence* of galvinoxyl, the simultaneous formation of $CH_2(CO_2Me)CH_2C_6F_5$ (**3**) *did not occur* (see Scheme 1). The formation of **2** was much slower (10% in 18 h) in the reaction **1** + 1 equiv of methyl acrylate + 1 equiv of galvinoxyl + 5 equiv of NBu_4Br.

Several conclusions can be drawn from these observations. First, it is clear that $Pd-C_6F_5$ bond homolysis does not occur and $C_6F_5^\bullet$ is not trapped by galvinoxyl. There are two possible ways that **2** (but *not* **3**) can be formed in the reaction **1** + 1 equiv of methyl acrylate + 1 equiv of galvinoxyl. One way is that $C_6F_5CH_2CH(CO_2Me)^\bullet$ is generated by homolysis following the insertion of acrylate into the $Pd-C_6F_5$ bond of **1** and that **2** is formed from this radical through hydrogen abstraction by galvinoxyl. The second possibility is that β-hydrogen abstraction from $Pd-CH(CO_2Me)CH_2C_6F_5$ results in the formation of **2** and Pd−H (see Scheme 1) and the galvinoxyl simply abstracts a hydrogen atom from the metal hydride, resulting in catalyst decomposition (the formation of metallic palladium is observed in the reaction). The first pathway is easily discounted for the following reason. If the $C_6F_5CH_2CH(CO_2Me)^\bullet$ radical is formed in the reaction of **1** with methyl acrylate, then polyacrylate formation should occur even in the absence of added ligand (phosphine or halide). The second possibility, the reaction of galvinoxyl with a putative Pd hydride formed by β-hydrogen abstraction from $Pd-CH(CO_2Me)CH_2C_6F_5$, finds full support in independent studies on other systems involving isolated hydrides, or in catalyzed olefin isomerization reactions, accepted to occur by an insertion/β-hydrogen abstraction mechanism.[21]

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 β-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 2. The first step involves the insertion of acrylate into the $Pd-C_6F_5$ bond (step **A**). In the absence of added ligand, this is quickly followed by β-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 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 has been observed in stable free radical polymerizations (SFRP)[22] and in cobalt-mediated radical polymerizations.[23]

Scheme 2



The actual polymerization occurs by successive addition of acrylate monomer to the alkyl radical (Scheme 2, step **E**). The growing radical chain is in equilibrium with the corresponding palladium-bound polymeric alkyl (steps **B** and **F**). Chain termination by β-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 methacrylate or 1-hexene rather than acrylate. Indeed, if methyl methacrylate is present from the outset, no polymerization occurs because of facile β-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 β-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 hydride by β-hydrogen elimination compared to methyl acrylate, and the decomposition rate of the catalyst increases.

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Phosphines and excess halide ions act as ancillary ligands in Scheme 2. Their effects are complex, as they can influence differently the rates of individual steps in the polymerization process. The presence of either class of ligands will be expected to retard the β-hydrogen elimination step (in the case of excess halide through the formation of anionic alkyl complexes, e.g. $[Pd_2(\mu\text{-}X)_2(CH(CO_2Me)CH_2Pol)_2X_2]^{2-}$).[24] However, the initial alkene insertion step will also be retarded. This is evident from the observation that the formation of **2** in the reaction **1** + 1 equiv of methyl acrylate + 1 equiv of galvinoxyl + 5 equiv of NBu_4Br is slower than in the absence of excess bromide. The phosphine provides an additional deactivation mechanism (path **G**) not observed with halide ions.

The deactivating effect of galvinoxyl or TEMPO is 2-fold. First, they react with the growing chains in the radical polymerization process. Additionally, they can react with the Pd hydride formed by β-hydrogen abstraction,[21] preventing its reentrance to initiate new chain growth. The first is presumably the faster of the two processes. In any case, it is clear that 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 hydride insertion based reactions.

Conclusion

We have discovered new palladium-based systems for the homopolymerization of acrylates and their copolymerization with simple 1-alkenes. The copolymers invariably contain much more acrylate than simple alkene. In this respect, the activity of our neutral and anionic palladium complexes is a mirror image of that provided by cationic complexes, which efficiently polymerize nonfunctionalized alkenes but not acrylates.[7] The polymerization occurs by a free radical mechanism that is tied to a β-H elimination chain termination/transfer step. Further mechanistic studies on this and related systems are in progress.

Experimental Section

General Considerations. ^1H, ^{13}C, ^{19}F, and ^{31}P NMR spectra were recorded on Bruker AC-300, PX-300, RX-400, and AMX2-500 instruments. Chemical shifts are reported in δ (ppm) downfield from Me_4Si (^1H), $CFCl_3$ (^{19}F), or H_3PO_4 (^{31}P). The spectra were recorded at 293 K. ESR spectra were recorded on a Bruker ER83CS/ER 041 X6 instrument. Size exclusion chromatography (SEC) was carried out on a Waters SEC system using a three-column bed (Styragel 7.8 × 300 mm columns: 100−10 000, 500−30 000, and 5000−6 000 000 D) and Waters 410 differential refractometer. SEC samples were run in $CHCl_3$ at room temperature and calibrated to polystyrene standards. Solvents were dried over CaH_2 and distilled and deoxygenated before use. Methyl acrylate, ethyl acrylate, butyl acrylate, methyl methacrylate, and methyl methacrylate-d_8 were purchased from Aldrich, distilled, and deoxygenated prior to use. 1-Hexene and styrene were purchased from Aldrich and deoxygenated before use. 2,2′-Azobis(isobutyronitrile) (AIBN), galvinoxyl, pyridine, TEMPO, tetrabutylammonium bromide (NBu_4Br), tetrabutylammonium chloride (NBu_4Cl), tetrabutylammonium iodide (NBu_4I), tetrabutylammonium tetrafluoroborate (NBu_4BF_4), ammonium tetraphenylborate (NH_4BPh_4), trimethyl phosphine (PMe_3), and triphenylphosphine (PPh_3) were purchased from Aldrich. *trans*-$Pd(C_6F_5)Br(CH_3CN)_2$ (**1**) was prepared according to the literature procedure.[11] Ethene was purchased from MG Industries. All the reactions described were carried out under an inert atmosphere. Polymer tacticity was determined by integration of the methine-coupled and -decoupled region in the ^1H NMR spectrum. The extent of monomer incorporation in the copolymers was determined by integration of the methoxy signals (methyl acrylate/methyl methacrylate copolymers) or methoxy/methyl signals (methyl acrylate/1-hexene copolymers) in the ^1H NMR spectra.

Reactions of 1 with Methyl Acrylate and Methyl Methacrylate. To a solution of **1** (0.0200 g, 0.046 mmol) in $CDCl_3$ (0.6 mL) was added methyl acrylate (0.004 mL, 0.046 mmol). The mixture was let stand for 2 h, and decomposition to metallic palladium was observed. It was checked by ^{19}F and ^1H NMR spectra, and a mixture of **2** and **3** (**2**:**3** = 2:1) was found.

2: ^{19}F NMR (282 MHz, $CDCl_3$, 293 K) δ −160.8 (m, $2F_{meta}$), −150.4 (t, $1F_{para}$), −138.8 (m, $2F_{ortho}$); ^1H NMR (300 MHz, $CDCl_3$, 293 K) δ 7.67 (d, J(H,H) = 16.0 Hz, 1H; $CH(C_6F_5)$), 6.77 (d, J(H,H) = 16.0 Hz, 1H; $CH(CO_2CH_3)$); MS (EI) *m*/*z* (relative intensity) 252 (M^+, 46), 221 (100), 193 (65), 173 (10), 143 (36), 123 (16), 117 (8), 59 (2).

3: ^{19}F NMR (282 MHz, $CDCl_3$, 293 K) δ −161.8 (m, $2F_{meta}$), −156.1 (t, $1F_{para}$), −142.9 (m, $2F_{ortho}$); ^1H NMR (300 MHz, $CDCl_3$, 293 K) δ 3.05 (t, J(H,H) = 7 Hz, 2H; $CH_2(C_6F_5)$), 2.64 (t, J = 7 Hz, 2H; $CH_2(CO_2CH_3)$); MS (EI) *m*/*z* (relative intensity) 254 (M^+, 44), 223 (17), 195 (71), 194 (100), 181 (77), 145 (16), 143 (11), 59 (12).

The reaction of **1** with methyl methacrylate was carried out in the same way, and a mixture of compounds **4** and **5** was obtained (**4**:**5** = 1:1).

4: ^{19}F NMR (282 MHz, $CDCl_3$, 293 K) δ −162.8 (m, $2F_{meta}$), −156.7 (t, $1F_{para}$), −142.9 (m, $2F_{ortho}$); ^1H NMR (300 MHz, $CDCl_3$, 293 K) δ 6.3 (s, 1H; H^1)*, 5.45 (s, 1H; H^2), 3.8 (s, 3H; OCH_3), 3.7 (s, 2H; $CH_2C_6F_5$); MS (EI) *m*/*z* (relative intensity) 266 (M^+, 95), 235 (47), 207 (48), 206 (48), 205 (20), 203 (27), 187 (100), 181 (81), 59 (10). In the ^1H NMR spectrum, H^1 is trans to $CH_2C_6F_5$ and H^2 is trans to CO_2CH_3.

5: ^{19}F NMR (282 MHz, $CDCl_3$, 293 K) δ −162.9 (m, $2F_{meta}$), −157 (t, $1F_{para}$), −143.2 (m, $2F_{ortho}$); ^1H NMR (300 MHz, $CDCl_3$, 293 K) δ 3.68 (s, 3H; OCH_3), 3.1 (m, 1H; CH), 2.8 (m, 2H; $CH_2C_6F_5$), 1.2 (d, J(H,H) = 8.9 Hz, 3H; CH_3); MS(EI) *m*/*z* (relative intensity) 268 (M^+, 22), 253 (19), 237 (6), 221 (11), 209 (11), 208 (26), 193 (11), 181 (100), 59 (7).

To a solution of **1** (0.0250 g, 0.057 mmol) in $CDCl_3$ (0.6 mL) was added methyl acrylate (0.0051 mL, 0.057 mmol) and galvinoxyl (0.0240 g, 0.057 mmol). The mixture was monitored by ^{19}F NMR, and after 30 min, compound **2** accounted for 86% of the C_6F_5-containing compounds (100% after 2 h).

Synthesis of $[Pd_2(\mu\text{-}Br)_2(C_6F_5)_2(PPh_3)_2]$ (6).[25] A solution of PPh_3 (0.105 g, 0.400 mmol) in CH_2Cl_2 (6 mL) was added dropwise to a stirred solution of **1** (0.175 mg, 0.400 mmol) in CH_2Cl_2 (20 mL). The mixture was stirred for 50 min and the solvent evaporated to dryness. Et_2O (5 mL) was added to the residue, and a yellow solid was obtained which was filtered, washed with Et_2O, and air-dried. Yield: 0.186 mg (75%). Anal. Calcd for $C_{48}H_{30}Br_2F_{10}P_2Pd_2$: C, 46.82; H, 2.45. Found: C, 45.98; H, 2.70. ^{19}F NMR (282 MHz, $CDCl_3$, 293 K): δ −163.1 (m, $2F_{meta}$), −160.8 (t, $2F_{para}$), −118.6 (m, $4F_{ortho}$). ^{31}P NMR (121.4 MHz, $CDCl_3$, 293 K): δ 33.6 (t, J(P,F) = 10.2 Hz).

Polymerizations in the Presence of Phosphine or Pyridine. Polymerization of Acrylates. To a solution of

(24) For anionic complexes formed by similar systems see: (a) Usón, R.; Forniés, J.; Nalda, J. A.; Lozano, M. J.; Espinet, P.; Albéniz, A. C. *Inorg. Chim. Acta* **1989**, *156*, 251−256. (b) Albéniz, A. C.; Espinet, P.; Martín-Ruiz, B.; Milstein, D. *J. Am. Chem. Soc.* **2001**, *123*, 11504−11505.

(25) Usón, R.; Royo, P.; Forniés, J.; Martínez, F. *J. Organomet. Chem.* **1975**, *90*, 367−374.

PPh_3 (0.0032 g, 0.012 mmol) in PhCl (2 mL) was added a solution of methyl acrylate (2.0554 g, 23.875 mmol) in PhCl (2 mL). This mixture was added to **1** (0.0052 g, 0.012 mmol), and the reaction proceeded at room temperature for 20 h, although stirring was halted after the initial 2.5 h. The polymer was precipitated from MeOH, the methanol was decanted, and the polymer was dried under vacuum to yield 1.88 g of poly(methyl acrylate) (91%). ^{1}H NMR (300 MHz, $CDCl_3$, 293 K): δ 3.68 (s, 6H; OCH_3), 2.34 (b, 2H; C*H*(CO_2CH_3)^s, C*H*(CO_2CH_3)^i)*, 1.95 (b, 1H; CH^i), 1.68 (b, 2H; CH_2^s), 1.51 (b, 1H; CH^i) (i = isotactic, s - syndiotactic). Polymer tacticity was determined by integration of the methine coupled and decoupled region of the ^{1}H NMR spectra.

The same procedure was used for other monomers, ligands, and/or solvents (see Table 1).

Poly(ethyl acrylate): 65% yield; ^{1}H NMR (300 MHz, $CDCl_3$, 293 K) δ 4.13 (b, OCH_2CH_3), 2.41−2.26 (b), 1,95 (b), 1.69(b), 1.28 (t, b, OCH_2CH_3); M_w (M_w/M_n) = 18.2 × 10^5 (2.7).

Poly(butyl acrylate): 75% yield; ^{1}H NMR (300 MHz, $CDCl_3$, 293 K) δ 4.04 (b, $OCH_2CH_2CH_2CH_3$), 2.38−2.18 (b), 2−1.85 (b), 1.68−1.54 (b), 1.38 (b), 0.91 (b); M_w (M_w/M_n) = 7.3 × 10^5 (11.5).

Copolymerization of Methyl Acrylate and 1-Hexene. To a solution of PPh_3 (0.0030 g, 0.011 mmol) in PhCl (2 mL) was added a mixture of methyl acrylate (0.8604 g, 9.994 mmol) and 1-hexene (1.1104 g, 13.194 mmol) in PhCl (2 mL). This mixture was added to **1** (0.0050 g, 0.011 mmol), and the reaction proceeded at room temperature for 21 h. The polymer was precipitated from MeOH, the methanol was decanted, and the polymer was dried under vaccum to yield 0.162 g of copolymer (8.2% yield, 9.4% hexene incorporation). The amount of hexene incorporated was determined by intergration of ^{1}H NMR signals.

Polymerizations in the Presence of Excess Halide. Polymerization of Acrylates. To a solution of the appropriate halide in PhCl (4 mL) was added methyl acrylate. The mixture was then added to **1**, and the flask was capped with a rubber septum and removed from the drybox. The reaction mixture was stirred at room temperature for the desired reaction time. $CHCl_3$ was added to the viscous crude product. The polymer was precipitated from MeOH, the MeOH was decanted, and the polymer was dried under vacuum. The same procedure was followed when other solvents were used.

Copolymerization of Methyl Acrylate with Methyl Methacrylate (or Methyl Methacrylate-d_8). To a solution of halide (10 equiv/Pd) in PhCl (4 mL) was added methyl acrylate and methyl methacrylate (or methyl methacrylate-d_8) in the appropriate proportion. The mixture was then added to **1**, and the flask was capped with a rubber septum and removed from the drybox. The reaction mixture was stirred at room temperature. The polymer was precipitated from MeOH, the MeOH was decanted, and the polymer was dried under vacuum.

Copolymerization of Methyl Acrylate with 1-Hexene. The polymerization was carried out by following a procedure analogous to that employed for the copolymerization of methyl acrylate and methyl methacrylate.

AIBN-Initiated Copolymerizations of Methyl Acrylate. A mixture of methyl acrylate (0.8610 g, 10.001 mmol) and 1-hexene (1.1120 g, 13.213 mmol) in PhCl (2 mL) was added to a solution of AIBN (0.0045 g, 0.027 mmol) in PhCl (2 mL). The reaction proceeded at 56 °C for 23 h. The polymer was precipitated from MeOH, the methanol was decanted, and the copolymer was dried under vacuum to yield 0.317 g (16% yield, 13.7% hexene incorporation). The amount of hexene incorporated was determined by integration of ^{1}H NMR signals.

The copolymerization of methyl acrylate and methyl methacrylate initiated by AIBN was carried out in a similar way, but using a monomer ratio (methyl acrylate:methyl methacrylate) of 1.1:1 and a temperature of 100 °C for 3 h. The copolymer obtained (68% yield) was methyl methacrylate rich (methyl acrylate:methyl methacrylate = 1:1.25).

ESR Experiments. A mixture of methyl acrylate (0.2390 g, 2.776 mmol) and AIBN (0.0005 g, 0.003 mmol) in CH_2Cl_2 (0.6 mL) was charged in an ESR tube. The sample was heated to 70 °C inside the probe, and a radical species was detected.

A mixture of methyl acrylate (0.2390 g, 2.776 mmol) and PPh_3 (0.0007 g, 0.003 mmol) in CH_2Cl_2 (0.4 mL) was added to a solution of **1** (0.0012 g, 0.003 mmol) in CH_2Cl_2 (0.2 mL), and the mixture was charged in an ESR tube. Spectra were taken in the temperature range 25−50 °C, after mixing and when the polymerization was taking place, and a viscous solution was present (1 and 3 h later). No signal was detected.

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