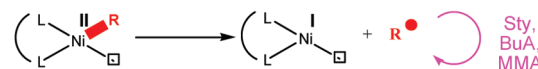# Homo- and Copolymerizations of (Meth)Acrylates with Olefins (Styrene, Ethylene) Using Neutral Nickel Complexes: A Dual Radical/Catalytic Pathway

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ABSTRACT: Nickel complexes $[(X,O)NiR(PPh_3)]$ (X = N or P), designed for the polymerization of ethylene, were found to be efficient for the homo- and copolymerization of butylacrylate (BuA), methylmethacrylate (MMA), and styrene. Their role as a radical initiator was demonstrated from the calculation of the copolymerization reactivity ratios. It was shown that the efficiency of the radical initiation is improved by the addition of PPh_3 to the nickel complexes as well as by increasing the temperature. The dual role of a nickel complex as radical initiator and catalyst was exploited to succeed in the copolymerization of ethylene with BuA and MMA. Multiblock copolymers containing sequences of both ethylene and polar monomers were thus prepared for the first time by a dual radical/catalytic mechanism.
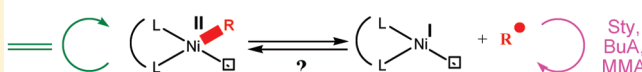
INTRODUCTION

Polar vinyl monomers such as (meth)acrylates are classically homopolymerized by anionic[1] or radical[2] mechanisms: both can be metal-mediated. Transition metal (TM)-based polymerizations involving coordination of the monomer have been investigated for the homopolymerizations of polar vinyl monomers. This topic, reviewed recently by Chen,[3] actually covers two very different polymerization mechanisms according to Chen definitions: migratory insertion (Cossee mechanism) and coordinative-anionic addition (anionic polymerization). On one hand, the early TM-based homopolymerization of polar vinyl monomers such as (meth)acrylates did not proceed via migratory insertion in a carbon—metal bond but via a coordinative-anionic mechanism involving an oxygen—metal bond with metal enolate intermediates.[3] From the pioneering works of Yasuda[4] with lanthanide-based complexes and Collins[5] with group 4 metallocenes, the homopolymerization of (meth)acrylates was developed with high degrees of control over the living character and the stereochemistry of the polymerization.[3] On the other hand, the late TM-based polymerization of polar vinyl monomers may proceed via a migratory insertion mechanism. A great number of metal complexes of iron,[6] nickel,[7−9] palladium,[10] and copper[11] were reported to homopolymerize (meth)acrylates in the presence of a large excess of MAO as the activator (or in the case of palladium-based systems without additional MAO). However, in most cases, it is still not clear whether the mechanism of polymerization is based on migratory insertion or free radical or ionic polymerization. In some cases, it has been clearly demonstrated that a free radical mechanism is involved,[9b,10] whereas in other cases, polymerization was induced by the cocatalyst (MAO) itself.[12] In the case of palladium complexes, it is assumed that the homolytic

cleavage of the carbon—metal bond generates radicals that are able to homopolymerize (meth)acrylates via a free radical mechanism.[10] Even though examples of pure migratory insertion-based homopolymerization of polar vinyl monomers are scarce,[13] consecutive units of polar vinyl monomers were observed in copolymers with nonpolar olefins such as ethylene.[3,14]

In the present work, we investigated the behavior of neutral nickel complexes $[(X,O)NiR(PPh_3)]$ (X = N or P) in the homo- and copolymerization of (meth)acrylates (in the absence of cocatalysts such as MAO). These catalysts were initially designed for the polymerization of nonpolar olefins and used in the presence of phosphine scavengers to allow the coordination of the olefin. It has been shown that the addition of phosphine to the polymerization of ethylene with these nickel catalysts leads to the deactivation of the catalyst.[15c] Counter-current of this "classical" mechanism for olefin polymerization, we present evidence that the addition of triphenylphosphine to the nickel complexes leads to a drastic increase in activity for the polymerization of (meth)acrylates. The rationalization of this unexpected effect is discussed in this Article; as a result, new routes for the copolymerization of ethylene and (meth)acrylates are described.

EXPERIMENTAL SECTION

All chemicals were handled under an argon atmosphere using standard Schlenk techniques. Ethylene (purity 99.95%) was purchased

from Air Liquide and used without any further purification. MMA, BuA, and styrene were purchased from Acros, dried over CaH_2, and distilled under partial pressure of argon. PPh_3 and the nickel precursors were purchased from Aldrich and used without further purification.

The salicylaldimine ligand was obtained by condensation of 2,6-diisopropylaniline with 3,5-iodosalicylaldehyde. Complex **1** was obtained by reaction of the sodium salt of the ligand with trans-$(PPh_3)_2NiPhCl$[16] in toluene according to a literature procedure.[15b,17a] An orange powder was obtained (yield 45%). ^{1}H NMR (benzene-d_6): δ 8.2 (d, CH=N, 1H), 6.3−7.2 (m, H_{arom}, 25H), 4.0 (m, C$\underline{H}$Me$_2$, 2H), 1.2 (d, CH$\underline{Me}_2$, 6H), 1.1 (d, CH$\underline{Me}_2$, 6H). ^{13}C NMR (benzene-d_6): δ 165.8 (C−O), 163.5 (C=N), 150.5 (C_{arom}), 149.9 (C_{arom}-N), 142.6 (C_{arom}), 140.8 (C_{arom}), 137.7 (o-C of Ni-Ph), 135.3 (o-C of Ni-PPh$_3$), 132.9 (i-C of Ni-Ph), 132.1−131.5 (i-C of Ni-PPh$_3$), 130.5 (p-C of Ni-PPh$_3$), 127.7 (m-C of Ni-PPh$_3$), 126.8 (p-C of Ni-Ph), 125.9 (C_{arom}), 123.4 (C_{arom}), 122.1 (C_{arom}), 121.0 (m-C of Ni-Ph), 97.6 (C−I), 73.9 (C−I), 29.4 (C$\underline{H}$Me$_2$), 26.0 (s, CH$\underline{Me}_2$), 23.2 (s, CH$\underline{Me}_2$). ^{31}P NMR (benzene-d_6): 23.5 (Ni-PPh$_3$). (The absence of the signal of free PPh$_3$ at −5 ppm was systematically checked.)

The phosphinoenolate ligand was obtained from the deprotonation of (ethoxycarbonyl methyl)triphenylphosphonium bromide by a weak base such as triethylamine, followed by the addition of benzoylchloride.[18] Complex **2** was obtained by the oxidative addition of the ligand to a zerovalent nickel complex $Ni(COD)_2$, leading to an alkylated metal complex by transfer of a phenyl group from the phosphorus to the nickel.[19a,e] The complex is stabilized by the presence of a coordinated triphenylphosphine molecule. A yellow solid was obtained (yield 60%). ^{1}H NMR (chloroform-d): δ 8.20−6.14 (m, H_{arom}, 35H), 3.8 (q, O−C$\underline{H}_2$CH$_3$, 2H), 0.6 (t, O−CH$_2$−C$\underline{H}_3$, 3H). ^{13}C NMR (chloroform-d): δ 165.4 (C=O), 134.3, 133.6, 133.5, 131.3, 129.7 − 129.3, 129.0, 127.8, 126.7, 126.0, 121.2, 91.0, 58.3 (O−C$\underline{H}_2$−CH$_3$), 13.8 (O−CH$_2$−C$\underline{H}_3$).

Homopolymerization of MMA, BuA, or Styrene. In a Schlenk tube, the desired amount of complex **1** or **2** was dissolved in the monomer (50 mL). The mixture was heated to the desired temperature under magnetic stirring. During the polymerization, samples were regularly collected to determine the yield of the reaction by gravimetry and thus its kinetic profile.

Copolymerizations of MMA, BuA, and Styrene. The same procedure as that for the homopolymerizations was followed with a total volume of monomers of 10 mL. Several mixtures of the two corresponding monomers A and B were investigated: A/B (wt %) = 20/80, 40/60, 50/50, 60/40, 70/30, 80/20. At the end of the polymerization, the mixture was cooled and the reaction was quenched by the addition of acidic ethanol.

Copolymerizations of Ethylene and MMA or BuA. *Caution: these polymerizations involve high pressure and explosive gas.* Ethylene copolymerizations were performed in a 160 mL stainless steel autoclave (equipped with safety valves, stirrer, oven) from Parr Instrument. High-pressure ethylene was stored in a 1.5 L intermediate tank. The tank was cooled to −20 °C to liquefy ethylene at 35 bar. When the thermodynamic equilibrium was reached, the intermediate tank was isolated and heated to reach an ethylene pressure of 150 bar. This tank was used to fill in the reactor and maintain a constant ethylene pressure during the reaction. The nickel complex and triphenylphosphine were dissolved in 50 mL of MMA or BuA in a Schlenk tube, then introduced to the reactor by cannulation. The stirred reactor (250 rpm) was then pressurized with ethylene, and the reaction mixture was heated to the desired temperature. The pressure was adjusted to the desired value. At the end of the polymerization, the reactor was slowly cooled and degassed. Polymer was then isolated by

evaporation of the polymerization medium and was then dried under vacuum at 70 °C.

Ethylene Copolymers Extractions with Methylethylketone. Copolymers (1 g) were extracted in a Kumagawa apparatus for 2 h in boiling methylethylketone (MEK) (80 °C). Two fractions were collected: the fraction soluble in boiling MEK (after evaporation of MEK and drying) and the insoluble fraction (after drying).

Polymer Analysis. The molecular weights of the homo- and copolymers of MMA, BuA, and styrene were determined by size exclusion chromatography (SEC) using a WATERS 717 injector and four columns (one precolumn PLgel Olexis guard and three columns PLgel 5 μm Mixed C) at 30 °C in THF (flow rate: 1 mL/min). Two detectors were used (light scattering and refractometer) to obtain the absolute values of molecular weight. The molecular weights of the ethylene-containing polymers (copolymers of ethylene and MMA or BuA and homopolyethylenes) were determined by size exclusion chromatography (SEC) using a Waters Alliance GPCV 2000 instrument (columns: PLgel Olexis) with two detectors (viscosimeter and refractometer) at 150 °C in trichlorobenzene (flow rate: 1 mL/min). The system was calibrated with polystyrene standards using universal calibration.

The thermal properties of the ethylene-MMA or ethylene-BuA copolymers or homopolyethylenes were determined by differential scanning calorimetry (DSC) on a Setaram DSC 131 apparatus at a heating rate of 5 or 10 K/min from −100 to 20 °C and from 20 to 150 °C. The samples were heated and cooled twice, and the reported data were obtained during the second heating.

The chemical composition and tacticity of the polymers were determined by high-resolution liquid nuclear magnetic resonance (NMR) spectroscopy. The analyses were carried out on a Bruker DRX 400 spectrometer operating at 400 MHz for ^{1}H and at 100.6 MHz for ^{13}C at the "Service commun de RMN des Polymères − Institut de Chimie de Lyon" in Villeurbanne. Spectra were obtained with a 5 mm QNP probe.

The homo- and copolymers of MMA, BuA, and styrene were examined as 10−15% (w/v) solutions in chloroform-d_1 at 323 K. The chemical shift values (δ) are given in ppm with reference to the internal standard tetramethylsilane (TMS). The tacticty of the MMA homopolymers was determined from the CH$_3$ signal at 0.7 to 1.3 ppm (^{1}H NMR). The composition of the copolymers was determined by ^{1}H NMR using signals at: (1) 0.5 to 1.3 ppm for MMA (C$\underline{H}_3$), at 3.5 to 4.0 ppm for BuA (O−C$\underline{H}_2$), and at 6.5 to 7.5 ppm for styrene (H_{arom}) in the case of styrene/BuA and styrene/MMA copolymers and (2) at 3.6 ppm for MMA (O−C$\underline{H}_3$) and at 4.0 ppm for BuA (O−C$\underline{H}_2$) in the case of BuA/MMA copolymer.

The copolymers of ethylene and MMA or BuA (and homopolyethylenes) were examined as 10−15% (w/v) solutions using a mixture of tetrachloroethylene (TCE) and benzene-d_6 (2/1 v/v) at 363 K. The chemical shift values (δ) are given in ppm with reference to the internal standard TMS for ^{1}H NMR and to the $(-(CH_2)_n-)$ signals of polyethylene at 30.00 ppm for ^{13}C NMR. The composition of the copolymers was determined by ^{1}H NMR. For E/MMA copolymers: % MMA = $100/(1 + ((A − 5)/4))$, where A is the integral of the signals between 1 and 2.5 ppm and the integral of O−CH$_3$ signal at 3.6 ppm calibrated at 3. For E/BuA copolymers: %BuA = $100/(1 + ((A − 10)/4))$, where A is the integral of the signals between 1 and 2.5 ppm and the integral of O−CH$_2$ signal at 4 ppm calibrated at 2.

■ RESULTS AND DISCUSSION

Homo- and copolymerizations of meth(acrylates) and styrene were investigated using two neutral square planar nickel
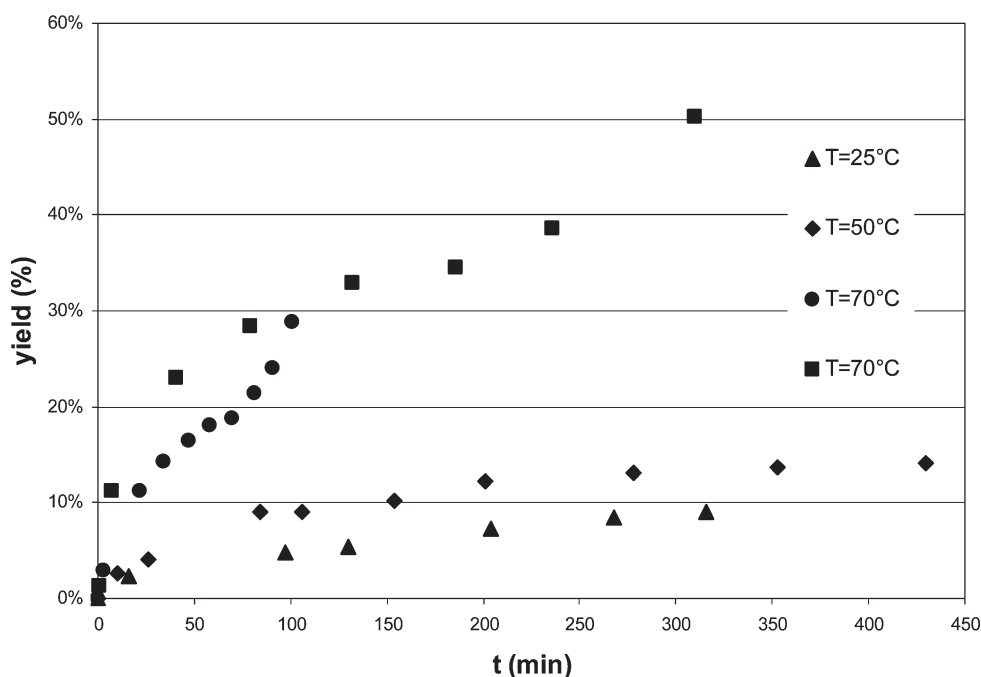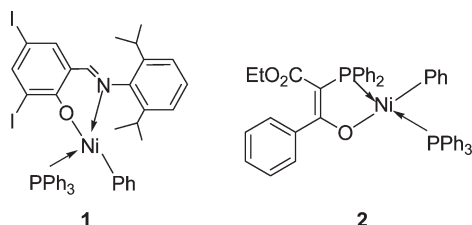
Figure 1. Homopolymerization of MMA with **1**/PPh$_3$ (1/3): [MMA] = 9.3 mol·L^{-1}; ▲,◆, ●: [Ni] = 2.3 mmol·L^{-1}; ■: [Ni] = 4.6 mmol·L^{-1}.

complexes: the nickel(II) salicylaldiminato complex **1** and the nickel(II) phosphinoenolate complex **2**.

These nickel complexes were developed for the oligo-/ polymerization of ethylene in organic[15,19] and aqueous dispersed media.[17] These systems generally require the presence of a phosphine scavenger to activate the polymerization by providing a vacant site for the olefin coordination. Moreover, such complexes and especially nickel(II) salicylaldiminato complexes have been reported as inefficient catalysts for the homopolymerization of (meth)acrylates,[20] as well as for the copolymerization of ethylene and (meth)acrylates[14d] in the absence of additional cocatalysts such as MAO.[3,8] In the present work, complexes **1** and **2** were used without phosphine scavenger and without any aluminum-based cocatalysts.

Homopolymerizations of Methyl Methacrylate and Butyl-acrylate. The homopolymerization of methyl methacrylate (MMA) was investigated using complex **1** in bulk at temperatures from 25 to 70 °C ([Ni] = 2.3 mmol·L^{-1} and [MMA] = 9.3 mol·L^{-1}). Under these conditions MMA does not polymerize by thermal self-initiation in the absence of the nickel complex. In the presence of complex **1,** polymerization occurred, but the polymer yields remained very low (up to 2% after 20 h at 70 °C). A high-molecular-weight, moderately syndiotactic poly-(methylmethacrylates) (PMMA) was produced (M_n = (3 to 4) × 10^5 g/mol, PDI = 3 to 4; %rr = 70%).

When triphenylphosphine was added to **1** (PPh$_3$/**1**: 3/1), the formation of PMMA was much more efficient (Figure 1). This

was completely unexpected for a "classical" olefin polymerization system: phosphine scavengers are indeed usually used to activate neutral nickel complexes.

Under these polymerization conditions, PPh$_3$ alone is not able to initiate the polymerization of MMA. With the combination **1**/ PPh$_3$, the PMMA conversions achieved after 2 h were ∼5% at 25 °C, ∼10% at 50 °C, and ∼30% at 70 °C and the initial slopes of the kinetic profiles increased with increasing temperature (Figure 1). Upon doubling the nickel concentration, the initial slope became steeper, and high PMMA yields (up to ∼50%) were obtained.

The number-average molecular weights of the PMMA increased slightly with polymerization temperature from about M_n = 8500 g/mol (PDI ∼ 2) at 25 °C to M_n = 20 000 g/mol at 50 °C (PDI ≈ 3) and M_n = 30 000 g/mol (PDI ≈ 2) at 70 °C (at 10% conversion). M_n was almost independent of conversion at 25 °C, whereas it first increased until 10−15% conversion before reaching a plateau at 50 and 70 °C (M_n = 26 000 and 37 000 g/mol, respectively). At higher nickel concentration, a decrease in the molecular weights was observed (M_n = 7500 g/mol at [Ni] = 4.6 mmol·L^{-1} versus 30 000 g/mol at [Ni] = 2.3 mmol·L^{-1}; T = 70 °C; ∼10% conversion). The synthesized PMMA were moderately syndiotactic (%rr = 62−66%).

Similar experiments were then performed with complex **2**. The activation effect of the phosphine was also observed with complex **2** but to a lesser extent (Figure 2). Complex **2** alone exhibited by itself a significant activity in the homopolymerization of MMA, unlike complex **1**. In both the presence and absence of additional phosphine, the MMA conversions remained low (up to 14%). The molecular weights of the PMMA were almost independent of conversion and slightly decreased upon heating (from about M_n = 250 000 g/mol (PDI ≈ 2.1) at 50 °C to M_n = 190 000 g/mol (PDI ≈ 2.1) at 70 °C; at 10% conversion).

The results obtained with complexes **1** and **2** and the "phosphine effect" observed were unexpected. These complexes
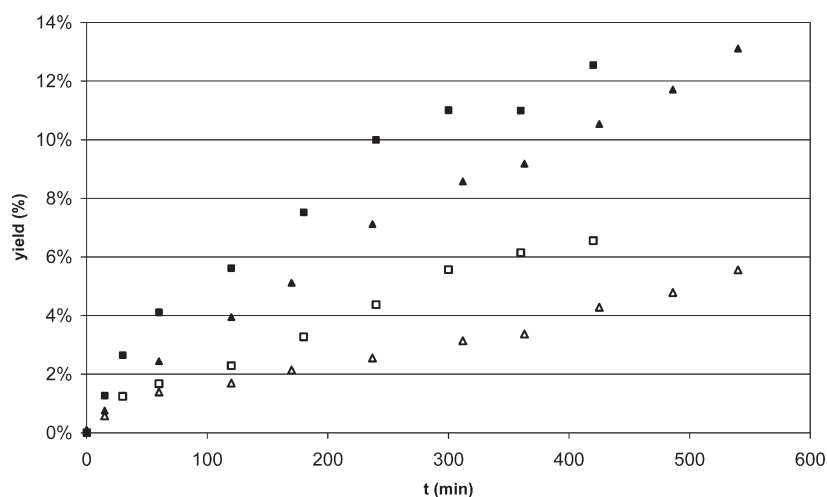
Figure 2. Homopolymerization of MMA with **2**: $[MMA] = 9.3 \, mol \cdot L^{-1}$; $[Ni] = 2.3 \, mmol \cdot L^{-1}$; $\triangle$: $T = 50 \,°C$; $\blacktriangle$: $T = 50 \,°C \, (+ \, 3 \, PPh_3)$; $\square$: $T = 70 \,°C$; $\blacksquare$: $T = 70 \,°C \, (+ \, 3 \, PPh_3)$.
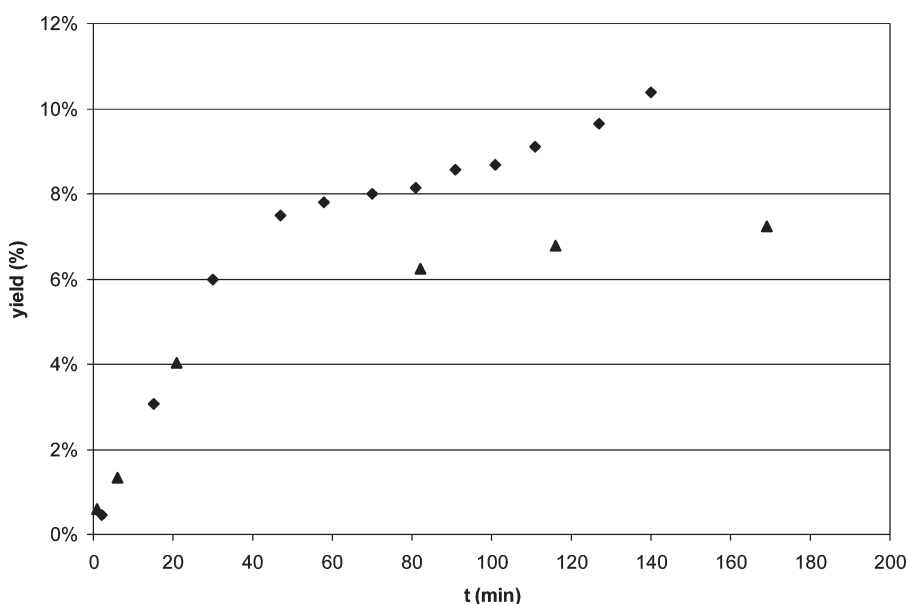
Figure 3. Homopolymerization of BuA with **1**/PPh$_3$: $[BuA] = 6.9 \, mol \cdot L^{-1}$; $[Ni] = 2.3 \, mmol \cdot L^{-1}$; $\blacktriangle$: $T = 50 \,°C \, (+ \, 3 \, PPh_3)$; $\blacklozenge$: $T = 70 \,°C \, (+ \, 3 \, PPh_3)$.

are known to be active catalysts for the polymerization of nonpolar olefins by classical migratory insertion mechanism in the presence of phosphine scavengers, whereas conversely they require additional phosphine to be active for the homopolymerization of MMA. The activating effect of the phosphine tends to indicate a polymerization mechanism involving the coordination of the phosphine to nickel. Several mechanisms may be considered. Mechanisms based on monomer coordination (migratory insertion or coordinative-anionic addition) would feature a competition for coordination sites between the monomer and the phosphine. Therefore these mechanisms should be disfavored by the presence of additional phosphine. A free radical mechanism based on the homolytic cleavage of the metal—carbon bond may be favored by the presence of additional phoshine, which could act to stabilize the nickel(I) fragment.

The homopolymerization of butyl acrylate (BuA) was also investigated from complexes **1** and **2** in bulk at $T = 50$ and $70 \,°C$

$([Ni] = 2.3 \, mmol \cdot L\text{-}1$ and $[BuA] = 6.9 \, mol \cdot L^{-1})$. In the absence of additional PPh$_3$, the conversions achieved were very low (<1 to 2% after 10 h) with both complexes **1** and **2**. When triphenylphosphine was added to **1** (3 equiv), the formation of poly(butylacrylate) was much more efficient (Figure 3) and high-molecular-weight polymers were formed ($M_n = 135\,000 \, g/mol$ (PDI $\approx$ 2.4) at 50 °C and $M_n = 160\,000 \, g/mol$ (PDI $\approx$ 2.5) at $T = 70 \,°C$ at ~7.5 to 8% conversion). Complex **2**, however, remained almost inactive when combined with PPh$_3$ (1.5% conversion after 10 h).

As in the case of MMA polymerization, the enhancing effect of the phosphine was observed for BuA polymerization. Similar hypotheses may be proposed regarding the mechanism of polymerization: free radical versus coordination mechanisms (migratory insertion or anionic).

Homo- and Copolymerization of Styrene with (Meth)Acrylates. To discriminate between the proposed polymerization

Table 1. Copolymerization of Styrene and Butyl Acrylate with Complexes 1 and 2[a]

nickel system	% wt BuA feed	% wt BuA polymer[b]	yield (g)	reactivity ratios rBuA/rSty (R^2)[c]
1	20	20	0.67	0.27/0.82 (1)
	50	41	0.62	
	70	54	0.6	
1/PPh$_3$ (1/3)	20	20	0.83	0.24/0.81 (1)
	50	40	0.87	
	70	54	0.8	
2	20	21	0.36	0.17/0.73 (0.999)
	40	35	0.33	
	60	44	0.26	
	80	58	0.22	
2/PPh$_3$ (1/3)	20	18	0.40	0.25/0.95 (0.997)
	40	33	0.36	
	60	45	0.32	
	80	58	0.23	

[a] Polymerization conditions: total volume 10 mL, T = 70 °C, [Ni] = 2.3 mmol·L^{-1}, t = 3 h. [b] Determined by ^{1}H NMR. [c] R^2 = coefficient of determination of linear least-squares method.

mechanisms, we performed experiments in the presence of TEMPO as a radical trap. We observed a deactivation of the polymerization of MMA by the addition of TEMPO, but the experiments were not considered to be conclusive. Radical traps have been shown to react with organometallic complexes, which could lead to catalyst deactivation.[10a,21]

An alternative discrimination method is to investigate copolymerizations and to determine the reactivity ratios. Hence, we investigated the copolymerizations of MMA with BuA and of styrene with these two meth(acrylic) monomers. Styrene is able to (co)polymerize via a radical mechanism or theoretically via migratory insertion, but it cannot copolymerize via coordinative-anionic addition.

The homopolymerization of styrene was first investigated for comparative purposes: in bulk at T = 70 °C with complexes **1** and **2** with or without additional PPh$_3$ ([Ni] = 2.3 mmol·L^{-1} and [Sty] = 8.73 mol·L^{-1}). In all cases, the homopolymerization took place, and the effect of the phosphine was less pronounced than that in the polymerizations of MMA and BuA (after 2 h of polymerization at T = 70 °C: ∼9% conversion with **1** vs ∼14% with **1**/PPh$_3$ (1/3); ∼14% for both systems with **2**).

The copolymerization of BuA with styrene was studied in bulk with various monomer compositions, with complexes **1** and **2** both in the presence and in the absence of additional PPh$_3$ (T = 70 °C, [Ni] = 2.3 mmol·L^{-1}). The results are summarized in Table 1. Higher copolymer yields were obtained using complex **1** than with complex **2**. For both complexes, the yields increased upon addition of the phosphine (a more pronounced effect with **1**) and slightly decreased upon addition of BuA. These results are consistent with the homopolymerization results. The composition of the copolymers is not modified by the addition of the phosphine. This tends to indicate that a single mechanism of polymerization is involved in both cases, with an increased concentration of active species in the presence of additional phosphine.

The reactivity ratios of the comonomers were calculated using the Kelen−Tudos method (terminal model) and are reported in Table 1. They are almost identical with both complexes, with or without additional phosphine and close to the reported reactivity ratios for the free radical copolymerization of styrene and butyl
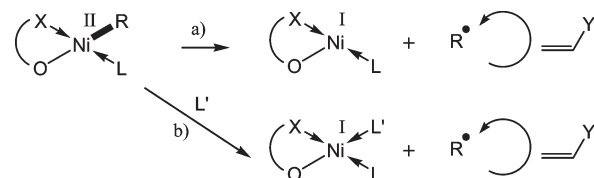

Figure 4. Homopolymerization of a polar vinyl monomer from radicals generated by homolytic cleavage of nickel carbon bond: (a) spontaneous and (b) assisted by phosphine addition (L, L′ = PPh$_3$, R = Ph, X = N or P (for salicylaldiminato or phosphinoenolate ligands, respectively)).

acrylate (rBuA = 0.19, rSty = 0.86).[22] Therefore, the coordinative-anionic mechanism can be excluded. The synthesis of diblock copolymers could theoretically occur via the latter mechanism; however, the calculated reactivity ratios are not in favor of a block structure (rBuA × rSty = 0.12 to 0.25 < 1). The reactivity ratios also exclude a migratory insertion mechanism that would likely be disfavored by the presence of additional phosphine. In conclusion, the calculated reactivity ratios clearly support a free radical mechanism.

We assume that the radicals are released upon the homolytic cleavage of the metal−carbon bond (Figure 4a), as has been reported in the literature with palladium complexes.[10] Hence, the nickel complex plays the role of a radical initiator. The homolytic cleavage of the metal−carbon bond may be favored by the addition of the phoshine through a stabilization of the nickel(I) fragment produced (Figure 4b). Therefore, adding phosphine would lead to a higher concentration of radicals and as a consequence to a higher activity of the system. Moreover, the results indicate that the addition of phosphine does not change the nature of the polymerization mechanism (same reactivity ratios) but reinforces it.

Similar investigations were performed with the two other monomer pairs, BuA/MMA and MMA/Sty. Similar effects were observed with respect to yields and copolymer compositions upon the addition of the phosphine to complex **1** or **2**. The reactivity ratios calculated by the Kelen−Tudos method are presented in Table 2.

Table 2. Copolymerization of MMA with Butyl Acrylate or Styrene with Complexes 1 and 2[a]

comonomer A	comonomer B	nickel system	rA	rB	$(R^2)^b$	rArB
MMA (rA = 2.15)[c]	BuA (rB = 0.40)[c]	**1**	0.74	0.17	1	0.13
		1/PPh₃	0.82	0.21	1	0.17
		2	0.97	0.30	0.989	0.29
		2/PPh₃	1.63	0.55	0.951	0.90
Sty (rA = 0.52)[c]	MMA (rB = 0.46)[c]	**1**	0.87	0.45	0.997	0.39
		1/PPh₃	0.79	0.11	0.980	0.87
		2	1.40	0.42	0.980	0.59
		2/PPh₃	1.06	0.39	0.980	0.41

[a] Polymerization conditions: total volume 10 mL, T = 70 °C, [Ni] = 2.3 mmol·L^{-1}, t = 3 h. [b] R^2 = coefficient of determination of linear least-squares method. [c] From ref 22.
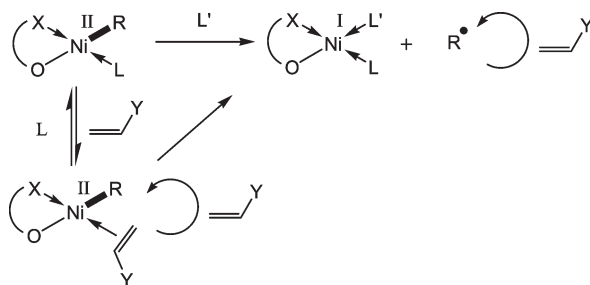

Figure 5. Free radical versus coordination–insertion mechanisms in homopolymerization of the polar vinyl monomers (L = PPh₃, L′ = PPh₃ or monomer, R = Ph, X = N or P (for salicylaldiminato or phosphinoenolate ligands, respectively)).

Figure 6. Copolymerization of ethylene and polar vinyl monomers: the dual radical/catalytic pathway.

In both cases, the calculated reactivity ratios deviate from those expected for a free radical copolymerization. It seems that the presence of MMA shifts the polymerization mechanism from a pure free radical mechanism toward a more complex mechanism (rBuA × rMMA = 0.13 to 0.90 < 1 and rSty × rMMA = 0.39 to 0.87 < 1 compared with 0.86 and 0.24, respectively, for free radical copolymerization). The simple terminal model used to describe the copolymerization may not be sufficient to describe the copolymerization with MMA. Indeed, the terminal model does not take into account the penultimate effects or the potential coordination of the polar monomers onto the nickel. The coordination of MMA (and potentially of the two other monomers) to the nickel center could be involved in the polymerization mechanism, which would influence the rate of homolytic cleavage of the nickel−carbon bond (as reported for the phosphine, see Figure 5). Another explanation for the discrepancy in reactivity ratios could be the coexistence of the free radical mechanism and the coordination/insertion mechanism (Figure 5).

On the basis of our results, the nickel complex appears to play a dual role: (1) as a radical initiator whose limited efficiency can be improved by increasing the temperature or adding a Lewis base such as a phosphine and (2) as a classical coordination/insertion catalyst.

The potential of this dual behavior led us to consider the copolymerization of nonpolar olefins (such as ethylene) with polar vinyl monomers. Because these nickel complexes are known catalysts for the polymerization of ethylene by migratory insertion, diblock copolymers of ethylene and polar olefins should be accessible. Moreover, if the homolytic cleavage of the metal−carbon bond can occur reversibly, multiblock copolymers may be accessible. An elegant pathway to the copolymerization of polar and nonpolar olefins using a dual radical/catalytic mechanism can thus be projected (Figure 6).
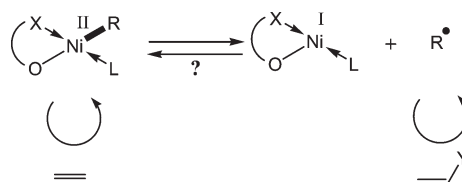
Copolymerization of (Meth)acrylates and Ethylene. The copolymerizations of ethylene and MMA or BuA were investigated in bulk (50 mL of polar monomer) using complex **1** at two constant ethylene pressures (25 and 100 bar) without the addition of alkyl aluminum cocatalysts.[23] Under these conditions (even at 100 bar), the polymerization medium was biphasic, with a liquid phase comprising **1** and ethylene in solution in the polar monomer and a second phase comprising mainly supercritical ethylene.[24] The results are presented in Table 3. In bulk polar monomer, polymers were obtained in satisfactory yields but in lower yields than those for the homopolymerization of ethylene.

Under the same conditions, homopolymerizations of ethylene by a migratory insertion mechanism (catalytic polymerization) produced 12 g of polyethylene from **1** at 100 bar in 50 mL of toluene versus 6.5 g of copolymer in 50 mL of MMA. A decrease in activity was observed upon PPh₃ addition to **1**, but PE properties were unchanged (T_m = 124.0 °C from **1** and T_m = 123.2 °C from **1**/PPh₃). Note that the low melting points of the PE obtained with **1** or **1**/PPh₃ are due to the "chain walking" mechanism,[14a] which leads to a branched polymer. Under these conditions (at 100 bar, using an AIBN concentration identical to the concentration of nickel complex **1**), only traces of low-molecular-weight polyethylene are produced by free radical homopolymerization of ethylene. Under similar conditions, the copolymerization of a polar monomer (MMA or BuA) and ethylene using higher concentrations of AIBN (×3) led to amorphous copolymers enriched in the polar monomer (94 mol % MMA for E/MMA copolymer and 83 mol % BuA for E/BuA copolymer).

The polymer obtained by the copolymerization of ethylene and MMA at 25 bar using **1** as catalyst contained 20.5 mol % MMA, whereas at 100 bar the MMA content dropped to 2.7 mol %. These two polymers, respectively, melt at 112 and 122 °C. When phosphine was added, the yields decreased and the incorporation of MMA in the copolymer increased to, respectively, 34 mol % at 25 bar and 7.7 mol % at 100 bar. The first polymer is amorphous, whereas the second exhibits a weak broad melting transition (T_m = 110−121 °C). No glass transition was observed between −100 °C and +150 °C, even in the case of the

Table 3. Copolymerization of MMA and Butyl Acrylate with Ethylene from Complex 1[a]

polar monomer (PM)	nickel system	ethylene pressure	yield (g)	M_n (PDI) g/mol	% PM polymer[c]	T_m (°C)
MMA	**1**	25	4.1	10 000 (3.0)	20.5	112.3
	1	100	6.5	12 000 (3.7)	2.7	122.4
	1/PPh₃	25	3.1	28 100 (1.7)	34.0	no T_m
	1/PPh₃	100	1.2	37 600 (1.9)	7.7	110−121
BuA[b]	**1**	25				
	1/PPh₃	25	2.2	58 000 (5.2)	86.3	no T_m

[a] Polymerization conditions: 50 mL of polar monomer (PM), T = 50 °C, [Ni] = 2.3 mmol·L⁻¹, t = 2 h. [b] t = 4 h. [c] mol %, determined by ¹H NMR.

amorphous polymer. The T_g of long MMA sequences potentially present (PMMA or long MMA sequences) can be expected at ~+100 °C, which overlaps with the temperature range for melting of the PE sequences (PE or long ethylene sequences).

The molecular weights of the polymers were one order of magnitude lower than in the case of the homopolymerization of MMA and in the same range as for homopolyethylenes (obtained using **1** under similar conditions).

In the case of BuA, no activity was observed at 25 bar with **1** only, whereas phosphine addition led to the formation of an amorphous polymer containing 86.3 mol % of BuA. The molecular weight of the polymer was lower than that of the corresponding homopolymer of BuA obtained using **1**/PPh₃. The glass transition of polymer was observed at −49 °C, indicative of long BuA sequences (Tg (homoPBuA) = −54 °C).

Even though MMA incorporation in the polymers was measured by ¹H NMR, the structure of the polymers formed with **1** and **1**/PPh₃ is not yet clear. In particular, the presence of homopolymers of ethylene, of MMA (or of MMA enriched copolymers from a pure free radical mechanism), or both together with block copolymers cannot be ruled out. The polymer properties can help to characterize the nature of these polymers. The fully amorphous polymer obtained from **1**/PPh₃ at 25 bar was found to contain 66% of ethylene. The absence of a melting transition for this polymer, however, suggests the absence of long ethylene sequences (homopolyethylene or polyethylene-*block*) and therefore indicates the presence of a copolymer structure.

Further characterization of the polymers was undertaken by extraction of the polymers with boiling MEK. (See Table 4 for E/MMA copolymers.) Because homoPMMA (and homoPBuA) are fully soluble in boiling MEK and homoPE (branched and synthesized with **1** or **1**/PPh₃) is insoluble, the extraction can help in determining the presence of homopolymers. The chemical composition of the two fractions of polymer (soluble and insoluble in MEK) was analyzed by ¹H NMR.

In the case of the ethylene/BuA copolymerization (86.3 mol % BuA), the polymer obtained is amorphous and fully soluble in MEK. This indicates the absence of polyethylene.

In the case of the crystalline polymer containing 20.5 mol % MMA, both fractions contain high levels of MMA inclusion (30 mol % MMA in the MEK soluble fraction and 16 mol % in the MEK insoluble one) while being composed mainly of ethylene units (70 and 84 mol %, respectively). Because the MEK soluble fraction cannot contain PE and the MEK insoluble fraction cannot contain PMMA, this indicates that copolymers were produced. Nevertheless, the presence of polyethylene in the MEK insoluble fraction and of PMMA in the MEK soluble fraction cannot be ruled out. Hence, the polymer produced using **1** can be characterized as a mixture of polymers, probably

Table 4. MEK Extractions of E/MMA copolymers Obtained from 1[a]

polymers (E/MMA)[b]	wt % soluble in MEK (MMA content mol %)[c]	wt % insoluble in MEK (MMA content mol %)[c]
homo PMMA (0/100)	100	0
homo PE (100/0)	0	100
copolymer (79.5/20.5)	32 (30)	68 (16)
copolymer (97.3/2.7)	6 (40)	94 (0.5)
copolymer (66/34)	100 (34)	0 (0)
copolymer (92.3/7.7)	66 (11)	34 (1)

[a] Extractions conditions: 2 h in boiling MEK. [b] Synthesized from **1** or **1**/PPh₃. [c] Determined by ¹H NMR.

containing diblock or potentially multiblock copolymers with a variety of block lengths. In the case of the crystalline polymer containing 2.7 mol % MMA, a mixture of ethylene-enriched (close to homopolyethylene containing 99.5 mol % of ethylene units) and MMA-enriched (40 mol %) copolymers was determined. The same trends are observed with the polymer containing 92 mol % of ethylene with different ratios between MEK soluble and insoluble fractions (corresponding to a mixture of 34 wt % of an ethylene enriched copolymer and 66 wt % of copolymer containing 11 mol % MMA). Finally, in the case of the amorphous polymer (34 mol % MMA), the absence of homopolyethylene was confirmed by the presence of only an MEK soluble fraction.

In conclusion, the MEK extractions indicate the formation of copolymers. Additionally, the formation of homopolymers appears to be limited or absent altogether. The complex mixture of copolymers obtained is consistent with the proposed dual catalytic/radical mechanism. Such a mechanism would indeed generate block copolymers with a chemical composition distribution (CCD, with respect to the comonomer levels and the block lengths). The CCD would then be determined by the equilibrium between the different nickel species, Ni(II) versus Ni(I), that is, catalytically active nickel for the polymerization of olefins versus radical initiating nickel for the polymerization of polar monomers. On the basis of the results of this study, the latter equilibrium is apparently displaced toward the release of radicals upon the addition of phosphine (which was demonstrated to promote the radical formation in the homo- and copolymerization of (meth)acrylates and styrene) and at low ethylene concentration (pressure). Higher ethylene pressures appear to displace the equilibrium toward the catalytically active species, resulting in ethylene-enriched copolymers.

Further characterization of the polymers was performed by ¹³C NMR analysis. The presence of a mixture of copolymers prevented detailed quantitative analyses, but a number of

conclusions could be drawn. The sequences of polar monomer (including identification of the tacticity of the MMA block) and of ethylene (branched ethylene block due to chain-walking mechanism) were identified on the ^{13}C NMR spectra. Additional new weak signals were observed in the case of MMA-enriched copolymers obtained at 25 bar, which may arise from the alternating E/MMA units and are present in both MEK soluble and insoluble fractions. These signals were absent from the spectra of ethylene-enriched copolymers obtained at 100 bar.

Copolymers with complex structures were obtained from the copolymerization of ethylene and polar monomer using complex **1**. The high copolymerization yields are significantly different from the yields expected from both a pure free radical polymerization and a pure coordination/insertion polymerization. Under the pressure and temperature conditions used, radical polymerization is inefficient, and coordination/insertion polymerization is inhibited by the presence of the polar monomer. The copolymers synthesized are not statistical and differ from MMA-enriched copolymers produced by a free radical mechanism. They instead exhibit a rather blocky character.

These results are consistent with the proposed polymerization mechanism involving both coordination/insertion and free radical mechanisms. This mechanism is based on the proposed dual role of the nickel complex, as a catalyst (by migratory insertion into the Ni^{II}—C bond) and as a radical initiator (by homolytic cleavage of the Ni^{II}—C bond), as illustrated in Figure 6. The efficiency of the radical initiation can be improved by the addition of phosphine. In the case of the BuA/E copolymerization, the addition of phosphine is even necessary to promote the polymerization.

The proposed mechanism-shuttling between coordination/insertion and radical polymerization still needs to be confirmed. Furthermore, reversible homolytic cleavage of the metal—carbon bond could provide access to the synthesis of multiblock copolymers of polar and nonpolar olefins. The term "reversible homolytic cleavage of the metal—carbon bond" refers to the equilibrium between the Ni(I) and Ni(II) species upon reoxidation of the Ni(I) species by addition of, for example, a propagating macroradical. Whereas the existence of such mechanism-shuttling still needs to be proven, the permanent consumption of ethylene during the polymerization and properties of the copolymers indicate that multiblocks copolymers of ethylene and polar monomers are formed.

CONCLUSIONS

The homopolymerizations of butylacrylate (BuA) and methylmethacrylate (MMA) (and styrene) were investigated in bulk with two neutral nickel olefin polymerization catalysts: the nickel(II) salicylaldiminato complex **1** and the nickel(II) phosphinoenolate complex **2**. Homopolymerization was found to be enhanced by heating and upon addition of triphenylphosphine, contrary to what is expected for the "classical" polymerization of olefins with these nickel complexes (which require phosphine scavengers).

The copolymerizations of BuA, MMA, and styrene indicated the involvement of a free radical mechanism initiated by complexes **1** and **2**, as demonstrated by the calculations of the comonomer reactivity ratios.

The dual role of the nickel complexes in the copolymerization was highlighted. On one hand, the nickel complexes act as classical catalysts for the polymerization of olefins (coordination—insertion

mechanism). On the other hand, the nickel complexes act as radical initiators, due to the homolytic cleavage of the nickel—carbon bond. The addition of triphenylphosphine appears to promote the homolytic cleavage.

On the basis of this feature of the nickel complexes, an original dual radical/catalytic pathway was postulated for the copolymerization of ethylene with polar monomers (e.g., MMA and BuA) by complex **1**. High copolymer yields were obtained. The addition of triphenylphosphine to complex **1** enhanced the rate of the copolymerization of ethylene and MMA, whereas its presence was necessary for the E/BuA copolymerization to proceed. Mixtures of copolymers were obtained, ranging from ethylene-enriched copolymers to polar monomer-enriched copolymers. The copolymers synthesized were found to exhibit a blocky microstructure, as demonstrated by thermal analysis, extraction in boiling MEK, and NMR analysis. The successful synthesis of E/MMA and E/BuA copolymers confirmed the potential dual role of the nickel complexes as a catalyst and radical initiator. The ethylene and polar monomer blocks are thought to be produced via a coordination/insertion mechanism and a free radical mechanism, respectively. The efficiency of the free radical mechanism seems to be improved by the addition of phosphine. The proposed mechanism shuttling between coordination/insertion and radical polymerization requires further study for confirmation. The shuttling would be facilitated by the reversibility of the homolytic cleavage of the metal—carbon bond and would give access to multiblock copolymers of polar and nonpolar olefins. Further investigations are in progress into the proposed dual radical/catalytic mechanism and the characterization of the copolymers synthesized (using HT-LC techniques and ^{13}C NMR).

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