

## Synthesis of copolymers of ethylene and (meth)acrylates or styrene by an original dual radical/catalytic mechanism\*

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**Abstract:** Neutral Ni<sup>II</sup> complexes, classically used for catalytic ethylene polymerization, can play an additional role as radical initiators of the homo- and copolymerizations of (meth)acrylates and styrene. Benefiting from this duality, the copolymerization of ethylene and various (meth)acrylates or styrene was successfully performed. Multiblock copolymers containing sequences of both ethylene and (meth)acrylates were prepared for the first time from an original dual radical/catalytic mechanism.

**Keywords:** catalysis; free radicals; (meth)acrylates; olefins; polymerization.

### INTRODUCTION

Homopolymers of polar vinyl monomers [e.g., (meth)acrylates] are traditionally synthesized by free radical polymerization involving occasionally transition metals (TMs). In some other cases, the coordination of the monomers on the TM is implied, i.e., for the polymerization via a coordinative anionic addition with early TMs (oxygen–metal bond; enolate intermediates) and via a migratory insertion with late TMs (carbon–metal bond) [1]. In the latter case, a great number of metal complexes of Fe, Ni, or Pd were reported to homopolymerize (meth)acrylates in the presence of large excess of methylaluminumoxane (MAO) as the activator (except for Pd-based systems) [1]. However, it is often not clear whether the mechanism of the polymerization is based on migratory insertion, free radical, or ionic polymerization (from MAO). In specific cases, it was clearly demonstrated that a free radical mechanism was involved from radicals possibly generated by the homolytic cleavage of the carbon–metal bond [2].

Even though there are only scarce examples of pure migratory insertion-based homopolymerization of polar vinyl monomers [3], consecutive insertions of polar vinyl monomers were observed in copolymers with nonpolar olefins such as ethylene [1,4]. These copolymers are in fact the most attracting materials as the incorporation of polar vinyl monomers in polyolefins remains one of the major challenges in polymer chemistry. Most of the promising catalysts for the synthesis of these copolymers are Pd-based [4]. The first breakthrough was achieved by Brookhart with the synthesis of highly branched copolymers of olefins and acrylates using cationic  $\alpha$ -diimine Pd<sup>II</sup> complexes [5]. In 2002, Drent reported another promising catalytic system based on a neutral Pd phosphino-sulfonate complex, which

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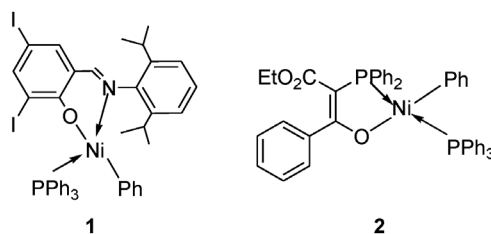
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is able to synthesize linear copolymers of ethylene and methylacrylate (MA) [6]. Lately, studies almost exclusively focused on these Pd complexes with some successes in the synthesis of ethylene copolymers with polar vinyl monomers such as acrylates, vinyl acetate, or acrylonitrile [3,4,6–8]. Despite scientifically attractive results, the activities of the complexes in copolymerization remain too low for any industrial application. The current commercial processes for the synthesis of such copolymers of non-polar olefins and polar vinyl monomers are based on free radical polymerization, thus limiting the range of available microstructures [9].

To overcome these various issues, we recently developed an original mechanism, the so-called dual radical/catalytic polymerization, which combines the catalytic coordination/insertion and the free radical mechanisms from one single organometallic complex [10]. Indeed, an additional role of neutral Ni complexes, initially designed for the catalytic polymerization of ethylene, was evidenced in the homo- and copolymerization of (meth)acrylates and styrene, as a radical initiator [10]. Benefiting from the dual role of these Ni complexes as catalyst and radical initiator, we succeeded in the copolymerization of ethylene with polar vinyl monomers such as methylmethacrylate (MMA) and butylacrylate (BuA) [10]. The present paper describes this dual radical/catalytic copolymerization of ethylene and polar vinyl monomers especially with new comonomers such as butylmethacrylate (BuMA), MA, or styrene.

## EXPERIMENTAL SECTION

The analytical techniques for the analysis of the polymers and the synthesis of the two neutral square planar Ni complexes used (the Ni<sup>II</sup> salicylaldiminato complex **1** and the Ni<sup>II</sup> phosphinoenolate complex **2**) were previously described by the authors [10].



The copolymerizations of ethylene and polar vinyl monomers were carried out in neat monomers in a 160-mL stainless steel autoclave according to the procedure described previously for MMA and BuA (50 mL of polar monomer) [10].

The copolymer composition was determined by <sup>1</sup>H NMR as previously depicted [10]. For E/MMA copolymers: mol % MMA = 100/{1 + [(A-5)/4]} with A the integral of the signals between 1 and 2.5 ppm and the integral of the O-CH<sub>3</sub> signal at 3.6 ppm calibrated for 3 protons. For E/BuA copolymers: mol % BuA = 100/{1 + [(A-10)/4]} with A the integral of the signals between 1 and 2.5 ppm and the integral of the O-CH<sub>2</sub> signal at 4.0 ppm calibrated for 2 protons. For E/BuMA copolymers: mol % BuMA = 100/{1 + [(A-12)/4]} with A the integral of the signals between 1 and 2.5 ppm and the integral of the O-CH<sub>2</sub> signal at 4.0 ppm calibrated for 2 protons. For E/MA copolymers: mol % MA = 100/{1 + [(A-3)/4]} with A the integral of the signals between 1 and 2.5 ppm and the integral of the O-CH<sub>3</sub> signal at 3.3 ppm calibrated for 3 protons. For E/styrene copolymers: mol % styrene = 100/{1 + [(A-3)/4]} with A the integral of the signals between 1 and 2.5 ppm and the integral of the phenyl signals between 5.7–7.4 ppm calibrated for 5 protons.

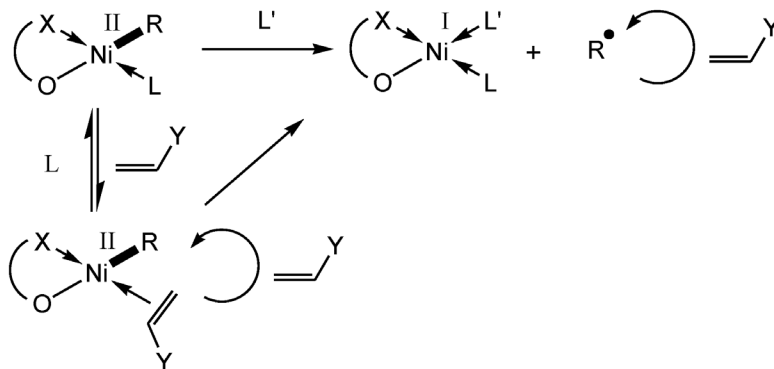
## RESULTS AND DISCUSSION

## The dual role of Ni complexes [10]

The homo- and copolymerizations of meth(acrylates) and styrene were first investigated using complexes **1** and **2**, without additional phosphine scavenger and without any Al-based cocatalysts. Under these conditions, almost no activity was observed for the homopolymerization of MMA or BuA at temperatures between 25 and 70 °C. When triphenylphosphine (PPh<sub>3</sub>) was added to **1** or **2** (molar ratio PPh<sub>3</sub>/Ni = 3/1), the formation of PMMA or PBuA was achieved efficiently [10]. This “phosphine effect” is completely unexpected for a “classical” olefin polymerization system for which phosphine scavengers are usually used in order to activate such neutral Ni complexes. More classically increasing the temperature led to higher polymerization yields.

Several mechanisms can be considered. On one hand, the mechanisms based on monomer coordination (migratory insertion or coordinative-anionic addition) usually imply a competition at the coordination site between the monomers and the phosphine. Thus, in first approximation, they should be disfavored by the presence of additional phosphine. On the other hand, a free radical mechanism based on the homolytic cleavage of the metal–carbon bond could be favored by the presence of additional phosphine, which could then, as Lewis base, stabilize the released Ni<sup>I</sup> complex.

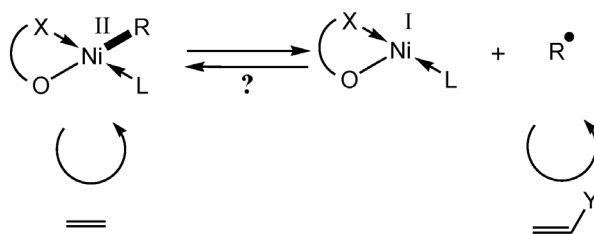
In order to discriminate the proposed polymerization mechanisms, we investigated the copolymerizations of MMA with BuA and the one of styrene with these two meth(acrylic) monomers [10]. In the copolymerization of BuA and Sty, the reactivity ratios calculated by the Kelen–Tudos method clearly support a free radical mechanism and the migratory insertion or the coordinative-anionic mechanisms can be ruled out. Reactivity ratios are very similar for both complexes, with or without additional phosphine. The radicals are assumingly released upon the homolytic cleavage of a Ni–C bond, with the Ni complex playing the role of a radical initiator (Fig. 1).



**Fig. 1** Dual role of Ni complexes in the homopolymerization of polar vinyl monomers (L = PPh<sub>3</sub>, L' = PPh<sub>3</sub> or monomer, R = Ph, X = N or P). Reprinted with permission from [10]. Copyright © 2011 American Chemical Society.

In both other cases (copolymerizations with MMA), the calculated reactivity ratios are deviating from the expected values 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. We assumed the coexistence of the free radical mechanism and the coordination/insertion mechanism as illustrated on Fig. 1.

Based on these results, the Ni complex seems to play a dual role: (1) as a radical initiator and (2) as a classical coordination/insertion catalyst. This led us to consider the copolymerization of ethylene



**Fig. 2** Dual radical/catalytic mechanism for the copolymerization of ethylene and polar vinyl monomers. Reprinted with permission from [10]. Copyright © 2011 American Chemical Society.

with polar vinyl monomers by an elegant way using the dual radical/catalytic mechanism illustrated in Fig. 2.

### Copolymerization of ethylene and MMA by a dual radical/catalytic polymerization mechanism

The copolymerization of ethylene and MMA was investigated in neat monomers with complex **1**, with or without additional PPh<sub>3</sub> at two constant ethylene pressures (25 or 100 bar) and at two different temperatures (50 or 80 °C) [10]. The results of the polymerizations are presented in Table 1.

**Table 1** Copolymerization of ethylene and MMA.<sup>a</sup>

Ni system	T polymerization (°C)	P ethylene (bar)	Yield (g)	% MMA polymer <sup>b</sup>	T <sub>m</sub> (°C)
<b>1</b>	50	25	4.1	20.5	112.3
<b>1</b>	50	100	6.5	2.7	122.4
<b>1</b>	80	100	1.8	53.3	no T <sub>m</sub>
<b>1</b> / 3 PPh <sub>3</sub>	50	25	3.1	34.0	no T <sub>m</sub>
<b>1</b> / 3 PPh <sub>3</sub>	50	100	1.2	7.7	110–121
<b>1</b> / 9 PPh <sub>3</sub>	50	100	1.8	50.1	no T <sub>m</sub>
<b>1</b> / 9 PPh <sub>3</sub>	80	100	2.7	87.7	no T <sub>m</sub>

<sup>a</sup>Polymerization conditions: 50 mL of MMA, [Ni] = 2.3 mmol l<sup>-1</sup>, t = 2 h.

<sup>b</sup>Mol %, determined by <sup>1</sup>H NMR.

Polymers were obtained in relatively good yields, significantly higher than the yields expected from both a pure free radical copolymerization or a pure coordination/insertion copolymerization (e.g., with Pd phosphine-sulfonate complexes). Note that under these conditions the free radical homopolymerization of ethylene cannot be expected.

The ethylene pressure, the temperature of polymerization, and the phosphine addition clearly influence the yield and the nature of the polymers obtained. The incorporation level of MMA drastically decreases with ethylene pressure, whereas it increases with temperature. The addition of PPh<sub>3</sub> (from 3 to 9 equiv to the Ni complex) interestingly results in an increasing incorporation level of MMA (from 7.7 to 50.1 mol % at 50 °C/100 bar).

In summary, a broad range of ethylene/MMA copolymers is obtained with MMA levels from 2.7 mol % at high pressure without additional phosphine up to 87.7 mol % at higher T and in the presence of additional phosphine. These compositions are significantly different from the copolymer compositions obtained by a pure free radical polymerization mechanism. Under the same conditions (50 °C/100 bar) with higher concentration of azobisisobutyronitrile (AIBN) as radical initiator (10 times

the Ni concentration mentioned in Table 1), a E/MMA copolymer containing 94 mol % MMA is obtained.

The molecular weights ( $M_n$ ) of the polymers are between 10 000 and 60 000 g/mol with relatively narrow molecular weight distributions ( $2 < \text{PDI} < 5$ ). The thermal properties of polymers seem to indicate long sequences of ethylene units in particular at high ethylene pressure and in the absence of additional phosphine since semicrystalline polymers are obtained. In other cases, fully amorphous polymers are obtained despite ethylene contents between 13.3 and 66 mol %.

The exact nature of the copolymers needs to be more precisely clarified, namely, with respect to the presence of homopolymers of ethylene and/or of MMA. To do so, MEK (methyl ethyl ketone) extractions of the polymers were performed and combined with in-depth  $^1\text{H}$  and  $^{13}\text{C}$  NMR analysis of the fractions as previously described [10]. Actually, the formation of homopolymers is negligible and a complex mixture of copolymers is formed. This is compatible with the proposed dual catalytic/radical mechanism. The formation of homopolyethylene was evidenced only in the case of the copolymers containing 2.7 and 7.7 mol % MMA (50 °C/100 bar, with and without additional phosphine).

The copolymers synthesized are clearly not statistical and seem to exhibit a rather blocky character. They are very different from MMA-enriched copolymers produced from a pure free radical mechanism. These findings are compatible with the proposed polymerization mechanism involving both coordination/insertion and free radical mechanisms. This polymerization is based on the dual role of the Ni complex, as a catalyst (with the migratory insertion in the  $\text{Ni}^{\text{II}}\text{-C}$  bond) and as a radical initiator (with the homolytic cleavage of the  $\text{Ni}^{\text{II}}\text{-C}$  bond) as illustrated in Fig. 2. On one hand, the efficiency of the radical initiation can be improved by the addition of phosphine or by the increase of the polymerization temperature. On the other hand, increasing the ethylene pressure apparently favors the migratory insertion mechanism, which results in the formation of ethylene-enriched copolymers and/or homopolyethylene.

The reversibility of the homolytic cleavage of the metal–carbon bond and the corresponding shuttling between coordination/insertion and radical polymerization still need to be confirmed. It would give access to the synthesis of multiblock copolymers of polar and nonpolar olefins. Based on the current results, namely, the permanent consumption of ethylene during the polymerization and the copolymers properties, the occurrence of this reversible radical/catalytic mechanism seems realistic.

### Copolymerization of ethylene and other polar vinyl monomers

Under similar conditions as for the E/MMA copolymerization, the copolymerization of ethylene and BuA was investigated (Table 2). No activity was observed at 25 and 100 bar with complex **1** without phosphine addition. At 25 bar, the addition of 3 equiv of phosphine led to the formation of a polymer containing 86.3 mol % of BuA [10]. At higher ethylene pressure (100 bar), a polymer containing lower amounts of BuA (51.3 mol %) was obtained when 9 equiv of  $\text{PPh}_3$  was added to complex **1**. Note that 3 equiv of phosphine was not enough at this ethylene pressure to observe any polymerization.

**Table 2** Copolymerization of ethylene and polar vinyl monomers or styrene.<sup>a</sup>

Polar monomer (PM)	Ni system	P ethylene (bar)	Yield (g)	$M_n$ (PDI) g/mol	% PM polymer <sup>c</sup>	$T_g$ ( $T_m$ ) (°C)
BuA	<b>1</b>	25	–	–	–	–
	<b>1</b>	100	–	–	–	–
	<b>1</b> / 3 PPh <sub>3</sub>	25	2.2	58 000 (5.2)	86.3	–49 (–)
	<b>1</b> / 9 PPh <sub>3</sub>	100	1.0	158 000 (3.3)	51.3	–53 (–)
BuMA	<b>1</b>	25	3.4	4500 (9.4)	7.2	– (100–120)
	<b>1</b> / 3 PPh <sub>3</sub>	25	3.3	134 000 (6.5)	46	– (–)
MA	<b>1</b>	25	1.7	85 000 (5.6)	15.4	20 (–)
	<b>1</b> / 3 PPh <sub>3</sub>	25	2.9	nd	86.3	0 (–)
Styrene <sup>b</sup>	<b>1</b>	25	1.2	4900 (1.8)	64.2	– (–)
	<b>1</b>	100	0.3	7900 (3.2)	16.5	– (110)
	<b>1</b> / 3 PPh <sub>3</sub>	25	2.2	3400 (2.4)	73.3	– (–)
	<b>1</b> / 3 PPh <sub>3</sub>	100	1.1	100 000 (1.2)	42.1	– (–)

<sup>a</sup>Polymerization conditions: 50 mL of PM,  $T = 50$  °C,  $[Ni] = 2.3$  mmol L<sup>-1</sup>,  $t = 4$  h.

<sup>b</sup> $t = 3$  h.

<sup>c</sup>Mol %, determined by <sup>1</sup>H NMR.

The polymers obtained are fully amorphous and fully soluble in MEK, which indicates the absence of homopolyethylene and of long ethylene sequences. The glass transitions of the polymers were measured at –49 and –53 °C, which points out the presence of long BuA sequences [ $T_g$  (homoPBuA) = –54 °C]. <sup>13</sup>C NMR analysis confirms the presence of BuA sequences and of ethylene sequences [signal at 30 ppm for  $-(CH_2)_n-$ ], indicating the presence of a sequence of at least 4 ethylene units.

Contrary to the case of MMA, the addition of PPh<sub>3</sub> is necessary for the E/BuA copolymerization to proceed which confirms homopolymerization results (no BuA homopolymerization without addition of PPh<sub>3</sub> on Ni complex). In the absence of phosphine ethylene-enriched E/MMA copolymers were produced at high ethylene pressure whereas no polymerization is observed in the case of E/BuA copolymerization. This indicates that the coordination-insertion mechanism favored in the absence of phosphine and at high ethylene pressure (as observed for E/MMA copolymerization) is more strongly hindered by acrylates than by methacrylates (possibly by the formation of a stronger chelate after polar monomer insertion as reported in the literature [11]). In the case of BuA the addition of phosphine promotes the homolytic cleavage of the Ni–C bond and the free radical polymerization becomes possible leading to the formation of BuA-enriched copolymers. Moreover the coordination/insertion mechanism on Ni is also possibly activated by phosphine coordination on Ni (diminution of chelate strength).

To get more insight into the results and support the hypotheses two other polar comonomers of the acrylate and methacrylate families were also studied as well (Table 2).

The behavior with complex **1** in the copolymerization of ethylene and BuMA is very similar to the one observed in the copolymerization E/MMA. BuMA does not inhibit the polymerization at 25 bar in the absence of additional phosphine and a low crystalline ethylene-enriched copolymer is obtained (7.2 mol % BuMA). The addition of PPh<sub>3</sub> leads to a significant increase of the BuMA incorporation up to 46 mol %. As in the case of E/MMA copolymerization an amorphous copolymer is formed when phosphine is added whereas a crystalline one is formed with the Ni complex alone.

Contrary to the case of the copolymerization of ethylene and BuA, E/MA copolymerization is not totally poisoned by the presence of the polar monomer at 25 bar in the absence of additional phosphine. The incorporation of MA drastically increases by the addition of PPh<sub>3</sub> and acrylate-enriched copoly-

mers are formed (such as in the case of E/BuA). Amorphous copolymers exhibiting  $T_g$  in the 0–20 °C range are formed, which is compatible with long acrylate sequences [ $T_g$  (homoPMA) = +10 °C].

The differences observed between acrylate and (meth)acrylate comonomers were confirmed. The control of polar monomer incorporation seems to be easier in the case of methacrylates: a broader range of copolymers is accessible upon tuning the temperature, the ethylene pressure, and the addition of PPh<sub>3</sub>. The copolymers properties are clearly different from those of statistical copolymers (obtained, e.g., by a pure free radical polymerization). They seem to exhibit a rather blocky character that is fully compatible with the dual radical/catalytic mechanism depicted on Fig. 2.

### Copolymerization of ethylene and styrene

Styrene is not strictly a polar monomer but it offers some interests in terms of mechanism understanding (in principle, no inhibition of the coordination–insertion polymerization will take place contrary to what was observed with the ester function of the (meth)acrylates). It will also give access to original ethylene-styrene copolymer microstructures. The copolymerization of ethylene and styrene was thus investigated in neat monomers with complex **1** with or without additional PPh<sub>3</sub> at two constant ethylene pressures (25 and 100 bar). These results are presented in Table 2.

Styrene behaves differently than acrylates and methacrylates especially in the absence of additional phosphine. The comonomer insertion is indeed much higher than in the case of the copolymerization of ethylene with MMA, BuMA, or MA. Such as with MMA, the copolymerization of ethylene is effective in the absence of phosphine, but the yield and styrene incorporation both decrease with increasing ethylene pressure. Such as previously observed with other polar comonomers, the addition of phosphine leads to an increase of the styrene incorporation, which tends to support the occurrence of a mechanism not solely based on coordination/insertion. The polymer produced at 100 bar and in the absence of phosphine is slightly crystalline, while the other polymers are fully amorphous despite ethylene levels between 27.7 and 58.9 mol %. This supports the absence of homopolyethylene and is only compatible with a blocky structure of styrene/ethylene copolymers. The mechanism of polymerization could be nevertheless more complex as proposed in Fig. 2 as styrene could theoretically be copolymerized with ethylene by a pure coordination/insertion mechanism on Ni.

### CONCLUSION

Incorporation of polar vinyl comonomers in polyolefins is a very challenging target in polymer chemistry. Pure coordination–insertion mechanisms have revealed their limits even if some attractive results were obtained with Pd-based catalysts. The dual radical/catalytic polymerization presented in this paper will certainly expand the horizon in this field.

Indeed, neutral Ni complexes were found to play a dual role as catalyst in olefin polymerization and as radical initiator in homo- and copolymerizations of (meth)acrylates and styrene (from the homolytic cleavage of the metal–carbon bond).

This duality of the Ni<sup>II</sup> salicylaldiminato complex was taken advantage to implement simultaneously free radical and catalytic mechanisms in the presence of ethylene and polar vinyl monomers from a single organometallic complex. A reversible polymerization shuttling from one mechanism to the other seems to proceed leading to the formation of multiblock copolymers. Indeed, the so-called “dual radical/catalytic polymerization” was efficient for the synthesis in high yields of original multiblock copolymers of ethylene and various acrylates and meth(acrylates) or styrene exhibiting original thermal properties. The important role of the PPh<sub>3</sub> addition to the Ni complex was evidenced in all cases, and it is believed to favor the radical polymerization. A broad range of copolymer compositions was achieved by varying the ethylene pressure, the temperature, and by using the “phosphine effect”.

Further investigations are in progress in order to gain more insight into both the polymerization mechanisms (combining EPR and NMR spectroscopy) and the precise characterization of the copolymers obtained (using HT-LC techniques and NMR).

## ACKNOWLEDGMENT

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## REFERENCES

1. E. Y.-X. Chen. *Chem. Rev.* **109**, 5157 (2009).
2. (a) G. Tian, H. W. Boone, B. M. Novak. *Macromolecules* **34**, 7656 (2001); (b) C. Elia, S. Elyashiv Barad, A. Sen, R. Lopez-Fernandez, A. C. Albeniz, P. Espinet. *Organometallics* **21**, 4249 (2002); (c) X. He, Q. Wu. *Appl. Organomet. Chem.* **20**, 264 (2006); (d) R. Lopez-Fernandez, N. Carrera, A. C. Albeniz, P. Espinet. *Organometallics* **28**, 4996 (2009).
3. (a) D. Guironnet, P. Roesle, T. Runzi, I. Göttker-Schnetmann, S. Mecking. *J. Am. Chem. Soc.* **131**, 422 (2009); (b) D. Guironnet, L. Caporaso, B. Neuwald, I. Göttker-Schnetmann, L. Cavallo, S. Mecking. *J. Am. Chem. Soc.* **132**, 4418 (2010); (c) T. Runzi, D. Guironnet, I. Göttker-Schnetmann, S. Mecking. *J. Am. Chem. Soc.* **132**, 16623 (2010).
4. (a) S. D. Ittel, L. K. Johnson, M. Brookhart. *Chem. Rev.* **100**, 1169 (2000); (b) L. S. Boffa, B. M. Novak. *Chem. Rev.* **100**, 1479 (2000); (c) A. Berkefeld, S. Mecking. *Angew. Chem., Int. Ed.* **47**, 2538 (2008); (d) A. Nakamura, S. Ito, K. Nozaki. *Chem. Rev.* **109**, 5215 (2009).
5. (a) L. K. Johnson, S. Mecking, M. Brookhart. *J. Am. Chem. Soc.* **118**, 267 (1996); (b) S. Mecking, L. K. Johnson, L. Wang, M. Brookhart. *J. Am. Chem. Soc.* **120**, 888 (1998).
6. E. Drent, R. Van Dijk, R. Van Ginkel, B. Van Oort, R. I. Pugh. *Chem. Commun.* 744 (2002).
7. K. M. Skupov, P. R. Marella, M. Simard, G. P. A. Gap, N. Allen, D. Conner, B. L. Goodall, J. P. Claverie. *Macromol. Rapid Commun.* **28**, 2033 (2007).
8. (a) T. Kochi, K. Yoshimura, K. Nozaki. *Dalton Trans.* 25 (2006); (b) T. Kochi, S. Noda, K. Yoshimura, K. Nozaki. *J. Am. Chem. Soc.* **129**, 8948 (2007); (c) S. Ito, K. Munakata, A. Nakamura, K. Nozaki. *J. Am. Chem. Soc.* **131**, 14606 (2009).
9. (a) K. W. Doak. In *Encyclopedia of Polymer Science and Engineering*, 2<sup>nd</sup> ed., H. F. Marks, N. M. Bikales, C. G. Overberger, G. Menges (Eds.), Vol. 6, pp. 386–429, Wiley-Interscience, New York (1985); (b) P. Ehrlich, G. A. Mortimer. *Adv. Polymer Sci.* **7**, 386 (1970).
10. A. Leblanc, E. Grau, J.-P. Broyer, C. Boisson, R. Spitz, V. Monteil. *Macromolecules* **44**, 3293 (2011).
11. (a) A. W. Waltman, T. R. Younkin, R. H. Grubbs. *Organometallics* **23**, 5121 (2004); (b) A. Berkefeld, M. Drexler, H. M. Moeller, S. Mecking. *J. Am. Chem. Soc.* **131**, 12613 (2009).