

## Copolymerization of Ethylene with Unsaturated Alcohols and Methacrylate Using a Silylated $\alpha$ -Diimine Nickel Catalyst: Molecular Modeling and Photodegradation Studies

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**ABSTRACT:** In this article, the experimental results obtained in the copolymerization of ethylene with polar monomers using a silylated  $\alpha$ -diimine nickel catalyst are described and compared with those obtained with a non-silylate similar one. The results show that the introduction of a silyl group in the para-position of the imine moiety turns the catalyst less sensitive toward polar functionalities. However, the reactivity observed in copolymerization reactions was found to be reduced both the global polymerization and incorporation rates. Molecular modeling calculation allowed us to understand both the preferred insertion mode and the intermediate product structures for E/MMA copolymerization. Photodegradation studies showed that the presence of polar groups in the copolymers increases their rate of oxidation and turn them more easily degradable. The stabilization performed by Tinuvin 770 showed that for long-exposure times, it is not very effective regardless it is only mixed or grafted to the copolymer. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 1820–1832, 2013

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### INTRODUCTION

Polyolefins are hydrophobic polymers. Thus, to improve their compatibility with inorganic fillers, reinforcers, and engineering plastics, which are hydrophilic, or to make them suitable for adhesives and dyeing agents<sup>1,2</sup> it is necessary to introduce some polar groups in the polyolefin chain. Several attempts have been made to achieve this goal and grafting polar monomers onto the polyolefinic chain is one of the most used methods to achieve it.<sup>3–9</sup> Nevertheless, these grafting techniques are

complex, pollute the environment, and lead to degradation of the polymer chains and crosslinking. In fact, it was found that competitive secondary reactions that occur simultaneously with the grafting reaction of polyethylene (PE) are mainly crosslinking<sup>10–15</sup> while PP undergoes essentially degradation.<sup>16,17</sup> Of course, it is possible to minimize this degradation process but never to prevent it completely. Thus, some degradation will always occur during the grafting processes. Furthermore, residues of graft monomers and other auxiliaries will bring negative

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effects on the properties of the blends. Therefore, direct copolymerization of the olefins with polar monomers will be a much more attractive method. These copolymerization reactions may be carried out either by a classic radical reaction or using a single-site catalyst.<sup>18–20</sup> The use of single site catalysts in this process would not only open new and less expensive routes for the synthesis of copolymers of olefins with polar comonomers but would also make it possible to get new materials with different properties from those of the commercially available ones, due to a better control of the comonomer in the polymer chain and different microstructures only possible to obtain in this case.

However, there are some difficulties in achieving this as the functional groups of the polar monomers poison the catalysts used, which are transition-metal-based complexes.

A great deal of attention has been directed recently toward the research of late-transition-metal-based complexes used as catalysts for the polymerization of olefins.<sup>2,21–23</sup> The lower oxophilicity and consequently greater functional group tolerance of late transition metals make them likely targets for the development of catalysts to be used in the copolymerization of ethylene with polar comonomers.<sup>1,2</sup> In fact, Ni and Pd complexes with bulky diimine ligands showed improved tolerance against polar functionality<sup>24–27</sup> due to the typically lower Lewis acidity of these late transition metals. However, even with these catalysts, a rather significant loss in activity was observed in the presence of the polar monomers.<sup>25–28</sup> To get a better performance of the catalyst in the presence of polar functionalities,  $\alpha$ -diimine Ni complexes with electron releasing para-substituents were synthesized.<sup>29,30</sup> Either in the case where a  $-\text{Si}(\text{tBu})\text{Ph}_2$  group was introduced at the para-position of the 2,6-dialkylaryl imine moiety<sup>29</sup> or in the case where the introduced group was  $-\text{OSi}(\text{tBu})\text{Ph}_2$ <sup>30</sup> an increase, although slight, in the electronic density on the metal was observed. In this work, the {bis[N,N'-(4-tert-butyl-diphenylsilyl)-2,6-diisopropylphenyl]imino}acenaphthene} dibromonickel **1** was used as catalyst precursor in copolymerization studies of ethylene with 5-hexen-1-ol, **H**, 10-undecen-1-ol, **U**, acrilamide AA and methyl methacrylate (MMA). The results thus obtained were compared with those previously observed for the precursor [bis(N,N'-dimesitylimino)acenaphthene] dibromonickel **2**.<sup>27</sup> Molecular modeling was used to gain insight into the polymerization process. To better evaluate the effect of the incorporation of the polar monomers in the stability of the obtained polymers, the photodegradation process of some of these copolymers was studied. Their stabilization by grafting the stabilizer onto the polymeric chain, through either the OH or the ester group of the incorporated 10-undecen-1-ol or methylmethacrylate, was also evaluated.

## EXPERIMENTAL

### Materials

{bis[N,N'-(4-tert-butyl-diphenylsilyl)-2,6-diisopropylphenyl]imino}acenaphthene} dibromonickel **1** was synthesized according to a literature procedure.<sup>29</sup> The polar monomers, 5-hexen-1-ol, **H**, 10-undecen-1-ol, **U**, acrylamide, AA, and MMA, were purchased from Aldrich. AA was heated under vacuum and nitrogen before

being used. The other comonomers were used after trap to trap distillation under nitrogen.

Methylaluminoxane (MAO) was supplied by Akzo Chemical. Trimethylaluminum (TMA), triisobutylaluminum, and diethylaluminum chloride (DEAC) were obtained from Aldrich.

### Polymerization

As described previously,<sup>27,31,32</sup> polymerizations of ethylene and copolymerization of the polar monomers with ethylene were carried out in a flame dried 250-mL crown-capped pressure bottle sealed with neoprene septum and pump filled with nitrogen atmosphere. This polymerization bottle was filled by 50 mL of dry toluene and then, in the case of the alcohols, a certain amount of the pretreated comonomer solution was added. The resulting solution was then saturated at an ethylene relative pressure previously stated, usually around 1 bar, which was maintained throughout the polymerization reactions. Then the cocatalyst in the proper Al/Ni ratio was added via a glass syringe. At this time, the solutions were brought to the desired temperatures and allowed to equilibrate for 15 min. After this, the corresponding amount of a toluene solution of the Ni catalyst was added to the polymerization reactors. In the case of MMA, no initial solvent was used. A certain volume of MMA was initially introduced in the reactor followed by the same procedure described above. The polymerizations were terminated after a certain period of time by quenching the mixture with 150 mL of a 2% (v/v) HCl/methanol solution.

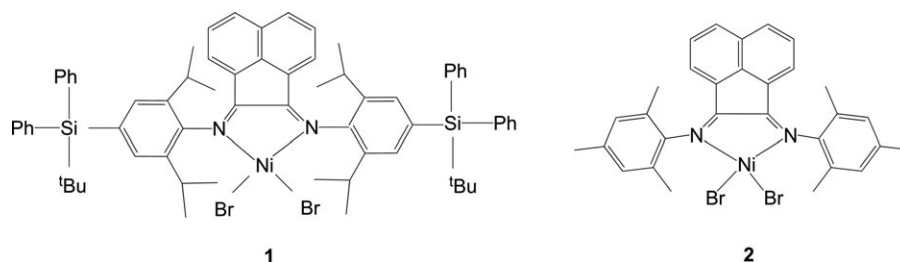
Both **H** and **U** were treated *in situ* with TMA 5 min before the introduction of the cocatalyst, MAO, and the catalyst precursor. The homopolymerization of MMA and its copolymerization with ethylene, **E** were carried out in bulk.

### Mixing and Grafting Procedures

**Grafting Procedure of Tinuvin 770.** Grafting of Bis (2,2,6,6-tetramethyl-4-piperidyl) sebacate (Tinuvin 770) on E/MMA copolymer was performed in a test tube under argon atmosphere. A weighed amount of E/MMA copolymer and Tinuvin 770 were loaded in test tube and then dried solvent was added and left for 24 h to attain the equilibrium swelling of the powder. The reaction system was deaerated by bubbling argon gas for 8 min, and then the test tube was sealed. The tube was placed into the radiation chamber at a suitable distance and height for a desired period. After 5 h the reaction was stopped by the addition of a large volume of acetone to the reaction mixture. Tinuvin 770 was used in an excess concentration of 1.2 wt % of copolymer E/MMA to get in the final sample a concentration of Tinuvin 770 as close of 1.00 wt % as possible. After photoreaction, the ungrafted stabilizer was removed by precipitation. The whole mass was filtered and washed with acetone. The residual Tinuvin 770 removed by Soxhlet extraction with methanol for 48 h. The graft copolymer was dried to constant weight under vacuum at 50°C. Percent grafting was calculated as follows:

$$\text{Percentage of grafting(\%)} = \frac{W_g - W_0}{W_0} \times 100 \quad (1)$$

where  $W_g$  and  $W_0$  represent the weight of grafted and initial powdered polymer, respectively. The results obtained for each



Scheme 1. Catalyst structures.

sample are: LNi 153 0.83 wt %, LNi 154 0.78 wt %, LNi 155 0.80 wt %, and LNi 160 0.81 wt %

**Mixing Procedure of Tinuvin 770.** In mixed blend samples, the conventional stabilizer Tinuvin 770 was mixed with copolymer E/MMA by melt blending in a Minimax mixer (CSI, CS-183 MMX) at 170°C for 10 min then extruded. Tinuvin 770 was used in 1.00 wt % concentration of copolymer E/MMA.

#### Polymer Characterization

Copolymers were analyzed by NMR as described previously.<sup>27</sup> <sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained on samples dissolved in a mixture of 1,2,4-trichlorobenzene with 35% C<sub>6</sub>D<sub>6</sub> at 110°C or CDCl<sub>3</sub> at room temperature. The instrument used was a Varian Unity 300 spectrometer. The internal reference is provided by hexamethyldisiloxane ( $\delta$  <sup>1</sup>H 0.06,  $\delta$  <sup>13</sup>C 1.9 relative to tetramethylsilane) or tetramethylsilane.

The thermal properties of the copolymers were determined by differential scanning calorimetry (DSC). The equipment used for the DSC analyses was a Perkin Elmer DSC-7. The samples were heated/cooled at a rate of 10°C/min under nitrogen environment. The melting temperature and heat of fusion were obtained from the heating thermogram.

For photodegradation studies, thin films (100  $\mu$ m) were prepared by a preheated carver press at 170°C by applying 150 kg/cm<sup>2</sup> platen pressure for 30 s and cooled rapidly by water circulation in the press under pressure.

The samples were irradiated in a polychromatic irradiation chamber SEPAP 12-24 (M/s Material Physico Chimique, Nueilly, Marne, France) at 60°C under air.<sup>33</sup> This polychromatic irradiation chamber consists of four 400 W medium-pressure mercury vapor lamps, supplying radiation longer than 290 nm.

The oxidative photodegradation was identified and estimated with FTIR spectroscopy (16PC Perkin-Elmer Spectrometer). The oxidized films were analyzed immediately to minimize the slow oxidation rate during storage. Surface morphology of the films was studied by using a Leica Cambridge (Stereoscan 440) Scanning Electron Microscope. The specimens were coated with gold (90 nm thick) in an automatic Sputter coater (Poloran Equipment, Scanning Electron Microscope coating unit E5000, U.K), the accelerating potential was 10 KV.

#### Molecular Modeling

Molecular modeling calculations were performed using PC Spartan 04 for PM3 calculations. The program was supplied by Wavefunction and the methods applied are described in the relevant literature.<sup>34</sup>

Full geometry optimizations, for all the complexes under analysis, were performed. As the molecules under investigation were rather large, a semiempirical PM3 model was used. Enthalpies of formation of all compounds and transition states were also computed under this approximation.

## RESULTS AND DISCUSSION

### Copolymerization Results

Different cocatalysts have been studied previously in the activation of the catalyst precursor 1. DEAC and MAO had been shown to be the best ones for this system in the polymerization of ethylene.<sup>28</sup> The PE obtained with this catalyst system is a branched polymer (N branches/1000C = 34 in the case of MAO, RT; 45 in the case of DEAC, RT and 92 in the case of DEAC,  $T = 60^\circ\text{C}$ ). However, when a similar Ni catalyst precursor, 2, is used, the PE obtained, under similar experimental conditions, is rather more branched than that obtained with precursor 1 (N branches/1000C = 93 in the case of MAO, RT, and 102 in the case of DEAC, RT for precursor 2). The structures of the two catalyst precursors studied are depicted in Scheme 1.

The catalyst system 1/MAO was also studied in copolymerization reactions of E with polar comonomers such as H, U, and MMA. When H or U, beside ethylene E, was introduced in the polymerization reactor, the activity of the polymerization was reduced to almost zero.

However, when these polar comonomers were pretreated with alkyl aluminium, it is possible to obtain some polymer although with a quite lower activity (Tables I and II). This behavior had already been observed previously when precursor 2 was used.<sup>27</sup> Nevertheless, the new catalyst precursor 1 was expected to show a better performance than 2 in the presence of polar functionalities as the introduction of the -Si(<sup>t</sup>Bu)Ph<sub>2</sub> group at the para-position of the 2,6-dialkylaryl imine led to an increase, although slight, of the electronic density over the metal (see below in Table V).

Unfortunately this was not enough to turn it into a completely tolerant complex against these polar functionalities. In fact, to get some polymer in the presence of H or U, it was necessary to use a protecting agent. However, the activity of the catalyst system 1/MAO was shown to be quite higher than that of 2/MAO either in the homopolymerization of ethylene or in the copolymerization of ethylene with unsaturated alcohols which may be ascribed to the inductive effect of the -Si(<sup>t</sup>Bu)Ph<sub>2</sub> group. In fact, the activity of 1/MAO is 2–3 times higher than that observed with 2/MAO both in E homopolymerization and in copolymerization of E/U or E/H.<sup>27</sup>

**Table I.** Copolymerization of E with H Using the System 1/MAO

Catalyst System	Run N	[H] <sup>a</sup> (mM)	Time (h)	Activity × 10 <sup>-6</sup> (g/molNi.[E].h)	Polymer OH <sup>a</sup> mol %
1/MAO	LNi 19 <sup>b</sup>	-	0.1	60.580	-
	LNi 30 <sup>c</sup>	H/33	1	0.283	0.49
	LNi 31 <sup>c</sup>	H/100	3	0.373	0.96
	LNi 48 <sup>d</sup>	H/100	3	0.143	1.46
	LNi 77 <sup>c</sup>	H/300	3	0.015	2.50

**Experimental conditions:** V = 50 mL toluene; H was pretreated with TMA in a molar ratio of 1:1.

<sup>a</sup>[H] accounts for the concentration of 5-hexen-1-ol in the feed and OH for the concentration of hydroxyl groups, and consequently the concentration of comonomer, incorporated in the polymer

<sup>b</sup>[Ni] = 5 μM, T = RT, [E] = 0.37 M, Al/Ni = 720.

<sup>c</sup>[Ni] = 30 μM, T = RT, [E] = 0.37 M, Al/Ni = 3000.

<sup>d</sup>[Ni] = 30 μM, T = 50°C, [E] = 0.28 M, Al/Ni = 3000.

The drop in the activity observed in the presence of the pretreated unsaturated alcohols is less pronounced when the comonomer is U (~ 3 to 60 times less than the activity of the homopolymerization of ethylene) than in the case of H (200 to 4000 times). This decrease in the activity seems to be better related to a decrease in the insertion rate of these comonomers than to the poisoning of the catalyst by the heteroatoms. It is interesting to note that the increase in the activity of system 1/MAO compared to system 2/MAO does not go along with an increase of the comonomer incorporation ratio. In fact, for the same comonomer concentration in the feed, the incorporation level in the polymer is 2–3 times lower for the system 1/MAO than that observed for the system 2/MAO.<sup>27</sup>

The -Si(<sup>t</sup>Bu)Ph<sub>2</sub> group seems to enhance the ethylene polymerization rate (Rate<sub>EP</sub>) more strongly than the unsaturated alcohols polymerization rates (Rate<sub>UAP</sub>). Thus, the increase of activity together with the decrease in the polar monomer incorporation level may be due to the higher ratio (Rate<sub>EP</sub>)/(Rate<sub>UAP</sub>) observed for the system 1/MAO compared with that of system 2/MAO.<sup>27</sup> The results in Tables I and II show that an increase

of the comonomer concentration in the feed leads to an increase of the incorporation level of both H and U in the polymer. No significant improvement in the performance of the catalyst system was observed by increasing the polymerization temperature. In the case of H, a slight increase in the concentration of polar monomer incorporated in the polymer was observed at higher temperatures, but this was accompanied by a slight decrease in the polymerization activity (Run LNi 48 vs. 31). In the case of the polar monomer U, both the activity and the incorporation ratio of comonomer in the polymer decreased by increasing the temperature from RT to T = 50°C (Run LNi 70 vs. 91).

The system 1/MAO was studied in the polymerization of MMA and copolymerization of E/MMA. The results were compared with those obtained with another system involving catalyst 2' activated also with MAO; catalyst 2', {bis[N,N'-2,6-diisopropylphenyl]imino}acenaphthene} dibromonickel,<sup>35</sup> is very similar to catalyst 2 and thus the results obtained were used to compare activities and conversion values. These polymerizations were carried out without any solvent and any pretreatment of the polar monomer. The results in Table III show that system

**Table II.** Copolymerization of E with U Using the System 1/MAO

Catalyst System	Run N	[U] <sup>a</sup> (mM)	Time (h)	Activity × 10 <sup>-6</sup> (g/molNi.[E].h)	Polymer OH <sup>a</sup> (mol %)
1/MAO	LNi19 <sup>b</sup>	-	0.1	60.58	-
	LNi26 <sup>c</sup>	U/50	1	18.09	0.42
	LNi89/LNi2 <sup>c</sup>	U/100	3	3.72	1.70
	LNi90/LNi1 <sup>c</sup>	U/200	3	4.71	2.70
	LNi91 <sup>c</sup>	U/300	3	3.94	4.04
	LNi70/LNi150 <sup>d</sup>	U/300	3	0.02	3.23
	LNi142 <sup>e</sup>	U/500	47	0.11	4.32

Experimental conditions: V = 50 mL toluene; U was pretreated with TMA in a molar ratio of 1:1;

<sup>a</sup>[U] accounts for the concentration of 10-undecen-1-ol in the feed and OH for the concentration of hydroxyl groups, and consequently the concentration of comonomer, incorporated in the polymer.

<sup>b</sup>[Ni] = 5 μM, Al/Ni = 720, [E] = 0.37 M, T = RT.

<sup>c</sup>[Ni] = 10 μM, t<sub>p</sub> = 3 h, Al/Ni = 720, [E] = 0.30 M, T = RT.

<sup>d</sup>[Ni] = 10 μM, t<sub>p</sub> = 3 h, Al/Ni = 720, [E] = 0.23 M, T = 50°C.

<sup>e</sup>[Ni] = 20 μM, Al/Ni = 930, [E] = 0.37 M, T = RT.

**Table III.** Copolymerization of E with MMA Using the Systems 1/MAO and Catalyst 2'/MAO

Catalyst System	Run N	[E] (M)	Conversion (mol %)	Activity $\times 10^{-3}$ (g/molNi.h)	Polymer MMA (mol %) <sup>a</sup>
1/MAO[32]	LNi153 <sup>b</sup>	-	13	3.70	-
	LNi158 <sup>c</sup>	-	6	5.80	-
	LNi155 <sup>b</sup>	0.34	14	3.80	60
	LNi160 <sup>d</sup>	0.63	13	12.70	20
	LNi162 <sup>b</sup>	0.50	11	3.20	50
2'/MAO[35]	-	-	19 <sup>e</sup>	5.30	-
	-	-	22 <sup>f</sup>	6.20	-
	-	-	9 <sup>g</sup>	3.3	-

Experimental conditions:  $V_{\text{MMA}} = 10$  mL,  $[\text{Ni}] = 1.4$  mM,  $\text{Al/Ni} = 500$ ; MMA was used in bulk; the catalyst solution was prepared in ODCB.

<sup>a</sup>Concentration of MMA incorporated in the copolymer, calculated by  $^1\text{H}$  NMR and confirmed by  $^{13}\text{C}$  NMR.

<sup>b</sup> $t_p = 24$  h,  $T_p = 30^\circ\text{C}$ .

<sup>c</sup> $t_p = 7$  h,  $T_p = -20^\circ\text{C}$ .

<sup>d</sup> $t_p = 7$  h,  $T_p = 0^\circ\text{C}$ .

<sup>e</sup> $t_p = 24$  h,  $T_p = 30^\circ\text{C}$ .

<sup>f</sup> $t_p = 24$  h,  $T_p = -10^\circ\text{C}$ .

<sup>g</sup> $t_p = 24$  h,  $T_p = -20^\circ\text{C}$ .<sup>32,35</sup>

2'/MAO leads to slightly better activities and conversions than system 1/MAO. The concentration of MMA in the polymer is rather higher than that observed for H or U but the activities are much lower. For system 1/MAO, the incorporation of MMA varies between 20 and 60%.

An attempt to obtain copolymers of E with AA using the catalyst system 1/MAO was also made. Since the activity of ethylene polymerization carried out in the presence of acrylamide was found to be close to zero (only traces of polymer could be obtained), no characterization of the polymer was possible. The reaction product of E with the pretreated AA (AA/TMA) showed to be a functionalized PE when system 2/MAO was used.<sup>36,37</sup> The activity found for a polymerization run of E with 110 mM of AA at RT was  $A = 12 \times 10^4$  g/mol/Ni/[E].h and the amount of AA incorporated in the copolymer was about 20 units of AA per macromolecule. Although only small amounts of AA were incorporated into the copolymers, their solubility and stiffness were found to be completely different from those of the parent homopolymers PAA and PE.<sup>19</sup> A more fundamental study using hexene and AA led to the conclusion that AA inserts in a 2,1 mode at the end of the polymer chain. However, due to the chain walking process, several AA molecules per macromolecule of copolymer could be found, located each one at the end of a PE branch.<sup>20</sup>

However, when E was polymerized in the presence of AA (AA/TMA) using system 1/MAO as catalyst, the polymer obtained, which was found to have similar solubility to PE, showed no evidence of the presence of AA units in the polymer chain. Either the number of AA units incorporated, possibly as end groups, was too small and the molecular weight of the polymer too high to be possible to detect them by NMR or no incorporation has occurred. Another possible explanation for the lower number of AA units incorporated, most probably located at the end of the branches, besides that resulting from a lower coordination/insertion rate for AA in the case of precursor 1, comes from the fact that the PE obtained

with this precursor is less branched than that obtained with precursor 2.

The results of DSC analysis of the homopolymers and copolymers obtained with the catalyst systems 1/MAO are depicted in Table IV. These results show that both the enthalpy of fusion and the melting point of the copolymers involving unsaturated alcohols decrease when the concentration of the incorporated alcohol increases, as expected. However, in the case of copolymers of E/MMA, this effect is not observed. This may be partially due to the fact that the PMMA sequences show some syndiotacticity.

Compared to PMMA, the presence of E in the chain decreases the melting point of the copolymer except in the case where the amount of E is as high as 80%. In this case, a slight increase of the melting point is observed. Interesting to note is that this copolymer shows a higher melting point than any of the related homopolymers, PE or PMMA.

### Molecular Modeling

Following a previous comparative study between these two catalyst precursors 1 and 2 regarding homopolymerization of E and copolymerization of E/U, molecular modeling calculations involving homopolymerization and copolymerization of AA and MMA with E were now performed to get also further insight into these polar monomers polymerization processes.

Since the main objective of the molecular modeling study is to compare the two catalyst precursors, no structural simplification should be made and the complete structures had to be modeled. This fact, coupled with the fact that the molecules in question are rather large and that a significant number of species had to be computed implied that a semiempirical method was used and PM3 was chosen. Molecular modeling calculations allowed us to observe that the electronic density over the metal increases when the group  $\text{Ar}_2\text{RSi-}$  substitutes the  $\text{CH}_3-$  one (Table V).



**Table IV.** Results of DSC Analysis of PE, PMMA, and Copolymers E/H, E/U, and E/MMA

Entry	% Polar Monomer H,U or MMA in the polymer	$\Delta H_f$ /J/g	$T_{onset}$ (°C)	$T_{max}$ (°C)	$\Delta T$ (°C)
LNi19 (MAO, 18°C) PE	-	108.2 (78.7)	89.5 (71.0)	109.9 (99.0)	~ 60 <sup>a</sup> (~ 80)
LNi30 E/H	-	90.1 (83.2)	85.2 (79.3)	106.4 (98.3)	21.2 (19)
LNi31 E/H	-	70.2 (52.7)	84.1 (77.3)	90.4 (84.1)	6.3 (6.8)
LNi 77 E/H	2.5	73.1 (71.3)	83.6 (78.4)	88.5 (83.3)	73.1 (71.3)
LNi 26 E/U	-	24.2 (19.2)	96.8 (89.1)	102.7 (95.9)	5.9 (6.8)
LNi 89 E/U	1.7	38.1 (35.6)	80.8 (78.7)	89.2 (91)	38.1 (35.6)
LNi 90 E/U	2.7	41.6 (38.8)	59.1 (45.9)	67.7 (59.5)	41.6 (38.8)
LNi 91 E/U	4.0	12.8 (8.7)	46.8 (41.8)	55.8 (50.5)	12.8 (8.7)
LNi153 PMMA	-	11.1 (9.01)	105.9 (99.7)	114.6 (107.4)	8.7 (7.7)
LNi155 E/MMA	60	12 (10.90)	101.6 (94.5)	110.5 (101.6)	8.9 (7.1)
LNi160 E/MMA	20	25.1 (21.6)	114.2 (104.3)	122.7 (111.6)	8.5 (7.3)
LNi162 E/MMA	50	6.7 (5.6)	94.3 (89.4)	101.3 (94.8)	7.0 (5.4)

<sup>a</sup>Scans performed from 30 to 200°C, scan rate: 10°C/min; values of a second scan between brackets.

The structure and energetics of various species that participate in the steps involved in the growing of the polymer chain both in the polymerization and copolymerization reactions were also estimated, by PM3 calculations, for the catalyst precursors 1 (SiPhNiBr<sub>2</sub>) and 2 (MesNiBr<sub>2</sub>). These calculations involved the stable species with and without coordinated monomer as well as the activated species in the insertion step, both when ethylene and the polar monomer are being inserted.

**Acrylamide.** Since in AA there are three possible ways of coordination to the metal active center, through the O, through the N, and through the double bond C=C, these three complexes were modeled and their heat of formation was estimated (data in Supporting Information Table I). The obtained values show that, for both precursors, the energetically most favorable complex corresponds to the coordination through the O. This explains why a pretreatment of AA with TMA is required before carrying out the polymerization reaction. Thus, next step was to study the interaction between AA and TMA.

Since AA has two basic atoms, the Al of TMA may either coordinate through the O or the N. The coordination of one molecule of AA with two of TMA must also be considered. Scheme 2 show the reaction between AA and TMA, including the case where a reaction between one hydrogen of the NH<sub>2</sub> group of the AA and a CH<sub>3</sub> of the TMA occurs with formation of CH<sub>4</sub>. The heats of formation of each of these complexes were

**Table V.** Energy and Electronic Density for the Dibromide  $\alpha$ -Diimine Ni Complexes 1 and 2

Catalyst precursor	Heat of formation (Kcal/mol)	Ni Mulliken Density
1	-338.5	-0.917
2	-348.8	-0.900

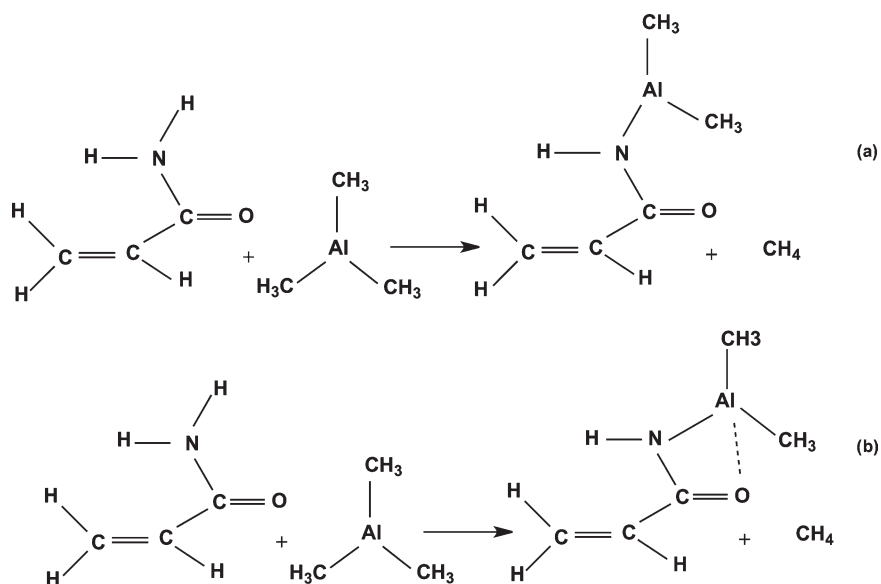
Geometry optimization and the energy of formation of the complexes were computed by PM3.<sup>34</sup>

also estimated and it was found that the adduct formed with one molecule of AA and two of TMA involving a methane elimination reaction was the most stable one. (data in Supporting Information-Table II)

However, experimentally it was observed that the activity of the reaction decreases when a ratio TMA/AA of two was used, which seems to indicate that the two/one adduct may be less reactive. Thus, as the adduct AA-TMA with the Al atom simultaneously bonded to the N and the O atoms of the AA with a simultaneous reaction between one hydrogen of the NH<sub>2</sub> group of the AA and a CH<sub>3</sub> of the TMA was the most stable among the remaining structures, it was this species (Me<sub>2</sub>AlNHOC<sub>3</sub>H<sub>3</sub>) [Scheme 2(b), Figure 1] that was used for the study for the coordination and insertion reactions.

The optimized structures of the cationic active center with a growing chain of different sizes, with a coordinated TMA protected acrylamide AA-TMA before and after its insertion in the growing chain show an agostic interaction of the  $\beta$ -hydrogen with the metal ( $d(\text{Ni}-\text{H}) \approx 1.68$  Å;  $d(\text{C}-\text{H})$  agostic  $\approx 1.51$  Å and if no agostic interaction occurs this distance would be  $d(\text{C}-\text{H}) \approx 1.1$  Å).

Calculations similar to those performed with the unsaturated alcohols<sup>28</sup> were also carried out with this system. Two modes of AA insertion were studied. The results in Table VI were obtained when both 1,2 and 2,1 insertion mode were considered for catalyst precursors 1 and 2 activated with MAO. These results show that the energetics of these reactions is roughly independent of the size of the growing chain after the first insertion ( $R > C3$ ). Thus, to simplify, after the two set of results obtained for the insertion mode 1,2 where all the calculated values are shown, it will be only shown the results obtained for a growing chain where  $R \geq C5$ . According to these results, it is expected the insertion rate of an AA molecule in the PE chain to be lower in the case of catalyst precursor 1 than in the case of 2. A much less stable coordination complex is obtained and a similar or higher Ea for the insertion is observed



**Scheme 2.** Reaction between AA and TMA with formation of CH<sub>4</sub>. (a) The Al atom of TMA is bonded only to the N of AA; (b) The Al atom is simultaneously coordinated through the O and the N of AA.

in the case of catalyst precursor 1 compared with 2. The experimental results obtained are in good agreement to these findings as when catalyst precursor 1 is used no evidence of AA insertion could be found. Conversely, when catalyst precursor 2 was used, a functionalized PE was obtained having AA molecules in the end of the PE branches.<sup>36,37</sup>

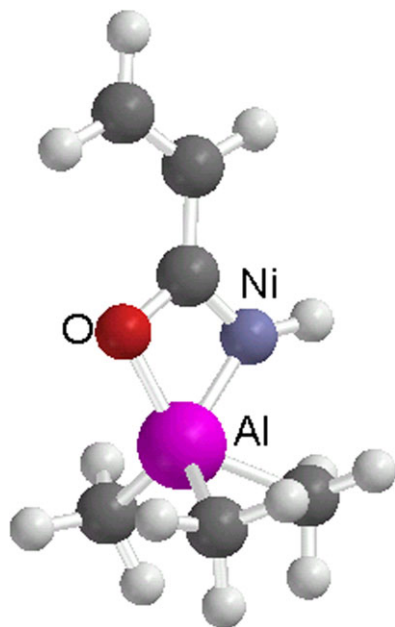
The experimental results obtained show that only functionalized PE, PE, or polyhexene, PHex are obtained when the polymerizations of E or Hex are carried out in the presence of AA. No co-

polymer of PE/PAA or PHex/PAA either block or random could be identified so far.<sup>36,37</sup> Thus, it seems that after the insertion of one molecule of AA no other insertion occurs (either of E or AA). Regarding the insertion mode, these calculations point to a slight preference for the 1,2 insertion mode no matter the catalyst precursor is. However, there is experimental evidence that a 2,1 insertion of an AA has occurred when hexen-1-ene, instead of ethylene, was used as main monomer.<sup>37</sup> This disagreement between the experimental results and the theoretical calculations may be probably due to different monomers being used (ethylene in the theoretical calculations and hexen-1-ene in the experimental runs) and is also related to the small difference that is observed for the two insertion modes.

**Methylmethacrylate.** In the case of MMA, different structures for the cationic active center with a growing chain of different sizes and an inserted molecule of MMA were modeled and the results are discussed below. In the case of MMA, as in the case of AA, the size of the growing chain seems not to significantly affect the energetics of the reactions provided that  $R > C3$ .

1-In the case of a 1,2 insertion (the less substituted carbon is bonded to the metal) as the  $\beta$ -carbon has no hydrogen atoms different complex structures may occur:

- i. Structures showing an agostic interaction between a hydrogen of the CH<sub>3</sub> group (a  $\gamma$ -carbon) and the metal. ( $d(\text{Ni}-\text{H}) \approx 1.74 \text{ \AA}$ ;  $d(\text{C}-\text{H}) \text{ agostic} \approx 1.27 \text{ \AA}$  and if no agostic interaction occurs, the distance would be  $d(\text{C}-\text{H}) \approx 1.1 \text{ \AA}$ ).
- ii. Structures where the interaction between this H of the CH<sub>3</sub> group and the Ni becomes even stronger looking like if the hydrogen becomes truly bonded to the Ni and not any more to the C (Figure 2). This complex is about 4.5 Kcal/mol more stable than the previous one in the case of catalyst 1 and about 2 Kcal/mol in the case of catalyst 2.



**Figure 1.** Adduct  $\text{C}_2\text{H}_3\text{C}=\text{ONHAl}(\text{CH}_3)_2$  formed in the reaction between AA and TMA showing the Al atom bonded simultaneously to the N and the O atoms. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

**Table VI.**  $\Delta H$  and  $E_a$  of TMA-AA Coordination and Insertion Step Assuming Two Insertion Modes, 1,2 and 2,1 for Catalyst Systems 1 and 2

Catalyst System	R	$H_{\text{Coord}}$ (Kcal/mol)	$E_{a\text{insertion}}$ (Kcal/mol)	$ \Delta H_{\text{insertion}} $ (Kcal/mol)
1/MAO Insertion mode 1,2	Me	-35.08	37.48	3.99
	Pr	-0.52	27.64	-9.32
	Pe	-1.73	27.76	-9.56
	Hp	-1.98	27.99	-9.38
1/MAO Insertion mode 2,1	Pe	-1.73	35.55	-5.65
	Hp	-1.98	35.76	-5.39
2/MAO Insertion mode 1,2	Me	-77.25	35.67	12.73
	Pr	-18.35	27.26	1.74
	Pe	-18.54	27.17	1.70
	Hp	-18.55	27.18	1.71
2/MAO Insertion mode 2,1	Pe	-18.54	30.23	3.14
	Hp	-18.54	30.22	3.15

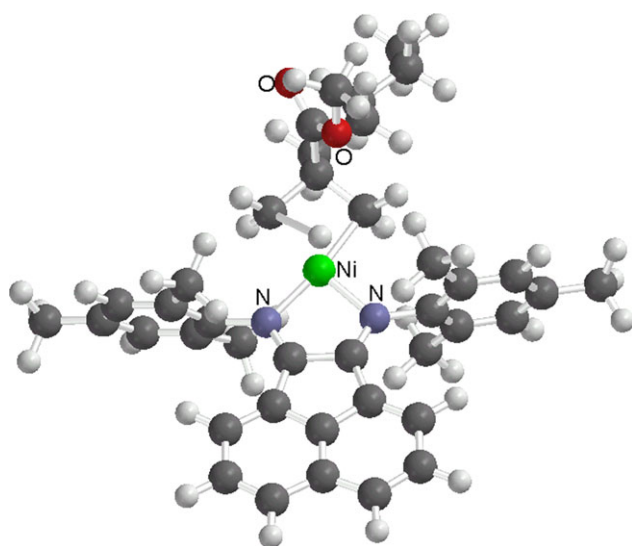
iii. Structures showing the oxygen of the carbonyl group coordinated to the metal. This complex, exhibiting a five-member ring, is much more stable (in 31.9 Kcal/mol for catalyst 1 and in 44.5 Kcal/mol for 2) than any of those mentioned earlier (Figure 3).

2-In the case of a 2,1 insertion, the following structures have to be considered:

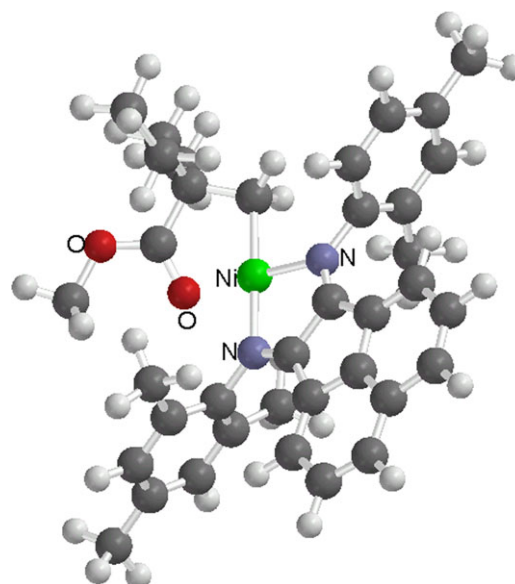
1. Structures showing a  $\beta$ -agostic interaction ( $d(\text{Ni}-\text{H}) \approx 1.66\text{\AA}$ ;  $d(\text{C}-\text{H})$  agostic  $\approx 1.5\text{\AA}$  and if no agostic interaction occurs, this distance would be  $d(\text{C}-\text{H}) \approx 1.1\text{\AA}$ ).
2. Structures with the oxygen of the carbonyl group coordinated to the metal.
3. If no chain-walking occurs, the complex showing a four-member ring was found to be about 48 Kcal/mol more

stable than the previous one for catalyst precursor 1 and 44 Kcal/mol in the case of 2 (Figure 4).

If rearrangements due to chain-walking take place, complexes with rings of different sizes may occur. The complex exhibiting a six-member ring in the case of catalyst precursor 2 was found to be as stable as the one with a four-member ring being both more stable than those with rings of either five or seven members. In the case of catalyst precursor 1, the complex exhibiting a six-member ring was found to be the most stable of all the possible complexes. These types of complexes, showing a six-member ring, have been detected by NMR in MMA polymerization reactions catalyzed by similar  $\alpha$ -diimine systems.<sup>25,26</sup>

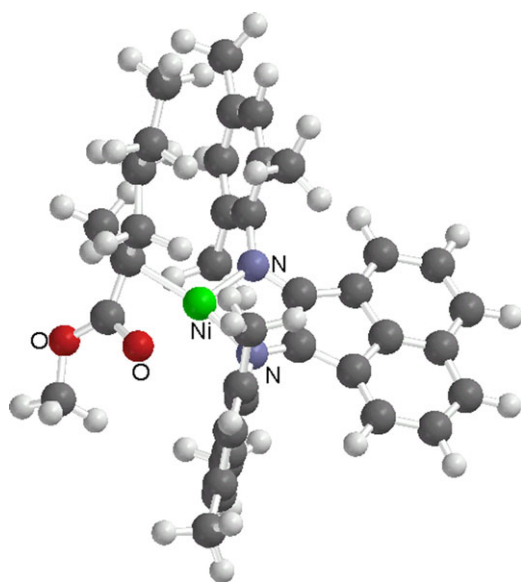


**Figure 2.** Complex structure after 1,2 MMA insertion for catalyst 2 showing a strong interaction between the H of the  $\text{CH}_3$  group and the Ni. ( $d(\text{Ni}-\text{H}) \approx 1.56\text{\AA}$ ;  $d(\text{C}-\text{H})$  agostic  $\approx 2.3\text{\AA}$ ; if no agostic interaction occurs, this distance would be  $d(\text{C}-\text{H}) \approx 1.1\text{\AA}$ ). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 3.** Complex structure after 1,2 MMA insertion for catalyst 2 showing the formation of a chelate between the O and the Ni (five-member ring). The difference between the heat of formation of this structure and that where no chelate is formed is  $\Delta\Delta H = -44.5\text{ Kcal}$ . [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]





**Figure 4.** Complex structure after 2,1 MMA insertion for catalyst 2 showing the formation of a chelate between the O and the Ni (four-member ring). The difference between the heat of formation of this structure and that where no chelate is formed is  $\Delta\Delta H = -48.6$  Kcal. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

A coordination of an ethylene molecule after the insertion of a MMA one was also studied. Tables VII and VIII show the enthalpies and activation energies for the coordination of a MMA molecule, its insertion, and the subsequent coordination of E and MMA molecules for the different structures.

**Structures showing a  $\gamma$ -agostic interaction.** Only one transition state could be found for both cases 1 i) and 1 ii). However, different values for the enthalpy of insertion will be reached in each case. Table VII shows the values obtained in Case 1 i) and 1 ii) for an insertion mode 1,2. The values obtained in Case 1 ii) show a stronger interaction between the  $\gamma$ -H and the Ni than that observed in Case 1 i).

**Structures showing a  $\beta$ -agostic interaction.** As mentioned earlier, these types of structures are only possible if a 2,1 insertion has occurred (Case 2). Table VIII shows the values obtained in this case.

**Structures showing a coordination of the oxygen of the carbonyl group to the metal.** In this case, one of the oxygen atoms of the MMA is also coordinated to the Ni which seems to stabilize the structure. Table IX shows a summary of the energetics involved in the coordination of E and MMA after the first MMA insertion for different insertion modes and structures. The values in Tables VII and VIII, where noncyclic structures were considered, show that after a 1,2 MMA insertion the coordination either of E or MMA is much more unfavorable than the first one. However if the MMA insertion mode is 2,1 subsequent coordination of E seems to be as favorable as in E homopolymerization and that of MMA is even more favorable than the first MMA coordination. Thus, it would be expected the copolymerization of E and MMA to occur at a similar rate as E homopolymerization. This, however, is not true since experimentally a considerable decrease in the rate is observed. The values in Table IX are able to explain why this happens. In fact, when a chelate structure is formed the coordination reaction of MMA is endothermic and that of E is much less exothermic than in homopolymerization even in the case of a previous 2,1 insertion of MMA which is the most favourable case.

Despite the  $E_a$  energy for 1,2 insertion being slightly lower than that of 2,1, these results explain not only why a 2,1 MMA insertion mode is observed experimentally<sup>25,26</sup> (Tables VII vs. VIII) but also why a significant decrease in the polymerization rate is observed.

#### Photodegradation and Stabilization Studies

There is a wide range of industrial applications for polyolefins-containing polar groups or copolymers of olefins with polar monomers. However, as the introduction of polar groups in a polyolefin chain is expected to cause an increase of the photodegradation process of the sample it would be necessary, before thinking of any application, to study this aspect to know how far this degradation will go when compared with the parent homopolymers. In this context, it would also be interesting to find out how to improve their stability. Thus, a thorough study on photodegradation and stabilization of the homopolymer and copolymer samples was performed. Tinuvin 770, which is a relatively new stabilizer that can be either mixed or grafted in the polymer samples, seemed to us to be a quite promising stabilizing agent and for this reason it was the first stabilizer studied.

**Table VII.**  $\Delta H$  and  $E_a$  of MMA Coordination, 1,2 Insertion and Subsequent E and MMA Coordination for Catalyst Systems 1 and 2 (Cases 1 i and 1 ii)

Catalyst systems	R	$\Delta H_{\text{CoordMMA}}$ (Kcal/mol)	$E_a$ insertion (Kcal/mol)	$\Delta H_{\text{insertion}}$ (Kcal/mol)	$\Delta H_{\text{CoordE}}$ (Kcal/mol)	$\Delta H_{\text{CoordMMA}}$ (Kcal/mol)
<b>1/MAO</b> Insertion mode 1,2 (Case 1 i)	Hp	-0.11	23.78	-18.64	-9.24	28.08
	No	-0.12	23.67	-18.63	-9.24	28.08
<b>1/MAO</b> Insertion mode 1,2 (Case 1 ii)	Hp	-0.11	23.78	-20.91	-6.97	30.35
	No	-0.12	23.67	-20.90	-6.97	30.35
<b>2/MAO</b> Insertion mode 1,2 (Case 1 i)	Hp	-12.33	19.60	-12.05	-22.22	7.30
	No	-12.33	19.60	-12.05	-22.22	7.30
<b>2/MAO</b> Insertion mode 1,2 (Case 1 ii)	Hp	-12.327	19.60	-16.70	-17.57	11.96
	No	-12.329	19.60	-16.70	-17.57	11.96

**Table VIII.**  $\Delta H$  and  $E_a$  of MMA Coordination, 2,1 Insertion and Subsequent E and MMA Coordination for Catalyst Systems 1 and 2

Catalyst Systems	R	$\Delta H_{\text{CoordMMA}}$ (Kcal/mol)	$E_{a\text{insertion}}$ (Kcal/mol)	$\Delta H_{\text{insertion}}$ (Kcal/mol)	$\Delta H_{\text{CoordE}}$ (Kcal/mol)	$\Delta H_{\text{CoordMMA}}$ (Kcal/mol)
1/MAO Insertion mode 2,1	Hp	-0.108	25.17	1.62	-67.29	-33.63
	No	-0.12	25.15	1.63	-67.29	-33.62
2/MAO Insertion mode 2,1	Hp	-12.33	25.36	-1.45	-69.79	-35.54
	No	-12.33	25.36	-1.45	-69.79	-35.54

Homopolymer of MMA and copolymers of E/MMA were prepared by using the 1/MAO catalyst system mentioned earlier. The photodegradation and stabilization of E/MMA copolymers with Tinuvin 770 led to the development of IR bands in the hydroxyl and carbonyl regions. This region used to be sharp and narrow. However, in the copolymer samples, the carbonyl region (1850–1550  $\text{cm}^{-1}$ ) shows several overlapping bands. This can be seen in Figure 5 that shows the carbonyl region of sample LNi 155 (copolymer E/MMA with 60% of MMA incorporated prepared using catalyst 1) + Tinuvin 770 mixed. The absorption at 1712, 1723, 1741, and 1783  $\text{cm}^{-1}$  have been assigned to carboxylic acid, ketone, ester, and lactone, respectively. The intensity of band at 1723  $\text{cm}^{-1}$  increases significantly as photodegradation time increases and a simultaneous increase in other bands was also observed to progress with irradiation, but at 1783  $\text{cm}^{-1}$  only a negligible increase was observed, which is in agreement with the observation of Li and Guillet.<sup>38</sup> Sample LNi 155, when compared with PE samples, shows a higher photodegradation which may be due to the MMA incorporated in the copolymer (Figure 5). The copolymer with the lower percentage of MMA (20% MMA) shows an increment in photostability when compared with the PE. However, this increment in the beginning and up to 100 h is lower than that observed with sample LNi155 (60% MMA). Nevertheless, the degradation rate increases with time and after 250 h, its photodegradation is very similar to that of the sample LNi155. The photodegradation behavior of sample LNi 155 does not show any big difference between the mixed or grafting of Tinuvin 770 on copolymer (Figure 5 vs. 6). A very broad hydroxyl absorption region (3700–3200  $\text{cm}^{-1}$ ) with a maximum centered at 3400  $\text{cm}^{-1}$  appeared during photoirradiation. This band is due to neighboring intramolecular hydrogen bonded hydroperoxides and alcohols. Hydrogen-bonded hydroperoxides (3421  $\text{cm}^{-1}$ ) and associated alcohols (3380  $\text{cm}^{-1}$ ) were also present. The hydroxyl absorption is more intense in LNi 155 when compared with

other samples (Figure 7). This can be due to the higher percentage of MMA present in this copolymer. The figures of the other samples studies are shown in Supporting Information (Figures S1–S5).

The photodegradation of ethylene copolymers led to the development of IR band in the hydroxyl and carbonyl regions, as stated earlier. It is observed that formation/developments of functional groups are more intense in copolymers than in PE<sup>39</sup> due to inherent alcohol and/or carbonyl contents in the matrix and they enhance the oxidation, thereby leading to intense development to hydroxyl and carbonyl group. Tinuvin 770 did not show to be an efficient stabilizer in the case of these E/MMA copolymers since after a long period of exposure to the light all the samples show similar photodegradation.

## CONCLUSIONS

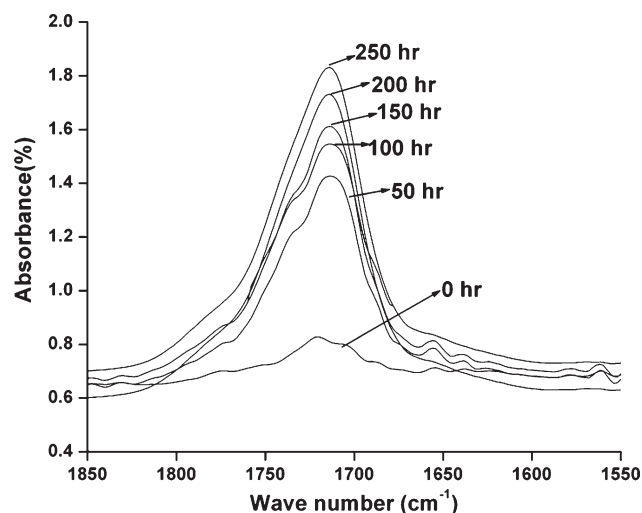
The new  $\alpha$ -diimine Ni complex bearing an electron donor -Si(<sup>t</sup>Bu)Ph<sub>2</sub> group in para-position of the imine moiety show lower incorporation levels of polar monomers (either for unsaturated alcohols or AA). However, the decrease of its oxophilicity due to the increase of the negative charge over the metal (Table V) leads to a better stability of the Ni compound in the presence of the polar monomers. Thus, the activities observed are in general higher than those of the parent compounds where, instead of -Si(<sup>t</sup>Bu)Ph<sub>2</sub> group, an alkyl group (catalyst 2) or an hydrogen atom (catalyst 2') are in the para-position. With catalyst 1, in opposition to what happens with alcohols and AA, it was possible to obtain copolymers of E with MMA having a quite high content of MMA incorporated.

As stated earlier, the incorporation of a polar group in a polyolefinic chain is crucial to improve the compatibility of the polyolefin with inorganic fillers and reinforcers making them suitable for adhesives and dyeing agents.<sup>1,2</sup> In particular, ethylene-methacrylates or methacrylic acid copolymers are

**Table IX.** Compared Values of E and MMA Coordination Enthalpies after Two Different Mode of Insertion of the First MMA Molecule for the Tree Catalysts Mentioned

Catalyst	$\Delta H_{\text{CoordE}}$ (after 1,2 insertion five-member chelate; Kcal/mol)	$\Delta H_{\text{CoordMMA}}$ (after 1,2 insertion five-member chelate; Kcal/mol)	$\Delta H_{\text{CoordE}}$ (after 2,1 insertion four-member chelate; Kcal/mol)	$\Delta H_{\text{CoordMMA}}$ (after 2,1 insertion, four-member chelate; Kcal/mol)
1	24.56 (-9.24)	61.86 (28.08)	-22.85 (-67.29)	10.82 (-33.62)
2	26.94 (-22.21)	56.43 (11.96)	-22.20 (-69,79)	12.05 (-35.54)
2'	25.61 (-7.03)	63.11 (30.47)	-23.33 (-66.89)	9.66 (-33.89)

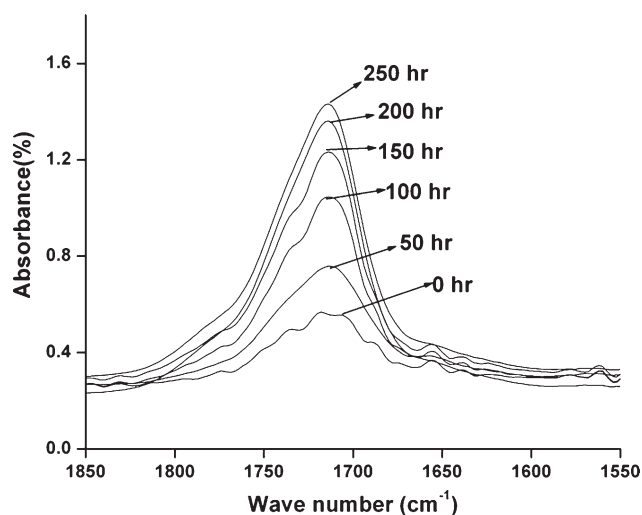
Calculations performed by PM3 for a growing chain with nine carbon atoms; noncyclic structures in brackets



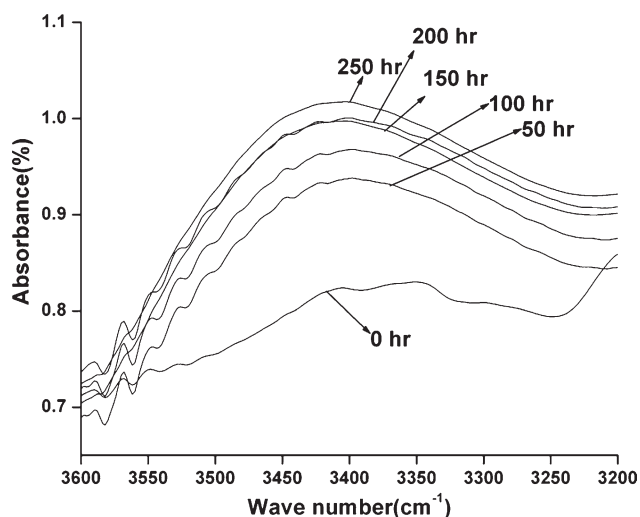
**Figure 5.** Carbonyl region of LNi 155 (copolymer E/MMA with 60% of MMA incorporated prepared using catalyst 1) + Tinuvin 770 mixed (1.00%).

preferably used in conventional extrusion coating, coextrusion coating, and so on.<sup>15</sup> They usually show an excellent adhesion to unprimed foil, paper, and metallized film, improving their structure reliability and barrier integrity.

They are also very useful to improve the interaction of the multiwall carbon nanotubes (MWNTs), which are very attractive fillers for increasing the electrical conductivity of the polymers<sup>40–44</sup> as well as for improving the modulus and strength of the composites,<sup>45–49</sup> with the polymer used to disperse them. In fact ultrahigh molecular weight PE (UHMWPE) is one of the polymers used to disperse the MWNTs. However, some MWNTs, having fewer defects than the current ones, may induce hard dispersions into the matrix of UHMWPE. This dispersion can be improved drastically if instead of UHMWPE



**Figure 6.** Carbonyl region of LNi 155 (copolymer E/MMA with 60% of MMA incorporated prepared using catalyst 1) + Tinuvin 770 grafted (0.80%).



**Figure 7.** Hydroxyl region of LNi 155 (copolymer E/MMA with 60% of MMA incorporated prepared using catalyst 1) + Tinuvin 770 mixed (1.00%).

alone a mixed solution of UHMWPE and ethylene-methyl methacrylate copolymer (E/MMA) is used as matrix.

Thus, the copolymers of E with MMA prepared with our catalyst 1 which properties are necessarily different from those obtained by radical polymerization, may be used, with improved results, as compatibilizer agents and in all the fields where commercial copolymers E/MMA usually are.

Molecular modeling calculation performed allowed us to understand better why, in the case of AA, a ratio AA/TMA of one is enough to protect both basic points of the AA. In the case of MMA, they explain why a 2,1 insertion mode is usually observed experimentally despite the activation energies for an 1,2 insertion being slightly lower than those obtained for the 2,1 mode. As mentioned earlier, after an 1,2 MMA insertion, the coordination of an E or a second MMA molecule is much less favorable than that observed after a 2,1 insertion. Thus, the reaction only goes on with those intermediate compounds resulting from a previous 2,1 insertion. Another conclusion we may draw from these calculations is that if no chelate structures, involving the O of the MMA and the metal of the catalyst, were formed the copolymerization rate would be much higher than that observed experimentally. It is the stabilization effect of these cyclic structures that leads to the very low homo-(MMA) and copolymerization (E/MMA) rates usually obtained.

These results compare quite well to those obtained by Ziegler and coworker<sup>50</sup> who performed the calculations by DFT and MD using both a model alpha-diimine Ni catalyst and a real one;  $2' = \{\text{bis}[\text{N},\text{N}'\text{-2,6-diisopropylphenyl}]\text{imino}\}\text{acenaphthene}\}$  dibromonickel. Our calculations performed by PM3 method provided, as stated earlier, a good account of the experimental results obtained. In those cases, where very large and complex molecules are involved, more elaborated calculation methods such as *ab initio*, DFT or HF must be avoided. Thus, it is important to show that the PM3 method, which is much less expensive and time-consuming than the previous ones, is also able

to be a very competitive tool in some areas of applications. In the cases studied in this article, as well as in other cases reported in literature,<sup>28,51,52</sup> PM3 was found to lead to quite adequate results all of them in good agreement to the experimental ones.

As mentioned earlier, the photodegradation of E/MMA copolymers shows that, both in the hydroxyl and carbonyl regions, the formation/developments of functional groups are more intense than in the homopolymer. This may be due to inherent alcohol and/or carbonyl contents in the matrix which enhance the oxidation, thereby leading to more intense developments to hydroxyl and carbonyl groups. It was also found that, for long periods of exposure to the light, grafting the stabilizer Tinuvin 770 on copolymer did not lead to a significant improvement compared to just mixing it to the copolymer.

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