Kinetic and UV−Visible Spectroscopic Studies of Hex-1-ene Polymerization Initiated by an α-Diimine-[*N*,*N*] Nickel Dibromide/MAO Catalytic System

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ABSTRACT: A study of the elementary reactions involved in the catalytic activation process of α-diimine $NiBr_2$ by methylaluminoxane (MAO), for α-olefins polymerization, was undertaken in toluene and chlorobenzene as solvents. The investigation is based on the comparative study of polymerization kinetics of hex-1-ene, UV−visible spectroscopic analysis of the catalytic system and structural analysis of the poly(hex-1-ene)s formed. Correlation between polymerization activities and changes in the UV−visible absorption spectrum of the transition metal derivative were found. Spectroscopic data have underlined the important role of the monomer in the stabilization process of the nickel-based active species. Partial polymerization orders with respect to MAO, nickel derivative and monomer were determined. Surprisingly, an apparently negative monomer order of the polymerization corresponding to a decrease of the polymerization rate with an increase of monomer concentration in the reacting medium was observed. A tentative interpretation based on the presence of two types of propagating active species of different reactivity, resulting from the walking migration mechanism, is discussed.

Introduction

Late transition metal complexes (Fe-, Co-, Ni-, and Pd-based), used in combination with methylaluminoxane (MAO) or borane derivatives, are highly attractive catalytic systems for the preparation of polyolefins[1] with tailored chain architecture.

A real breakthrough in this field came out after that Brookhart and co-workers disclosed the synthesis of a series of new square planar nickel(II) and palladium(II) derivatives bearing substituted α-diimine-[*N*,*N*] ligands as catalyst precursors for the preparation of polyolefins with special chain topology.[2−4] These late transition metal derivatives, in association with MAO as cocatalyst, enable in particular the following:

First is the preparation of highly branched polyethylene without any α-olefin comonomer. The extent of branching drastically varies with the structure of the late transition metal derivative as well as with the experimental conditions.[5−7]

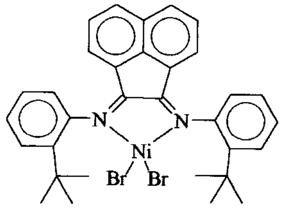
Second is the synthesis of block copolymers from two different α-olefins.[8] This results both from a rapid initiation of the polymerization and from a propagation reaction which proceeds, in selected conditions, through persistent active species without noticeable chain termination and chain transfer.

Third is the preparation of functional polyethylenes by "co-insertion" of ethylene and acrylate monomers.[9−10]

The possibilities to polymerize, in a proper way, cycloolefins using late transition metal derivatives has been also demonstrated.[11,12]

Although much more versatile in polymerization, it is admitted that late transition metal polymerization active species are relatively similar in nature to those formed with group IV metallocenes. To be active in olefin polymerization, transition metal derivatives (procatalyst) should be transformed into coordinatively unsaturated cationic metal−alkyl complexes. In the case of MAO as cocatalyst, activation of late transition metal derivative might involve successive alkylation and cationization,[2] in a manner quite similar to that of group IV metallocenes.[13] However, it is worthy noting that these new systems require for their activation a much smaller amount of MAO[2].

Scheme 1



We report in this paper an investigation of α-diimine-[*N*,*N*] $NiBr_2$ complex (Scheme 1)/MAO system and in particular of the elementary reactions yielding polymerization-active species.

To that purpose, a kinetic study of hex-1-ene polymerization, an UV−visible spectroscopic investigation of the catalytic system, and a structural analysis of the poly(hex-1-ene)s formed were conjointly performed. A rather similar approach was recently used to investigate the elementary reactions involved in metallocene-based/MAO catalytic systems. Indeed, UV−visible spectroscopy provides information on the metal complex electronic structure and is a valuable tool for catalyst characterization.[14−22]

The correlation observed between the polymerization kinetics, the UV−visible spectrum of the nickel-based/MAO catalytic system, and the poly(hex-1-ene) structure are stressed and discussed in terms of reaction mechanisms.

Results and Discussion

Kinetic Study of Hex-1-ene Polymerization. Hex-1-ene polymerization in the presence of the α-diimine-

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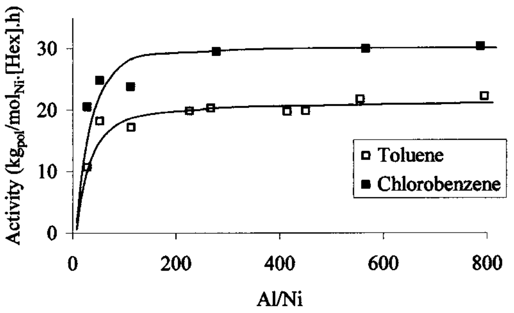


Figure 1. Influence of [MAO]/[Ni] ratio on hex-1-ene polymerization in toluene and in chlorobenzene at −10 °C. [Ni] = 10^{-4} M; [hex-1-ene] = 1 M.

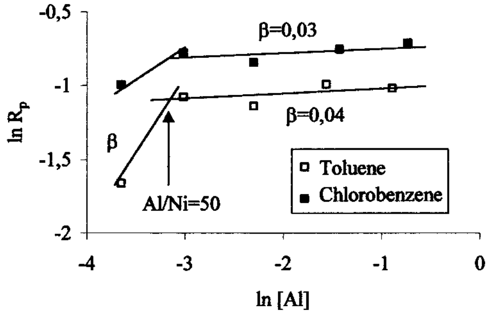


Figure 2. Logarithmic variations of the hex-1-ene polymerization rate vs MAO concentration, in toluene and in chlorobenzene at −10 °C. [Ni] = 0.90 mM and [Hex] = 0.83 M; 0.025 < [MAO] < 0.97 M; 28 < Al/Ni < 1075).

[*N*,*N*] nickel dibromide complex /MAO catalytic system was investigated, at −10 °C, both in toluene and in chlorobenzene. The kinetics of the hex-1-ene polymerization were followed by dilatometry.

The influence on the catalytic activity of the relative proportion of MAO, with respect to Ni, is presented in Figure 1 for experiments performed in toluene and in chlorobenzene.

As it may be seen, the activity increases sharply with the MAO/Ni ratio (r) to finally reach a plateau of maximal activity for r higher than about 50, in the two solvents. This suggests that the formation of active species is already complete (but not necessarily quantitative) for this MAO/Ni ratio. It is worthy noting that the maximum activity is reached for r values much lower than for metallocenes of group IV.[18−22] Besides, as already noticed with zirconocene/MAO systems, the catalytic activity is higher in the more polar chlorinated solvent.[23] This might be related to the ionic structure of active species.

To further characterize the reaction mechanisms involved in the Ni-based catalytic system, a kinetic study of hex-1-ene polymerization was undertaken and the dependence of the polymerization with respect to the MAO, the Ni complex procatalyst, and the monomer was determined.

Assuming that the polymerization rate, R_p, can be expressed by the following kinetic equation, $R_p = k_{p_{app}}[Ni]^{\alpha}[Al]^{\beta}[Hex]^{\gamma}$, the kinetic orders α, β, and γ were measured.

To determine the kinetic order with respect to MAO, the nickel complex and hex-1-ene initial concentrations were kept constant, respectively, to 0.90×10^{-3} M and to 0.83 M, while the MAO concentration was varied from 0.025 to 0.97 M. Indeed, this corresponds to Al/Ni ratios ranging from 28 to 1075. As could be postulated from the variation of the polymerization activity with the MAO/Ni ratio, plotting ln [R_p] vs ln [MAO], Figure 2, yields two distinct dependence laws. The first one, for MAO/Ni ratios lower than 50, shows a dependence of the polymerization, approximately of one order, with respect to MAO, in agreement with an increase of the number of active species proportional to the MAO concentration. For higher MAO concentrations, corresponding to MAO/Ni ratios higher than 50, a zero-order dependence is observed in agreement with a steady-state concentration in active species.

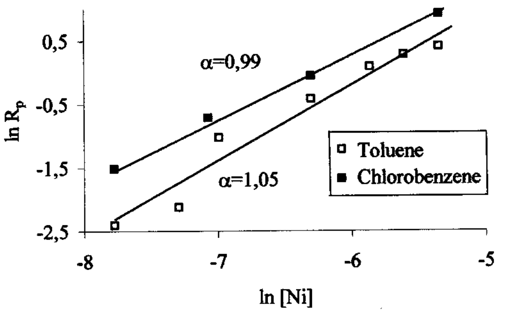


Figure 3. Logarithmic variations of the hex-1-ene polymerization rate vs Ni concentration, in toluene and in chlorobenzene at −10 °C. [MAO] = 0.38 M and [Hex] = 0.83 M; 0.42 < [Ni] < 4.74 mM; 80 < Al/Ni < 915).

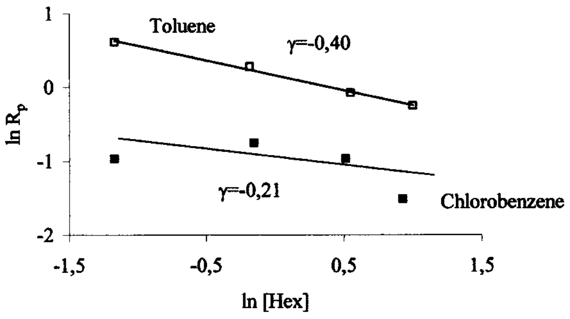


Figure 4. Logarithmic variations of the hex-1-ene polymerization rate vs monomer concentration, in toluene and in chlorobenzene at −10 °C. [Ni] = 0.90 mM and [MAO] = 0.23 M; Al/Ni = 260), 0.31 < [Hex] < 2.78 M).

It is worth noting that the same behavior is observed in the two solvents, although R_p is higher in chlorobenzene.

The kinetic order with respect to the nickel complex procatalyst was determined in the same way; see Figure 3. MAO and hex-1-ene concentrations were kept constant and respectively equal to 0.38 and 0.83 M whereas the nickel complex concentration was varied from 4.74 × 10^{-3} to 0.42 M. The values correspond to MAO/Ni ratios ranging from 915 to 80, for which we may assume that the proportion of MAO is high enough to allow the maximal formation of active species corresponding to the plateau of activity.

In the two solvents, the kinetic order with respect to nickel, α, is close to unity, in agreement with monomeric active species, contrary to other nickel-based polymerization systems.[24]

Finally, the kinetic order with respect to the monomer was determined using a constant and elevated MAO/Ni ratio (Al/Ni = 260), to ensure the complete formation of active species. MAO and nickel complex concentrations were fixed respectively to 0.23 M and to 0.90×10^{-3} M whereas the hex-1-ene concentration was varied from 0.31 to 2.78 M.

Surprisingly, an apparent negative monomer order is observed in the two solvents, see Figure 4. In other

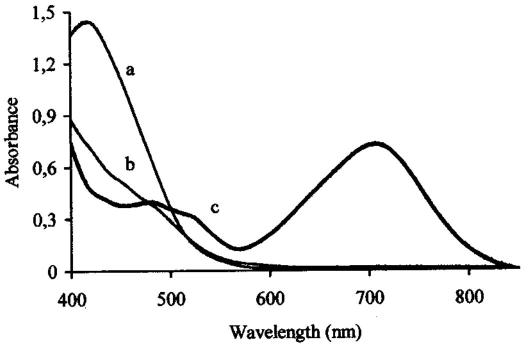


Figure 5. UV-visible absorption spectra of α-diimine ligand (a), α-diimine-[*N*,*N*] $NiBr_2$ (b), and α-diimine-[*N*,*N*] $NiBr_2$/MAO catalytic system (Al/Ni = 100) (c) in toluene at 20 °C.

words, the rate of hex-1-ene polymerization diminishes with increasing the initial monomer concentration. This very specific behavior will be discussed in connection with the "walking" mechanism described by Brookhart, later in this paper.

According to kinetic data, the hex-1-ene polymerization rate in the presence of the α-diimine-[*N*,*N*] nickel bromide/MAO system, at −10 °C, may be expressed by a series of two kinetic equations:

in toluene

$$\text{Al/Ni} < 50 \quad R_p = k_{p_{app}}[\text{Ni}]^1[\text{Al}]^1[\text{Hex}]^{-0.4}$$

$$\text{Al/Ni} > 50 \quad R_p = k_{p_{app}}[\text{Ni}]^1[\text{Al}]^0[\text{Hex}]^{-0.4}$$

in chlorobenzene

$$\text{Al/Ni} < 50 \quad R_p = k_{p_{app}}[\text{Ni}]^1[\text{Al}]^1[\text{Hex}]^{-0.2}$$

$$\text{Al/Ni} > 50 \quad R_p = k_{p_{app}}[\text{Ni}]^1[\text{Al}]^0[\text{Hex}]^{-0.2}$$

UV−Visible Spectroscopic Study of the α-Diimine-[*N*,*N*] $NiBr_2$ /MAO System. The UV−visible spectroscopic investigation of several zirconocene/MAO systems has been recently reported.[18−22] This technique was found to be very effective for the observation of the successive elementary steps yielding cationic active species. To further characterize the elementary processes leading to the formation of active species in α-diimine-[*N*,*N*] $NiBr_2$ /MAO systems, an UV−visible spectroscopic analysis of the catalytic system was thus implemented in toluene and chlorobenzene. Since very similar trends were observed in toluene and chlorobenzene, only the toluene UV−visible spectroscopic study is presented.

A first series of spectroscopic experiments was performed at 20 °C. The corresponding results are presented in Figure 5.

As it may be seen, the absorption spectrum of the α-diimine-[*N*,*N*] ligand alone is characterized by an intense absorption band centered at 415 nm (a) whereas the corresponding α-diimine-[*N*,*N*] $NiBr_2$ complex does not show any characteristic UV−visible absorption maximum between 400 and 850 nm (b). Addition of MAO (MAO/Ni = 100) to the toluene solution of the Ni complex results in the formation of three new absorption bands (c), Figure 5; the main one is centered at 710 nm whereas two other peaks of much lower intensity are observed at 480 and 510 nm. These important changes in the absorption spectrum of the initial α-diimine-[*N*,*N*] $NiBr_2$ complex can be attributed to the structural and electronic modifications on the Ni complex after reaction with MAO. It is worthy to note that a green-black coloration of the reaction medium, followed by a precipitation of black solid particles and a decrease of the 480−510 nm bands intensity to the benefit of the 710 nm band rapidly occurs. This could be attributed to the structural modification of the soluble complex as well as to the partial reduction of nickel(II) to the zero oxidation state. These changes are accompanied by a rapid deactivation of the catalytic system. Indeed, a very low polymerization activity was noticed when the catalytic system was prepared in such a way, i.e., by direct addition of MAO on the Ni derivative, in absence of hex-1-ene.

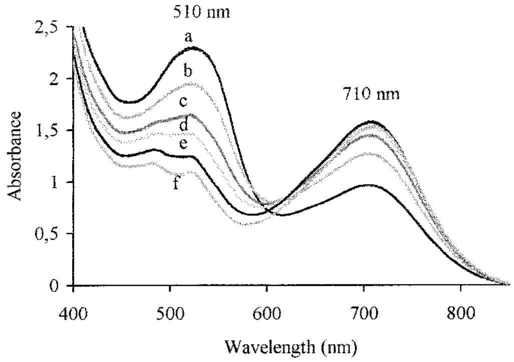


Figure 6. UV−visible absorption spectrum of α-diimine-[*N*,*N*] $NiBr_2$/MAO catalytic system in the presence of hex-1-ene at various polymerization times in toluene at 20 °C. (a) $t = 0$ h, (b) $t = 1$ h, (c) $t = 2$ h, (d) $t = 3$ h, (e) $t = 5$ h, (f) $t = 19$ h. ([Ni] = 1.33 mM; Al/Ni = 100; [Hex] = 0.37 M.)

The catalytic system was thus formed in the presence of the monomer, MAO being systematically added last. It was shown that hex-1-ene polymerization readily occurs in these conditions, although that, at 20 °C, reactivity tends to decrease with time and it was not possible to restart the polymerization after addition of a second batch of monomer. The UV−visible spectrum of the catalytic system prepared under these new experimental conditions (Ni complex, hex-1-ene, MAO at 20 °C) is presented in Figure 6.

At the initial time, the UV/visible spectrum of the system is now characterized by a main absorption band centered at 510 nm whereas the band at 710 nm, although still present, is of much lower intensity. However, with increasing time, the intensity of the absorption band at 510 nm continuously decreases and transforms through an isosbestic point into the band located at 710 nm; during this transformation, the formation of another band at 480 nm is also noticed. These findings suggest that the active species could be those exhibiting an absorption at 510 nm whereas the species corresponding to the band at 710 nm are likely inactive for polymerization.

The results also highlight the low stability of active species, at 20 °C, even in the presence of monomer, as already noticed from polymerization kinetics. Since a "living" character of the polymerization was reported at lower temperature (−10 °C), we investigated by UV−visible spectroscopy the formation and the stability of the active species at −10 °C, in the presence of hex-1-ene. Results are presented in Figure 7.

As it may be seen, the main species formed are those with the absorption band at 510 nm whereas the band at 710 nm is still present. On the basis of the 510/710

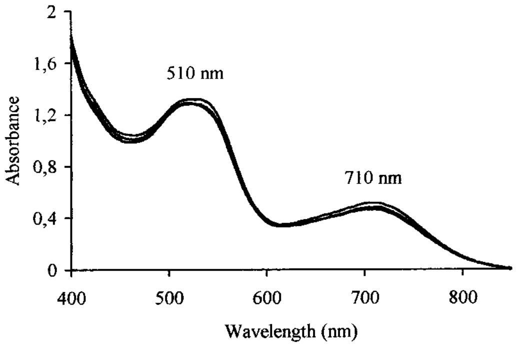
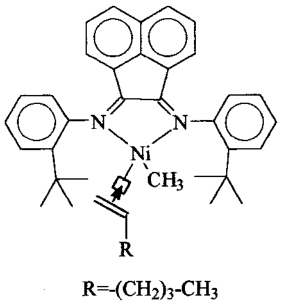


Figure 7. UV−visible absorption spectrum of α-diimine-[*N*,*N*] $NiBr_2$/MAO catalytic system in the presence of hex-1-ene at various polymerization times in toulene at −10 °C. ($t = 0$ h, $t = 1$ h, $t = 20$ h). ([Ni] = 1.27 mM, Al/Ni = 100, [Hex] = 0.68 M.)

Scheme 2



nm band intensity ratio, we may conclude that the active species are obtained in much higher proportion than at 20 °C. At −10 °C, the UV−visible spectrum does not evolve with time over a period of several days, showing that active species are stable in these low-temperature conditions. Interestingly, it was shown that the addition to this system of a second hex-1-ene feed, after 12 h, has no effect on the profile and intensity of the absorption spectrum. Under similar conditions (−10 °C, addition of a second monomer batch), kinetics show that the polymerization activity remained close to its initial value, in agreement with the absence of termination during the hex-1-ene polymerization. It is worthy noting that the small fraction of inactive species (710 nm band) is produced at the very beginning, likely during the reaction between MAO and the Ni complex, indeed.

Given the spectroscopic and kinetic data, it may be conclude that the formation and the stability of Ni-based active species is very much dependent on the experimental conditions and procedure. They depend, in particular, on the introduction order of the various catalyst components and the presence of the olefin monomer appears to be essential for the stabilization of active species. A coordination of the monomer onto the vacant site of the Ni, in agreement with the low monomer order observed for the polymerization, might explain this stabilizing effect. The possible structure of active species is shown in Scheme 2.

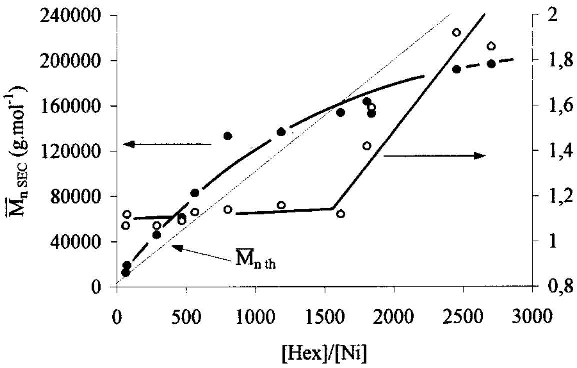


Figure 8. $\bar{M}_n$ and molar mass distribution (I) vs [hex-1-ene]/[Ni] ratios.

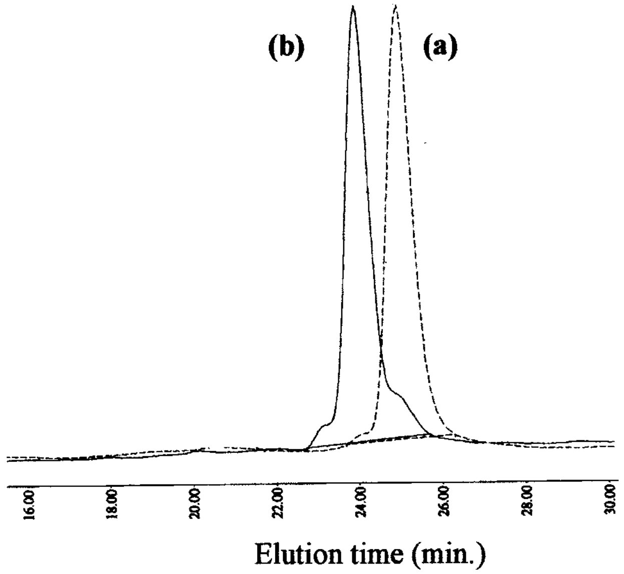


Figure 9. SEC chromatograms of a polyhexene: (a) after the first monomer feed, $\bar{M}_{n_{SEC}} = 86\,000$ g mol^{-1}, $I_p = 1.08$; (b) after the second monomer feed: $\bar{M}_{n_{SEC}} = 162\,600$ g mol^{-1}, $I_p = 1.16$.

Structure of Poly(hex-1-ene) Chains and Interaction with the Polymerization Kinetics. The livingness of α-olefin polymerization, already reported by Brookhart,[8] was systematically checked by measuring the molar masses of poly(hex-1-ene)s prepared under different polymerization conditions. Experimental $\bar{M}$ values were determined by size exclusion chromatography, using both a polystyrene calibration (RI detection) and a laser light scattering detection to get absolute molar mass; indeed, the two methods give $\bar{M}$ in good agreement.

The experimental molar masses of poly(hex-1-ene)s obtained under various polymerization conditions are reported in Figure 8, where they can be compared with theoretical values determined assuming one chain formed by initial Ni complex. Depending on the initial [hex-1-ene]/[Ni] ratio, two domains can be distinguished.

(a) The experimental $\bar{M}$ increases almost linearly with the initial [hex-1-ene]/[Ni] ratio up to a value of about 1000, while the molar mass distribution remains narrow and close to 1.1, supporting a living type polymerization mechanism. Addition of a second monomer feed to one of this polymerization system, after complete conversion of the monomer, results in an increase of the polymer molar mass without significant broadening of the chain distribution, in agreement with a restart of the polymerization from the same polymer ends; see Figure 9. The small shoulder observed at high elution volume likely corresponds to a slight deactivation of active chains upon addition of the second batch of hex-1-ene.

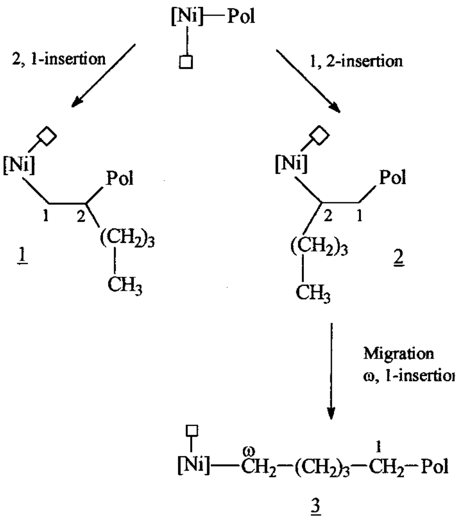
Comparison of $\bar{M}$(exptl) and $\bar{M}$(theor), calculated as $\bar{M}$(theor) = ([M]/[Ni]) × conv, see Figure 8, reveals that the experimental molar masses are higher than predicted. This indicates that a fraction of α-diimine-[*N*,*N*] Ni species could not be activated or is deactivated at

Table 1. Influence of A_{510}/A_{710} Intensity Ratio on the Poly(hex-1-ene)s Molar Masses

Al/Ni	A_{510}/A_{710}[a]	$\bar{M}$(theor),[b] g/mol	$\bar{M}$(exptl),[c] g/mol	$\bar{M}$(exptl)/$\bar{M}$(theor)
100	2.87	45 000	127 500	2.83
100	5.50	42 000	97 900	2.33
250	5.93	45 000	86 800	1.93

[a] Intensity ratio of absorption bands located at 510 nm (active species) and 710 nm (inactive species), respectively [b] $\bar{M}$(theor) = $[M]_0/[Ni]_0$ × conv. [c] $\bar{M}$(exptl) is determined by SEC using a polystyrene calibration

Scheme 3



the very beginning of the reaction, in agreement with UV–visible observations of the catalytic system. The deviation between experimental and theoretical molar masses, expressed by the ratio $\bar{M}$(exptl)/$\bar{M}$(theor) (see data in Table 1) follows an inverse course than the intensity ratio between the 510 nm (attributed to active species) and the 710 nm (inactive species) absorption bands. In other words, the higher the fraction of active species formed, the closer $\bar{M}$(exptl) and $\bar{M}$(theor) are. Even under optimal conditions, the efficiency of the catalytic system with respect to α-diimine-[*N*,*N*] $NiBr_2$ does not exceed 50%.

(b) For initial [hex-1-ene]/[Ni] ratio higher than 1500, the $\bar{M}$(exptl) values clearly level off and polydispersity increases sharply; the hex-1-ene polymerization deviates from its "living" character, in agreement with Brookhart's findings,[8] indicating that noticeable chain transfer takes place at a high [hex-1-ene]/[Ni] ratio corresponding to high initial monomer concentration (>1 M).

The very peculiar chain structure of polyolefins obtained with α-diimine$NiBr_2$/MAO catalytic system has been already widely studied and described by Brookhart and colleagues.[2] Formation of ethylene sequences in polyolefins, is explained by migration of active centers along the chains through the so-called "walking" mechanism depicted in Scheme 3.

Whereas 1,2-monomer-insertion affords propagating active species **1**, 2,1-insertion results in the formation of species **2**, inactive for monomer addition. The latter is believed to rearrange into active species, **3**, through migration of the metal to the ω position of the last hex-1-ene branch, thus yielding polyethylene sequences. The proposed mechanism involves, successively, formation, by β-hydrogen abstraction, of a Ni-complexed unsaturated polyolefin and migratory reinsertion of the unsaturated polyolefin in the Ni–H species. The frequency of the migration process can be evaluated by ^1H NMR spectroscopy from the proportion of methyl groups in the polyolefin. In a normal poly(hex-1-ene), the number of methyl groups (and thus of butyl branches) is equal to 167 for 1000 carbons. This proportion can be much lower in poly(hex-1-ene)s prepared with Ni-based Brookhart catalysts.

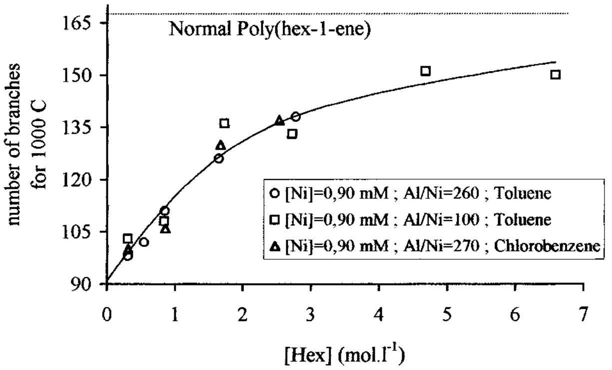


Figure 10. Effect of the initial hex-1-ene concentration on the number of branching, in toluene at −10 °C (*T* = −10 °C, α-diimine-[*N*,*N*] $NiBr_2$/MAO as catalytic system).

It was previously shown that the structure of the catalyst (metal and nature of the ligands) as well as the polymerization temperature has a strong influence on the branching.[7]

A strong influence of the monomer concentration on the poly(hex-1-ene) branching structure was also noticed in this study; see data collected in Figure 10. Rearrangement is more frequent in polymerization performed at low monomer concentration, suggesting a lower dependence with respect to monomer of the migration process, compared to propagation. However, interpretation of the kinetic data is not simple as indicated by the apparent negative monomer order of the propagation reaction. This behavior might result from the competition between propagation and migration processes. Indeed, it is worthy noting that migration yields different propagating species, **3**, with primary alkyl–Ni structure, similar to those involved in ethylene polymerization. These species exhibit a much higher reactivity than β-substituted alkyl nickel species **1**, responsible for α-olefin polymerization. The polymerization rate will therefore depend both on the intrinsic reactivity of species **1** and **3** and on their relative concentrations.

Since, according to poly(hex-1-ene) structures, species **3** are present in higher proportion (higher proportion of ethylene sequences) at low monomer concentration, the overall polymerization rate will increase when decreasing monomer concentration, thus leading to an apparent negative kinetic order of the polymerization with respect to monomer, as experimentally observed.

It is of particular interest to examine the thermal characteristics of the poly(hex-1-ene)s, as a function of the proportion of butyl branches. The DSC-traces of poly(hex-1-ene)s prepared with Ni catalysts are presented in Figure 11. In the case of poly(hex-1-ene)s with 117 branches per 1000 carbons corresponding to about 30% rearrangement, a T_g is observed at −57 °C, a temperature close to the normal poly(hex-1-ene) one. However, for poly(hex-1-ene)s with 52 and 61% rearrangement of hex-1-ene units, a broad melting peak is observed, in addition to the glass transition, indicating

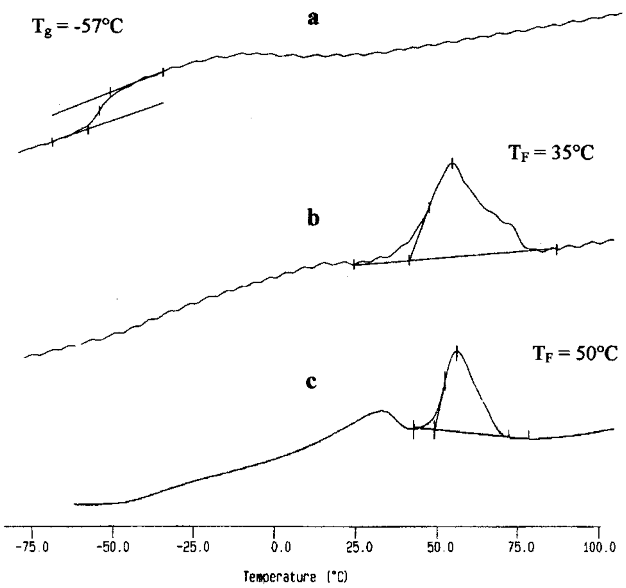


Figure 11. DSC traces of polyhex-1-enes exhibiting 117 CH_3 groups for 1000 C (a), 81 CH_3 groups for 1000 C (b), and 66 CH_3 groups for 1000 C (c).

the formation of polyethylene sequences long enough to crystallize: the lower the number of branches, the higher the melting temperature. This confirms that poly(hex-1-ene)s with versatile properties can be easily prepared with Ni catalysts only by tuning the monomer concentration.

In conclusion, we have attempted to correlate the polymerization kinetics of hex-1-ene initiated by α-diimine-[*N*,*N*] $NiBr_2$/MAO both with a spectroscopic study of the catalytic system and with the poly(hex-1-ene) structure. Catalytic active species resulting from the activation of the nickel complex by MAO were identified by UV−visible spectroscopy. This study revealed than the active species formed are quite unstable, even at low temperature, in absence of monomer. The presence of an α-olefin during the nickel activation by MAO is essential. The monomer is presumed to stabilize the active species by complexation.

Besides, the contribution of two distinct propagating species of different intrinsic reactivity, present in different proportion according to the reaction conditions are believed to govern the polymerization kinetics. The first species (**1**) corresponds to normal poly(hex-1-ene)-Ni termini; the second (**3**) results from active centers migration to the ω position of the terminal polyolefin branch. This complex scheme could explain the observed negative order of the polymerization with respect to the α-olefin monomer.

Further kinetic and spectroscopic investigations of Ni-based catalytic moieties in the presence of styrene and norbornene, stressing the important role of the monomer in these polymerization systems, are in progress and will be reported in forthcoming papers.

Experimental Part

Materials. Toluene (J. T. Baker) was distilled twice over sodium/benzophenone and just before use. Chlorobenzene (Prolabo) was distilled under reduced pressure over CaH_2 before the polymerization. Hex-1-ene (Sigma Aldrich) was purified over alumina (Merck) and trihexylaluminum (Witco GmbH). MAO (Witco GmbH), 10 wt % in toluene, was used as received.

Synthesis of the Nickel Derivative. The catalyst was synthesized according to ref 8.

Polymerization Procedure. All products were transformed through a cannula under nitrogen atmosphere.

Polymerizations were carried out in toluene or chlorobenzene in a dilatometer chamber equipped with PTFE stopcocks, at −10 °C. The nickel derivative was first introduced in the dilatometer chamber, previously degassed and thermostated at −10 °C. A solution of monomer and MAO was then added through a cannula into the dilatometer. The polymerization kinetics were immediately followed by recording the volume contraction of the polymerization solution in the dilatometer. After a given reaction time, the polymerization mixture was precipitated into ethanol and a small amount of hydrochloric acid. The organic phase was filtered and the recovered polymer dried under vacuum.

UV−Visible Spectroscopy. The absorption spectra of the catalytic system, in the absence and in the presence of the monomer, were recorded under dry nitrogen atmosphere on a Varian carry 3E UV−visible spectrometer; a quartz cell attached to the glass reactor was used for measurements, as already described in ref 18.

Characterization of the Polymers. ^1H NMR polymer spectra were recorded on a Brüker AC200 spectrometer, in $CDCl_3$ at room temperature. The molar masses of the poly(hex-1-ene)s were measured by size exclusion chromatography in THF on a Varian chromatograph fitted with a refractive index detector and equipped with polystyrene gel columns (TSK gel). Number-average molar mass ($\bar{M}_n$) and weight-average molar mass ($\bar{M}_w$) were estimated on the basis of a polystyrene calibration. The actual molar masses of the poly(hex-1-ene)s were calculated from the response of a multiangle laser light scattering detector (Wyatt technology) that was connected to a size exclusion chromatography (MALLS/SEC) line. The d*n*/d*C* value for poly(hex-1-ene) in THF solution was found to be equal to 0.068 $cm^3\ g^{-1}$. Thermal properties were determined on a Perkin-Elmer DSC7 after the second heating cycle at 10 °C/min temperature increase.

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