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Homo- and copolymerisation of norbornene and styrene with nickel bis(acetyl acetonate)/methylaluminoxane system

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Abstract

The homo and copolymerisations of norbornene and styrene with nickel bis(acetyl acetonate)/methylaluminoxane system were systematically investigated. This catalytic system shows a high activity towards homopolymerisation of both norbornene and styrene. For random copolymerisation, an increase in the initial styrene feed content leads to a gradual loss of activity relative to norbornene homopolymerisation. On the other hand, a drastic loss of activity, relative to styrene homopolymerisation, was found for very low norbornene feed contents. These results are qualitatively interpreted using the trigger coordination mechanism proposed by Ystenes.

The structural characterisation of the polymers showed that norbornene polymerisation occurs via a 2,3 addition mechanism and that true copolymers are formed by random copolymerisation. At low styrene feed contents, only isolated styrene units or very short styrene sequences are present in the resulting copolymer. At higher styrene feed contents, short polystyrene sequences with more than eight styrene units may be formed. Determination of the reactivity ratios shows a much higher reactivity for norbornene ($r_{\text{norbornene}} = 17.8$ and $r_{\text{styrene}} = 0.16$). Size exclusion chromatography measurements have shown that polynorbornenes possess high molecular weights. Relatively low molecular weights were observed for homopolystyrene and copolymers.

Keywords: Homo- and copolymerisation; Nickel bis(acetyl acetonate)/methylaluminoxane; Polynorbornene; Norbornene/styrene copolymers; Trigger mechanism

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1. Introduction

Norbornene and its derivatives can be polymerised via ring-opening olefin metathesis [1,2], cationic polymerisation [3] and more recently by olefin addition polymerisation. In the latter case, the bicyclic structure of the monomer is retained. Depending on the catalytic system used, different polynorbornenes may be obtained ranging from amorphous to more stereoregular and crystalline ones [4–6]. Molecular dynamic simulations have shown that addition polynorbornenes display a characteristic rigid random coil conformation, and may be included in a special class of materials showing restricted rotation about the main chain [7,8]. Based on their peculiar structural features, many interesting properties are expected for polynorbornenes. For example, these polymers exhibit very high decomposition temperatures, increased thermal stability, excellent dielectric properties and unusual transport properties. Therefore, they are attractive materials not only for microelectronics and optical applications [7] but also for other potential uses in packing and gas separation [9].

On the other hand, polynorbornene homopolymers present some disadvantages. They are very brittle materials at room temperature, and their solubility in

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common organic solvents is rather low, specially for high molecular weight polymers. The processability of the homopolymers is also rather poor.

In order to improve their processability, copolymers of norbornene with other traditional vinyl monomers, mainly ethylene, have been synthesised. By introducing these monomer units into the polymer chains, the solubility of the polymers in common organic solvents can be increased. Meanwhile, we may expect that a proper control of the incorporation rate and microstructure will keep the rigid coil conformation of the polymers to a high extent.

Norbornene polymerisation can be catalysed by some selected catalysts based on metallocenes [6,10,11] or on Pd(II) [4,5,7–9,12–14] and Ti(IV) [15] complexes. Metallocene based systems lead to a stereospecific and highly crystalline homopolymer, but the monomer conversion rate is rather low. On the other hand, palladium catalysts usually give amorphous polymers.

The use of organo-nickel complexes for the polymerisation of norbornene or of substituted functional norbornene monomers has also been described in patent literature [16–18]. Recently, it was also reported [19] that styrene–norbornene copolymers can be synthesised with the nickel stearate/methylaluminoxane (MAO) catalytic system. Nickel bis(acetyl acetonate) is another cheap commercial catalyst. When combined with the common cocatalyst MAO, this system can polymerise styrene and methyl methacrylate [20,21]. The polymerisation of norbornene with this catalyst was also mentioned in Japanese patents [22,23]; however, no details were given.

This paper addresses the investigation of the homo and copolymerisations of norbornene and styrene in the presence of a nickel bis(acetyl acetonate)/MAO, [Ni(acac)$_2$/MAO] catalytic system.

2. Experimental part

2.1. Materials

Nickel bis(acetyl acetonate) and norbornene, with a purity of 99%, were supplied by Aldrich. Styrene (Aldrich, 99%), was dried over calcium hydride, and then freshly distilled under vacuum prior to use. Toluene (Petrogal Galp Quimicos, 99.5%), was dried over butyllithium/styrene and then distilled under reduced pressure. MAO was provided by Witco GmbH, Germany, as 10% w/v solution in toluene.

2.2. Polymerisation procedure

The Schlenk technique was used in all the polymerisation and solvent drying processes, and except where indicated, the nickel concentration was controlled at 0.001 mol/l.

Two polymerisation procedures based upon different catalyst activation processes were examined in this work (Fig. 1). In procedure I, nickel and MAO were first mixed and stirred for a certain time to pre-activate the catalyst, and then, the monomer solution was added and polymerised. In procedure II, there was no pre-activation step. First, the monomer solution was mixed with nickel bis(acetyl acetonate), then the MAO was added to nickel in the presence of the monomer(s) and the polymerisation initiated.

The polymerisations were terminated by the addition of acidified methanol. The resulting polymer was precipitated and separated by filtration, washed with methanol several times and finally dried under vacuum at 70°C for more than 12 h.

The polymerisation yield in percentage was calculated as the weight fraction of converted monomer over the total monomer:

$$\text{yield (\%)} = (\text{weight}_{\text{resulting polymer}}/\text{weight}_{\text{total monomer}})100. \tag{1}$$

The catalytic activity was defined as the weight of the resulting polymer divided by the amount of introduced Ni(II) (expressed in grams) and the polymerisation time (in hours):

$$\text{catalyst activity} = \text{weight}_{\text{resulting polymer}}/(\text{weight}_{\text{Ni(II)}} \cdot \text{time}_{\text{polymerisation}}). \tag{2}$$

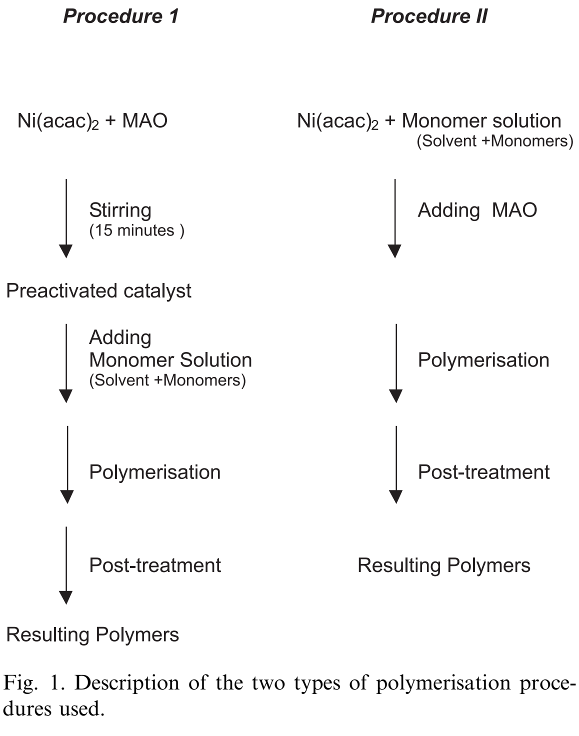

Fig. 1. Description of the two types of polymerisation procedures used.

2.3. Characterisation of the polymers

The molecular weight of the polymers was measured by size exclusion chromatography (SEC) on a Waters 150C instrument at 135°C and using 1,2,4-trichlorobenzene as solvent. Polystyrene standards were used for calibration.

The Fourier transform infrared (FTIR) spectra of the polymers were recorded on a Perkin Elmer 1600 spectrometer.

The nuclear magnetic resonance (NMR) spectra of the polymers were acquired on a Brüker MSL 300P spectrometer operating at 300 MHz for ^{1}H and at 75.4 MHz for ^{13}C. Spectra were recorded at 380 K using 1,1,2,2-tetrachloroethane (d_2) as solvent and hexamethyldisiloxane as chemical shift reference.

3. Results and discussion

3.1. Polymer synthesis

It is well known that the polymerisation activity of Ziegler–Natta or metallocene catalysts depends on several parameters, such as aluminium/transition metal ratio, polymerisation temperature, polymerisation time, monomer/transition metal ratio and monomer composition. In this work, we have investigated how such parameters can affect the activity of the Ni(acac)$_2$/MAO catalytic system in homo and copolymerisations of norbornene and styrene.

3.1.1. The catalyst

Preliminary experiments were made to check the polymerisation activity of each one of the two single components of the system, Ni(acac)$_2$ and MAO. It was found that Ni(acac)$_2$ in the absence of MAO is inactive for the norbornene polymerisation, and that MAO alone can initiate norbornene polymerisation. In the literature [19], it is also mentioned that MAO alone can polymerise styrene with very low activity. As already pointed out by some authors, this fact may be the result of the ability of MAO to initiate the polymerisation of various monomers by a cationic mechanism. However, as shown in Fig. 2, the polymer yield obtained in the presence of MAO alone is much lower than that obtained in the presence of the whole Ni(acac)$_2$/MAO system. This result shows that the combination of Ni(acac)$_2$/MAO is the real catalytic system and that active centres are formed by the interaction between these two components.

3.1.2. The polymerisation procedures

Two different polymerisation procedures were tested (Fig. 1). As already mentioned, in procedure I, there is a previous mixing of Ni(acac)$_2$ with MAO in order to allow the formation of the active sites before monomer introduction. In procedure II, the activation of Ni(acac)$_2$ with MAO was done in the presence of the monomers. As may be seen in Fig. 3, for each monomer or monomer mixture, procedure II gives higher yields than procedure I. Two possible explanations for this fact are that the presence of monomer during the formation process of active species would: (a) stabilise these species towards decomposition or irreversible deactivation and (b) facilitate the complexation of the monomer to the MAO activated Ni complexes and thus increase the catalytic activity. Therefore, procedure II was used for the following polymerisation tests.

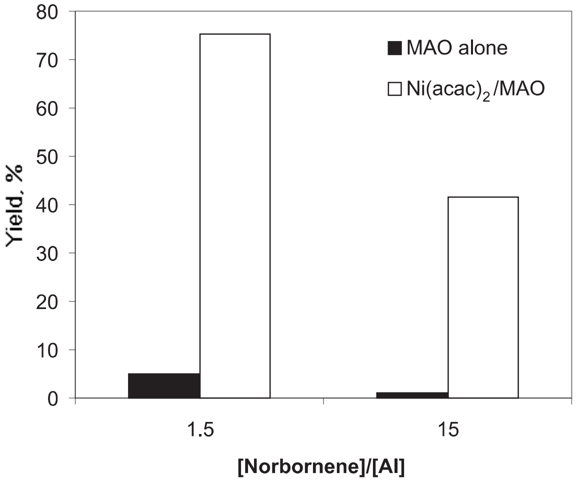

Fig. 2. Norbornene polymerisation yields. ([Norbornene] = 1.5 mol/l, polymerisation time = 4 h and temperature = 25°C).

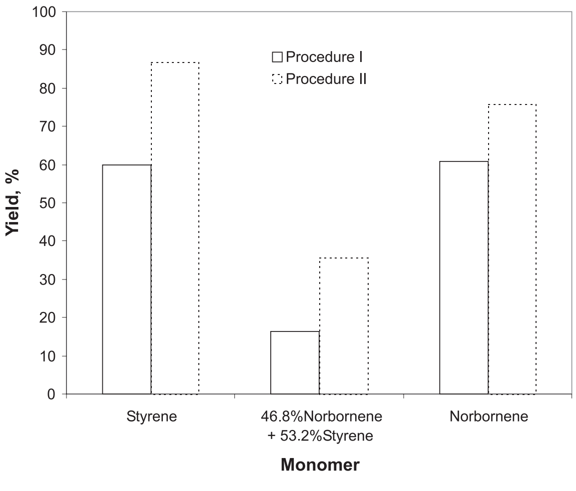

Fig. 3. Polymerisation yields given by two polymerisation procedures.

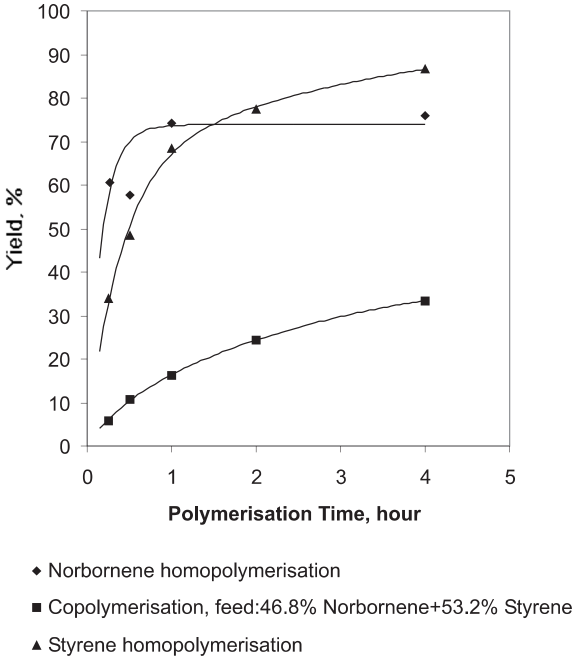

Fig. 4. Dependence of yield on the polymerisation time. (polymerisation conditions: [Ni] = 0.001 mol/l, Al/Ni = 1000, at room temperature).

3.1.2.1. The influence of polymerisation time. Fig. 4 displays the influence of polymerisation time on the yield for both homo and copolymerisations. Polymer yield increases with time and two distinct periods can be observed in the polymerisation process. In the first period, about 30–50 min depending on the monomer used, a rapid increase of the yield with time is observed. In the second period, the polymer yield increases very slightly and tends to a constant value (at 4 h polymerisation time) as a consequence of a significant decrease of the polymerisation rate.

3.1.2.2. The influence of polymerisation temperature. A series of polymerisation runs were performed at temperatures between 25°C and 50°C, while keeping the other parameters constant. As shown in Fig. 5, no significant effect of temperature on polymer yield or catalyst activity is observed both for homo and copolymerisations.

3.1.2.3. The influence of Al/Ni ratio. The dependence of the polymerisation yield on the Al/Ni mole ratio is shown in Fig. 6. For both homo and copolymerisations the observed behaviour is common to many Ziegler–Natta and metallocene systems: the catalytic activity increases markedly at first, followed by a gradual increase (up to the maximal value) and then remains

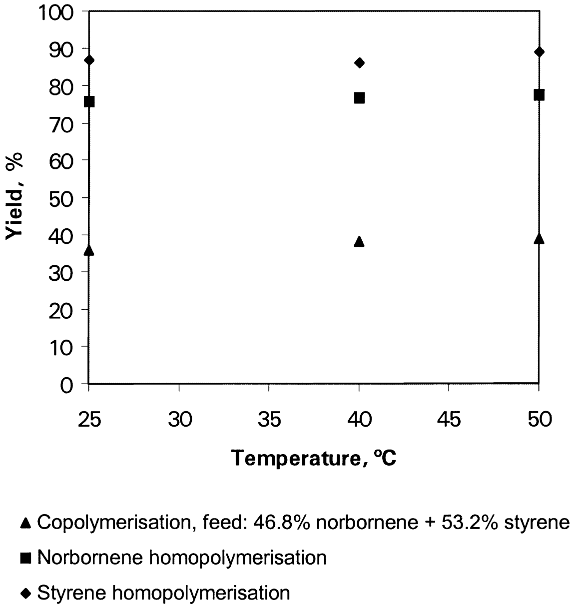

Fig. 5. Dependence of yield on the polymerisation temperature. (polymerisation conditions: [Ni] = 0.001 mol/l, Al/Ni = 1000, for 4 h).

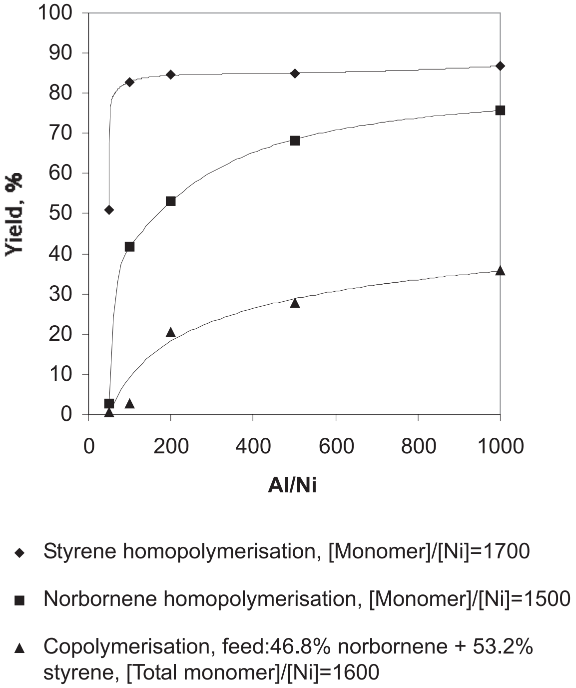

Fig. 6. Dependence of yield on the Al/Ni ratio. (polymerisation conditions: [Ni] = 0.001 mol/l, 4 h at 25°C).

constant. These results may be explained by the formation and stabilisation of an increasing number of active species, at higher Al/Ni mole ratios, until it attains the maximal concentration in active species.

The main difference observed between the two homopolymerisation reactions is that in the case of styrene homopolymerisation, the maximal conversion level is obtained at a rather low Al/Ni ratio (about 100) while for norbornene homopolymerisation, much higher Al/Ni ratios (over 500) are necessary to obtain the maximal conversion.

Despite the high yields obtained in both the homopolymerisation reactions (~75% for norbornene and ~85% for styrene), a maximum conversion of only 30% is obtained when copolymerising styrene and norbornene (53:47 by mole) at a rather high Al/Ni ratios (between 500 and 1000).

3.1.2.4. The influence of monomer/nickel molar ratio.

Fig. 7 shows the dependence of the catalytic activity on the monomer/nickel ratio. For norbornene and styrene homopolymerisations, a linear increase in activity with the monomer/nickel ratio is observed. The random copolymerisation of norbornene and styrene follows a different pattern; the catalytic activity reaches a maximum at a total monomer/nickel mole ratio of about 5000, and then decreases.

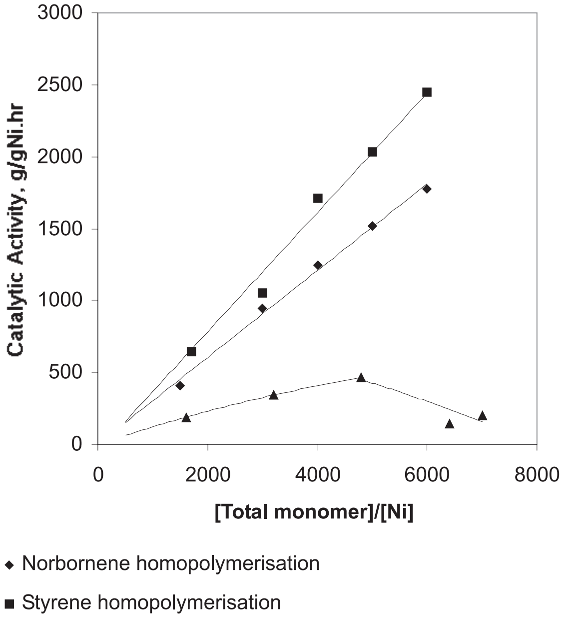

Fig. 7. Catalyst activity vs. monomer/nickel ratio. (polymerisation conditions: Al/Ni = 500, 4 h at 25°C, [Ni] was controlled at 0.001 and 0.0008 mol/l for a very high monomer/nickel ratio).

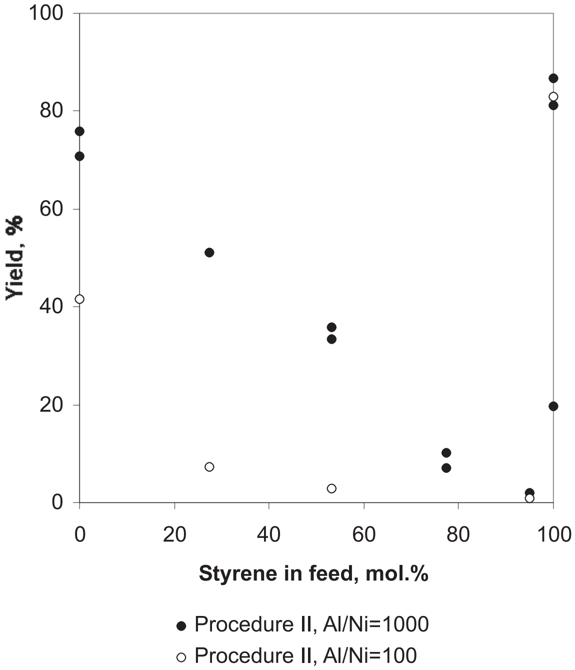

Fig. 8. Influence of feed composition on the yield. (polymerisation conditions: [Ni] = 0.001 mol/l, [monomer]/[Ni] = 1500–1700, 4 h at 25°C).

3.1.2.5. The influence of monomer composition.

A series of copolymerisation reactions were performed using different feed compositions, while keeping the [norbornene + styrene]/[Ni] molar ratio constant. Fig. 8 shows the dependence of polymerisation yield on the initial feed composition at two different Al/Ni ratios (100 and 1000). For comparison, the yields of the respective homopolymerisations are also indicated. It may be seen that an increase in the initial styrene feed content leads to a gradual loss of activity relative to norbornene homopolymerisation. On the other hand, and despite the high activity observed for norbornene homopolymerisation, a very low content of norbornene (~0.06 mol%) in the initial feed leads to a drastic loss of activity when compared with styrene homopolymerisation.

In order to confirm this unexpected result, additional tests were performed. As illustrated in Fig. 9a, styrene was polymerised using four different schemes. In all the four schemes, the [styrene]/[Ni] molar ratio was controlled at 1500. Scheme I refers to styrene homopolymerisation. In all the other schemes, a very low concentration of norbornene, in stoichiometric amounts, to nickel ([norbornene]/[nickel] = 1), was introduced. In Scheme II, the two monomers and the nickel catalyst were mixed together in the beginning, and then MAO was added to initiate the polymerisation. In Schemes III and IV, norbornene was first mixed with nickel, then two-thirds of the necessary MAO was added and the solution

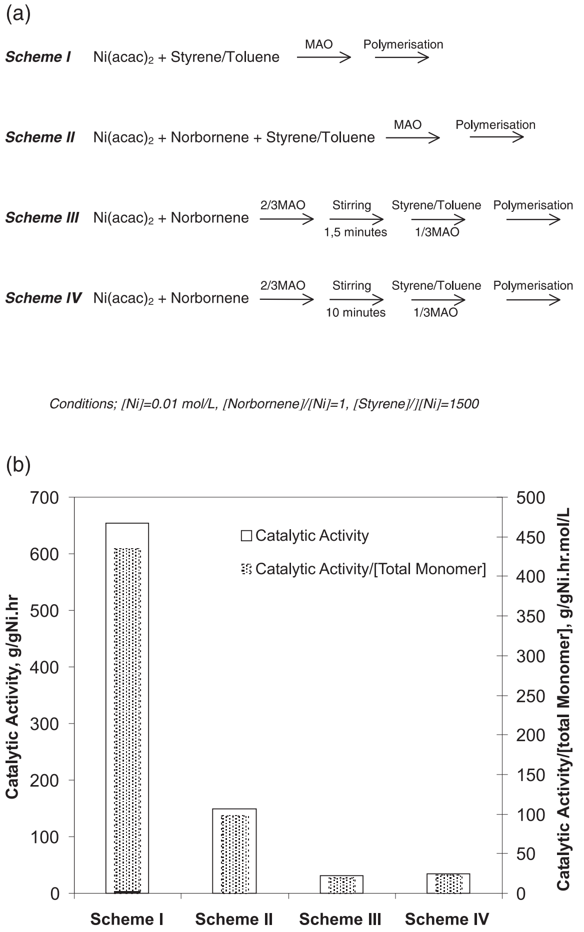

Fig. 9. (a) Controlled polymerisation schemes and (b) corresponding catalytic activity.

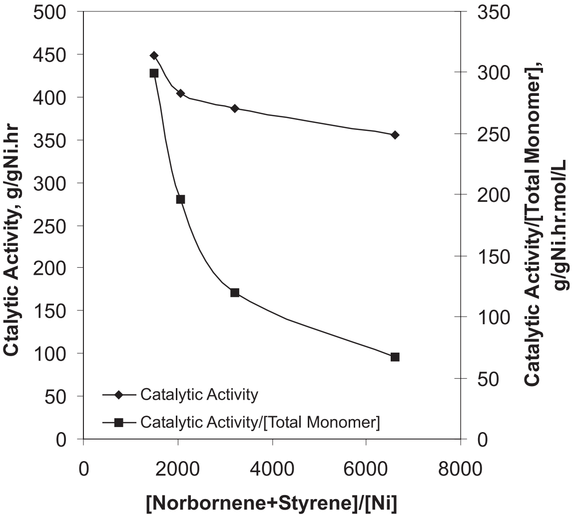

Fig. 10. Dependence of catalytic activity on the styrene content in the feed. (polymerisation conditions: 25°C, [norbornene]/[Ni] = 1500, [Ni] = 0.001 mol/l for the first three experiment and [Ni] = 0.0008 mol/l for the last experiment, Al/Ni = 1000).

was stirred for 1.5 to 10 min and finally, the styrene monomer and the remaining MAO were added and polymerisation started. The experimental results shown in Fig. 9b confirm our first data. Even in the presence of a very small amount of norbornene (stoichiometric to nickel), the catalytic activity is markedly low. In Schemes III and IV, as norbornene was first mixed with nickel, the blocking effect is even more pronounced.

Additional tests were performed in order to examine the effect of increasing styrene contents on the copolymerisation activity, while keeping the [norbornene]/[Ni] molar ratio controlled at 1500. As indicated in Fig. 10, the catalytic activity is lowered, but slightly and slowly. These results put in evidence, again the sharp contrast with the strong influence of norbornene on the styrene homopolymerisation activity.

This peculiar behaviour of the $Ni(acac)_2$/MAO system in norbornene/styrene copolymerisation will be discussed later on.

Another series of copolymerisation experiments were performed at low conversion levels in order to determine the monomer reactivity ratios by the Kelen–Tudos method [24]; results are listed in Table 1.

3.2. Polymer characterisation

3.2.1. Molecular weight characterisation by SEC

The average molecular weights and the molecular weight distribution of several homo and copolymers were measured by SEC. The experimental $\overline{M}_w$ and $\overline{M}_n$ values as well as the theoretical $\overline{M}_n$ values are listed in Table 2. Polystyrene samples possess low molecular

Table 1
Low yield copolymerisations and the reactivity ratios

Styrene in feed (mol%)	27.5	53.2	77.3	95
Polymerisation time (min)	2.5	15	20	240
Yield (%)	11.0	5.9	2.2	2.1
Styrene in copolymer (mol%)	2.0	9.5	28.4	65.8
Reactivity ratio by the Kelen–Tudos method [24]	$r_{styrene} = 0.156$		$r_{norbornene} = 17.8$	

Table 2
Molecular weight of the resulting polymers[a]

Norbornene content in the feed norbornene/styrene (mol%)	Al/Ni ratio	$\overline{M}_{\mathrm{w}} \times 10^{-3}$ [b]	Polydispersity ($\overline{M}_{\mathrm{w}}/\overline{M}_{\mathrm{n}}$)	$\overline{M}_{\mathrm{n}} \times 10^{-3}$ [b] (g mol^{-1})	$\overline{M}_{\mathrm{n}} \times 10^{-3}$ Theoretical [c](g mol^{-1})
100	100	593	2.0	291	58.8
100	200	609	1.9	325	74.9
100	500	765	1.9	405	96.3
100	1000	730	1.9	388	106
72.5	1000	40.8	2.0	23.5	76.5
46.8	1000	18.6	2.5	7.3	52.5
22.7	1000	8.3	1.9	4.4	15
0	1000	33.4	1.9	18.3	134
0	100	35.7	1.4	25.1	137
0	50	35.6	1.5	23.6	79.6

[a] Polymerisation conditions: [Ni] = 0.001 mol/l, [total monomer]/[Ni] = 1500, for 4 h, at room temperature.

[b] By GPC calibrated with polystyrene standard.

[c] $\overline{M}_{\mathrm{n}}(\text{theoretical}) = \text{yield} \times \text{weight}_{\text{total monomer}}/[\text{Ni}]$.

weight ($\overline{M}_{\mathrm{n}} \approx 2\times10^4$). On the contrary, the molecular weight of polynorbornene is much higher in the order of 10^5. In accordance with the data of Haselwander et al. [25], we may assume that the average molecular weight measured by the SEC technique and using polystyrene standards is in good agreement with the absolute value obtained with static light scattering technique.

The influence of the aluminium/nickel ratio on the molecular weight was analysed. For norbornene polymerisation, the polymer average molecular weight increases with the Al/Ni ratio. For styrene polymerisation, no significant effect of Al/Ni ratio on the average molecular weight is observed for Al/Ni ratios higher than 50.

Both homo and copolymer samples present unimodal elution SEC curves, and the calculated $\overline{M}_{\mathrm{w}}/\overline{M}_{\mathrm{n}}$ ratios are around 2. These data suggest that homo and copolymerisations take place at a single active site and that the polymers obtained from random copolymerisation are really "true" copolymers and not mixtures of homopolymers. The absence of polystyrene in the copolymer samples was confirmed using a dual detector, i.e., refractive index and ultraviolet detectors, in SEC analysis.

It was also noticed that the average molecular weights of the copolymers are low and depend on feed composition, decreasing with the increasing styrene content in the monomer feed. These results suggest that styrene plays a significant role as transfer agent. In Table 2, the theoretical $\overline{M}_{\mathrm{n}}$ values are listed and compared with the experimental ones. Polynorbornenes possess experimental molecular weights much higher than the theoretical ones. The opposite occurs for polystyrene and copolymers.

3.2.2. *Structural and composition characterisation by NMR and FTIR*

Polynorbornene, polystyrene and norbornene–styrene copolymers of different compositions have been investigated by FTIR spectroscopy, ^{1}H-NMR and ^{13}C-NMR (Figs. 11–13).

The FTIR spectra (Fig. 11) and the ^{1}H-NMR spectra (Fig. 12) of polynorbornene and copolymers shows the absence of the vibration bands of carbon–carbon double bond at 1620–1680 cm^{-1} and of the resonance of the proton atom connected to the double bond at about 6 ppm, respectively. The ^{13}C-NMR spectrum of polynorbornene (Fig. 13), presents four groups of resonances (30.3–31.5 ppm); (35.6–37.7 ppm); (38.8, 39.8 and 42.8 ppm); (47.9, 48.3, 50.9, 52.4 ppm). Each region of resonance is characterised by several signals with small chemical shift differences. The results indicate that

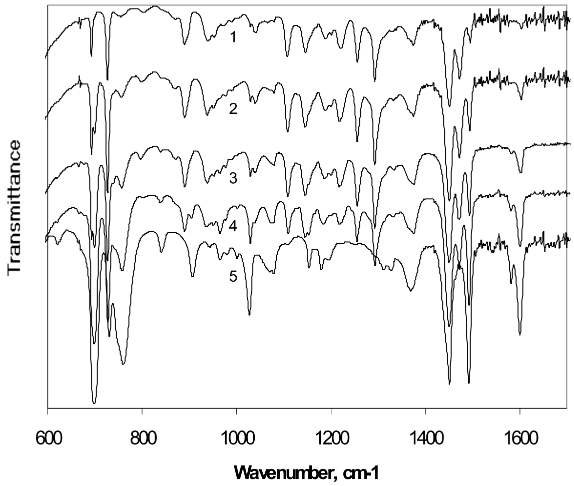

Fig. 11. FTIR spectra of the polymers synthesised from different monomers: (1) norbornene, (2) 72.5 mol% norbornene + 27.5 mol% styrene, (3) 46.8 mol% norbornene + 53.2 mol% styrene, (4) 22.7 mol% norbornene + 77.3 mol% styrene, (5) styrene.

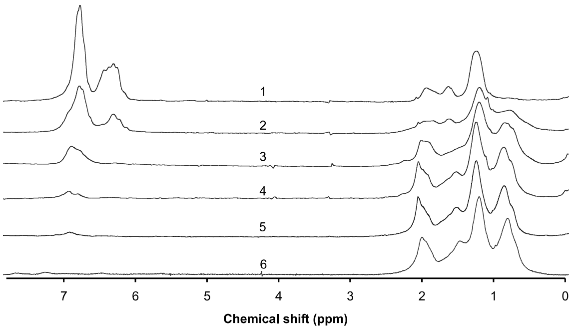

Fig. 12. ^{1}H-NMR spectra of the polymers synthesised from different monomers: (1) styrene, (2) 5% norbornene + 95% styrene, (3) 22.7 mol% norbornene + 77.3 mol% styrene (4) 46.8 mol% norbornene + 53.2 mol% styrene, (5) 72.5 mol% norbornene + 27.5 mol% styrene, (6) norbornene. The HTNS signal (not shown) is 0.2 upfield shifted from the usual assigned value (0.055 ppm).

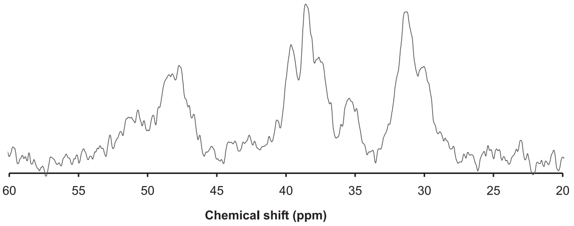

Fig. 13. ^{13}C-NMR spectrum of polynorbornene in 1,1,2,2-tetrachloroethane (d_2) at 380 K.

polymerisation of norbornene with Ni(acac)$_2$/MAO system occurred without ring opening and via a 2,3 addition.

The proton NMR spectrum of polystyrene (Fig. 12) revealed two peaks in the aromatic region, one at 6.5 ppm corresponding to the *ortho*-protons and the other at around 7.0 ppm corresponding to the *meta*- and *para*-protons. The integral ratio between them is about 3/2, in close agreement with the theoretical value.

For norbornene–styrene copolymers the FTIR spectra (Fig. 11) shows an increase in the intensity of the bands related to the phenyl ring (e.g., the out-of-plane phenyl ring deformation band at 698 cm^{-1}, the out-of-plane aromatic hydrogen deformation band at 760 cm^{-1} and the in-plane phenyl ring bending–stretching vibrations at 1600, 1492 and 1452 cm^{-1}) with the styrene feed content.

The ^{1}H-NMR spectra of copolymers also shows some differences on the aromatic proton region, as function of the styrene feed content (Fig. 12). For a styrene molar fraction below 50% in the feed, only one peak at around 7.1 ppm was observed, evidencing that no blocks with more than eight styrene units are formed in the resulting polymer [26]. This fact is consistent with the formation of a random copolymer presenting only isolated styrene units or very short styrene sequences. For a styrene molar fraction in the feed above 50%, the proton spectra show two peaks at about 6.5 and 7.1 ppm, but the ratio of the areas between them is much higher than 3/2, indicating that short polystyrene sequences with more than eight styrene units may be formed in the resulting copolymer. These results confirm that the polymers obtained by random copolymerisation are really copolymers.

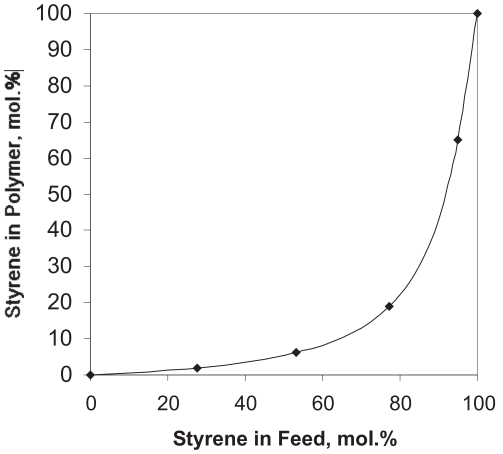

Fig. 14. Copolymer composition vs. feed composition.

The composition of the copolymers obtained at variable comonomer feed was determined by ^{1}H-NMR. In Fig. 14, the compositions of the copolymers obtained at high conversion are represented. The composition of the copolymers obtained at low yields, and the calculated reactivity ratios of the two monomers are listed in Table 1. As may be seen, the styrene incorporation increased with the styrene content in monomer feed. The styrene reactivity ratio ($r_{\text{styrene}} = 0.16$) is much lower than the norbornene reactivity ratio ($r_{\text{norbornene}} = 17.8$), indicating that the incorporation of styrene into the copolymer chains is much slower than that of norbornene.

The ^{13}C-NMR spectra of the copolymers were also acquired. An analysis of the microstructure of copolymers, e.g., the norbornene incorporation mode, is being carried out.

3.3. Mechanistic consideration and discussion

Some authors [16] have already pointed out that the polymerisation with Ni-based catalysts may proceed by a coordination mechanism. The results presented in the previous paragraphs also support this mechanism.

In fact, the ^{1}H- and ^{13}C-NMR spectra of polynorbornene samples show that polymerisation of norbornene with Ni(acac)$_2$/MAO system occurs without ring opening and via 2,3 addition, in a way similar to that described by Kaminsky et al. [6] in the case of metallocene systems. This 2,3 addition mode is characteristic of a coordination mechanism. As shown by Gaylord et al. [3], radical or cationic polymerisation leads to 2,7 addition.

Another point is that the reactivity ratios, determined by the Kelen–Tudos method, for the norbornene/styrene copolymerisation show a much higher reactivity for norbornene ($r_{\mathrm{norbornene}}$) (100 times) than that for styrene (r_{styrene}). As is well known, in radical polymerisation the observed reactivity order is the opposite, $r_{\mathrm{styrene}} \gg r_{\mathrm{norbornene}}$. These results also suggest that a coordination mechanism operates with the Ni(acac)$_2$/MAO system.

Based on this mechanism, we may assume that reaction between nickel complex and MAO produces a cationic centre. In the absence of monomer, MAO and nickel centres will be closely interacting and some less stable and/or less active complexes may form, leading to lower activities. In the presence of monomers, σ–π bond complexes likely involving cationic nickel centres and the monomer may be formed, which along with MAO, will play a role in the formation and stabilisation of the active species. These complexes will present increased activity. The complexated monomer will then be inserted between the alkyl group and the nickel centre. Repetition of the complexation–insertion steps will lead to polymer chain growth. Finally, the growth of polymer chain may be terminated via the β-elimination of hydrogen atom.

Most of the results of the previous sections may be easily understood on this basis and from other literature data. Both primary and secondary addition modes are known for styrene polymerisation [28,29]. Longo et al. [30] have shown that styrene insertion proceeds preferentially by a secondary way in the Ni(acac)$_2$/MAO system. In this case, the last inserted secondary styrene unit can form a η^3-nickel–benzyl ring bond that allows an additional stabilisation of the cationic centre to some degree. This may be a plausible reason for the low Al/Ni ratio (near 100) necessary to achieve a high conversion in styrene homopolymerisation. On the other hand, it is well known that the chain termination and transfer reactions can occur easily by the β-elimination of hydrogen from a last inserted styrene unit [28]. In contrast, the β-elimination of hydrogen would be much more difficult for a last inserted norbornene, otherwise, some strain effect would be created in the cyclo-ring, which is thermodynamically unfavourable. This explains the much higher molecular weight of polynorbornene when compared with polystyrene or copolymers. Also it explains the difference in dependence of polymer molecular weight on the Al/Ni ratio, for the two homopolymers.

Nevertheless, assuming the coordination mechanism, some results are difficult to explain. Very low contents of norbornene in the initial feed (0.06 mol%, or even in stoichiometric amount to Ni) lead to a drastic loss of activity when compared with styrene homopolymerisation, a much more gradual loss of activity relative to norbornene homopolymerisation is observed in the presence of significant amounts of styrene (Figs. 8–10).

We will try to interpret this peculiar behaviour in a qualitative way, on the basis of the trigger mechanism proposed by Ystenes some years ago [27]. This mechanism seems to be more suitable to explain complex copolymerisation behaviours, because the complexation of the first monomer is a step distinctly different from the propagation step. Hence, different monomers may have different abilities to activate the catalytic centre and may give different numbers of active species. It is assumed in this mechanism that the active centres are never free, they are always occupied by a complexated monomer. The complexated monomer will be inserted into the growing chain if and only if another monomer is ready to complexate. On this basis, we will assume that the propagation step may proceed via a trigger mechanism and that the complexated monomer is inserted if and only if a new monomer is able to complexate.

Taking into account the strain effect of the cyclo-ring, we may assume that norbornene has a stronger tendency to complexate with the cationic Ni centres than styrene. Due to this tendency, norbornene monomer would always be ready to trigger the insertion of previously complexated norbornene or styrene units into the growing polymer chain, and to complexate itself with the cationic centre. A styrene monomer would also be able to trigger a complexated styrene, but its ability to force the insertion of an already complexated norbornene into the polymer chain and to complexate itself with the nickel centre is rather weak. This latter trigger action is possible, but its probability is very low and increases slowly with the concentration of styrene.

Therefore, for norbornene/styrene copolymerisation, norbornene displays a much higher rate of incorporation into the polymer chains than does styrene. The use of higher styrene concentration may slightly increase the complexation and incorporation of styrene but even then, the styrene monomer would have difficulty to trigger and replace the complexated norbornene, leading to styrene incorporation levels in the polymer much lower than that in the feed (in accordance with the experimental reactivity ratios), and to reduced activities. On the other hand, the styrene polymerisation is strongly inhibited, by the addition of low levels of norbornene. As assumed before, nickel centres will complexate preferentially with norbornene, but the norbornene concentration is rather low; therefore, polymerisation must proceed by styrene complexation and as mentioned before, the ability of styrene to complexate with the nickel centre while forcing norbornene insertion is very low.

In accordance with our assumption of a trigger mechanism operating in our polymerisation system, Endo and Masaki [31] reported for styrene homopolymerisation in the presence of the Ni(acac)$_2$/MAO system, a second-order dependence on the monomer. However, a detailed kinetic investigation of both homo and copolymerisations of norbornene and styrene initiated by Ni(acac)$_2$/MAO will be necessary to provide further support to the present statements.

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