

Polymerization of Higher α -Olefins Using a C_s -Symmetry Hafnium Metallocene Catalyst. Kinetics of the Polymerization and Microstructural Analysis

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Received 23 April 2009; accepted 23 April 2009

DOI: 10.1002/pola.23483

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The C_s -symmetry hafnium metallocene $[(p\text{-Et}_3\text{Si})\text{C}_6\text{H}_4]_2\text{C}(2,7\text{-di-}t\text{-BuFlu})(\text{C}_5\text{H}_4)\text{Hf}(\text{CH}_3)_2$ and tetrakis(pentafluorophenyl) borate dimethylanilinium salt $([\text{B}(\text{C}_6\text{F}_5)_4]^-[\text{Me}_2\text{NHPH}]^+)$ were used as the catalytic system for the polymerization of higher α -olefins (from hexene-1 to hexadecene-1) in toluene at 0 °C. The evolution of the polymerization was studied regarding the variation of the molecular weight, molecular weight distribution and yield with time. The effect of the monomer structure on the polymerization kinetics was established. The role of trioctylaluminum in accelerating the polymerization was investigated. ^{13}C NMR spectroscopy was used to study the microstructure of the poly(α -olefins) by the determination of the pentad monomer sequences. The thermal properties of the polymers were obtained by differential scanning calorimetry, DSC. The results were discussed in connection with the polymer microstructure. © 2009 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 47: 4314–4325, 2009

Keywords: α -olefins; glass transition; kinetics; metallocene catalyst; microstructure

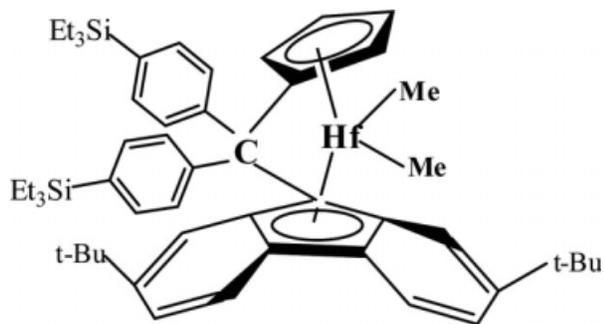
INTRODUCTION

Polyolefins are by far the most important class of synthetic polymers. They are used in a wide range of applications since they provide excellent mechanical properties, chemical resistance, and processability.¹ The primary goal of polymer

chemistry over the last half century is the development of chain-growth polymerization methods that lead to the synthesis of polyolefins with controlled molecular weights, molecular weight distributions, and stereochemistry.² Since the discovery of Ziegler-Natta catalysts³ remarkable advances have been reported concerning the controlled synthesis of polyolefins. Homogeneous polymerization catalysts now exist that are unparalleled in the control of the molecular and structural characteristics of the products.⁴

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Journal of Polymer Science: Part A: Polymer Chemistry, Vol. 47, 4314–4325 (2009)
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Scheme 1. The C_s -symmetry hafnium metallocene catalyst $[(p\text{-Et}_3\text{Si})\text{C}_6\text{H}_4]_2\text{C}(2,7\text{-di-}t\text{-BuFlu})(\text{C}_5\text{H}_4)\text{Hf}(\text{CH}_3)_2$.

Three mutually interconnected approaches have been developed for the controlled synthesis of polyolefins. The first one involves the use of the Group 4 metallocenes.⁵ Extensive studies have been devoted over the past two decades regarding the synthesis of these metallocenes and their evaluation as catalysts for the polymerization of olefins, in combination with suitable cocatalysts. This area of research has also been expanded to the use of Groups 3 and 5 metallocenes and half-metallocenes bearing amine, alkoxide, amide groups etc.⁶ The second approach includes the use of the late transition metal complexes as the catalytic species promoting the polymerization of olefins.⁷ The development of cationic α -diimine palladium and nickel complexes led to highly active catalysts for the synthesis of polyolefins exhibiting high molecular weights and unique branched structures. The knowledge acquired during the years regarding the electronic and steric effects of the ligands led to the third approach, which is the use of early transition metals bearing non-Cp ligands, such as diamido, alkylthio, and amine-phenolate ligands.⁸

In this report the polymerization of higher α -olefins (from hexene-1 to hexadecene-1) using the C_s -symmetry hafnium metallocene catalyst $[(p\text{-Et}_3\text{Si})\text{C}_6\text{H}_4]_2\text{C}(2,7\text{-di-}t\text{-BuFlu})(\text{C}_5\text{H}_4)\text{Hf}(\text{CH}_3)_2$, (Scheme 1) was studied. Emphasis was given on the kinetics of the polymerization, the control over the molecular characteristics and the microstructure of the polyolefins. The polymers produced from α -olefins bearing up to 10 carbon atoms are amorphous and can be used as impact strength modifiers when blended with polypropylene.⁹ The polymers produced from α -olefins bearing more than 12 carbon atoms exhibit side chain crystallinity and can be combined with amorphous blocks to provide samples with improved mechanical properties.¹⁰ Very extensive studies

have been devoted to the copolymerization of ethylene with higher α -olefins leading to linear low density polyethylenes having controlled density and crystallinity depending on the amount and the nature of the α -olefin.¹¹ In a previous study, the same catalytic system was used for the synthesis of functionalized polyolefins coming from the copolymerization of octene-1 and tetradecene-1 with silyl-protected 10-undecen-1-ol (1-*tert*-butyldimethylsilyloxy-10-undecene).¹²

Limited results were reported for the homopolymerization of higher α -olefins, due to the low catalytic activities and molecular weights produced by these monomers.¹³ In general, the polymerization rate decreases with increasing steric requirements.¹⁴ Therefore, ansa metallocene catalysts have been developed for the homogeneous polymerization of higher α -olefins to obtain products of high molecular weight and high rate of polymerization.¹⁵ It was observed that zirconocenes lead to poly(α -olefin)s bearing lower molecular weights but with higher catalytic activities than the corresponding hafnocenes.¹⁶ The nature of the catalytic system and the monomer, the temperature of the polymerization and the concentrations of the catalyst and the monomer are the major parameters influencing the kinetics of the polymerization and the microstructure of the produced polymers.^{14a,15,17}

EXPERIMENTAL

Materials

All manipulations were performed using high-vacuum and/or Schlenk techniques. The hafnium catalyst $[(p\text{-Et}_3\text{Si})\text{C}_6\text{H}_4]_2\text{C}(2,7\text{-di-}t\text{-BuFlu})(\text{C}_5\text{H}_4)\text{Hf}(\text{CH}_3)_2$, (Scheme 1) was donated by Exxon-Mobil.¹⁸ Tetrakis(pentafluorophenyl) borate dimethylanilinium salt $([\text{B}(\text{C}_6\text{F}_5)_4]^-[\text{Me}_2\text{NHPH}]^+)$ was synthesized¹⁹ or purchased from Strem Chemicals. Trioctylaluminium (TOA, 25 wt % in hexane) was purchased from Aldrich. Toluene (Aldrich) was dried and vacuum-distilled from calcium hydride (CaH_2), sodium metal and polystyryllithium consecutively. Methylene chloride (CH_2Cl_2 , Aldrich) was dried and vacuum-distilled from CaH_2 . The monomers hexene-1, octene-1, decene-1, tetradecene-1, and hexadecene-1 (Aldrich), were vacuum-distilled from CaH_2 in the vacuum line.

Polymerization of α -Olefins

The polymerizations were carried out at 0 °C in a 0.1-dm³ Schlenk-type reaction flask. A typical

polymerization process is the following: Toluene (5 mL) and tetradecene-1 (1.5 mL) were added to the reaction flask. The mixture was stirred at 0 °C followed by the addition of 5.0 mL of the hafnium catalyst solution (4.69×10^{-2} mmol) with the borane cocatalyst (4.69×10^{-2} mmol) to initiate the polymerization. The polymerization was quenched by the addition of an HCl/methanol solution, and the polymer was precipitated in methanol, washed with methanol, filtered, and dried in high vacuum at room temperature.

Kinetic Experiments

The kinetic experiments were carried out following two different protocols. According to the first, appropriate samples were taken from the reaction mixture via gas-tight syringe utilizing standard Schlenk techniques, at specific periods of time. The aliquots were quenched immediately in the appropriate amount of MeOH/HCl. The precipitated polymer was filtered, rinsed with methanol and dried in high vacuum until constant weight. In the second protocol independent experiments were conducted under the same conditions. Termination of the polymerization reaction took place at the determined time followed by precipitation, filtration, rinsing, and drying of the resulting polymer.

Both protocols were utilized to record the polymerization time evolution. The experimental results of the aforementioned protocols did not show any significant differentiation, in all cases.

Characterization Techniques

Size exclusion chromatography (SEC) experiments were carried out using a modular instrument consisting of a Waters Model 510 pump, a Waters Model U6K sample injector, a Waters Model 401 differential refractometer, and a set of four μ -styragel columns with a continuous porosity range of 10^6 – 10^3 Å. The columns were housed in an oven-thermostatted at 40 °C. Tetrahydrofuran was the carrier solvent at a flow rate of 1 mL/min. The instrument was calibrated with polystyrene (PSt) standards (six samples covering a molecular weight range of 10,000–900,000).

Static light scattering measurements were performed with a Chromatix KMX-6 low angle laser light scattering photometer at 25 °C equipped with a 2 mW He-Ne laser operating at $\lambda = 633$ nm. The eq 1 describing the concentration dependence of the reduced intensity is:

$$Kc/\Delta R_{\theta} = 1/M_{w,app} + 2A_2c + \dots \quad (1)$$

where K is a combination of optical and physical constants, including the refractive index increment, dn/dc , and the excess Rayleigh ratio of the solution over that of the solvent, ΔR_{θ} . Stock solutions were prepared, followed by dilution with solvent to obtain appropriate concentrations. All solutions and solvents were optically clarified by filtering through 0.22 μ m pore size nylon filters directly into the scattering cell.

Refractive index increments, dn/dc , at 25 °C were measured with a Chromatix KMX-16 refractometer operating at 633 nm and calibrated with aqueous NaCl solutions.

The polymer microstructure was determined from ^{13}C NMR spectra utilizing the inverse gated proton decoupling sequence incorporated in the library of the 600 MHz Varian NMR spectrometer which eliminates the NOE. The time delay used was 20 s and was established running T_1 experiments (delay time used was $> 5 T_1$ of the longest relaxing nucleus). The 90° pulse applied was 6.7 μ s while the number of transients was 2500.

DSC experiments were performed with a 2910 Modulated DSC model from TA instruments. The samples were heated or cooled at a rate of 10 °C/min. The second heating results were recorded.

RESULTS AND DISCUSSION

Polymerization of Hexene-1

The hafnium catalyst $[(p\text{-Et}_3\text{Si})\text{C}_6\text{H}_4]_2\text{C}(2,7\text{-di-tert-BuFlu})(\text{C}_5\text{H}_4)\text{Hf}(\text{CH}_3)_2$ in combination with the tetrakis(pentafluorophenyl) borate dimethylanilinium salt ($[\text{B}(\text{C}_6\text{F}_5)_4]^- [\text{Me}_2\text{NHPH}]^+$) cocatalyst were used for the polymerization of hexene-1. The reactions were conducted in toluene at various temperatures from 0 up to 120 °C. The results concerning the variation of the molecular weight, molecular weight distribution, and polymer yield with polymerization temperature are displayed in Table 1. The reactions were conducted under the same experimental conditions regarding the catalyst, cocatalyst and monomer concentrations. It is obvious that upon decreasing the temperature the yield and the molecular weight considerably increase, whereas the molecular weight distribution decreases. This behavior can be attributed to the substantial decrease of the rate of termination and chain transfer reactions upon decreasing the temperature. Therefore, the best control over the molecular characteristics and the polymerization

Table 1. Polymerization of Hexene-1 at Different Temperatures^a

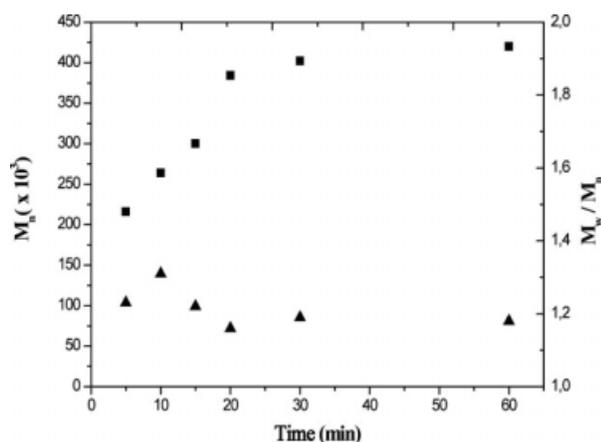
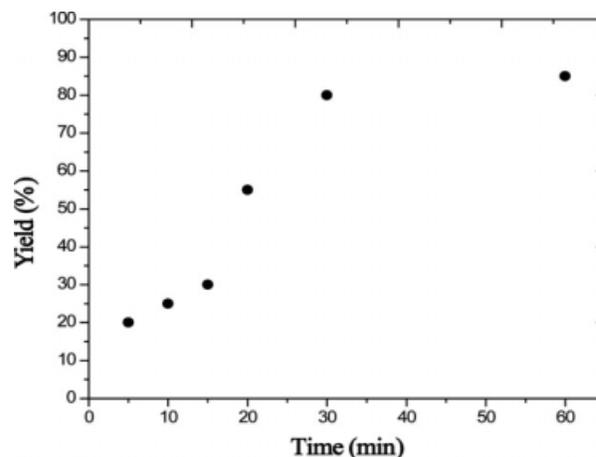
Polymerization Temperature, °C	$M_n \times 10^{-3b}$	M_w/M_n^b	Yield (%)
0	380	1.19	90
25	330	1.28	80
80	200	1.55	70
120	170	1.60	65

^a Polymerization conditions: [catalyst] = [cocatalyst] = 5.2 mM, [monomer] = 2.35 mM, polymerization time = 1 h.

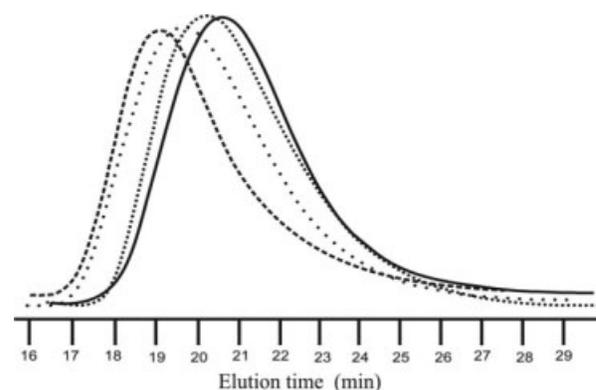
^b By SEC in THF at 40 °C.

yield is achieved when the polymerization is conducted at 0 °C. At lower temperatures the rate of polymerization will be lower rendering the polymerization of hexene-1 under these conditions nonpractical. Consequently, all the other experiments were conducted at 0 °C.

The evolution of the polymerization is depicted in Figures 1 and 2 showing the change of the molecular weight, molecular weight distribution and yield with time. The system is characterized by an induction period, which is equal to a few minutes. This period is devoted for the activation of the catalyst by the cocatalyst and the complexation of the first monomer unit for the initiation of the polymerization process. This behavior was reported earlier for the polymerization of hexene-1 with zirconocenes²⁰ and also for the polymerization of other monomers as well.²¹ After this period the molecular weight and the yield increase linearly with time. The maximum molecular weight and the maximum yield were obtained 30 min after the initiation of the polymerization. The

**Figure 1.** Molecular weight and molecular weight distributions versus time for the polymerization of hexene-1, (■) $M_n = f(t)$ and (▲) $I = f(t)$.**Figure 2.** Yield versus time for the polymerization of hexene-1.

final yield is close to 90%. Taking into account the extended purification processes of the samples it can be concluded that the yield is near quantitative. The SEC traces of the samples taken from the reactor during the polymerization are given in Figure 3. The molecular weight distribution is relatively narrow ($M_w/M_n \sim 1.20$) and almost stable during the polymerization. All these results give direct evidence that the polymerization proceeds in a well controlled manner. Compared to other catalytic systems used for the polymerization of hexene-1 the present catalytic system leads to products having higher molecular weights and the polymerization reaction is very fast.²² In addition, the molecular weight distribution is very narrow. However, there are other catalytic species, which are based on titanium or other metals providing products of even lower polydispersities but with low molecular weights and yields.²³

**Figure 3.** SEC traces for the synthesis of P(Hexene-1) in different polymerization times (—) 5 min, (···) 10 min, (---) 15 min, (-·-) 20 min.

Polymerization of Octene-1

The polymerization of octene-1 was conducted under similar experimental conditions as hexene-1 regarding the monomer, catalyst and cocatalyst concentration and the polymerization temperature. The variation of the molecular characteristics and yield with time are displayed in Figures 4 and 5 respectively, whereas SEC traces of samples withdrawn during the polymerization are presented in Figure 6. As in the case of hexene-1 an induction period of ~ 3 min was obtained. The molecular weight and the yield increase linearly with time and the molecular weight distribution slightly reduce reaching values equal to 1.20. The maximum degree of polymerization and the maximum yield are similar with those observed for poly(hexene-1). However, the time where these maximum values were obtained was equal to 20 min instead of 30 min for poly(hexene-1).

This result indicates that octene-1 polymerizes faster than hexene-1. For the explanation of this effect several phenomena have to be considered. The larger the size of the α -olefin the more difficult is its insertion in the growing polymer chain, due to steric hindrance effects.¹⁷ On the other hand, the longer lateral polymer chain opens the π -ligands wider than a shorter α -olefin and facilitates the insertion of the longer α -olefin.^{17,24} A third effect that should be considered is associated with the nature of the active centers. They are formed *in situ* by the interaction between the catalyst and the fluoroarylborane cocatalyst and consist of alkyl metal cations that are attended by weakly coordinated counter anions. Although the

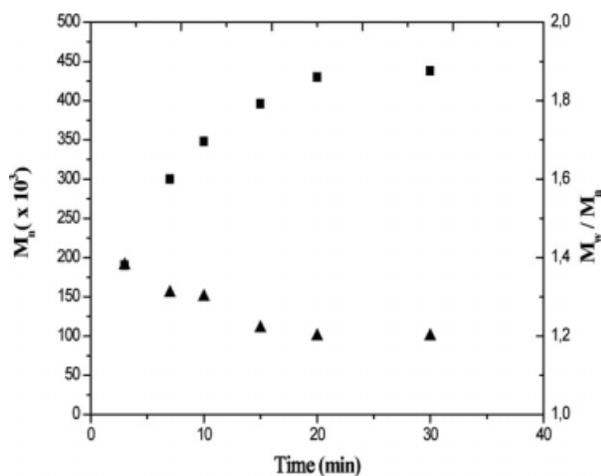


Figure 4. Molecular weight and molecular weight distributions versus time for the polymerization of octene-1, (■) $M_n = f(t)$ and (▲) $I = f(t)$.

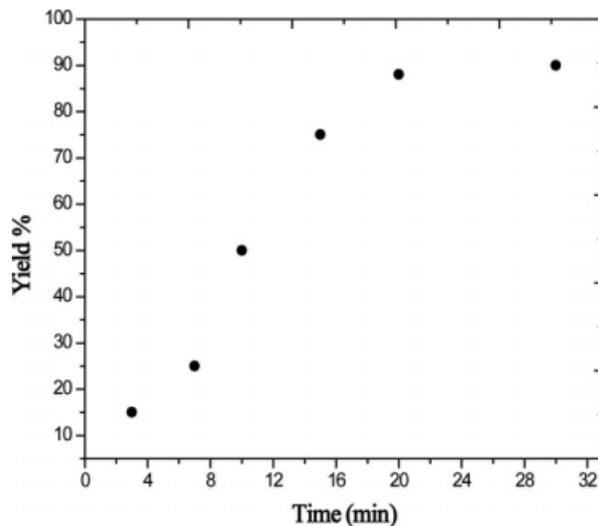


Figure 5. Yield versus time for the polymerization of octene-1.

cation-anion interaction is very weak the counter anion remains in the proximity with the metal cation to form a contact ion pair. This is facilitated in low permittivity solvents, such as toluene used in the present work. For the specific catalytic system under investigation the fluoroarylborane anion is relegated to the second coordinating sphere, rendering the ion pair more ionic and allowing for the formation of aggregates, at least quadruples in non polar solvents.²⁵ The less aggregated the active centers the higher is the acceleration of the polymerization reaction. In polar solvents the enhanced ion separation reduces the degree of aggregation leading to higher polymerization activities.^{21,26} The same effect can be observed using bulky monomers. Upon increasing the size of the monomer the

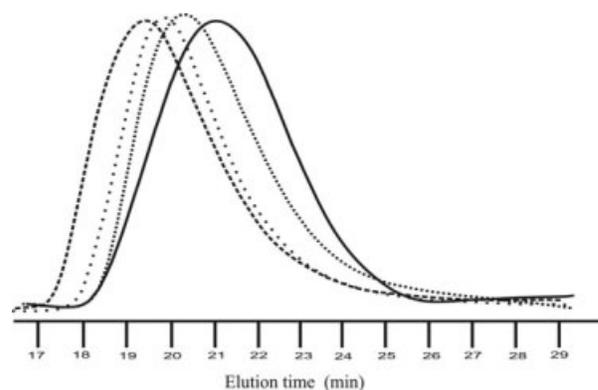


Figure 6. SEC traces for the synthesis of P(Octene-1) in different polymerization times (—) 3 min, (···) 7 min, (-·-) 10 min, (---) 20 min.

steric hindrance effects become more pronounced leading to reduced degrees of associations and thus to increased catalytic reactivities. Consequently, the first effect leads to a lowering, whereas the other two to an increase of the polymerization rate. Therefore, the increased polymerization rate of octene-1 compared to hexene-1 indicates that the second and third effect prevail over the steric hindrance exercised by the monomer side group.

Polymerization of Decene-1

Kinetic experiments were also conducted during the polymerization of decene-1 to further explore the earlier statements regarding the effect of the monomer structure on the polymerization reactivity using the specific C_s -symmetry catalyst. The results are given in Figures 7–9. It is obvious that the maximum molecular weight is obtained in 10 min, meaning that the polymerization is even more accelerated compared to octene-1. The steric hindrance induced by the monomer side group is overbalanced by the opening of the π -ligands of the catalyst and the reduction of the degree of association of the active centers leading to a considerable increase of the polymerization rate. This effect is so pronounced that even the induction period is minimized to only 1 min, compared to the 3 min, which was obtained for the polymerization of hexene-1 and octene-1.

The polymerization yield is also very high, as shown in Figure 8. However, the maximum yield was obtained after 15 min. This result indicates that in the period between 5 and 15 min the poly-

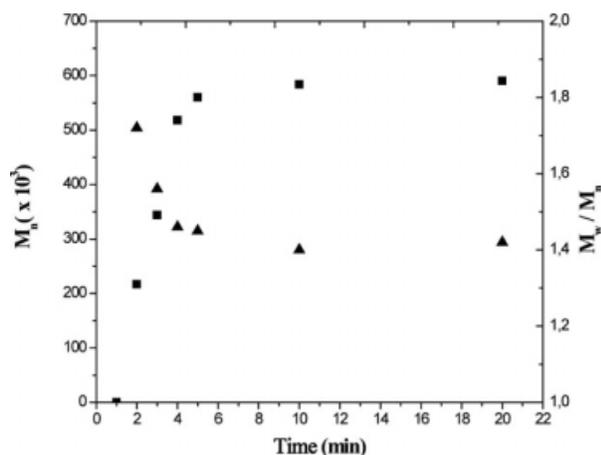


Figure 7. Molecular weight and molecular weight distributions versus time for the polymerization of decene-1, (■) $M_n = f(t)$ and (▲) $I = f(t)$.

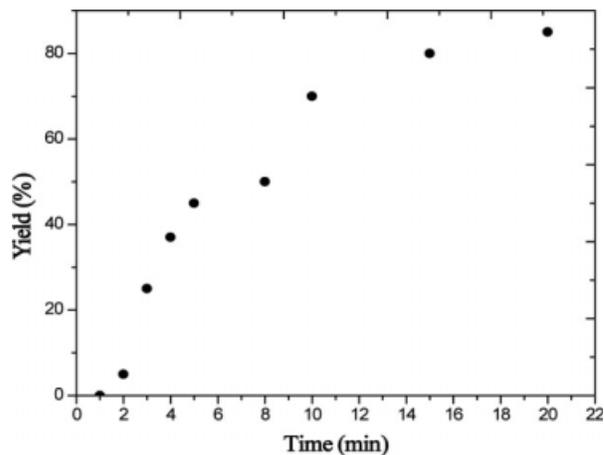


Figure 8. Yield versus time for the polymerization of decene-1.

mer chains do not grow further to higher molecular weights but instead more chains are produced. A possible scenario for this effect is that at the beginning of the polymerization, the unassociated active catalytic sites polymerize immediately and very fast the monomer. The aggregated ion pairs are much less reactive. Gradually, the equilibrium is shifted towards the free ion pairs providing new very active catalytic species producing new polymer chains. This procedure is accompanied with a rather poor control over the molecular characteristics. The final degree of polymerization is comparable with those obtained for poly(hexene-1) and poly(octene-1). However, the molecular weight distribution is much higher for poly(decene-1) gradually reducing from values around 1.8 to values around 1.4. This result is a direct indication that the active centers are not uniform throughout the polymerization. At the

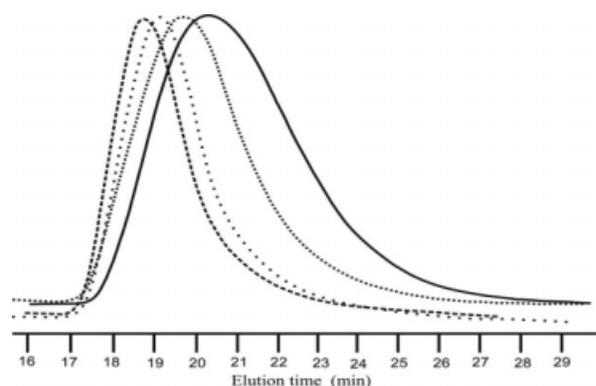


Figure 9. SEC traces for the synthesis of P(Decene-1) in different polymerization times (—) 2 min, (····) 3 min, (---) 4 min, (-·-·) 5 min.

initial stages of the reaction the very active free ion pairs coexist with the less active aggregated ion pairs leading to products of broad molecular weight distributions. Gradually, more free ion pairs are produced, the active centers become more uniform and the polydispersity of the products is considerably reduced.

Polymerization of Tetradecene-1

A different situation was observed for the polymerization of tetradecene-1, as shown in Figures 10-12. The rate of polymerization is drastically reduced compared to the other α -olefins bearing smaller side groups. It is evident that for this monomer the steric hindrance induced by the bulky side chain prevails leading to much lower polymerization rates. It is characteristic that the induction period is higher than 30 min, instead of 2 to 3 min for the other α -olefins, and the maximum molecular weight is obtained 7 h after the initiation of the polymerization, instead of 5 to 30 min for the other α -olefins. However, during this period the molecular weight increases linearly with time indicating that despite the delay in the reaction progress the polymerization still remains well-controlled. The molecular weight distribution is rather broad at the initial stages of the polymerization ($M_w/M_n \sim 1.6$) and gradually decreases ($M_w/M_n \sim 1.3$) meaning that the active catalytic centers become progressively more uniform. The retardation of the polymerization of tetradecene-1 was also observed in the past utilizing zirconocene catalytic systems, such as

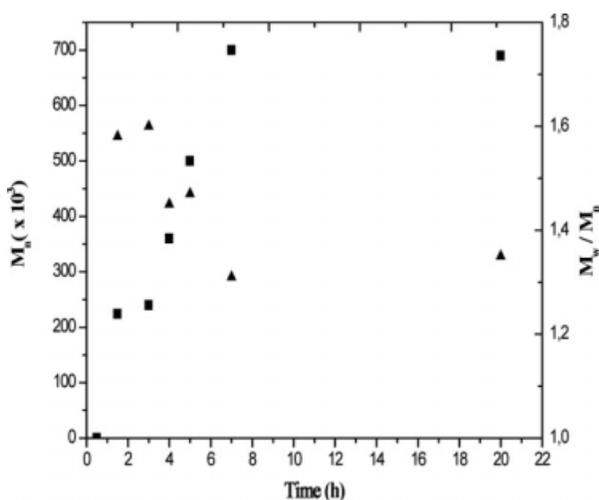


Figure 10. Molecular weight and molecular weight distributions versus time for the polymerization of tetradecene-1, (■) $M_n = f(t)$ and (▲) $I = f(t)$.

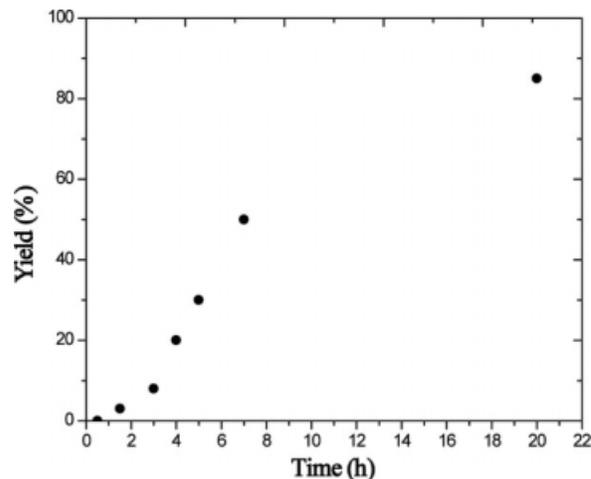


Figure 11. Yield versus time for the polymerization of tetradecene-1.

$\text{Et}(\text{Ind})_2\text{ZrCl}_2$ and $\text{Me}_2\text{C}(\text{Cp}(9\text{-Flu}))\text{ZrCl}_2$ in the presence of methylaluminoxane, MAO, as cocatalyst.^{22a} The polymerization yield increases also linearly during the first 7 h of the reaction, where the maximum molecular weight is obtained, and then gradually levels off leading after 20 h of reaction to the maximum values, up to 90%. The same behavior was observed for the polymerization of decene-1 and can be attributed to similar reasons.

Due to the high sensitivity of the metallocene catalytic systems towards trace impurities it was found that the addition of aluminium alkyls is very beneficial in accelerating the polymerization reaction.²⁷ For example highly active catalytic species were developed based on mixtures of metallocene dichlorides and fluoroarylboranes in the presence of an excess AlMe_3 or AlEt_3 . Therefore, to accelerate the polymerization of tetradecene-1

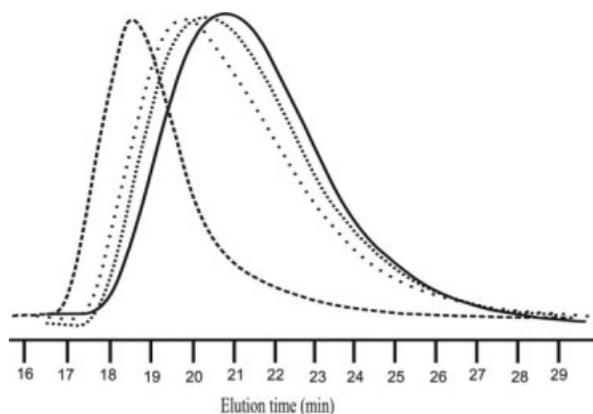


Figure 12. SEC traces for the synthesis of P(Tetradecene-1) in different polymerization times (—) 1.5 h, (···) 3 h, (---) 4 h, (-·-·) 7 h.

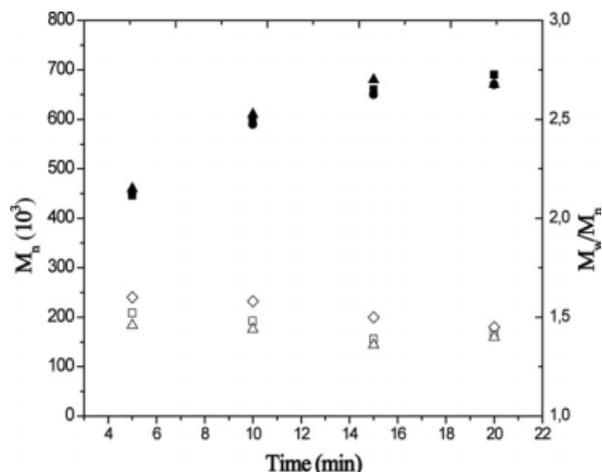


Figure 13. Molecular weight and molecular weight distributions versus time for the polymerization of tetradecene-1, using the catalytic system of $L_1L_2HfMe/[B(C_6F_5)_4]^- [Me_2NHPH]^+ /Al(n-Oct)_3$ in specific ratios of Al/Hf: 1/1 (\blacktriangle and \triangle , respectively), 5/1 (\blacktriangledown and \diamond , respectively) and 10/1 (\blacksquare and \square , respectively).

the reaction took place in the presence of $AlOct_3$ in different molar ratios with respect to the Hf metal. The results concerning the variation of the molecular weight, molecular weight distribution and yield with time are given in Figures 13 and 14. The acceleration of the polymerization is impressive, since the reaction is completed in less than 20 min. The best results were obtained when the molar ratio of Al to Hf, $[Al]/[Hf]$, was equal

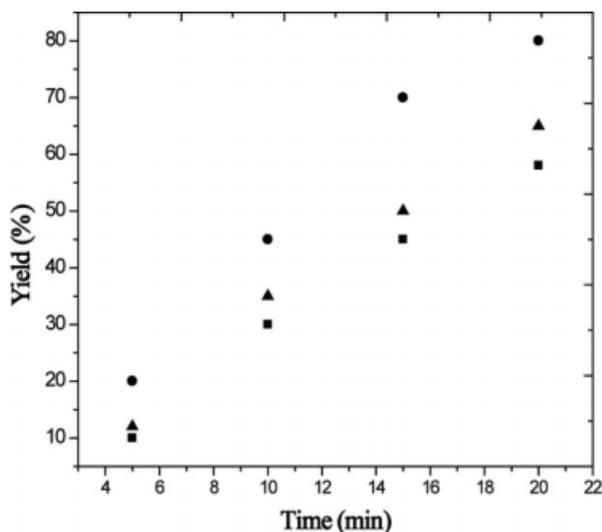
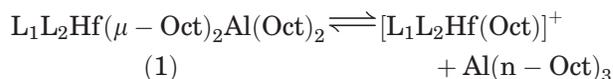


Figure 14. Yield versus time for the polymerization of tetradecene-1 using the catalytic system of $L_1L_2HfMe/[B(C_6F_5)_4]^- [Me_2NHPH]^+ /Al(n-Oct)_3$ in specific ratios of Al/Hf: 1/1 (\blacksquare), 5/1 (\bullet), and 10/1 (\blacktriangle).

to 5. For $[Al]/[Hf] = 1$ the amount of Al is not enough to provide the maximum effect, whereas for $[Al]/[Hf] = 10$ the large excess of $AlOct_3$ leads to the formation of the less active cationic dinuclear μ -complexes (1), due to the shift of chemical equilibrium to the left according to the following reaction:



It has to be mentioned that the acceleration of the polymerization of hexene-1, octene-1, and decene-1 in the presence of $AlOct_3$ was extremely high so that the reaction was completed in a few seconds. For this reason kinetic experiments were not conducted for these monomers in the presence of $AlOct_3$.

Polymerization of Hexadecene-1

The polymerization behavior of hexadecene-1 using the catalytic system 1 was similar with that reported for tetradecene-1. The results are displayed in Figures 15–17. The maximum molecular weight is obtained after 7 h, whereas the maximum yield after 20 h from the initiation of the polymerization. In addition, the molecular weight distribution gradually reduces from values equal to 1.6 to values equal to 1.3. Therefore, it can be concluded that the increase of the monomer side chain by two carbon atoms does not appreciably change the polymerizability of the monomer.

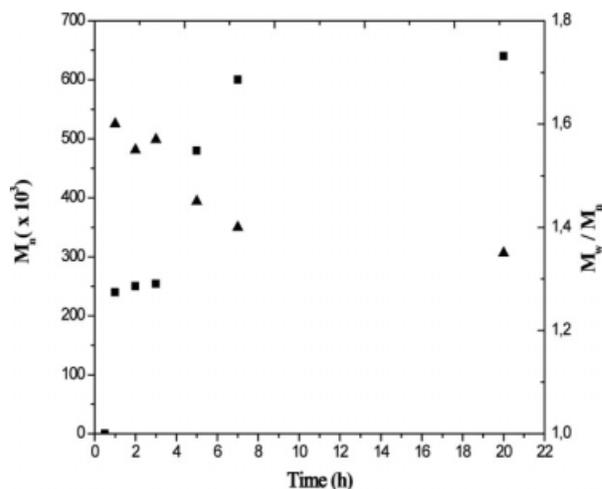


Figure 15. Molecular weight and molecular weight distributions versus time for the polymerization of hexadecene-1, (\blacksquare) $M_n = f(t)$ and (\blacktriangle) $I = f(t)$.

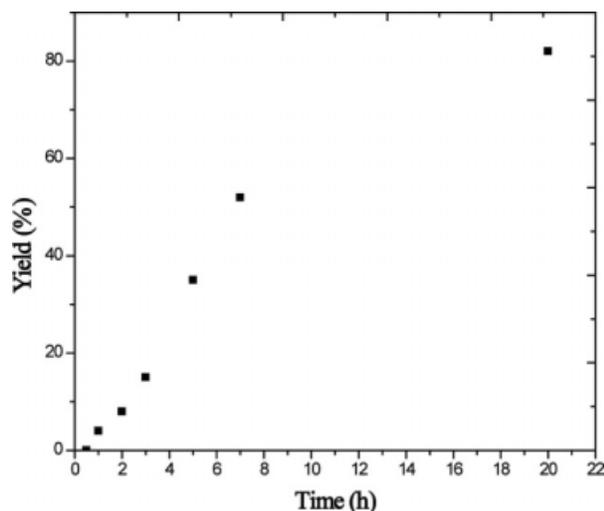


Figure 16. Yield versus time for the polymerization of hexadecene-1.

Microstructural Analysis

It is well known from previous studies that C_s -symmetry metallocenes promote the syndioselective polymerization of olefins.²⁸ The determination of the microstructure was conducted by ^{13}C NMR spectroscopy and was based on data previously reported in the literature regarding the stereochemical pentad sequence analysis.^{17,13b,29}

It has to be mentioned that the *rrrr* and the *mrrm* pentads overlap to some extent but without affecting much the accuracy in the determination of the syndiotactic pentads, due to the low isotactic sequences in the specific samples. The results of the microstructural analysis are shown in Table 2, whereas a characteristic example of a ^{13}C NMR spectrum is given in Figure 18.

It is evident that all the samples are predominantly syndiotactic, since the *rrrr* sequences are more than 50% in all cases. The poly(α -olefins) with the smaller side chains exhibit higher syn-

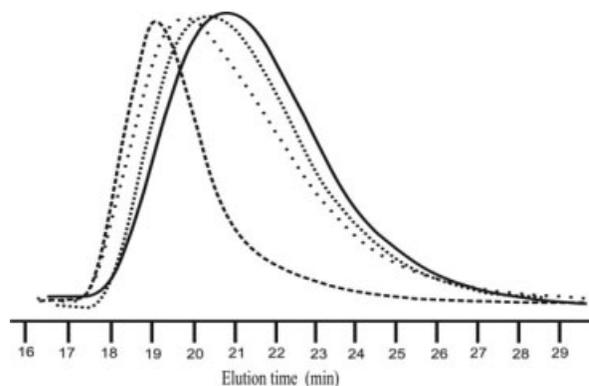


Figure 17. SEC traces for the synthesis of P(Hexadecene-1) in different polymerization times (—) 1 h, (····) 3 h, (---) 5 h, (-·-·) 7 h.

diotacticities than poly(tetradecene-1) and poly(hexadecene-1), as shown in Table 2. It seems that the large steric hindrance introduced by the side chains of these monomers prohibits the rotation of the monomer unit, thus reducing the level of syndiotacticity. On the other hand the isotactic pentads are limited and slightly increase only in the case of poly(tetradecene-1) and poly(hexadecene-1).

Thermal Properties of the Poly(α -olefins)

Differential scanning calorimetry, DSC, was used to study the thermal properties of the produced poly(α -olefins). The results are displayed in Table 3. Poly(hexene-1), poly(octene-1), and poly(decene-1) are amorphous showing only the presence of glass transition. It is obvious that the steric hindrance induced by the side groups prevent the crystallization of the polymer chains. The T_g values decrease upon increasing the size of the monomer's side group, due to their progressively increased flexibility³⁰ in agreement with literature results from similar homologous series of

Table 2. Microstructures of Poly(α -olefins)

Poly(α -olefins)	Pentads (%)					
	<i>mmmm</i>	<i>mrrr</i>	<i>mmrm</i>	<i>rrrr</i>	<i>mrrr</i>	<i>mrrm</i>
P(Hexene-1)	3.5	4	8	67	14.5	3
P(Octene-1)	4	6	8.5	64	12.5	5
P(Decene-1)	3	3.5	5	65	21	2.5
P(Tetradecene-1)	8	9	10.5	52	11.5	9
P(Hexadecene-1)	10	8.5	9.5	51	10	11

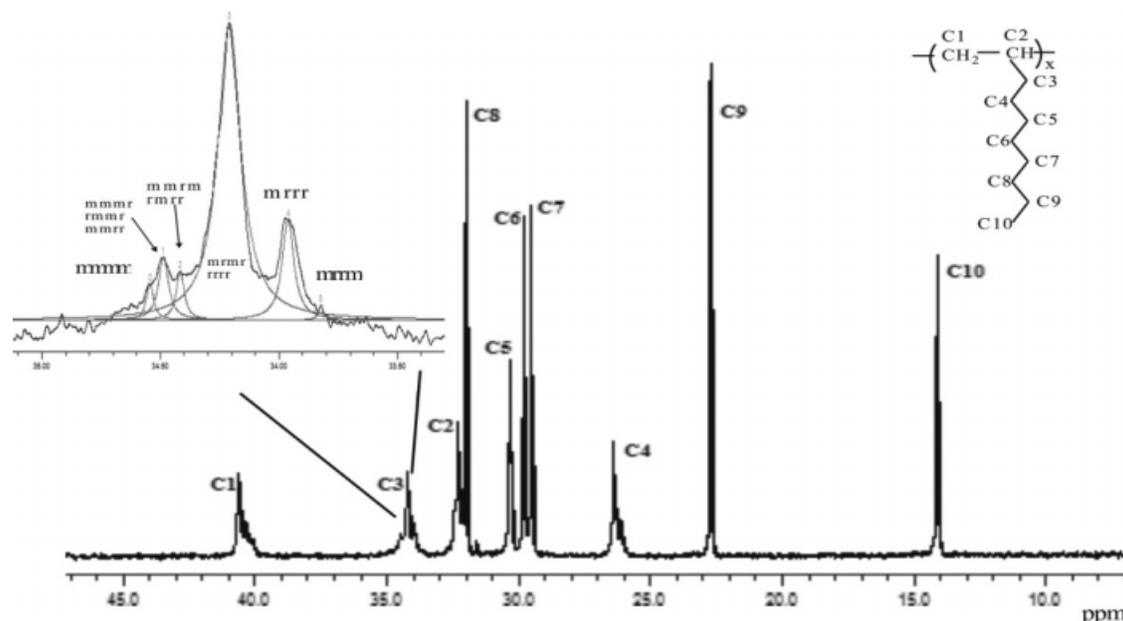


Figure 18. ^{13}C NMR (600 MHz) spectrum of PDec in CDCl_3 at $25\text{ }^\circ\text{C}$.

polymers, such as polyacrylates and polymethacrylates.²⁹ The corresponding T_g values for the isotactic polyolefins are also included in Table 3 for comparison. Only poly(decene-1) shows similar T_g values for syndiotactic and isotactic microstructure. For the other samples the isotactic polymers have lower T_g values than the syndiotactic ones. On the other hand poly(tetradecene-1) and poly(hexadecene-1) are crystalline showing T_m values upon heating. The crystallinity can be mainly attributed to the organization of the side chains, since their large size allows the development of crystalline domains, in agreement with other homologous series of polymers bearing large side groups.³¹ In the literature the corresponding isotactic polymers often present two endothermic peaks upon heating, attributed to both main chain and side chain crystallinity.^{14a,15,17,29}

Table 3. Thermal Properties of Poly(α -olefins)

Poly(α -olefins)	T_g ($^\circ\text{C}$)	T_m ($^\circ\text{C}$)	$(T_g)_{\text{iso}}^a$ ($^\circ\text{C}$)	$(T_m)_{\text{iso}}^a$ ($^\circ\text{C}$)
P(Hexene-1)	-32.7		-47.0	
P(Octene-1)	-59.0		-63.8	
P(Decene-1)	-66.1		-66.1	
P(Tetradecene-1)		7.1		50.0
P(Hexadecene-1)		32.1		60.0

^a T_g and T_m values for the isotactic polyolefins from ref. 22.

CONCLUSIONS

Hexene-1, octene-1, decene-1, tetradecene-1, and hexadecene-1 were polymerized using a C_s symmetry hafnocene catalyst and $[\text{B}(\text{C}_6\text{F}_5)_4]^- [\text{Me}_2\text{NHPH}]^+$ as the cocatalyst in toluene at $0\text{ }^\circ\text{C}$. The kinetics of the polymerization was studied by monitoring the molecular weight, molecular weight distribution and yield with time. It was found that the rate of polymerization strongly depends on the structure of the monomer. It gradually increases going from hexene-1 to decene-1 and then substantially decreases for tetradecene-1 and hexadecene-1. This behavior is attributed to the relative contribution of the steric hindrance induced by the side group of the α -olefin, which prevents its insertion in the growing polymer chain, the opening of the angle between the π -ligands, which becomes more pronounced the larger the α -olefin facilitating the insertion of the monomer and finally, the reduction of the degree of association of the catalytic ion pairs by increasing the size of the monomer leading to more active catalytic species. The polymerization of tetradecene-1 was substantially accelerated in the presence of triethylaluminum. The effect was more pronounced using a molar ratio of aluminum to hafnium, $[\text{Al}]/[\text{Hf}]$ equal to 5. High molecular weights of relatively narrow molecular weight distributions were obtained in all cases. ^{13}C NMR spectroscopy allowed for the determination of the

pentad monomer sequences revealing that the polymers are highly syndiotactic. The syndiotacticity is slightly higher for the polyolefins bearing smaller side groups. DSC analysis showed that poly(hexene-1), poly(octene-1), and poly(decene-1) are amorphous, whereas poly(tetradecene-1) and poly(hexadecene-1) display side chain crystallinity.

The financial support of the Ministry of Education through the Operational Program and Initial Educational Vocational Training on "Polymer Science and its Applications" and the Research Committee of the University of Athens is greatly appreciated.

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