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Living/controlled olefin polymerization initiated by nickel diimine complexes: The effect of ligand *ortho* substituent bulkiness

Jan Merna [a,*], Zdeněk Hošťálek [a], Jan Peleška [b], Jan Roda [a]

[a] Institute of Chemical Technology, Prague, Department of Polymers, Technická 5, 166 28 Prague 6, Czech Republic
[b] Institute of Materials Chemistry, Brno University of Technology, Purkyňova 118, 612 00 Brno, Czech Republic

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ABSTRACT

Polymerization of hex-1-ene and propene initiated by several methylalumoxane-activated diimine complexes was critically investigated. Effect of bulkiness of *ortho* aryl diimine substituents on extent of transfer reactions was examined. All of the complexes allowed us to prepare poly(hex-1-ene) with a very narrow molar mass distribution, molar mass being controlled by stoichiometry in a broad range of reaction conditions. Poly(hex-1-ene)s with molar mass between 15 and 220 kg mol^{-1} and dispersity (M_w/M_n) between 1.01 and 1.20 were prepared by varying the catalyst, temperature and monomer concentration. Livingness of hex-1-ene polymerization was demonstrated for the first time for nickel complex bearing ethyl *ortho* aryl substituents by reinitiation of chain growth upon addition of a new portion of monomer. Complexes with *ortho* methyl substituents did not allow complete reinitiation of chain growth and despite its good control over molar mass cannot be classified as a living polymerization catalyst. Chain branching can effectively be controlled by the choice of the ligand structure due to the chain-walking mechanism. Transfer reactions were more pronounced in propene polymerization. Polypropylene with narrow molar mass distribution could not be prepared using complexes with methyl substituents.

1. Introduction

Presently, polyolefins represent the largest group of commodity polymers. Considerable attention (both academic and industrial) is therefore focused on the development of new catalytic systems and polymerization processes [1]. To improve material properties of polyolefins, it is highly desirable to develop methods allowing one to control polymer chain parameters, such as molar mass and its distribution, stereoregularity or degree of branching. One of the most powerful methods to control polymer architecture [2] is living/controlled olefin polymerization [3]. Significant number of catalytic systems based on both early and late transition metal complexes was used for living/controlled olefin polymerization in last two decades [4]. Nickel diimine complexes represent an attractive group of such catalysts due to their high polymerization activity, lower oxophility, easy synthesis and the fact that they do not need high Al/metal ratios for catalyst activation [5].

Original Brookhart's publication claims a living character of alk-1-ene polymerization for methylalumoxane (MAO) and modified methylalumoxane activated acenaphthenchinone derived nickel complexes bearing bulky isopropyl and *tert*-butyl substituents in *ortho* aryl positions of ligand (Fig. 1, **1** and **2**) [6].

Living/controlled polymerization behavior was described for low polymerization temperatures and low monomer concentrations only, which limits the practical use of these complexes.

Marked suppression of transfer reactions by increased bulkiness of ligand *ortho* substituents was explained by hindering of axial positions of diimine complexes that prevents formation of the

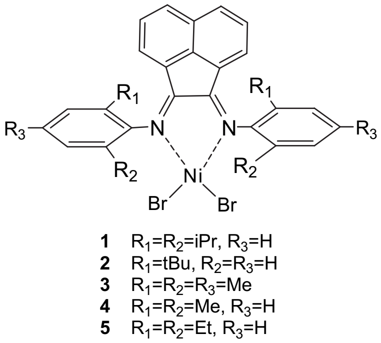

Fig. 1. Structure of nickel diimine complexes applied.

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[*] Corresponding author. Tel.: +420 220443194; fax: +420 220443175.
E-mail address: jan.merna@vscht.cz (J. Merna).

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transfer-reaction transition state represented by pentacoordinated *bis*-olefin hybrid species (Fig. 2) [5].

Living polymerization of hexe-1-ene initiated by the **2**/MAO system was examined more in detail by Peruch [7]. Formation of poly(hex-1-ene) with narrow molar mass distribution was observed for the monomer/initiator ratio (*M*/*I*) up to 1500 at −10 °C; within this limit, a reinitiation of polymerization was achieved. Later, we observed living/controlled hex-1-ene polymerization behavior using **1**/MAO system in chlorobenzene in much broader range of reaction temperatures and monomer concentrations, affording poly(hex-1-ene)s with narrow molar mass distribution [8]. Recently investigated hex-1-ene and dec-1-ene polymerizations catalyzed by MAO activated complex **1** and its analogue with -NCS leaving groups instead of Br anions gave polyolefins with narrow molar mass distribution at 0–30 °C [9]. Effect of pressure on hex-1-ene polymerization catalyzed by the bulky complex **1** and its analogue with butandione backbone was investigated by Suzuki et al. Poly(hex-1-ene)s with narrow molar mass distribution were prepared at room temperature only at ambient pressure. However, polymer yields were not quantitative and molar masses were significantly higher than those expected from the given *M*/*I* ratio [10]. Other more sophisticated catalytic systems bearing bulky diimine substituents were reported to show the living polymerization behavior [11,12]. High temperature stability of catalyst and good control over molar mass and dispersity was achieved by Guan using cyclophane diimine Ni complex for α-olefin polymerization [11]. In addition to the control over polymer molar mass and its distribution, chiral nickel diimine complexes reported by Coates allow one to control the regioselectivity at low temperatures [12]. However, a better chain growth and microstructure control of these systems are paid by more complicated diimine ligand synthesis and often much lower catalyst activity.

Poly(hex-1-ene) with low dispersity was also prepared with the **3**/MAO system having methyl diimine substituents in *ortho* and *para* positions at −11 °C [13]. An analogous nickel complex, namely {*bis*[*N*,*N*′-(4-*tert*-butyl-diphenylsiloxy-2,6-dimethylphenyl)imino]-acenaphthene} dibromonickel (**6**), bearing methyl groups in *ortho* positions and bulky *tert*-butyldiphenylsiloxyl group in *para* position yielded polypropylene and poly(hex-1-ene) with narrow molar mass distribution at −11 °C and even at 16 °C [14]. Di- and triblock copolymers of hex-1-ene and propene were prepared by the complex **6** at −15 °C. In case of both complexes **3** and **6**, however, the polymerization was not carried out to complete monomer conversion to prove unambiguously the living character of polymerization. Further, hex-1-ene homopolymerizations initiated by **3** and **6** displayed the linear increase of molar mass with time. This would rather suggest a deviation from the living/controlled polymerization behavior which is usually demonstrated by the linear dependence of molar mass on the monomer conversion in closed systems, assuming first order kinetics with respect to the monomer concentration. Similarly, Sivaram recently questioned the existence of the true living polymerization behavior of the **1**/MAO system in hex-1-ene polymerization by kinetic observations [15]. Noticeable chain transfer reactions were observed for *M*/*I* above 1500 and temperatures above 20 °C.

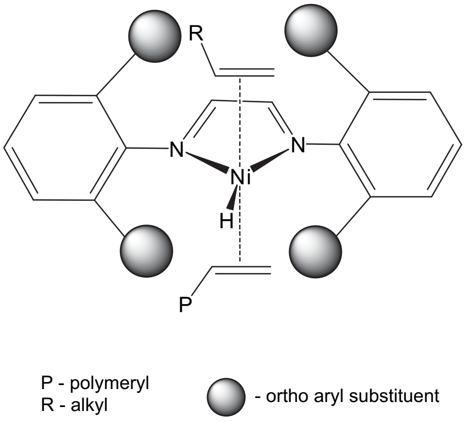

Fig. 2. Structure of the transfer reaction transition state.

In this paper, we report on a critical comparative study of living/controlled olefin polymerization behavior of five basic nickel diimine complexes (Fig. 1, **1**–**5**) in a broad range of reaction conditions with focus on the effect of *ortho* aryl substituents bulkiness on the extent of transfer reactions. Several criteria defining living/controlled polymerization behavior are examined to show the level of polymerization controllability and classify the catalysts either as “living” or only “controlled” according to IUPAC and ACS recommendations [3]. Possibilities to tune also polymer microstructure by catalyst choice are outlined.

2. Experimental section

2.1. Materials

All manipulations with air-sensitive compounds were done using standard Schlenk techniques. Nitrogen (SIAD, 99.999%) was purified by passing through a column packed with Cu-catalyst and molecular sieves to remove traces of oxygen and water. Chlorobenzene (p.a., Penta) was refluxed over CaH_2 and distilled under nitrogen. Hex-1-ene (99%, Aldrich) was dried over sodium/potassium alloy and distilled under nitrogen. MAO (10 wt% solution in toluene, Aldrich) was used as received. Nickel complexes were synthesized and purified according to reported procedures [6]. Purity of diimine ligands was proved by ^{1}H NMR and catalyst purity was checked by elemental analysis. Solutions of catalysts in chlorobenzene were stored at 5 °C.

2.2. Polymerization procedures

2.2.1. Hex-1-ene polymerization

Polymerizations were carried out under dry nitrogen in magnetically stirred 15 mL glass ampoules. Ampoules with chlorobenzene, hex-1-ene and initiator were placed in a bath kept at a desired temperature and tempered for 15 min. Polymerization was initiated by addition of MAO solution. After desired reaction time the polymerization was quenched by 1 mL of 10% HCl in MeOH, polymer was precipitated in 200 mL of MeOH and shortly dried at 50 °C under vacuum. The polymer product was dissolved in toluene, the solution centrifuged and polymer in the supernatant was reprecipitated in a large excess of MeOH in order to remove the insoluble rest of catalytic system. Polymer was separated and dried at 50 °C under vacuum until constant weight. To get the dependence of molar mass on the degree of monomer conversion, samples (3–4 mL each) were taken from the polymerization mixture (total volume 30 mL), quenched by pouring into acidified EtOH, separated and dried under vacuum. Kinetics of hex-1-ene polymerization was followed in 10 mL dilatometer equipped with a PTFE valve.

2.2.2. Propene polymerization

Polymerizations of propene were carried out in chlorobenzene in a magnetically stirred jacketed 100 mL glass reactor under 110 kPa dynamic pressure. The solvent and the catalyst solution were injected against propene flux and reactor was cooled to −10 °C. Polymerization was initiated by addition of the MAO solution. After 90 min the polymerization was quenched by addition of 1 mL of 10% HCl in MeOH, and polymer was precipitated in 300 mL of MeOH. After short drying, polymer was dissolved in toluene, centrifuged and polymer in the supernatant was reprecipitated in a large excess of MeOH to remove the insoluble rests of catalytic system. Polymer was separated and dried at 50 °C under vacuum until constant weight was achieved.

2.3. Polymer characterization

The microstructure of poly(hex-1-ene)s and polypropylenes was determined by ^{1}H and ^{13}C NMR spectroscopies. NMR spectra of polymers were measured on 500 MHz Bruker Avance DRX 500 spectrometer in $CDCl_3$ solution (15–20% w/v) at 30 °C.

^{13}C NMR INVGATE spectra of poly(hex-1-ene)s were collected typically 15–20 h (5000–7000 scans) using 90° pulse and relaxation delay of 10 s to allow the quantification of methyl carbon signals. Chemical shifts were referenced internally to the major backbone methylene carbon resonance, which was taken at 30.00 ppm from TMS. Interpretation of ^{13}C NMR spectra was based on APT and previously published assignments [16–18]. The nomenclature used is that of Usami [16] and Galland [18]. On labels *x*B*y*, B*y* is a branch of length *y* carbons, *x* is the carbon being discussed, and the methyl at the end of the branch is numbered 1. Thus, the second carbon from the end of a butyl branch is 2B4. *x*B*y*+ refers to the branches of length *y* and longer.

The total number of branches per 1000 carbon atoms (N) was determined by integrating methyl proton signals with respect to signals of all protons in ^{1}H NMR spectrum and calculated using the formula:

$$N = \frac{2(I_{CH_3})}{3(I_{CH+CH_2+CH_3})} \times 1000$$

Molar masses were determined using Waters Breeze chromatographic system equipped with RI detector operating at 880 nm and multi-angle laser light scattering (MALLS) miniDawn TREOS from Wyatt operating at 658 nm. Separations were performed with two columns (Polymer Laboratories Mixed C) at 35 °C in THF at an elution rate of 1 mL min^{-1}. The values of d*n*/d*c* of polyolefins in THF at 35 °C were obtained by two methods:

(1) Off-line determination for 5 selected poly(hex-1-ene) samples with low and high degree of branching using Wyatt Optilab REX detector at 658 nm by measuring polymer solutions in THF at 4 concentration levels ($dn/dc = 0.078 \pm 0.002$ mL g^{-1}).
(2) On-line measurements [19] using Waters 2414 refractometer at 880 nm giving $dn/dc = 0.077 \pm 0.001$ mL g^{-1} for large series of poly(hex-1-ene)s and $dn/dc = 0.079 \pm 0.001$ mL g^{-1} for 6 polypropylene samples.

Average d*n*/d*c* value 0.078 ± 0.002 mL g^{-1} in THF at 35 °C was found to be independent of the degree of polymer branching and used for SEC-MALLS evaluation of both poly(hex-1-ene)s and polypropylenes. D*n*/d*c* value determined by us is consistent with previously reported $dn/dc = 0.078 \pm 0.003$ mL g^{-1} obtained for THF solutions of highly branched polyethylenes prepared by Pd diimine catalyst at 932 nm [20]. Another d*n*/d*c* value for poly(hex-1-ene) prepared by **2**/MAO was reported to be 0.068 mL g^{-1} in THF at 633 nm [7].

3. Results and discussion

3.1. Polymerization of hex-1-ene

Polymerization of hex-1-ene was investigated using nickel diimine complexes differing in their substituents in *ortho* aryl positions (Fig. 1, **1**–**5**). In addition to bulky isopropyl and *tert*-butyl substituents (Fig. 1, **1**,**2**) described in original Brookhart's paper [6], complexes with smaller (methyl and ethyl) *ortho* aryl substituents were also employed (Fig. 1, **3**–**5**). Chlorobenzene was chosen as a solvent for the reaction due to a better solubility of nickel complexes as compared to toluene. Further, good solubility of high molar mass poly(hex-1-ene)s in chlorobenzene prevents the separation of polymer-containing less polar phase from relatively more polar catalyst phase at low polymerization temperatures, as was observed using dichloromethane and cyclohexane.

To assess the living character/controllability of polymerization, the values of the number of polymer molecules produced per one catalyst molecule, NPM/N(Ni), were calculated. To achieve correct values of this parameter, an exact value of polymer molar mass must be known, for which we used the SEC-MALLS method. We have observed in many experiments that rubbery poly(hex-1-ene)s, separated by standard precipitation of polymerization mixture to acidified methanol, encapsulated significant amounts (up to 20 wt.%) of MAO decomposition products. This would bring an error not only into monomer conversion values calculated from the weight of polymer but also into values of specific refractive index increment (d*n*/d*c*) used for the molar mass determination. Consequently, the values of NPM/N(Ni) derived from monomer conversion and molar mass would be erroneous. For that reason, polymers were purified by centrifugation as described in Experimental section. The NPM/N(Ni) values can finally be influenced by inactive impurities in the catalyst precursor which is difficult to characterize properly by, e.g., NMR spectroscopy due to its paramagnetic character. Purity of the nickel complexes was satisfactory, as found by elemental analysis; despite a relatively low sensitivity of the method we have estimated the maximum error of the NPM/N(Ni) determination to be smaller than 10%.

3.1.1. Control of molar mass

Our previous observations [8], namely that the hex-1-ene polymerization with complex **1** activated by MAO has a living/controlled character even at higher temperatures and higher monomer concentrations than initially claimed by Brookhart, led us to investigate the polymerization in detail in a broad range of reaction conditions. Thus, polymerizations were carried out between −10 °C and 25 °C in a wide *M*/*I* ratio range (200–3200) to explore reaction conditions under which living/controlled polymerization can be achieved (Table 1).

Results of the hex-1-ene polymerization with complexes **1** and **2** activated by MAO are in agreement with Brookhart's observations that nickel catalysts with bulky *ortho* aryl substituents of diimine ligand are capable to initiate the living/controlled polymerization of α-olefins [6]. Polymerizations reach almost complete monomer conversion after several hours and polymers prepared show a very narrow molar mass distribution within the whole temperature and *M*/*I* ratio range explored. Increase of dispersity is observed only in experiments with the highest *M*/*I* ratio (3200) suggesting an important role of the transfer reactions to monomer (Table 1, run 3 and 8). The NPM/N(Ni) values for both catalytic systems are lower than one, suggesting incomplete activation of complexes **1** and **2** by MAO, as reported in literature [7,8,15]. However, for complex **1** only a small part (<10%) of catalyst species is inactive and molar masses are in good agreement with the predicted values. In the case of complex **2**, catalyst efficiency is more decreased and approximately 20% of Ni complex remains untransformed to growing centers. An increased importance of the transfer reactions at high *M*/*I* ratio is reflected, beside in higher dispersity values, also in an increase of NPM/N(Ni) values above one (run 3 and 8). The effect of temperature on the increase of the transfer reaction extent is not detectable and the NPM/N(Ni) values remain almost constant between −10 °C and 25 °C.

Table 1
Polymerization of hex-1-ene initiated by **1**–**5**/MAO in chlorobenzene.

Run	Catalyst	M/I	T_p [°C]	Y_w[a] [%]	M_n[b] [kg mol^{-1}]	M_w/M_n[b]	NPM/N(Ni)[c]	N[d]
1	**1**	200	−10	93	16.5	1.05	0.94	
2		800	−10	92	67.0	1.01	0.92	127
3		3200	−10	73[e]	149.3	1.36	1.31	140
4		800	0	93[e]	70.8	1.01	0.88	
5		800	25	95[e]	73.1	1.01	0.87	
6	**2**	200	−10	80	17.3	1.01	0.77	
7		800	−10	93	71.6	1.05	0.87	109
8		3200	−10	85	205.5	1.26	1.11	138
9		800	25	95	79.8	1.06	0.80	98
10	**3**	200	−10	94	19.3	1.04	0.82	
11		800	−10	96	61.4	1.11	1.05	148
12		3200	−10	94	116.7	1.57	2.16	161
13		800	0	97	56.3	1.18	1.15	
14		800	25	96	49.7	1.32	1.29	113
15	**4**	200	−10	58	15.7	1.14	0.65	
16		800	−10	75	60.1	1.13	0.85	146
17		3200	−10	97	144.5	1.50	1.86	
18		800	0	82	55.6	1.20	0.99	
19		800	25	84	45.9	1.50	1.26	
20	**5**	200	−10	87	18.7	1.08	0.87	108
21		800	−10	90	66.0	1.08	1.09	131
22		3200	−10	84	219.7	1.12	1.05	148
23		800	0	95	68.2	1.04	0.99	120
24		200	25	98	21.6	1.09	0.76	84
25		800	25	92	62.7	1.13	1.01	100

[Ni] = 1.0 mM, Al/Ni = 200, polymerization time 5 h, total volume 10 mL.

[a] Monomer conversion.

[b] Number average molar mass (M_n) and dispersity (M_w/M_n) determined by SEC-MALLS.

[c] NPM/N(Ni) = polymer mass/($\mathrm{mol_{Ni}} \cdot M_n$).

[d] Number of branches per 1000 C atoms determined by ^{1}H NMR spectroscopy.

[e] Polymerization time 1 h.

Recently, living/controlled behavior was reported for the hex-1-ene polymerization initiated by MAO-activated complexes **3** and **6** bearing only small methyl substituents in *ortho* aryl positions [13,14]. We have therefore decided to investigate polymerizations of hex-1-ene with complex **3** in more detail in the next step. In addition to that, other two complexes **4** and **5** bearing methyl and ethyl groups (Fig. 1) have been prepared to prove the potential of diimine complexes with small aryl substituents to catalyze the polymerization in living/controlled manner. Both **4** and **5** were substituted in *ortho* aryl positions that probably represent the crucial substitution pattern for protecting growing centers against transfer reactions. Results of the hex-1-ene polymerization initiated by **3**–**5**/MAO in a wide range of reaction temperatures and monomer concentrations are collected in Table 1. Polymers with narrow dispersity were obtained below 0 °C and below 800 for all the three complexes **3**–**5** activated by MAO indicating controlled polymerization. In case of complexes **3** and **4** with methyl substituents, considerable extent of side reactions, i.e. loss of control, could be observed at high M/I and at room temperature, as indicated by the increase of dispersity and NPM/N(Ni) values (Table 1, run 12, 14, 17, 19). Further, complex **4** showed lower monomer conversions, suggesting the increased contribution of termination reactions. Similarly as for **1** and **2**, complexes **3** and **4** often feature incomplete activation by MAO and, despite their increased sensibility to transfer reactions, yield fewer polymer chains than could be expected from the amount of catalyst molecules present (Table 1, runs 10, 15, 16).

Interestingly, complex **5** bearing relatively small ethyl substituents has been proved to perfectly control the polymerization even at a very high M/I ratio (3200) as well as at room temperature (Table 1, runs 20–25). Moreover, catalyst efficiency of the **5**/MAO system, expressed by NPM/N(Ni), is the best of all the catalysts under study. Within the limits of experimental error, the number of polymer molecules is in agreement with the number of catalyst molecules and does not change in a broad range of experimental conditions. This makes **5**/MAO a very suitable system for the preparation of uniform polyolefins with tailored molar mass in the range of 10^3 to 10^5 g mol^{-1}, as controlled by the pre-set M/I ratio in the feed. The negligible extent of transfer reactions indicates that the bulkiness of ethyl groups is sufficient to suppress the transfer-reaction transition state formation (Fig. 2).

3.1.2. *Livingness of polymerization*

The possibility to prepare low dispersity polymers is only one of living/controlled polymerizations attributes and reflects high initiation rate as compared to propagation, as well as only insignificant amount of irreversible transfer and termination reactions [3]. To investigate more properly the livingness/controllability of olefin polymerization initiated by complexes with sterically less demanding ligands, we followed the dependence of molar mass on monomer conversion in hex-1-ene polymerization initiated by **4**/MAO and **5**/MAO at −10 °C and at M/I = 800 (Fig. 3). In both cases,

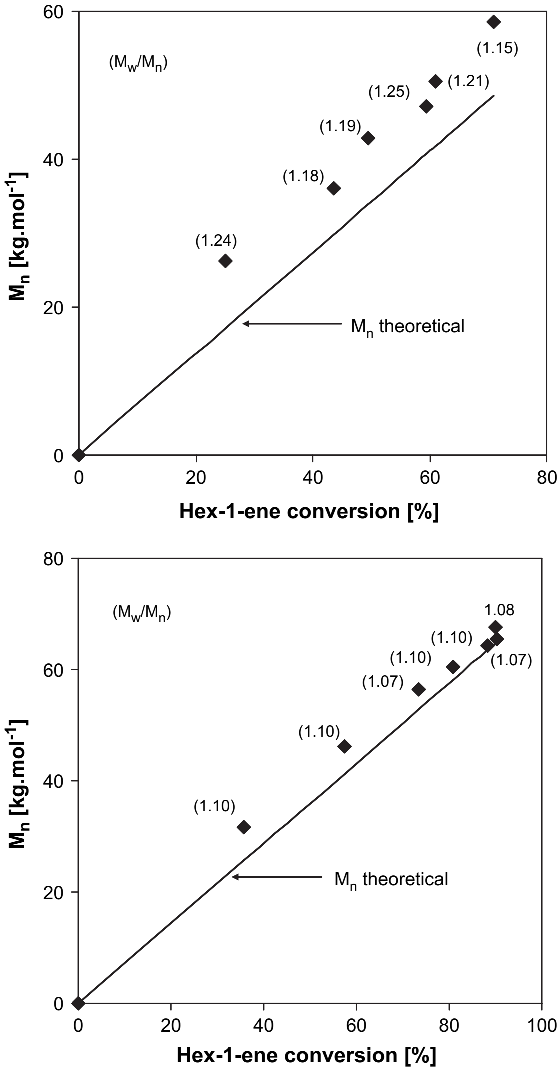

Fig. 3. Dependence of number average molar mass and dispersity (M_w/M_n) on monomer conversion in hex-1-ene polymerization initiated by **4**/MAO (upper chart) and by **5**/MAO (lower chart). T = −10 °C, [hex-1-ene] = 0.8 M, [Ni] = 1 mM, Al/Ni = 200, Total volume 30 mL, M_n(theoretical) = conversion $^*m$(hex-1-ene)/mol$_{\mathrm{Ni}}$.

the controllability of polymerization is confirmed by the fact that the plot of molar mass vs. hex-1-ene conversion is linear and molar mass distribution does not broaden in course of polymerization. The complex **4** yields poly(hex-1-ene) with higher dispersity values as compared to **5**. For the complex **4**, the experimentally determined molar masses are higher than those calculated from the *M*/*I* ratio. The average efficiency of **4** is 0.82 implying incomplete activation by MAO. In case of complex **5**, experimental molar masses are in good agreement with those predicted. A higher deviation of molar masses from the theoretical values is observed at lower conversions for both complexes. This could be caused by a higher experimental error of determination of polymer yield from relatively small samples at lower monomer conversions, or, alternatively, by a slower initiation, as observed previously by Sivaram for complex **1** [15]. However, dispersity values of poly(hex-1-ene)s prepared by any of the two initiation systems remain low and do not evolute in course of the whole experiment which indicates a fast initiation and a negligible extent of the transfer reactions at given conditions.

To examine the polymerization livingness/controllability [15] and to compare polymerization activities of all complexes, we performed kinetic investigation by means of dilatometry (Fig. 4). At −10 °C all complexes showed first order kinetics with respect to monomer concentration at least up to 50% monomer conversion as proved by the linearity of the plot of $\ln[M_0]/[M_t]$ vs. polymerization time; this indicates that propagation is accompanied by only negligible transfer and termination reactions. At higher conversions, however, complex **4** has shown substantional deviation from the linearity, suggesting the presence of termination reactions. Propagation rates of complexes **1**–**5** are not directly proportional to the bulkiness of their ligands. Two opposing effects can be responsible for this behavior. On the one hand, a higher steric demand restrains the access of the monomer to the growing center, decreasing thus the polymerization rate. On the other hand, a bulky ligand lowers the insertion barrier by destabilizing the ground state of monomer insertion relative to transition state which results in an increase of the propagation rate. A similar behavior was previously observed for ethylene and propylene polymerizations catalyzed by nickel diimine complexes [20,12b]. The complex **2** derived from monosubstituted bulky 2-*tert*-butylaniline displayed a significantly lower polymerization rate than the complexes derived from disubstituted anilines with substituent size varying from small methyl to large isopropyl groups.

Finally, to show the possibilities to control olefin polymerization initiated by diimine complexes **4** and **5**, we tried to reinitiate the growth of the chain by adding a second portion of monomer, after all monomer in the original feed had been consumed (Figs. 5 and 6). As is known, the nickel diimine catalysts are instable and decompose fast in absence of the monomer [7]. Thus, to protect most of growing centers, it is important to add the second portion of monomer shortly after the initial monomer feed is converted to polymer. This time period was estimated on the basis of dilatometry results. For the complex **4** (Fig. 5), molar mass is almost doubled after reinitiation but dispersity is increased and higher molar mass peak shows a tail of lower molar mass fraction indicating a certain extent of transfer and termination reactions. Therefore, the polymerization of hex-1-ene catalyzed by **4**/MAO cannot be considered as the living one but as the controlled polymerization at the most. In the reinitiation experiment with complex **5** (Fig. 6), polymer molar mass was doubled almost exactly and dispersity remained very low as a consequence of a negligible extent of transfer reactions. Hex-1-ene polymerization catalyzed by **5**/MAO can therefore be assigned as an exceptionally good example of living coordination polymerization at the current state of the knowledge in the field.

3.2. Polymerization of propene

Polymerization of propene was investigated at ambient pressure using complexes **1**–**5** activated by 200 equiv. MAO in chlorobenzene at −10 °C (Table 2). The order of the propene polymerization activity for all of the complexes **1**–**5** is similar to that of propagation rates observed in the case of hex-1-ene (Fig. 4). The complexes **1** and **4** differing essentially in ligand bulkiness were found to have highest activities, confirming thus complexity of the reaction mechanism. The lowest activity was consistently observed for the complex **2** with monosubstituted diimine ligand. Compared to the hex-1-ene polymerization, propene polymerization is, in most cases, accompanied by a larger extent of transfer reactions, as indicated by higher dispersity values of polypropylenes prepared. This could be explained by a higher propensity of diimine

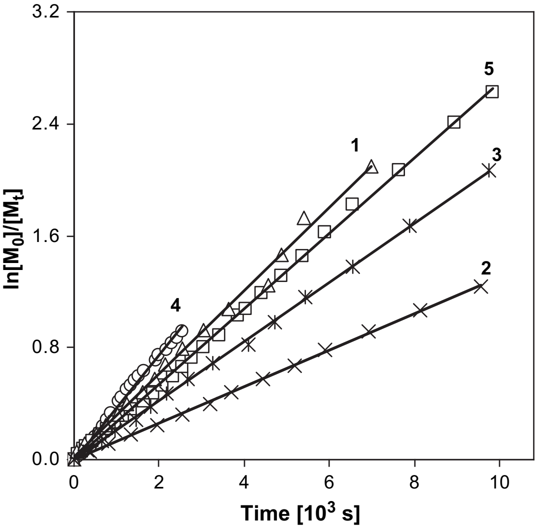

Fig. 4. Semilogarithmic dependence of $\ln[M_0]/[M_t]$ on time in hex-1-ene polymerization initiated by **1**–**5**/MAO at −10 °C in chlorobenzene. [hex-1-ene] = 0.8 M, [Ni] = 1 mM, Al/Ni = 200.

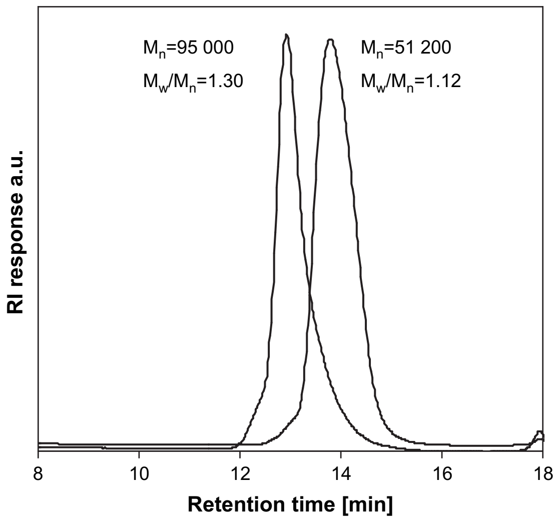

Fig. 5. SEC chromatograms of poly(hex-1-ene)s initiated by **4**/MAO and reinitiated by addition of a second portion of monomer after 5 h. T = −10 °C, [hex-1-ene] = 0.4 + 0.4 M, [Ni] = 1 mM, Al/Ni = 200.

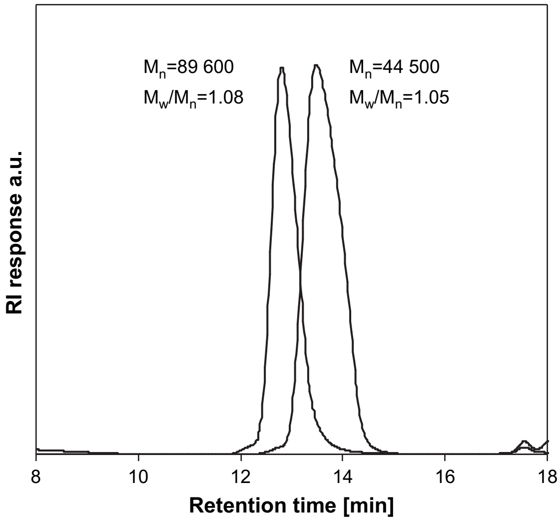

Fig. 6. SEC chromatograms of poly(hex-1-ene)s initiated by **5**/MAO and reinitiated by addition of a second portion of monomer after 5 h. T = −10 °C, [hex-1-ene] = 0.4 + 0.4 M, [Ni] = 1 mM, Al/Ni = 200.

complexes to transfer to monomer as a consequence of an easier access of smaller propene molecule to growing center and subsequently higher probability to form transfer-reaction transition state (Fig. 2). Reasonably narrow molar mass distribution was observed for polypropylenes obtained by the bulky complexes **1** and **2**, as reported previously by Brookhart [6]. The complexes **3** and **4** with small methyl substituents display substantially increased dispersity values. Extraordinary good suppression of the transfer was surprisingly observed in case of the catalyst **5** which yielded polypropylene with dispersity as low as 1.08. Comparison of NPM/N(Ni) values for the complexes **1**, **2**, **3** and **5** revealed that the extent of transfer reactions is quite limited in spite of molar mass distribution broadening. However, NPM/N(Ni) values can be influenced by an incomplete activation of the catalysts by MAO. Hence, the only reliable indication of living/controlled behavior could be assigned to the complex **5**, where a good correlation between the number of produced polymer chains and that of initiator molecules is accompanied by low dispersity values. In case of the complex **4**, the NPM/N(Ni) value (1.80) indicates an important role of the transfer reactions.

3.3. *Control of microstructure*

In addition to the control over polymer molar mass, simultaneous control of polymer microstructure represents another important challenge. A very good control over stereoselectivity by changing the reaction temperature in propylene polymerization using chiral nickel diimine complexes was recently reported by Coates [12]. However, crystalline isotactic polypropylene is formed only at very low reaction temperatures which leads to relatively low polymerization activity and low molar mass of resulting polymers. Another strategy to control polymer microstructure could be used in the case of diimine catalysts, based on their natural sensitivity to undergo β-H elimination followed by a subsequent olefin reinsertion, so called chain-walking mechanism allowing the growing center to migrate along the polymer chain [5,21]. The extent of chain-walking can be influenced by reaction temperature, monomer concentration and catalyst structure. In case of longer α-olefins, chain-walking leads to 1,ω- or 2,ω- monomer insertions. 1, ω-insertions lead to straightening of chain and formation of linear “polyethylene-like” domains that are capable of crystallization [7,9]. The possibility to control polyolefin molar mass using several complexes differing significantly in the bulkiness of their ligands, as in the case of the complexes **1**–**5**, gives us a new simple tool for synthesizing polymers controlled both in molar mass and microstructure. All poly(hex-1-ene)s and polypropylenes prepared by complexes **1**–**5** (Tables 1 and 2) are, as a consequence of chain-walking, less branched than would correspond to regular 1,2-monomer insertion, i.e. 167 branches/1000 C atoms for poly(hex-1-ene) and 333 branches/1000 C atoms for polypropylene. As seen from Table 1, the choice of the catalyst can significantly influence branching of the poly(hex-1-ene) chain under given reaction conditions (e.g. Table 1, run 7, 35% rearrangement vs. runs 11 and 16, 11% rearrangement). Moreover, due to a broad range of reaction temperatures and *M*/*I* ratios under which most of nickel complexes allow one to prepare polyolefins with controlled molar mass and low dispersity, it is possible to prepare poly(hex-1-ene) with even larger degree of rearrangement (run 24, 68% rearrangement). Similarly to poly(hex-1-ene)s, the degree of polypropylene rearrangement is affected by the bulkiness of diimine ligand (e.g. Table 2, run 27, 28% rearrangement vs. run 28, 10% rearrangement).

Table 2
Polymerization of propene initiated by **1**–**5**/MAO in chlorobenzene.

Run	Catalyst	A[a] [kg mol^{-1} h^{-1}]	M_n[b] [kg mol^{-1}]	M_w/M_n[b]	NPM/N(Ni)[c]	N[d]
26	**1**	63.6	101.5	1.27	0.94	292
27	**2**	25.9	32.1	1.29	1.21	241
28	**3**	39.2	66.0	1.42	0.89	299
29	**4**	65.6	54.7	1.43	1.80	292
30	**5**	38.8	61.2	1.08	0.95	262

[Ni] = 0.5 mM, Al/Ni = 200, T = −10 °C, p(propene) = 110 kPa, polymerization time 1.5 h, total volume 30 mL.
[a] Polymerization activity.
[b] Molar mass and dispersity (M_w/M_n) determined by SEC-MALLS.
[c] NPM/N(Ni) = polymer mass/(mol$_{Ni}\cdot M_n$).
[d] Number of branches per 1000 C atoms determined by ^{1}H NMR spectroscopy.

In the case of selected poly(hex-1-ene)s, more detailed structural analysis was performed by means of ^{13}C NMR spectroscopy (Fig. 7). Intensities of methyl signals, relaxed quantitatively under employed measurement conditions, are collected in Table 3 along with ^{1}H NMR data. The most abundant are butyl (e.g. 1B4+ at 14.39 ppm, 2B4 at 23.48 ppm) and methyl (1B1, 19.98 ppm) branches for all four poly(hex-1-ene)s samples. Poly(hex-1-ene) prepared by catalyst **4** (Table 3, run 16) surprisingly showed also the presence of ethyl (1B2, 11.12 ppm) and propyl (1B3, 14.83 ppm) branches despite the fact that this polymer shows, according to ^{1}H

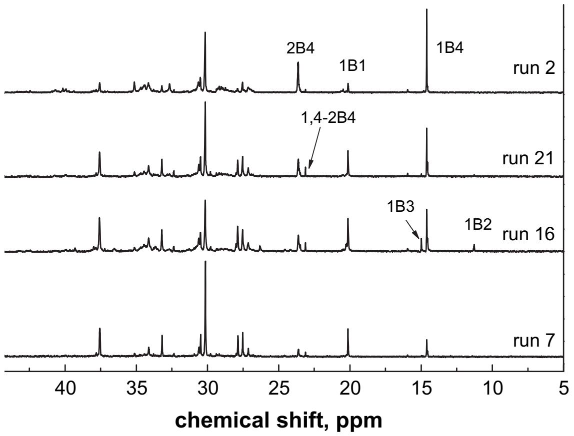

Fig. 7. ^{13}C NMR spectra of poly(hex-1-ene)s prepared by MAO activated catalysts **1** (Table 1, run 2), **2** (run 7), **4** (run 16), **5** (run 21) at −10 °C. [hex-1-ene] = 0.8 M, [Ni] = 1 mM, Al/Ni = 200.

Table 3
Microstructure of poly(hex-1-ene)s prepared by **1**,**2**,**4**,**5**/MAO.

Catalyst	Run	N[a]	%1,2-ins.[b]	1B1[c]	1B4[c]	1B1/1B4
1	2	127	76	17	82	0.21
2	7	109	65	56	33	1.70
4	16	140	84	63	51	1.24
5	21	131	79	42	54	0.78

[a] Total amount of branches determined by ^{1}H NMR.

[b] Fraction of 1,2-insertions determined by ^{1}H NMR assuming only insertions into primary alkyl – nickel bonds; %1,2-ins. = N/167 × 100.

[c] Relative numbers of selected branches determined by ^{13}C NMR.

NMR, the lowest degree of chain rearrangement. Presence of these types of branches, usually observed with palladium catalysts [8,17], might be caused by more facile monomer insertion into less sterically hindered secondary alkyl-nickel bonds. Similar behavior was recently observed for hex-1-ene polymerization catalyzed by complexes **1** and **2**, when 2,5- and 1,5-insertions of hex-1-ene were detected as a consequence of monomer insertion into the secondary alkyl-nickel bonds [22]. Semi-quantitative comparison of insertion fashions for investigated catalysts could be done calculating relative numbers of butyl and methyl branches per 1000 C atoms obtained from the ratio of butyl or methyl signals intensity to intensity of all ^{13}C NMR spectra signals. According to ^{1}H NMR data the highest degree of rearrangement (lowest %1,2-ins.) was displayed by bulky monosubstituted complex **2** which display the highest 1B1/1B4 ratio. This indicates a higher fraction of 2,1-insertions followed by chain-walking and resulting in 1,6-hex-1-ene enchainment. Energetically less favorable 2,1-insertion is probably facilitated by more open geometry of complex **2**. On contrary much lower chain straightening is observed for bulky disubstituted complex **1** that produced polyhexene with 127 branches/1000 C atoms and, according to ^{13}C NMR, high amount of monomer was inserted regularly in 1,2-fashion leading to butyl branches. Less bulky complexes **4** and **5** afforded polyhexene with approximately same degree of chain rearrangement and similar ratio of methyl to butyl branches.

Obviously, the changes of branching influence the thermal properties of polymer. The DSC traces of poly(hex-1-ene)s with approximately the same molar mass and different branching are shown in Fig. 8.

Samples with a higher degree of branching are completely amorphous and only glass transition could be observed (Fig. 7, run 16). Performing the hex-1-ene polymerization with a bulky catalyst like **2**, poly(hex-1-ene) with significantly rearranged monomer units is produced leading to the formation of linear “polyethylene-like” domains long enough to crystallize which is reflected by appearance of the broad melting endotherm in DSC trace beside the glass transition (run 7). The same behavior is observed when the polymerization is carried out with a less bulky catalyst under reaction conditions favorable for chain-walking, i.e. at a higher temperature and a lower monomer concentration (run 25).

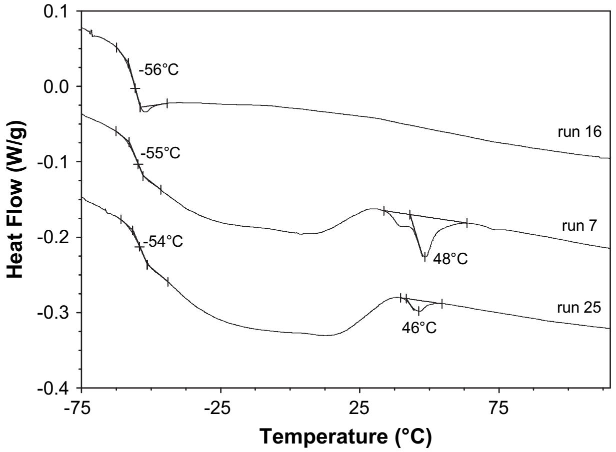

Fig. 8. DSC traces of poly(hex-1-ene)s with 146 branches/1000 C atoms (run 16), 109 branches/1000 C atoms (run 7) and 100 branches/1000 C atoms (run 25).

4. Conclusions

Benchmark investigation of olefin polymerization catalyzed by five basic nickel diimine complexes with different substituents in *ortho* aryl positions was performed in order to assess the degree of their livingness/controllability. The reaction condition range within which polyolefins having narrow molar mass distribution could be prepared was expanded to higher temperatures and higher monomer/initiator ratios for selected catalysts, allowing one to prepare polyolefins with molar masses 10^3 to 10^5 g mol^{-1} and dispersity below 1.15. Despite the evidence of the presence of the side reactions, even complexes **3** and **4** with methyl groups in *ortho* positions of diimine ligand can be used for the preparation of polyolefins with *controlled* molar mass and low dispersity. The *control* of polymerization was demonstrated by linear evolution of molar mass on polymer conversion for complexes **4** and **5** with methyl and ethyl *ortho* substituents. According to all examinations performed, the complex **5** bearing ethyl groups shows almost perfect *living polymerization* behavior in hex-1-ene as well as propene polymerizations (beside previously reported and well documented living polymerization of complexes **1** a **2**) and is a good candidate for e.g. preparation of block olefin copolymers. In addition, kinetic investigations confirmed a negligible extent of transfer and termination reactions at low temperatures for the most of catalysts. By choice of the catalyst, monomer and reaction conditions, polymer microstructure could effectively be varied in a large extent simultaneously with control over polymer molar mass.

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