Vinyl polymerization of norbornene with nickel catalysts bearing [*N*,*N*] six-membered chelate ring: Important influence of ligand structure on activity

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Abstract

Norbornene polymerizations with nickel complexes bearing [*N*,*N*] six-membered chelate ring activated with methylaluminoxane were investigated. The influence of ligand structure such as β-diimine, β-diketiminate, fluorinated β-diketiminate, and anilido-imine ligand on catalytic activities for norbornene polymerization was evaluated in detail. Ligands led to different electrophilicity of the nickel metal center, and a relatively positive nickel metal center would result in high catalytic activities for norbornene polymerization. The influences of polymerization temperature and Al/Ni ratio on norbornene polymerization with nickel catalysts bearing β-diimine, β-diketiminate, and fluorinated β-diketiminate ligands were also examined. All of the obtained polymers catalyzed by these nickel catalysts bearing [*N*,*N*] ligand are vinylic addition polynorbornenes with different molecular weights.
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1. Introduction

Interests in polymers of cyclic olefins such as norbornene (NBE) (bicyclo-[2.2.1]hept-2-ene) have increased dramatically over the past decade. The attractive properties of this addition type of polymer such as high chemical resistance, good UV resistance, low dielectric constant, high glass transition temperature, excellent transparency, large refractive index, and low birefringence have been the reasons for the increased interest [1–7]. Driven by industrial application [5–7], vinyl-addition homopolymerization of norbornene has already been reported using Ziegler-Natta catalysts (titanium) [8,9], metallocene/methylaluminoxane (MAO) catalytic systems (titanium, zirconium) [10–14], and late transition metal/MAO catalytic systems (iron, cobalt, nickel, and palladium) [1,2,15–32]. Conventional Ziegler-Natta catalysts, such as the $TiCl_4/AlR_3$, $TiCl_3/AlMe_3$, and $TiCl_4/LiAlH_4$ systems, can cause ROMP or addition polymerization [8,9]. It is well known that norbornene can also be efficiently polymerized with metallocene/MAO catalytic systems [4]. Most of the obtained polynorbornenes are insoluble in common solvents and show poor processability due to high crystallinity, though the half-titanocene complexes have recently been reported to produce soluble polynorbornenes [12]. Recently, late transition metal catalysts (typical Pd- and Ni-based catalysts) have been developed due to their high catalytic activities for norbornene addition polymerization [15–32]. Janiak have given a full literature and patent account on the work describing the addition polymerization to homo-polynorbornene [1,2], and also summarized different classes of air- and moisture- or shelf-stable Ni and Pd complexes for norbornene addition polymerization in a recent review [32]. For late transition metal nickel or palladium catalysts, the polynorbornenes catalyzed by the palladium-based catalysts are usually insoluble in common solvents, while those catalyzed by the nickel-based catalysts are soluble in chlorohydrocarbons.

During the past few years, we have focused our attention on the vinylic addition homo- and co-polymerization of norbornene with other monomers. Several series of nickel

complexes chelating [N,O] and [*N,N*] ligands were designed, synthesized, and their catalytic properties were investigated toward norbornene [33–39]. [*N,N*] ligands got our more attentions due to their more easily modified features on steric and electronic effect. Previously, we prepared nickel complexes chelating β-diimine, β-diketiminate, fluorinated β-diketiminate ligands, and studied their catalytic properties for ethylene polymerization [40–42]. Besides, we also prepared anilido-imino nickel complexes and investigated catalytic properties for norbornene and ethylene polymerization [33–35]. The aim of this work is to further investigate norbornene polymerization with nickel complexes chelating β-diimine, β-diketiminate, and fluorinated β-diketiminate ligands activated with MAO. To gain more insight into the effect of catalyst structure on catalytic activity for norbornene polymerization, the influence of [*N,N*] ligand structure such as β-diimine, β-diketiminate, fluorinated β-diketiminate, and anilido-imine ligand on catalytic activities was evaluated in detail.

2. Experiments

2.1. Materials

All manipulations involving air- and moisture-sensitive compounds were carried out under an atmosphere of dried and purified nitrogen using standard Schlenk and vacuum-line techniques. Toluene was dried over sodium metal and distilled under nitrogen. Norbornene (bicyclo-[2.2.1]hept-2-ene; Acros) was purified by distillation over potassium and used as a solution (4.26 mol/L) in toluene. Methylaluminoxane (MAO) was prepared by partial hydrolysis of trimethylaluminum (TMA) in toluene at 0–60 °C with $Al_2(SO_4)_3 \cdot 18H_2O$ as water source. The initial $[H_2O]/[TMA]$ molar ratio was 1.3. Other commercially available reagents were purchased and used without purification.

2.2. Polymerization

In a typical procedure, the appropriate MAO solid was introduced into the round-bottom glass flask, and then a toluene solution of norbornene (4.26 mol/L) was added via syringe. Toluene and nickel complexes solution (10^{-3} M) were syringed into the well-stirred solution in order, and the total reaction volume were kept at 20 mL. The reaction was continuously stirred for an appropriate period at polymerization temperature, which was controlled with an external oil bath in polymerization experiments. Polymerizations were terminated by addition of 200 mL of the acidic ethanol (ethanol–HCl, 95:5). The resulting precipitated polymers were collected and treated by filtering, washing with ethanol several times, and drying in vacuum at 60 °C to a constant weight.

2.3. Characterization

Gel permeation chromatography (GPC) analyses of the molecular weight and molecular weight distribution of the polymers were performed on a Waters 150C instrument using standard polystyrene as the reference and with chlorobenzene as

the eluent at 40 °C. The polymer samples were processed into KBr thin films for IR measurements. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet NEXUS-670 FTIR spectrometer. ^{1}H NMR spectra were carried out on an INOVA 500 MHz at room temperature in *o*-dichlorobenzene-d_4 solution for polymers (using TMS as internal standard). ^{13}C NMR spectra of the polymers in *o*-dichlorobenzene-d_4 were recorded on an INOVA 500 MHz spectrometer operating at 120 °C. The chemical shift value (127.3 ppm) of *o*-dichlorobenzene was used as an internal standard. Differential scanning calorimetry (DSC) analysis was conducted with a PerkinElmer DCS-7 system. The DSC curve was recorded at a heating rate of 10 °C/min. The cooling rate was 10 °C/min. TGA data was measured with a TG-290C thermal analysis system instrument under a nitrogen atmosphere up to 600 °C at heating rate of 10 °C/min. Wide-angle X-ray diffraction (WAXD) curve of the polymer powder was obtained using a D/Max-IIIA powder X-ray diffractometer.

3. Results and discussion

β-Diimine, β-diketiminate, fluorinated β-diketiminate, anilido-imine ligands and the corresponding nickel complexes were synthesized according to the reported methods [34,40,42,43] (see Fig. 1). All of the nickel complexes bearing [*N,N*] six-membered chelate ring showed high catalytic activities (up to 10^6 g PNBE/(mol Ni h)) for norbornene polymerization activated with MAO. Compared to nickel complexes reported by Janiak [32], four classes of nickel complexes bearing [*N,N*] six-membered chelate ring exhibited comparative activity. Influences of ligand structure, polymerization temperature, and Al/Ni ratio on norbornene polymerization were discussed, respectively.

3.1. Influence of ligand structure

Although all of nickel complexes bear [*N,N*] six-membered chelating ligand, ligand structure has an important influence on catalytic activities for norbornene polymerization. Fig. 2 shows that the order of the catalytic activity values for norbornene polymerization catalyzed by **1–4**/MAO is **1 > 3 > 2 > 4** at the same conditions. According to a commonly accepted Cossee mechanism of the catalytic polymerization [44,45], cooperation
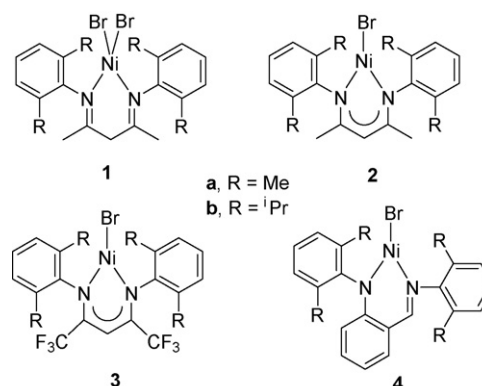

Fig. 1. Nickel complexes bearing [*N,N*] six-membered chelate ring.
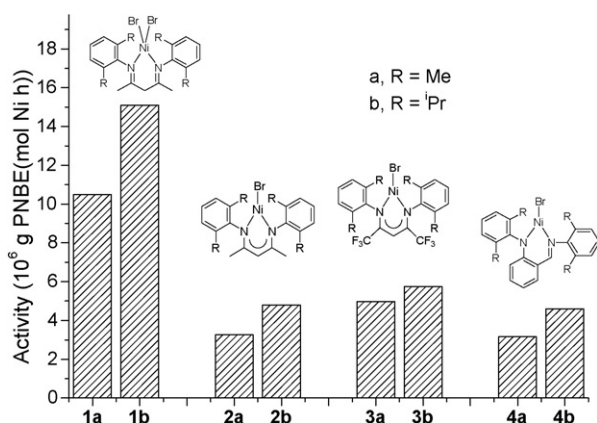
Fig. 2. Influence of ligand structure on norbornene polymerization with nickel complexes **1–4**/MAO. Polymerization conditions—polymerization temperature: 70 °C; Al/Ni = 3000; reaction time, t = 30 min; catalyst addition: 1 μmol, monomer concentration [NBE] = 2.13 mol/L, solvent: 20 mL toluene. Activities of **4a** and **4b** come from reference [34].

between complex **1** and MAO will produce cation active species [LNiMe]$^+$ (L: ligand **1**), while cooperation between complex **2–4** and MAO will produce neutral active species [LNiMe] (L: ligand **2–4**) (see Section 3.5). The cation active species [LNiMe]$^+$ has the most positive nickel metal center, thus **1**/MAO shows the highest catalytic activity for norbornene polymerization among four catalytic system. Other groups also reported that cation nickel or palladium catalysts or naked metal catalysts showed very high catalytic activity for norbornene polymerization [31,46–48]. In comparison of β-diketiminate ligands **L2** with fluorinated β-diketiminate ligands **L3**, the latter have two strong electron-withdrawing groups CF$_3$, thus resulting in a relatively positive nickel metal center. In comparison of β-diketiminate ligands **L2** with anilido-imine ligands **L4**, the latter has a conjugated benzene ring, which is a strong electron-donating group, thus resulting in a relatively negative nickel metal center. Therefore, a conclusion can be drawn that ligands lead to different electrophilicity of the nickel metal center, and a relatively positive nickel metal center will exhibit high catalytic activities for norbornene polymerization.

A reasonable explanation for the catalytic activity enhancement and molecular weight of product increase is that a more electrophilic nickel center can reduce activation energy for norbornene monomer insertion, and favor the norbornene coordination and insertion in the growing chain [47–49].

Moreover, catalytic activities of **4** for norbornene polymerization (3.16 × 10^6 g PNBE/(mol Ni h) for **4a**, 4.60 × 10^6 g PNBE/(mol Ni h) for **4b**) are slightly lower than that of **2** (3.26 × 10^6 g PNBE/(mol Ni h) for **2a**, 4.78 × 10^6 g PNBE/(mol Ni h) for **2b**), though anilido-imine ligands **L4** have a strong electron-donating benzene ring. This result may be ascribed to π–π conjugation between benzene ring and [N,N] chelate ring, which can stabilize active center and increase activity. Therefore, anilido-imino nickel complexes have the comparative activity to β-diketiminato nickel complexes because of cooperation of conjugation and electron-donation of benzene ring.

Table 1
Influence of the reaction temperatures on norbornene polymerizations with complexes **1–3**/MAO[a]

Run	Complex	T_p (°C)	Activity[b]	M_w[c]	M_w/M_n
1	**1a**	30	6.35	23.4	3.31
2	**1a**	50	8.21	20.8	2.83
3	**1a**	70	10.5	19.4	2.42
4	**1a**	90	7.62	16.5	2.67
5	**1b**	30	9.76	25.3	3.62
6	**1b**	50	10.2	22.2	3.25
7	**1b**	70	15.1	20.1	2.28
8	**1b**	90	11.1	17.9	2.56
9	**2a**	30	2.50	12.5	2.57
10	**2a**	50	4.56	11.1	2.01
11	**2a**	70	3.26	10.7	2.16
12	**2a**	90	2.56	8.80	2.42
13	**2b**	30	3.83	13.3	2.65
14	**2b**	50	5.12	12.1	2.15
15	**2b**	70	4.78	11.8	2.20
16	**2b**	90	3.15	9.25	2.51
17	**3a**	30	2.80	13.4	2.12
18	**3a**	50	4.26	12.3	2.03
19	**3a**	70	4.98	11.9	2.09
20	**3a**	90	6.12	9.80	2.24
21	**3b**	30	2.98	15.6	2.11
22	**3b**	50	4.90	13.8	1.92
23	**3b**	70	5.75	12.4	2.08
24	**3b**	90	6.70	10.3	2.27

[a] Polymerization conditions—reaction time, t = 30 min; catalyst addition: 1 μmol; Al/Ni = 3000; monomer concentration [NBE] = 2.13 mol/L; solvent: 20 mL toluene.
[b] In units of 10^{-6} g PNBE/(mol Ni h).
[c] In units of 10^{-5} g/mol.

Besides, a comparison of the catalytic activities of complexes with different bulky substituents shows that the steric hindrance of the nickel complexes influences their catalytic activities. In general, the complexes with 2,6-diisopropyl substituent (series **b**) exhibit higher catalytic activities than those with 2,6-dimethyl substituent (series **a**), and molecular weights of the polynorbornenes catalyzed by series **b**/MAO are higher than those of catalyzed by series **a**/MAO (see Table 1). This result is consistent with substituent effect reported in norbornene polymerization catalyzed by anilido-imino nickel/MAO system [34].

Compared to the other nickel complexes with [N,N] six-membered chelate ring, four classes of reported nickel complexes also showed higher activities for norbornene polymerization than nickel bisbenzimidazole complexes (*ca.* 10^4 g PNBE/(mol Ni h) on the given conditions) [50]. The polymerizations of norbornene were also investigated with nickel complexes bearing [N,N] five-membered chelate rings, such as nickel complexes with α-dioxime, diiminopyridine, and α-diimine ligand, in combination with MAO. On the given conditions, nickel complexes with diiminopyridine, and α-diimine ligand showed low activity (*ca.* 5 × 10^3 g PNBE/(mol Ni h)) [15], while nickel complexes with α-dioxime ligand showed moderate activity (*ca.* 10^5 g PNBE/(mol Ni h)) [29,32]. Considering that norbornene is a sterically encumbered monomer, four classes of reported nickel complexes with [N,N] six-membered chelate rings exhibited higher activity than those with [N,N]

five-membered chelate rings, which may be the consequence of more sterically open nature [41] and the weaker Ni–Br bond strength of the nickel complexes [31].

3.2. Influence of polymerization temperature

The reaction temperature strongly affected the catalytic activities, and the results of norbornene polymerizations using **1**–**3**/MAO at various temperatures were listed in Table 1. For **1** and **2**/MAO catalytic system, with an increase in the reaction temperature, the catalytic activities increased and then decreased. **1** and **2** showed the highest activity for norbornene polymerization at 70 and 50 °C, respectively. A higher temperature caused a decrease in the catalytic activity for the norbornene polymerization because of the instability or decomposition of the active species. For **3**/MAO catalytic system, with an increase in the reaction temperature from 30 to 90 °C, the catalytic activities increased consistently. **3a** and **3b** showed the highest activity 6.12×10^6 g PNBE/(mol Ni h) and 6.70×10^6 g PNBE/(mol Ni h) for norbornene polymerization at 90 °C, respectively. Fluorinated β-diketiminato nickel catalysts are more thermally robust than β-diketiminato nickel catalysts, which is obviously attributed to strong electron-withdrawing effect of CF$_3$ groups.

The polymerization temperature also affected the molecular weights of the polymers. The M_W values of the obtained polymers decreased with an increase in the reaction temperature, and this suggests that chain transfer or termination begins to accelerate at high temperature [35].

3.3. Influence of Al/Ni ratio

Al/Ni mole ratio played an important role in affecting the catalytic activities, thus complexes with bulky aryl group (**b** series) were chosen to investigate influence of Al/Ni ratio at the optimized temperature. As shown in Fig. 3, for **1b**/MAO catalytic system, with an increase in Al/Ni ratio from 500 to 5000, the catalytic activities for norbornene polymerization increased consistently. However, **2b** and **3b**/MAO catalytic systems showed
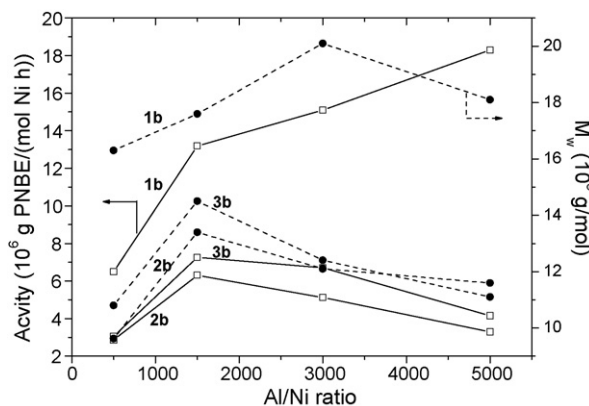

Fig. 3. Influence of Al/Ni ratio on norbornene polymerization with **1b**, **2b**, **3b**/MAO. Polymerization conditions—polymerization temperature: 70 °C for **1b**, 50 °C for **2b**, 90 °C for **3b**; reaction time, $t = 30$ min; catalyst addition: 1 μmol; monomer concentration [NBE] = 2.13 mol/L; solvent: 20 mL toluene.
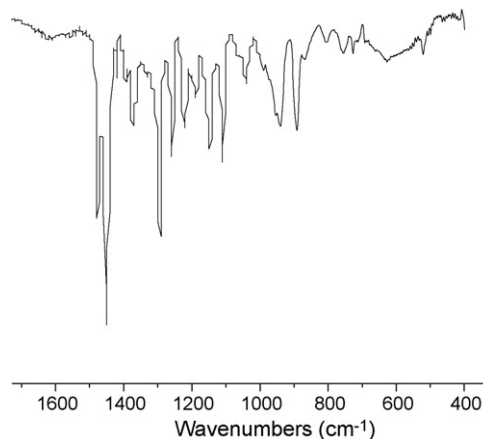

Fig. 4. Magnified FTIR spectrum of polynorbornene prepared by **1b**/MAO.

the different tendency. When Al/Ni ratio was 500, low activities for norbornene polymerization were obtained. With an increase in Al/Ni ratio, the catalytic activities for norbornene polymerization increased, and then decreased. When Al/Ni ratio was 1500, the highest catalytic activities were observed.

Besides, Al/Ni ratio slightly influenced the molecular weight of the obtained polynorbornene. All of the catalytic systems showed the same tendency. With an increase in Al/Ni ratio, the molecular weights of polynorbornenes increased, and then decreased, which suggests that excess MAO gives rise to easy chain transfer because of the action of AlMe$_3$ as a chain-transfer agent. The similar polymerization result involving nickel complexes with α-dioxime ligands, fluorinated β-diketiminate ligands, and anilido-imine ligand for norbornene polymerization was also reported [29,33,34].

3.4. Polynorbornene characterizations

All of the obtained polymers catalyzed by nickel catalysts bearing [N,N] ligand are vinylic addition polynorbornenes with different molecular weights, and soluble in chlorobenzene, o-dichlorobenzene, and cyclohexane solvents. The IR spectrum (Fig. 4) revealed no traces of double bond, which often appear at 1620–1680, 966 and 735 cm^{-1}, while the existence of vibration bands of bicyclics of norbornene at 941 cm^{-1}. ^{1}H NMR spectrum (0.86–2.38 ppm) (Fig. 5) also proved no traces of any double bond, ensuring the occurrence of vinyl-type polymerization rather than ring-opening metathesis polymerization [51]. ^{13}C NMR spectrum (Fig. 6) also further confirmed that the obtained polymers were vinyl-type polynorbornene [52]. Several signals were observed from 28 to 55 ppm. The absence of any signal at 20–24 ppm strongly indicates that the polynor-
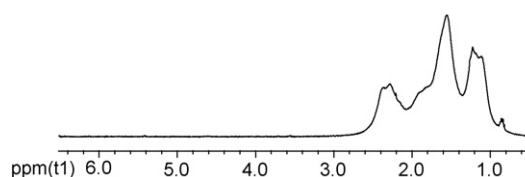

Fig. 5. ^{1}H NMR spectrum of polynorbornene catalyzed by **1b**/MAO.
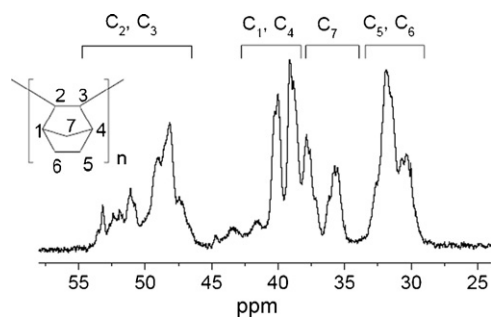
Fig. 6. ^{13}C NMR spectrum of polynorbornene catalyzed by **1b**/MAO.

bornene is *exo* enchained [53]. The resonances of methenes and methines appear at 29.7–32.0 ppm for C_5 and C_6, 35.5–37.9 ppm for C_7, 38.8–41.8 ppm for C_1 and C_4, and 48.1–54.0 ppm for C_2 and C_3. TGA curves of the obtained polynorbornenes showed that the polymer samples were stable up to 450 °C. Attempts to measure glass transition temperature (T_g) of poly-norbornene from DSC curve was unsuccessful because T_g was close to decomposition temperature [34,54]. The wide-angle X-ray diffraction analysis of the obtained polynorbornene showed two major broad peaks ($2\theta = 9$–11° and 17–19°) (Fig. 7), which indicates that the obtained polymer is non-crystalline and has low stereoregularity [55,56].

3.5. Mechanistic consideration

NMR and IR spectra of the obtained polymers clearly show that the polymerizations of norbornene with four classes of nickel catalysts proceed by a coordination mechanism. Detail mechanistic investigations with MAO as a cocatalyst are difficult since the exact composition and structure of MAO is still not entirely clear [31]. Janiak's group reported that diphosphane nickel and palladium complexes showed high activities for norbornene polymerization activated with $B(C_6F_5)_3$/AlEt$_3$ and investigated activation process. They found that highly active "naked" metal cations could be produced through ligand redistribution reaction due to open steric space [31]. For four classes of reported nickel catalysts, ligand redistribution reaction hardly proceeded because of bulky steric hindrance. Besides, there is a strong coordinating bond strength between neutral β-diimine ligand and nickel metal, and there is a more strong bond strength

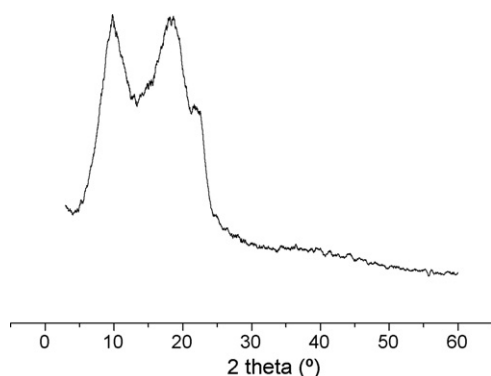between anionic β-diketiminate, fluorinated β-diketiminate, as well as anilido-imine ligand and nickel metal. Therefore, naked nickel cations are hardly produced by abstraction of the ligand. A possible activation process is that activation with MAO of four classes of nickel precursors can generate a pristine monochelate methyl nickel species characterized by the presence of a vacancy able to coordinate norbornene and initiate its polymerization. Similar activation mechanism was also proposed for bis(salicylaldiminate) nickel/MAO and anilido-imino nickel/MAO catalytic system [35,48,49,57].

4. Conclusion

All of the nickel complexes bearing [*N*,*N*] six-membered chelate ring showed high catalytic activities for norbornene polymerization activated with MAO. The ligand structure had an important influence on catalytic activity. The bulky steric hindrance of nickel complexes resulted in higher catalytic activity; ligands led to different electrophilicity of the nickel metal center, and a relatively positive nickel metal center would exhibit high catalytic activities. Polymerization temperature and Al/Ni ratio also played important roles in affecting catalytic activities for norbornene polymerization. All of the obtained polynorbornenes catalyzed by four classes of nickel catalysts bearing [*N*,*N*] ligand are vinylic type polymers with high molecular weight.

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Fig. 7. WAXD diagram of polynorbornenes obtained with **1b**/MAO.

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