



Polymerization of 5-norbornene-2-methyl acetate catalyzed by air-stable cationic (η^3 -substituted allyl) palladium complexes of *N*-heterocyclic carbene

Il Gu Jung^a, Young Tak Lee^a, Soo Young Choi^a, Dae Seung Choi^b, Youn K. Kang^{c,*}, Young Keun Chung^{a,*}

^a Intelligent Textile System Research Center, Department of Chemistry, College of Natural Sciences, Seoul National University, Seoul 151-747, Republic of Korea

^b Research Park, LG Chemical Limited, Yu Seong, Science Town, Daejeon, Republic of Korea

^c Division of Chemistry and Molecular Engineering, Department of Chemistry, College of Natural Sciences, Seoul National University, Seoul 151-747, Republic of Korea

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ABSTRACT

In situ generated cationic (η^3 -substituted allyl) palladium *N*-heterocyclic carbene (NHC) complexes are air-stable active catalysts for the olefin polymerization of (bicyclo[2.2.1]hept-5-en-2-yl)methyl acetate (5-norbornene-2-methyl acetate) (*endo:exo* = 7:3). Catalytic activities, polymer yields, molecular weights, and molecular weight distributions of polymers were investigated under various reaction conditions. The catalytic activity was highly dependent not only on the reaction condition such as a solvent or the reaction temperature but also on the structure of the catalyst that include substituents of the allyl group in the catalyst and the counter anion. As the bulkiness of the allyl group increased, the catalytic activity of the catalysts increased.

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1. Introduction

Late transition metal catalysts for the olefin polymerization have attracted considerable attention from both academic and industrial fields [1–3]. Particularly, the recent interest in the olefin polymerization of bicyclo[2.2.1]hept-2-ene (norbornene) is driven by its many interesting properties that include high mechanical strength, high thermal stability, high chemical resistivity, excellent optical transparency, good UV resistance, large refractive index, low birefringence, and low dielectric constant [4–6]. Due to these characteristic features, polynorbornene is an active candidate for a variety of specialty applications such as a deep UV photolithography, a matrix material of organic optoelectronic device, a cover layer for liquid-crystal display, an inter-level dielectric in microelectronics as well as bulk condensers [4]. Major drawbacks of polynorbornene, however, are its extreme brittleness mainly due to the high glass-transition temperature (>300 °C) [7], low solubility, and poor adhesion toward the film or substrates [8]. Reconciling these problems is crucial for the wide expansion of this material toward many applications described above.

Incorporation of a polar functional group into the polymer chain is a clever way to solve such problems [7,9–15]. Such functional groups can enhance miscibility or compatibility with organic sol-

vents and reduce the rigidity of the conformationally constrained polynorbornene backbone, which give rise to noticeable decrease of T_g or higher elongation-to-break values [7,8]. Moreover, the poor adhesion has been surely improved by attaching such functional groups to the polymer backbone [8].

Developing high-activity polymerization catalyst for the olefin polymerization of functionalized norbornene has been thus a keen interest. Although a variety of transition metal complexes of Ti and Zr [6,16–25], Co [26–32], Ni [5,33–50], and Pd [7,9–13,34,40,51–54] metals have been synthesized and tested for the olefin polymerization of norbornene, only a limited number of catalyst species have been proved to be effective for functionalized norbornenes. When functionalized norbornenes are employed, most transition metal catalyst systems become inactive for the polymerization reaction, which restrict their practical utility. Even for the catalyst systems that have a certain degree of activity toward functionalized norbornenes, the magnitudes of activities were far less than those for the bare norbornene.

Recently, we reported the cationic (η^3 -allyl)Pd(NHC) complexes as catalysts for the olefin polymerization of 5-norbornene-2-carboxylic acid methyl ester [15]. The catalytic activities were critically dependent on the chemical structure of *N*-substituted phenyl moiety of NHC group. Other important parameters that affect the catalytic activities include the identity of counter ions and solvents. Average activities during 12 h of polymerization were up to 1341 g_{poly}/mol_{cat}/h with the *endo:exo* = 5:95 mixture. The maximum activity for the pure *endo* isomer was limited to 155 g_{poly}/mol_{cat}/h.

* Corresponding authors. Tel.: +82 2 880 6662; fax: +82 2 889 0310 (Y.K. Chung), tel.: +82 2 880 4390 (Y.K. Kang).

E-mail addresses: younkang@snu.ac.kr (Y.K. Kang), ykchung@snu.ac.kr (Y.K. Chung).

Among a number of reports regarding the catalytic application of (η^3 -allyl)Pd(NHC) structural motif, we noticed the Nolan's recent study that reported the Suzuki–Miyaura and Buchwald–Hartwig reactions with (η^3 -allyl)Pd(NHC)X (X = halide ion) type catalyst systems in relation with the role of substituent(s) of allyl moiety [55]. The effect of substituent(s) in the allyl moiety was remarkable; the reaction yield was increased a factor of 7 even with the single additional methyl substituent. This result inspired us to study the effect of the structure of allyl group for the olefin polymerization of functionalized norbornene. Herein, we describe the olefin polymerization of 5-norbornene-2-methyl acetate with *in situ* generated cationic (η^3 -allyl)Pd(NHC) complex (**6⁺**) or (η^3 -substituted allyl)Pd(NHC) complexes (**7⁺**–**10⁺**) in which the bulkiness of allyl moiety was systematically modulated.

2. Experimental

2.1. Materials

All manipulations were carried out under nitrogen atmosphere unless otherwise noted. Standard Schlenk techniques were employed to manipulate air sensitive solutions. Solvents utilized in this work were obtained from Fisher Scientific (tetrahydrofuran, CH₂Cl₂, HPLC grade), Aldrich Chemical Co. (toluene, chlorobenzene, ACS grade), and Samchun Pure Chemicals (hexanes, ethyl acetate). Tetrahydrofuran (THF), toluene, and chlorobenzene were dried over Na/benzophenone and subsequently distilled from these reagents under nitrogen. CH₂Cl₂ was dried over P₂O₅ and subsequently distilled from this reagent under nitrogen. These solvents were degassed via three freeze–pump–thaw cycle prior to use. Hexanes and ethyl acetate were used without further purification. Reagents were purchased from Aldrich Chemical Co. or Strem Chemical Co. unless otherwise noted and were used as received. Lithium tetrakis(pentafluorophenyl)borate etherate (Li[B(C₆F₅)₄] · 2.5Et₂O) was purchased from Boulder Scientific Company and used as received. 5-norbornene-2-methyl acetate (*endo:exo* = 7:3) isomers were synthesized by literature method [55]. For the *endo:exo* = 1:1 mixture, pure *exo* isomer was added to the *endo:exo* = 7:3 mixture. The known compounds **2**–**8** were prepared by the published procedures [10,56,57].

2.2. Instrumentation

The ¹H NMR spectra were recorded on a Bruker 300 (300 MHz) spectrometer. Chemical shifts for ¹H NMR spectra are relative to a residual protium in the deuterated solvents (CDCl₃, δ = 7.26 ppm). ¹³C NMR spectra are also referenced to deuterated solvents (CDCl₃, δ = 77 ppm). The molecular weights and molecular weight distributions of polymers were determined by gel permeation chromatography (GPC) using a Waters system equipped with two Styragel columns (HR 5E, HR 2) connected in a serial fashion, a Waters 1515 solvent delivery system, and a Waters 2414 refractive index detector. Molecular weights are reported relative to polystyrene standards purchased from Sigma–Aldrich, Co. The calibrations as well as the measurement processes were carried out at 35 °C. THF was used as an eluent at a flow rate of 1.0 mL/min. High-resolution mass spectra (HRMS) were obtained at Korea Basic Science Institute (Daegu). Elemental analyses were done at the Analytical Center, School of Chemical and Biological Engineering, Seoul National University. Thermal gravimetric analysis (TGA) experiments were performed using a TGA2050, TA Instruments. Polymer samples were heated at 10 °C min⁻¹ heating rate under nitrogen. The glass-transition temperature (*T*_g) data were collected with DCS-Q100, TA Instruments.

2.3. Catalyst syntheses

2.3.1. Synthesis of **9**

1,3-Bis-(2,6-diisopropylphenyl)imidazolium chloride (0.30 g, 0.63 mmol) and potassium *tert*-butoxide (78 mg, 0.70 mmol) in 20 mL of THF were stirred at room temperature for 4 h. Compound **4** in 10 mL of THF was added to the reaction mixture and the resulting solution was stirred overnight at room temperature. After the solvent was evaporated, the product was separated by column chromatography on a silica gel column eluting with hexane and ethyl acetate (v/v, 7:3). Yield: 0.38 g (94%). ¹H NMR (CDCl₃): δ 7.45–7.39 (m, 2H), 7.25–6.97 (m, 16H), 5.01 (d, *J* = 7.4 Hz, 1H), 3.03 (sep, *J* = 6.6 Hz, 2H), 2.92 (sep, *J* = 6.6 Hz, 2H), 2.89 (d, *J* = 6.9 Hz, 1H), 2.12 (d, *J* = 12.3 Hz, 1H), 1.40 (d, *J* = 6.6 Hz, 6H), 1.17 (d, *J* = 6.6 Hz, 12H), 1.08 (d, *J* = 6.7 Hz, 6H). ¹³C NMR (CDCl₃): δ 184.9, 145.9, 145.8, 143.4, 138.4, 136.0, 130.7, 129.7, 128.6, 128.2, 127.6, 126.7, 126.5, 124.1, 123.7, 123.6, 108.2, 108.0, 46.4, 28.6, 28.5, 26.4, 26.1, 22.8, 22.1. HRMS Calc. for C₄₂H₄₉N₂Pd [M–Cl⁺]: 687.2930, found: 687.2926. Anal. Calc. for C₄₂H₄₉N₂PdCl: C, 69.70; H, 6.82; N, 3.87. Found: C, 69.88; H, 6.66; N 3.80%.

2.3.2. Synthesis of **10**

The procedure of the synthesis of **10** was the same manner as the synthesis of **9** except **5** instead of **4** was used. Yield: 93%; ¹H NMR (CDCl₃): δ 7.39–7.25 (m, 6H), 7.15–7.06 (m, 10H), 6.87 (t, *J* = 7.4 Hz, 2H), 3.17 (sep, *J* = 6.4 Hz, 2H), 2.74 (sep, *J* = 6.4 Hz, 2H), 2.66 (s, 1H), 2.18 (s, 1H), 1.43 (d, *J* = 6.6 Hz, 6H), 1.24 (d, *J* = 7.2 Hz, 6H), 1.20 (s, 3H), 0.95 (m, 12H). ¹³C NMR (CDCl₃): δ 186.2, 146.1, 146.0, 142.4, 142.2, 136.3, 130.9, 130.6, 129.6, 128.1, 127.1, 126.1, 125.8, 124.1, 123.8, 123.7, 120.7, 105.8, 49.3, 28.7, 28.4, 27.0, 25.7, 23.1, 21.6, 21.2. HRMS Calc. for C₄₃H₅₁N₂Pd [M–Cl⁺]: 701.3086, found: 701.3088. Anal. Calc. for C₄₃H₅₁N₂PdCl: C, 70.01; H, 6.97; N, 3.80. Found: C, 70.46; H, 6.93; N 3.56%.

2.4. Crystal structure determinations of **10**

An X-ray quality single crystal of compound **10** was mounted in a thin-walled glass capillary on an Enraf–Noius CAD-4 diffractometer with graphite-monochromated Mo K α radiation (λ = 0.71073 Å) at 25 ± 1 °C. Unit cell parameters were determined by least-squares analysis of 10 reflections (10° < θ < 13°). Intensity data were collected with θ range of 1.88°–24.97° in $\omega/2\theta$ scan mode. Three standard reflections were monitored every 1 h during data collection. The intensity data were corrected for Lorentz and polarization effects. The structure was solved by using Patterson method and refined by full-matrix least-squares techniques on *F* using SHELX-97 program packages [58,59]. All non-hydrogen atoms were refined positioned geometrically using riding model with fixed isotropic thermal factors (*U* = 0.08 Å²). The final cycle of the refinement converged with *R*₁ = 0.034 and *wR*₂ = 0.067.

2.5. General procedure for polymerization of 5-norbornene-2-methyl acetate (*endo:exo* = 7:3)

Compound **10** (1.6 mg, 2.2 μ mol) and Li[B(C₆F₅)₄ · 2.5Et₂O] (3.0 mg, 3.4 mol) were dissolved in chlorobenzene (3 mL). After the resulting solution was stirred at room temperature for 8 h, the reaction mixture was filtered through a syringe filter and the filtrate was slowly added to a stirred solution of 5-norbornene-2-methyl acetate (1.0 g, 6.6 mmol) in chlorobenzene (1 mL). After the reaction mixture was stirred at the predetermined temperature for 20 h, the reaction mixture was triturated in methanol (50 mL). The precipitates were collected and washed with methanol (20 mL \times 3) and dried in vacuum. Yield: 70%. ¹H NMR (CDCl₃): δ 4.3–3.6 (br, 2H), 2.5–0.5 (br, 12H).

allyl group [55]. As the size of substituent(s) increased, torsional angles sequentially decreased to 79.9°, 68.6°, and 62.2° for the methylallyl, dimethylallyl, and phenylallyl groups, respectively. Another important difference between previously reported (η^3 -allyl)Pd(NHC)X (X = halide ion) type complexes and **10** is dihedral angles between NHC ring plane and that of phenyl ring attached to the N atoms of NHC moiety. In most cases of (η^3 -allyl)Pd(NHC)X complexes, these dihedral angles are near 90°. In **10**, however, values are 109.7° and -73.8° for C(10)–C(5)–N(1)–C(1) and C(6)–C(5)–N(1)–C(1), respectively.

3.3. Polymerization reaction

An olefin polymerization of 5-norbornene-2-methyl acetate (*endo:exo* = 7:3) with five different cationic catalyst species, **6**⁺X⁻–**10**⁺X⁻ (X⁻ = counter anion), *in situ* generated from their corresponding neutral precursor molecules, **6**–**10**, was studied. Our previous work regarding the olefin polymerization of 5-norbornene-2-carboxylic acid methyl ester with similar type of cationic catalyst species revealed that the efficacy of polymerization critically dependent on the proper choice of a counter anion and a solvent. Based on this information, we thus tested the effect of counter anions and solvents first for the preliminary optimization of the polymerization condition. The monomer-to-catalyst ([M]/[cat]) ratio was fixed at 3000. Three different kinds of counter anions and two different solvents were chosen for the catalyst **6**⁺ (Table 1, entry 1–6). While all conditions listed in entry 1–5 of Table 1 provided less than 20% yield, more than 50% of yield obtained by B(C₆F₅)₄⁻/chlorobenzene couple was noteworthy.

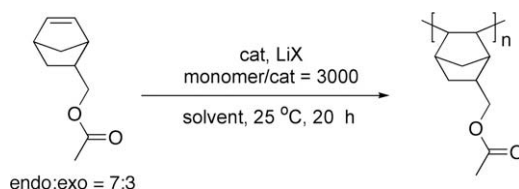
With this condition at hand, we tested the performance of catalyst species next. Yield of polymerization increased from 53% to 70% concomitantly with the increasing size of the allyl group. Con-

trol reaction with catalyst **1**⁺ or **5**⁺ in which NHC group was not involved did not give any polymer long enough to be insoluble in methanol. Obviously, the NHC group plays a crucial role in the activity and the stability of the catalyst. However, it is also important to emphasize that there is noticeable differences in catalytic activities by simple change of substituents in the allyl group. The trend indicates that the bigger allyl group performs better. It is somewhat against our intuition because an allyl group with bulkier substituent(s) prevents a norbornene monomer from approaching to metal center. Opposite results suggest that the effect of the steric hindrance is minimal; there seems to be other factors that enhance the polymerization activity by compensating the steric hindrance of increasing bulkiness of the allyl group. The elucidation of the detailed background of this phenomenon needs further study.

Interestingly, the polymerization reaction carried out in air gave almost similar results with that operated in a glove box (entry 10 versus 11). Not only the yield but also the molecular weight as well as the molecular weight distribution were virtually identical with each other. It has been reported that complexes derived from [(allyl)PdCl]₂/AgSbF₆ and [(allyl)PdCl]₂/AgBF₄ are stable in solution at 20 °C only for 1 h or so [38,63]. However, our new catalytic systems are quite stable under ambient condition for several days. While the cationic species **6**⁺ and **10**⁺ with BF₄⁻ counter anion in air exposure lead to the rapid formation of black particles indicating the decomposition of the catalyst, the similar phenomenon was observed only after 5 days for **6**⁺ with B(C₆F₅)₄⁻. In case of **10**⁺/B(C₆F₅)₄⁻ system, there was no change during the same period.

Increasing the [M]/[cat] ratio from 3000 to 8000 gave rise to the decrease of the yield. Maximum yield of 70% obtained with **10**⁺/B(C₆F₅)₄⁻ catalyst system with [M]/[cat] = 3000 was reduced to 41% when the [M]/[cat] ratio was increased to 8000. In case of

Table 1
Polymerization of 5-norbornene-2-methyl acetate catalyzed by cationic (η^3 -allyl)Pd(NHC) catalyst systems.^a



Entry	Catalyst	Counteranion	Solvent	M _n (kD)	M _w (kD)	PDI ^b	Yield (%) ^c	Activity (kg _{poly} /mol _{pd} /h) ^d
1	6	BF ₄ ⁻	Toluene/CH ₂ Cl ₂				n.r.	
2	6	SbF ₆ ⁻	Toluene/CH ₂ Cl ₂				18	4.5
3	6	B(C ₆ F ₅) ₄ ⁻	Toluene/CH ₂ Cl ₂				14	3.5
4	6	BF ₄ ⁻	Chlorobenzene				Trace	
5	6	SbF ₆ ⁻	Chlorobenzene				Trace	
6	6	B(C ₆ F ₅) ₄ ⁻	Chlorobenzene	121	209	1.73	53	13.2
7	7	B(C ₆ F ₅) ₄ ⁻	Chlorobenzene	124	225	1.82	55	13.7
8	8	B(C ₆ F ₅) ₄ ⁻	Chlorobenzene	128	230	1.80	56	13.9
9	9	B(C ₆ F ₅) ₄ ⁻	Chlorobenzene	128	231	1.80	60	14.9
10	10	B(C ₆ F ₅) ₄ ⁻	Chlorobenzene	151	272	1.80	70	17.4
11 ^e	10	B(C ₆ F ₅) ₄ ⁻	Chlorobenzene	148	267	1.81	70	17.4
12 ^f	6	B(C ₆ F ₅) ₄ ⁻	Chlorobenzene	128	240	1.87	19	12.6
13 ^f	10	B(C ₆ F ₅) ₄ ⁻	Chlorobenzene	166	293	1.76	41	27.2
14	1	B(C ₆ F ₅) ₄ ⁻	Chlorobenzene				n.r.	
15	5	B(C ₆ F ₅) ₄ ⁻	Chlorobenzene				n.r.	

^a [LiX]/[Cat] = 1.5.

^b Polydispersity index (M_w/M_n) determined by GPC calibrated with polystyrene standards at 35 °C.

^c Insoluble powder in methanol.

^d Average value for 20 h.

^e Reaction carried out in air.

^f [Monomer]/[Cat] = 8000.

$6^+/\text{B}(\text{C}_6\text{F}_5)_4^-$ catalyst system, this trend is more significant and the yield with $[\text{M}]/[\text{cat}] = 8000$ was 19%, which is only 36% of that obtained with $[\text{M}]/[\text{cat}] = 3000$.

If the olefin polymerization reaction of norbornene undergoes via living polymerization mechanism, the number averaged molecular weight (M_n) of the polymer is expected to be $\sim Y \times M \times R$ approximately, where Y is the yield, M is the molecular weight of a monomer, and R is the $[\text{M}]/[\text{cat}]$ ratio. Observed M_n s of polynorbornenes ranged from 121 to 151 kD for five different catalyst systems (Table 1, entry 6–10). Although these values are linearly dependent on the magnitudes of the yields at the given M and R values, they are at least a factor of 2 smaller than those predicted theoretically. Moreover, M_n values obtained with $[\text{M}]/[\text{cat}] = 8000$ (Table 1, entry 12 and 13) are even more deviated from the predicted ones. Similar trends were observed for $[\text{M}]/[\text{cat}] = 5000$ (Table 2) and $[\text{M}]/[\text{cat}] = 2000$ (Table 3). M_n values larger than predicted ones can be attributed to the decrease of active catalyst species due to the imperfect reaction condition. However, smaller-than-theoretical values of M_n are not usual for the polymerization reaction under the living polymerization mechanistic regime. From the results mentioned above, it is thus reasonable to assume that the major mechanism of olefin polymerization of 5-norbornene-2-methyl acetate with cationic (η^3 -allyl)Pd(NHC) catalyst systems is most likely a chain transfer mechanism.

We also investigated the effect of reaction temperature on the polymerization yield (Table 2). The $[\text{M}]/[\text{cat}]$ ratio was increased to 5000 for this experiment to magnify the differences of the catalytic performances among five catalyst systems. The trend of catalyst performance observed in the entry 6–10 in Table 1 have recurred at three different temperature points of 25, 50 and 70 °C; the polymerization yield increased as the steric bulkiness of the substituent(s) on the allyl group increased. An optimum reaction temperature for all catalyst systems was 50 °C and the best yield (56%), which was slightly lower than that obtained with $[\text{M}]/$

Table 3Polymerization yields, molecular weight and activity at various time period.^a

Time (h)	$M_n (\times 10^5)$	$M_w (\times 10^5)$	PDI ^b	Yield (%) ^c	Activity ($\text{kg}_{\text{poly}}/\text{mol}_{\text{Pd}}/\text{h}$)
1	0.65	1.34	2.05	37	123
2	0.88	1.58	1.80	51	46
4	1.26	1.99	1.57	60	15
20	1.12	2.30	2.04	70	2

^a Reaction conditions: Cat = $10^+/\text{B}(\text{C}_6\text{F}_5)_4^-$, monomer = 5-norbornene-2-methyl acetate, $[\text{Li}\{\text{B}(\text{C}_6\text{F}_5)_4\}]/[\text{Cat}] = 1.5$, solvent = chlorobenzene, *endo:exo* = 1:1, $[\text{monomer}]:[\text{cat}] = 2000$, temp = 50 °C.

^b Polydispersity index (M_w/M_n) determined by GPC calibrated with polystyrene standards at 35 °C.

^c Insoluble powder in methanol.

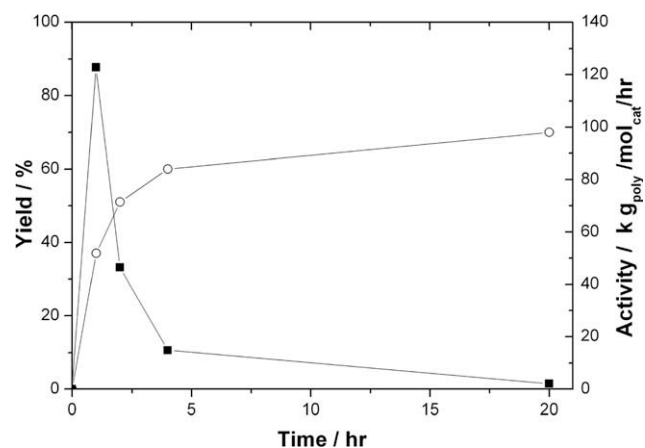
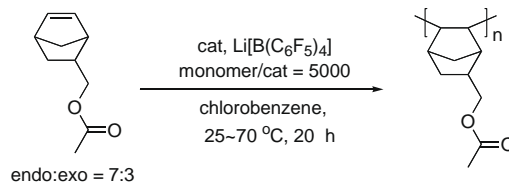


Fig. 3. Plots of activity (solid square) and yield (open circle) values as a function of time. For reaction conditions, see footnote a of Table 3.

Table 2Temperature effect of polymerization of 5-norbornene-2-methyl acetate catalyzed by cationic (η^3 -allyl)Pd(NHC) catalyst systems.^a

Entry	Catalyst	Temperature (°C)	$M_n (\times 10^5)$	$M_w (\times 10^5)$	PDI ^b	Yield (%) ^c	Activity ($\text{kg}_{\text{poly}}/\text{mol}_{\text{Pd}}/\text{h}$) ^d
1	6	25	0.89	1.43	1.60	19	7.9
2	7	25	1.03	1.73	1.68	23	9.5
3	8	25	1.16	1.86	1.61	31	12.9
4	9	25	1.18	2.09	1.77	33	13.7
5	10	25	1.24	2.27	1.83	40	16.6
6	6	50	0.88	1.42	1.61	22	9.1
7	7	50	0.98	1.60	1.63	21	8.7
8	8	50	1.55	2.71	1.75	47	19.5
9	9	50	1.59	2.78	1.75	49	20.3
10	10	50	1.69	3.00	1.78	66	27.4
11	6	70				0	0.0
12	7	70	0.58	1.47	2.53	14	5.8
13	8	70	1.31	2.51	1.91	24	10.0
14	9	70	1.36	2.32	1.71	33	13.7
15	10	70	1.53	2.80	1.83	42	17.4

^a $[\text{Li}\{\text{B}(\text{C}_6\text{F}_5)_4\}]/[\text{Cat}] = 1.5$.

^b Polydispersity index (M_w/M_n) determined by GPC calibrated with polystyrene standards at 35 °C.

^c Insoluble powder in methanol.

^d Average value for 20 h.

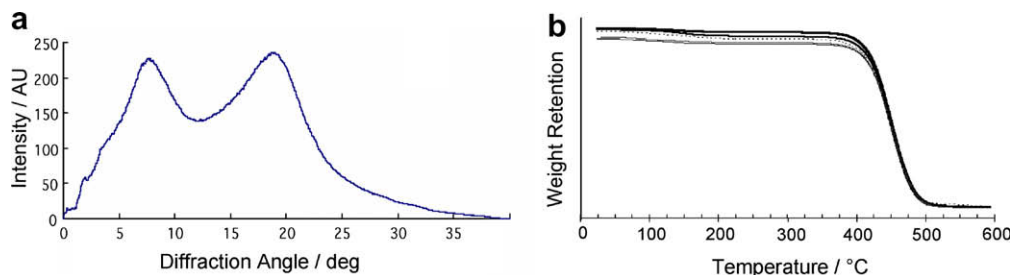


Fig. 4. WAXD pattern (a) and TGA diagram (b) of polymer (entry 1, Table 2).

[cat] = 3000, was obtained when catalyst **10⁺** was used (entry 10). Interestingly, when the polymerization operated at 70 °C using **6⁺** as a catalyst (entry 11), no reaction was observed presumably due to the low stability (or decomposition) of **6⁺** at this temperature.

With the optimized polymerization condition, we tested the activity of the **10⁺**/B(C₆F₅)₄⁻ catalyst system in chlorobenzene at 50 °C. Polymerization yields as well as activities are plotted as a function of the time (Table 3, Fig. 3). The activity was highest at the first one hour of the polymerization and rapidly decreased at longer time period. The maximum value of activity was 122.8 kg_{poly}/mol_{pd}/h. This value is *ca.* two orders of magnitude larger than that obtained for the polymerization of 5-norbornene-2-carboxylic acid methyl ester with cationic (η^3 -unsubstituted allyl)Pd(NHC) catalyst system in our previous work [15]. This result clearly shows the high catalytic activity of cationic (η^3 -substituted allyl)Pd(NHC) system toward the olefin polymerization of functionalized norbornene.

The crystallinity of the resultant polymers was investigated by wide-angle X-ray diffraction (WAXD). The WAXD pattern of polymer (entry 1, Table 2), shown in Fig. 4a, indicates that the polymer is a non-crystalline material. Two broad halos at $2\theta = 8^\circ$ and 19° were observed and attributed to a short-range order. Thus, the first peak ($2\theta = 8^\circ$) was the reflection of the interchain, or intersegment, distance of the polymer, while the second peak ($2\theta = 19^\circ$) was the reflection of the intrachain distance. This observation is in agreement with the results reported by Haselwander et al. [63] Observed glass-transition temperature (T_g) of this polymer was $\sim 280^\circ\text{C}$, which is significantly lower than that of normal polymorborene (380–390 °C) [8]. This polymer was stable up to 450 °C (Fig. 4b).

4. Conclusions

In sum, we have demonstrated that catalysts generated from cationic (η^3 -substituted allyl)Pd(NHC) complexes **6⁺**–**10⁺** are active in the olefin polymerization of norbornene bearing an methyl acetate group. As the steric bulkiness of the substituent(s) on the allyl group increases, the catalyst becomes more stable and the catalytic activity of the catalyst increases. Maximum activity was up to 122.8 kg_{poly}/mol_{pd}/h and the M_w of obtained polymer was near 3×10^5 . The polymers were amorphous, soluble in various organic solvents such as THF, CH₂Cl₂, chloroform, and chlorobenzene, and stable up to 350 °C. Despite the intended lowering of T_g by the incorporation of functional group, clear T_g was not observed.

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Appendix A. Supplementary material

CCDC 626303 contains the supplementary crystallographic data for compound **10**. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2008.10.058](https://doi.org/10.1016/j.jorganchem.2008.10.058).

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