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Norbornene polymerization and ethylene/norbornene copolymerization catalyzed by constrained geometry cyclopentadienyl-phenoxytitanium catalysts

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Abstract

Norbornene polymerization and ethylene/norbornene copolymerization were studied using constrained geometry complexes 2-(tetramethylcyclopentadienyl)-4,6-di-*tert*-butylphenoxytitanium dichloride (**1**), 2-(tetramethylcyclopentadienyl)-6-*tert*-butylphenoxytitanium dichloride (**2**), and 2-(tetramethylcyclopentadienyl)-6-phenylphenoxytitanium dichloride (**3**) as catalysts with Al^iBu_3 and $Ph_3CB(C_6F_5)_4$ as cocatalysts. Polymerization results indicate that these catalyst systems are highly active for both the homopolymerization of norbornene and the copolymerization of ethylene with norbornene. The norbornene homopolymerization is vinyl addition polymerization. Ethylene/norbornene copolymers with high norbornene incorporation (>50%) were easily obtained with these catalyst systems by increasing the norbornene feed concentration. The produced polymers were characterized by ^{13}C NMR, IR, DSC and GPC.

Keywords: Constrained geometry catalyst; Ethylene/norbornene copolymerization; Norbornene homopolymerization

1. Introduction

Since 1990s, homopolymerization of norbornene and copolymerization of norbornene with ethylene [1–3] catalyzed by single site catalysts have received extensive attention for the potential applications of the produced norbornene-containing polymers [4–7]. Ethylene/norbornene (E–N) copolymer is one of the most promising new industrial thermoplastic polymers with high glass transition temperature (T_g), excellent moisture barrier properties, chemical resistance, and optical clarity. It has been very attractive as a novel substrate material for high density data storage devices, packaging, and optical/biomedical applications [1b]. One of the interesting characteristics of E–N copolymer is that its glass transition temperature can be tuned from about 20 to 260 °C [8] by varying the norbornene content in the copolymer and modifying its microstructure. By carefully selecting the catalyst and controlling the reaction conditions, E–N copolymers with different compositions and properties can be produced. Some group 4 metallocene-based catalysts [9], especially some constrained geometry catalysts (CGCs) [10], have been reported to be good at catalyzing the homopolymerization of norbornene and the copolymerization of norbornene with ethylene. The constrained geometry titanium catalysts with a pendant nitrogen donor on the cyclopentadienyl ring, such as $Me_2Si(\eta^5\text{-}Me_4C_5)(^tBuN)TiCl_2$ [11], were found to show remarkable catalytic activity with efficient norbornene incorporation for the ethylene/norbornene copolymerization. From the structural point of view, constrained geometry titanium catalysts with a pendant oxygen donor on the cyclopentadienyl ring might show similar catalytic properties for the ethylene/norbornene copolymerization. However, no such kind of research work has been reported so far although a number of nonbridged (aryloxo)(cyclopentadienyl) titanium(IV) complexes have been

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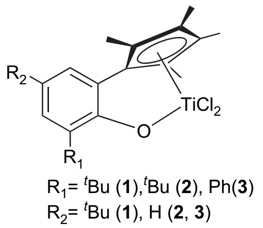

Chart 1. The constrained geometry catalysts used in this study.

tested as catalyst precursors for ethylene/norbornene copolymerization by Nomura et al. [12]. We have recently synthesized a number of constrained geometry titanium complexes with a pendant aryloxy side chain on the cyclopentadienyl ring [13,14]. These complexes were found to be good catalysts for the ethylene/norbornene copolymerization and E–N copolymers with high norbornene incorporation (>50%) similar to that obtained with constrained geometry catalyst with fluorenylamido ligand [15], which cannot be produced by monocyclopentadienylamido-titanium complexes [$Me_2Si(Cp')(N^tBu)]TiCl_2$ ($Cp' = Me_4Cp$, 2,4-Me_2Cp, 3-^tBuCp, Ind) [11], were easily obtained by increasing the norbornene feed concentration. In this paper, we wish to report the results of the norbornene homopolymerization and the ethylene/norbornene copolymerization catalyzed by these type of constrained geometry catalysts (Chart 1), 2-(tetramethylcyclopentadienyl)-4,6-di-*tert*-butylphenoxytitanium dichloride (**1**), 2-(tetramethylcyclopentadienyl)-6-*tert*-butylphenoxytitanium dichloride (**2**), and 2-(tetramethylcyclopentadienyl)-6-phenylphenoxytitanium dichloride (**3**) in the presence of Al^iBu_3 and $Ph_3CB(C_6F_5)_4$.

2. Experimental

2.1. Materials

Complexes **1–3** [13,14] and $Ph_3CB(C_6F_5)_4$ [16] were synthesized according to the literature procedure. Al^iBu_3, ^nBuLi, $TiCl_4$ and norbornene were purchased from Aldrich. Norbornene dissolved in toluene was dried with CaH_2 and stored over 4 Å molecular sieves. Toluene was distilled from sodium/benzophenone ketyl under nitrogen prior to use. Polymerization grade ethylene (from PetroChina Company) was further purified by passage through a 5 Å molecular sieve column containing MnO.

2.2. Polymerization

Norbornene polymerization experiments were performed as follows: a prescribed amount of norbornene in toluene (45 ml) and Al^iBu_3 (120 μmol) in toluene (2 ml) was added into a 100 ml glass flask under N_2, and the solution was heated to a desired temperature in an oil bath. The polymerization was started by the addition of $Ph_3CB(C_6F_5)_4$ (1.2 μmol) in toluene (2 ml) into the above solution soon after the addition of a precatalyst (1 μmol) in toluene (1 ml). After a certain period of time, the polymerization was terminated by injecting acidified methanol [HCl (3 M)/methanol = 1:1]. The polymer was collected by filtration, washed with water and methanol, and dried at 60 °C in vacuo to a constant weight.

E–N copolymerization experiments were carried out using a 250 ml jacketed stainless steel autoclave equipped with a magnetic stirrer. The autoclave was first charged with a prescribed amount of norbornene and Al^iBu_3 (2/3 of total amount) in 75 ml toluene, and saturated with ethylene (1 atm). The polymerization reaction was started by injection of a mixture of a precatalyst (1 μmol) and Al^iBu_3 (1/3 of total amount) in toluene (2 ml) and a solution of $Ph_3CB(C_6F_5)_4$ in toluene (3 ml) at the same time. The reactor was repressurized to needed pressure with ethylene immediately, and the pressure was maintained by continuously feeding ethylene. After a certain period of time, the polymerization was terminated by venting the reactor and the reaction mixture was discharged into a container filled with acidified methanol. The polymer was collected by filtration, washed with acidified methanol and fresh acetone, dried at 60 °C in vacuo to a constant weight.

2.3. Characterization

Molecular weight and molecular weight distribution of the polymer samples were measured on a PL-GPC220 at 140 °C with 1,2,4-trichlorobenzene as solvent and calibrated by polystyrene standards. The microstructures were analyzed by ^{13}C NMR spectroscopy on a Bruker AV400 spectrometer with *o*-dichlorobenzene-d_4 as solvent. Differential scanning calorimetric (DSC) analysis was conducted on a NETZSCH DSC 204, under nitrogen atmosphere from 20 to 400 °C at a heating/cooling rate of 10 °C/min. IR spectra were recorded on a Perkin–Elmer 2000 FT-IR spectrometer.

3. Results and discussion

3.1. Norbornene polymerization

The homopolymerization of norbornene catalyzed by complexes **1–3** in the presence of Al^iBu_3 and $Ph_3CB(C_6F_5)_4$ was studied in detail and the results are summarized in Table 1. It can be seen from the data that all complexes **1–3** can catalyze the homopolymerization of norbornene at temperatures from 20 to 100 °C upon activation with Al^iBu_3 and $Ph_3CB(C_6F_5)_4$. The order of the catalytic activity is **1** > **2** > **3** (Fig. 1), which might be attributed to the nature of the substituents on the phenolate group. It seems that the electronic effect of the substituent groups at both the *para* and the *ortho* positions of the phenolate plays a significant role. The catalytic activity of these catalyst systems increases first with the increase in polymerization temperature from 20 to 80 °C and begins to decrease with further increasing the polymerization temperature. The catalytic activity also increases with the increase in monomer concentration, which is similar to the previously reported results obtained with ($^tBuNSiMe_2Flu)TiMe_2$ as catalyst [17]. The molecular weight of the obtained polymers decreases with increasing the polymerization temperature, while the

Table 1
Results of norbornene polymerization with **1**–**3**/$Al^{i}Bu_3/Ph_3CB(C_6F_5)_4$[a]

Run	Catalyst	T (°C)	Concentration (mol/l)	Yields (g)	Conversion[b] (%)	Activity ($kg\,mol^{-1}\,h^{-1}$)	M_η[c] ($\times10^{-3}$)
1	**1**	20	2	2.59	28	863	25
2	**1**	40	2	2.68	29	894	25
3	**1**	60	2	2.92	31	972	25
4	**1**	80	1	2.12	45	706	21
5	**1**	80	2	3.86	41	1286	24
6	**1**	80	3	5.51	39	1835	47
7	**1**	80	4	6.78	36	2259	91
8	**1**	80	5	8.12	35	2706	155
9	**1**	100	2	3.77	40	1255	19
10	**2**	20	2	2.35	25	784	27
11	**2**	40	2	2.49	27	831	25
12	**2**	60	2	2.73	29	910	21
13	**2**	80	2	3.62	39	1208	20
14	**2**	100	2	3.34	36	1114	20
15	**3**	20	2	1.60	17	533	17
16	**3**	40	2	1.93	21	643	16
17	**3**	60	2	2.21	24	737	17
18	**3**	80	2	2.59	28	863	16
19	**3**	100	2	2.35	25	784	15

[a] Polymerization conditions: catalyst = 1 μmol; Al/Ti = 120; B/Ti = 1.2, solvent = toluene, total volume = 50 ml, polymerization time = 3 h.

[b] conversion was calculated by the weight of polymer fraction to monomer weight.

[c] Intrinsic viscosity measured at 135 °C in decahydronaphthalene, M_η calculated according to the following formula $[\eta] = 1.85\times10^{-4}M_\eta^{0.757}$.

polymer yield and the norbornene conversion increase with the increase in polymerization temperature. Under similar conditions, the increase in monomer concentration results in an increase in the polymer yield and a decrease in the monomer conversion. The molecular weight of the polymers also increases with the increase in the monomer concentration.

^{13}C NMR analysis indicates that the polynorbornene is formed via vinyl addition polymerization [17]. The ^{13}C NMR spectrum of a typical sample is shown in Fig. 2. There are several groups of signals in the range from 28 to 55 ppm, which come from norbornene units with different stereochemical environments in the polymer chain. By comparing the spectrum with the one reported in literature, the main peaks can be assigned to four groups: C5/6 (29.5–33.5 ppm), C7 (35–38.5 ppm), C1/4 (38.5–44 ppm), and C2/3 (47.5–55 ppm). All polynorbornene samples exhibit similar IR spectra. The absence of IR absorption in the range from 1680 to 1620 cm^{-1} indicates no double bond in the polymer chain, which further proves that the polynorbornene is produced from the vinyl addition polymerization and not the ring-opening metathesis polymerization [18]. DSC analysis of the polynorbornene samples shows no endothermic signal upon heating to the decomposition temperature (450 °C).

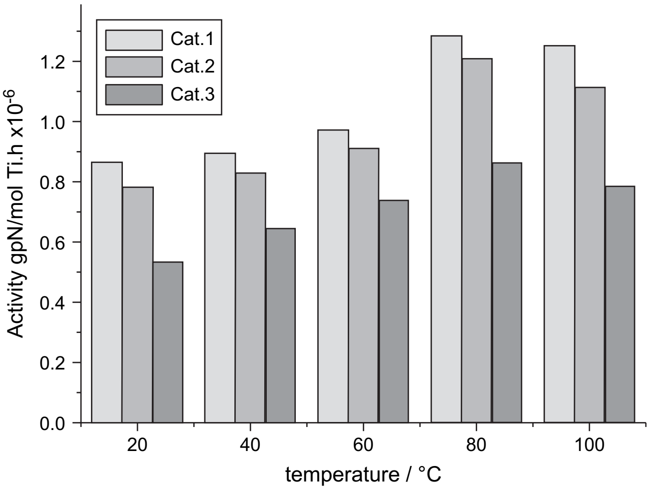

Fig. 1. The effect of temperature on the catalytic activity of norbornene polymerization. Polymerization conditions: catalyst = 1 μmol, Al/Ti = 120, B/Ti = 1.2, Al = $Al^{i}Bu_3$, B = $Ph_3CB(C_6F_5)_4$, solvent = toluene, total volume = 50 ml, polymerization time = 3 h.

3.2. Ethylene/norbornene copolymerization

Complexes **1**–**3** all can catalyze the copolymerization of norbornene with ethylene in the presence of $Al^{i}Bu_3$/$Ph_3CB(C_6F_5)_4$. It was studied in detail and the results are summarized in Table 2. As seen for the homopolymerization, the catalytic activity for the copolymerization under similar conditions is also in the order of **1** > **2** > **3**, which should mainly owe to the electronic effect of the substituent groups on the phenolate [19]. In order to optimize the reaction conditions, the copolymerization experiments from 30 to 90 °C using complex **1** were carried out at a fixed norbornene concentration and Al/Ti molar ratio. Experimental results indicate that the catalytic activity is sensitive to the reaction temperature, which is similar to the systems with $[Me(H)C(C_5H_4)(2,5\text{-}Me_2C_5H_2)]ZrCl_2$ or $[Pr(H)C(C_5H_4)(2,5\text{-}Me_2C_5H_2)]ZrCl_2$ as catalyst [10a]. The catalytic activity increases dramatically from 30 to 70 °C and reaches the highest value at about 70 °C. Further increase in the polymerization temperature results in a decrease in the catalytic activity. The molecular weight of the copolymers produced from these reactions also

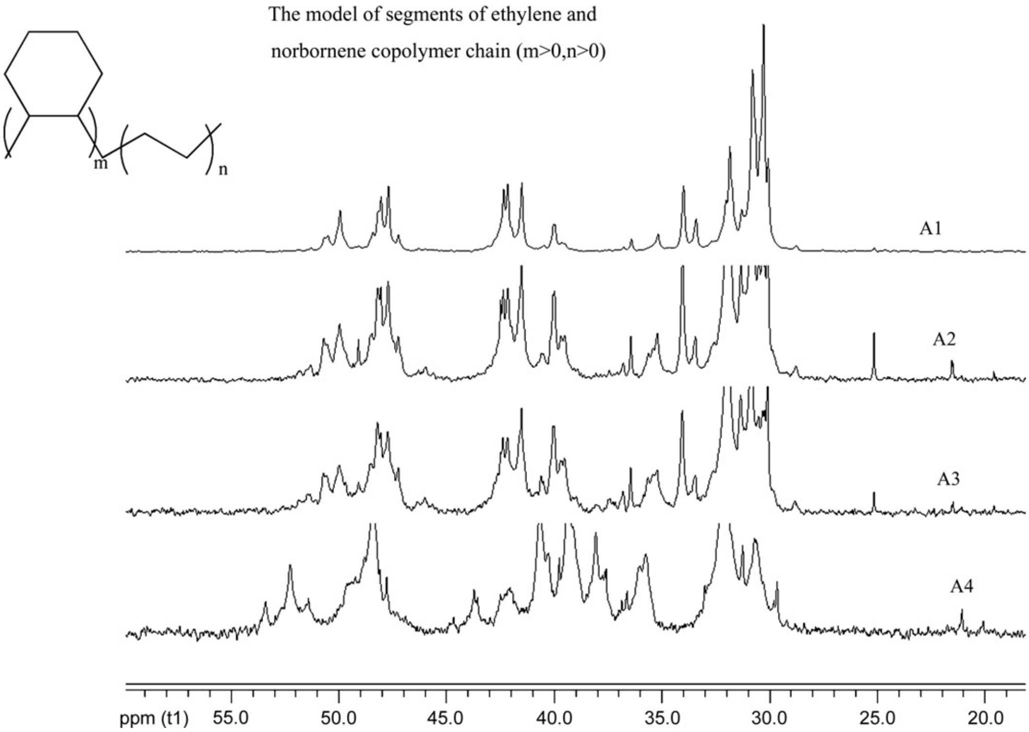

Fig. 2. The ^{13}C NMR spectra of the typical samples from E–N copolymers and norbornene homopolymer. A1: ^{13}C NMR spectrum of copolymer for Run 11; A2: ^{13}C NMR spectrum of copolymer for Run 12; A3: ^{13}C NMR spectrum of copolymer for Run 13; A4: ^{13}C NMR spectrum of homopolymer.

increases with the increase in polymerization temperature and reaches the highest point at about 50 °C. The glass transition temperature (T_g) of the copolymers increases with the polymerization temperature too since the incorporation of norbornene in the copolymer increases with the increase in polymerization temperature due to the decrease in the concentration of ethylene. The effect of the Al/Ti molar ratio on the copolymerization reaction was examined in a range from 60 to 150. As seen from Table 2, no polymer was obtained with an Al/Ti molar ratio of 60, which is obviously due to that the impurities in the reaction system cannot be effectively cleaned at this Al/Ti molar radio [20]. The catalytic activity increases first with the increase in the Al/Ti molar ratio and reaches the maximum with the Al/Ti ratio of about 120. Further increase in the Al/Ti molar ratio results in a decrease in the catalytic activity. Similar result has been observed previously [19].

The effect of the monomer concentrations on the copolymerization reaction was also investigated. Copolymerization experiments under 5 atm of ethylene with different norbornene feed concentrations were carried out and obvious comonomer effect was observed. The catalytic activity increases with the increase in norbornene concentration and reaches the highest value with the norbornene concentration being 1 M. Further increase in the norbornene concentration leads to a decrease in the catalytic activity. The molecular weight of the copolymer changes with the norbornene concentration in similar way. The incorporation of norbornene in the polymer chain, which was calculated according to a literature method [21], also increases with increasing the norbornene feed concentration in similar way to the system with $[(\mathrm{Ph})\mathrm{NC}(\mathrm{R}_2)\mathrm{C}(\mathrm{H})\mathrm{C}(\mathrm{R}_1)\mathrm{O}]_2\mathrm{TiCl}_2$ as catalyst [7]. The T_g of the copolymers also increases from 37.5 to 133.3 °C with the increase in the norbornene concentration from 0.5 to 5 M. The effect of ethylene pressure on the copolymerization reaction was also examined by keeping the norbornene concentration constant (5 M) and changing the ethylene pressure from 5 to 1 atm. It was found that the incorporation of norbornene in the copolymers increases from 57% (5 atm ethylene) to 85% (1 atm ethylene). The T_g of the copolymers also increases with the decrease in the ethylene pressure, while the molecular weight of the copolymers decreases at the same time. Our results indicate that E–N copolymers with different norbornene contents, especially copolymers with high norbornene contents (>50%), can be easily obtained with complexes **1–3** as catalysts by modulating the ratio of norbornene to ethylene. These results make these catalysts quite different from the nitrogen-containing constrained geometry titanium catalysts $[\mathrm{Me}_2\mathrm{Si}(\mathrm{Cp}')(\mathrm{N}^t\mathrm{Bu})]\mathrm{TiCl}_2$ ($\mathrm{Cp}' = \mathrm{Me}_4\mathrm{Cp}$, 2,4-$\mathrm{Me}_2\mathrm{Cp}$, 3-$^t\mathrm{BuCp}$, Ind), which can only produce E–N copolymers with less than 46 mol% norbornene incorporation [11]. The reason for the ability of complexes **1–3** to produce E–N copolymers with high norbornene incorporation may be resulted from the more open coordination environment of these catalysts. The ethylene/norbornene reactivity ratios (r_E and r_N) for the catalyst **1**/$\mathrm{Al}^i\mathrm{Bu}_3/\mathrm{Ph}_3\mathrm{CB}(\mathrm{C}_6\mathrm{F}_5)_4$ were calculated according to the Fineman–Ross method [22] (Fig. 3). The obtained monomer reactivity ratios of r_E and r_N are 1.18 and 0.08, respectively, with the product of reactivity ratio $r_E r_N = 0.094$. The r_E is smaller while the r_N is larger compared to the results reported in the literature [8,11,15,23]. The reactivity ratios

Table 2
Results of E–N copolymerization with **1**–**3**/Al^{i}Bu$_3$/Ph$_3$CB(C$_6$F$_5$)$_4$[a]

Run	Catalyst	T (°C)	C_N/P_{eth}[b]	Al/Ti	Yields (g)	Activity (kg mmol^{-1} h^{-1})	Incorp[c] (%)	M_η[d] ($\times10^{-3}$)	M_w[e] ($\times10^{-3}$)	M_w/M_n[e]	T_g[f] (°C)
1	**1**	30	1/5	120	2.83	5.66	n.d[g]	350	n.d	n.d	57.4
2	**1**	50	1/5	120	3.43	6.86	n.d	492	n.d	n.d	67.5
3	**1**	70	1/5	120	4.45	8.90	19.8	453	583	3.09	76.2
4	**1**	90	1/5	120	4.06	8.12	n.d	319	n.d	n.d	80.4
5	**1**	70	1/5	60	0	0	0	0	0	0	0
6	**1**	70	1/5	90	1.28	2.56	n.d	450	n.d	n.d	n.d
7	**1**	70	1/5	150	2.65	5.30	n.d	447	n.d	n.d	n.d
8	**1**	70	0/5	120	2.61	5.22	0	110	n.d	n.d	n.d
9	**1**	70	0.5/5	120	3.73	7.46	7.9	384	442	3.25	37.5
10	**1**	70	3/5	120	4.11	8.22	38	376	383	2.65	94.3
11	**1**	70	5/5	120	3.34	6.68	57	342	369	2.93	133.3
12	**1**	70	5/3	120	2.99	5.98	72	224	273	2.93	163.3
13	**1**	70	5/1	120	1.92	3.84	85[h]	82	92	2.32	194.3
14	**2**	30	1/5	120	2.28	4.56	n.d	344	n.d	n.d	n.d
15	**2**	70	1/5	120	3.70	7.40	n.d	438	n.d	n.d	n.d
16	**3**	30	1/5	120	1.83	3.66	n.d	277	n.d	n.d	n.d
17	**3**	70	1/5	120	2.89	5.78	n.d	324	n.d	n.d	n.d

[a] Polymerization conditions: catalyst = 1 μmol, B/Ti = 1.2, solvent = toluene, total volume = 80 ml, polymerization time = 0.5 h.

[b] C_N = concentration of norbornene (mol/l), P_{eth} = pressure of ethylene (atm).

[c] Incorporation of norbornene calculated by ^{13}C NMR with the following formula [20] $f_{(N)} = [N]/([N]+[E]) = (1/3(I_{C1}+I_{C2}+2I_{C7}))/I_{CH_2}$.

[d] Intrinsic viscosity measured at 135 °C in decahydronaphthalene, M_η calculated according to the following formula $[\eta] = 1.85\times10^{-4}M_\eta^{0.757}$.

[e] Weight-average molecular weight and molecular weight distributions were measured by GPC using polystyrene standard.

[f] T_g measured by DSC measurement.

[g] Not tested.

[h] For the C7 signal overlaps with the methylene signal in ^{13}C NMR spectrum, the integration of C7 signal was estimated as the average of C1–C4 integrations.

indicate that the coordination and insertion velocity of norbornene are relatively high in our catalyst system compared to most of other catalyst systems which leads to the high norbornene incorporation in the copolymer chains.

The ^{13}C NMR spectra of some typical E–N copolymer samples are shown in Fig. 2. These ^{13}C NMR spectra are similar to those reported in literature for E–N copolymers produced by *rac*-Et(indenyl)$_2$ZrCl$_2$ [24]. The main peaks can be assigned to the resonances of the tertiary carbons C2/C3 between 45 and 55 ppm, C1/C4 between 38 and 44 ppm, C7 between 32 and 37 ppm, and C5/C6 as well as methylenes of ethylene units below 31.5 ppm. The ^{13}C NMR spectrum with lower norbornene content is relatively simple since the norbornene units in the polymer chains are mainly isolated EENEE with only a few of alternating sequences ENENE and no ENNE and ENNNE sequences. With the increase in the norbornene incorporation, the ^{13}C NMR spectrum becomes complex with the appearance of signals at 19.17, 20.04, 21.59, 25.19 and 46.34 ppm in the spectra of A1–A3 for NENEN, ENNE, ENNNE and longer norbornene sequences in the polymer chains [7]. The peak at 39.54 ppm can be assigned to the C1/C4 signal of the racemic alternating sequence, whereas the peaks at 39.9 and 40.04 ppm can be assigned to signals of the same carbon atoms in the isotactic alternating sequences NENEE and NENEN [6]. The C2/C3 signal of the racemic alternating sequence appears at 45.21 ppm whereas the signals for the same carbon atoms in the *meso* alternating sequence appear at 45.73 and 45.82 ppm [6]. The signals at 38.94 ppm can be assigned to C1/C4 carbons of ENNNE and longer norbornene sequences [24].

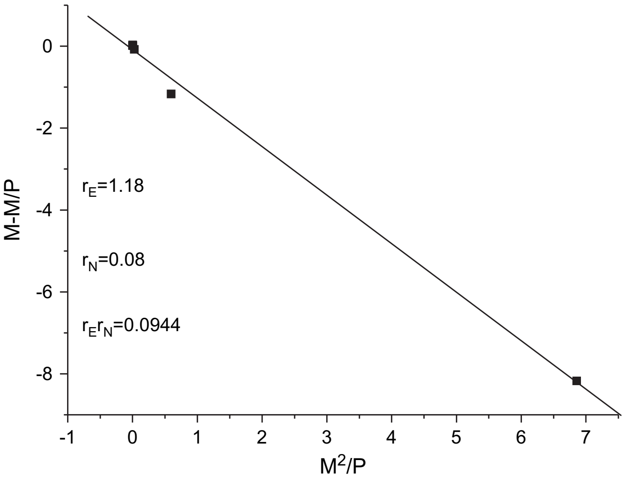

Fig. 3. Fineman–Ross plot of E–N copolymers obtained with **1**/Al^{i}Bu$_3$/Ph$_3$CB(C$_6$F$_5$)$_4$.

The GPC analysis reveals that the obtained copolymer samples possess high molecular weights and normal molecular weight distributions (M_w/M_n = 2.32–3.25). The DSC analysis of the copolymer samples indicates that the copolymers with wide range of T_g values have been obtained, and the T_g increases with the increase in norbornene incorporation in copolymers [25].

4. Conclusion

Upon activation with Al^{i}Bu$_3$/Ph$_3$CB(C$_6$F$_5$)$_4$, complexes **1**–**3** all can catalyze the norbornene homopolymerization and ethylene/norbornene copolymerization with high activity and produce high molecular weight polymers. The order of catalytic activity for norbornene polymerization and ethylene/norbornene copolymerization under similar conditions is **1** > **2** > **3**. ^{13}C NMR analysis of the norbornene polymers indicates that the norbornene homopolymerization is vinyl addition polymerization and not ring-opening metathesis polymerization. For the ethylene/norbornene copolymerization, obvious comonomer effect was observed. The norbornene incorporation was found to increase with the increase in temperature and the ratio of norbornene to ethylene in the feed. E–N copolymers with high norbornene incorporation (>50%) can be easily obtained by increasing the norbornene feed concentration.

Acknowledgments

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