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Copolymerization of Norbornene and Styrene with Anilinonaphthoquinone-Ligated Nickel Complexes

Samiul Islam Chowdhury, **Ryo Tanaka**, **Yuushou Nakayama** and **Takeshi Shiono** *

Graduate School of Engineering, Hiroshima University, Hiroshima 739-8527, Japan
* Correspondence: tshiono@hiroshima-u.ac.jp; Tel.: +81-824-24-773

Abstract: Poly(norbornene-*co*-styrene)s were synthesized by the use of anilinonaphthoquinone-ligated nickel complexes [Ni($C_{10}H_5O_2$NAr)(Ph)(PPh_3): **1a**, Ar = C_6H_3-2,6-^{i}Pr; **1b**, Ar = C_6H_2-2,4,6-Me; **1c**, Ar = C_6H_5] activated with modified methylaluminoxane (MMAO) or $B(C_6F_5)_3$ in toluene. The effects of the cocatalysts were more significant than those of the nickel complexes, and MMAO gave higher activity than $B(C_6F_5)_3$. The structural characterizations of the products indicated the formation of statistical norbornene copolymers. An increase of the styrene ratio in feed led to an increase in the incorporated styrene (S) content of the resulting copolymer. The molecular weight of the copolymer decreased with increasing the S ratio in feed at 70 °C. The copolymerization activity, using MMAO as a cocatalyst, decreased with lowering of the temperature from 70 to 0 °C, accompanied by an increase in the molecular weight of the copolymer. The S incorporation up to 59% with M_n of 78,000 was achieved by the **1b**-$B(C_6F_5)_3$ catalytic system. The glass transition temperatures of the norbornene (N)/S copolymers determined by differential scanning calorimetry, decreased from 329 to 128 °C according to the S content.

Keywords: nickel catalyst; copolymerization; norbornene; styrene

1. Introduction

The polymerization of cycloolefins such as norbornene (N) has been one of the key developments in the area of polymer chemistry because of its vast range of applications [1–3]. There are three types of mechanism for polymerization of N, which are ring-opening metathesis polymerization (ROMP) [4,5], cationic or radical polymerization [6–9], and coordination–insertion polymerization [10–12]. Each route of the polymerization leads to the polymers with different structures and properties. Polynorbornenes (PNBs) produced by coordination–insertion polymerization show excellent physical properties, such as good heat and chemical resistance, high decomposition temperature, high optical transparency, and low dielectric constant [13,14], but exhibit some negative properties such as brittleness and glass transition temperature (T_g) close to the decomposition temperature due to the presence of a rigid ring in the polymer chain.

The inferior properties of PNBs can be improved in cyclic olefin copolymers (COCs). The most representative COC is a copolymer of N and ethylene (E) [15]. The properties of COCs can be easily controlled by a kind of comonomer, comonomer content, and sequence distribution. Copolymerization of N with 1-alkene was also reported to modify the physical properties [16–24]. The introduction of styrene (S) should decrease the *birefringence* of COCs [25] because PNB and polystyrene possess positive and negative *birefringence,* respectively. Several examples of the copolymerization of N with S have been reported. The first N/S copolymerization was achieved by Ni-based catalysts using methylaluminoxane (MAO) as a cocatalyst [26]. Afterwards, some nickel and copper catalysts were used to synthesize N/S copolymers [27–33]. The S incorporation was improved by β-diketiminato nickel complexes [34]. The highest S incorporation was 52.4%, with the highest S feed ratio of 83%, but the M_w value was

around 10^3. Recently, bis(β-ketoamino) copper complexes were used for copolymerization of N and S, whereas the results were almost the same as those of β-diketiminato nickel complexes [35].

We have also reported N/S copolymerization by an *ansa*-fluorenylamidodimethyltitanium-based catalyst and shown the potentiality of the copolymer as a plastic substrate for flexible display materials [25]. However, the maximum S incorporation in the N/S copolymer with sufficient molecular weight was approximately 5 mol %. We have synthesized N/E/S terpolymer by using the same catalyst and obtained a zero-*birefringence* terpolymer with the S content of 12%, but the introduction of E unit (58 mol %) caused a significant drop of the T_g to 86 °C [36].

Therefore, we are interested in the copolymerization of N with S to obtain high molecular weight copolymers with controlled S content. We have previously reported that anilinonaphthoquinone-ligated nickel complexes activated with $B(C_6F_5)_3$ as a cocatalyst exhibit high activity for N polymerization to give high molecular weight polymer soluble in cyclohexane [37]. In the present paper, we report the N/S copolymerization using nickel complexes $[Ni(C_{10}H_5O_2NAr)(Ph)(PPh_3)$: **1a**, Ar = C_6H_3-2,6-^{i}Pr; **1b**, Ar = C_6H_2-2,4,6-Me; **1c**, Ar = C_6H_5], where **1c** was newly synthesized in this work, in the presence of modified MAO (MMAO) or $B(C_6F_5)_3$ (Figure 1).
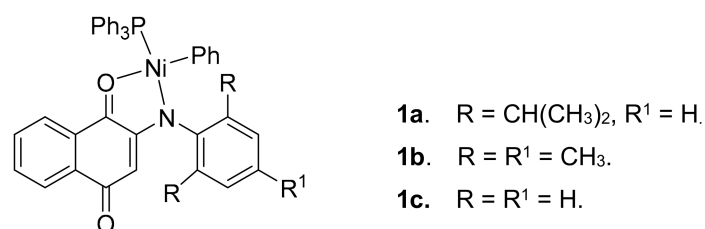

1a. R = $CH(CH_3)_2$, R^1 = H.
1b. R = R^1 = CH_3.
1c. R = R^1 = H.

Figure 1. Anilinonaphthoquinone-ligated nickel complexes used in this study.

2. Materials and Methods

2.1. Materials

All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques. All solvents were refluxed and distilled over sodium/benzophenone or calcium hydride. Norbornene was purified by stirring it over calcium hydride at 60 °C for one day, and then distilled. The stock solution of N (5.5 M) was prepared in toluene. Styrene (Wako Chemical Co. Ltd., Odawara, Japan) was dried over CaH_2, and then freshly distilled under vacuum prior to use. Modified methylaluminoxane (MMAO) solution (6.6 wt % in toluene) and toluene solution of $B(C_6F_5)_3$ were donated from Tosoh Finechem. Co. (Tokyo, Japan) and used as received. The nickel complexes **1a,1b** were synthesized according to the literature and the references therein [38,39]. The complex **1c** was synthesized using a similar procedure to that for **1a** and **1b** (Supporting Information).

2.2. Analytical Procedure

Molecular weights and molecular weight distributions of polymers were determined by gel permeation chromatography (GPC) with a Viscotec HT-350 GPC (Malvern, Great Malvern, UK) with one guard column and two 30 cm columns. This system was equipped with a triple-detection array consisting of a differential refractive index (DRI) detector, a two-angle (7, 90) light scattering (LS) detector, and a four-bridge capillary viscosity detector. Polymer characterization was carried out at 150 °C using *o*-dichlorobenzene as an eluent, and calibrated with polystyrene standards. The ^1H and ^{13}C NMR spectra of polymers were measured at room temperature on a Bruker 500M Hz instrument (Bruker, Rheinstetten, Germany) operated by the pulse Fourier-transform mode. Sample solution of ^{13}C NMR was prepared in $CDCl_3$ up to 10 wt %, and the pulse angle was 45°, and about 8000–10,000 scans were accumulated in pulse repetition of 5.0 s. The central peak of $CDCl_3$ (7.13 ppm for ^1H and 77.13 ppm for ^{13}C NMR) was used as an internal reference. Differential scanning calorimetry (DSC) was performed on a SII EXSTER 600 system (Seiko Instruments Inc., Chiba, Japan) under nitrogen

atmosphere. Thermal history difference in the polymers was eliminated by first heating the specimen to 380 °C, cooling from 10 to 20 °C/min, and then recording the second DSC scan at a heating rate of 10 °C/min.

2.3. Copolymerization of N and S

In a typical procedure, prescribed amounts of N and S in toluene solution were introduced into a 100 mL round-bottomed glass flask. Then, the cocatalyst (0.24 mL 500 μmol of MMAO toluene solution or 1 mL 20 μmol of $B(C_6F_5)_3$ toluene solution) and 1 mL of the nickel complex (5 μmol) solution in toluene were syringed into the well-stirred monomer solution in this order, and the total solution volume was made up to 25 mL by adding toluene. The copolymerization was conducted under continuous stirring for a required time under a certain temperature as controlled using an external oil or ice bath. The copolymerization was terminated by adding 300 mL of acidic methanol (methanol/concentrated hydrochloric acid, 95: 5 in volume). The resulting precipitated polymer was collected by filtration, adequately washed with methanol, and dried in vacuum at 60 °C for 6 h.

3. Results and Discussion

3.1. Homopolymerization of N and S

Homopolymerizations of N and S were performed using **1**-MMAO at 70 °C in toluene. The results are shown in Table 1. In the N polymerization, complex **1a** displayed the highest activity, and gave the polymer with the highest molecular weight among the complexes used. The opposite trends were observed in S polymerization, but the differences were not significant.

Table 1. Effects of monomer ratio of norbornene (N)/styrene (S) copolymerization by **1**-MMAO.

Run	N/S [a] (mmol/mmol)	Complex	Yield (g)	Act. [b]	f_S [c] (mol%)	M_n (10^3)	M_w/M_n [d]	N [e] (μmol)
1	40/00	1a	1.10	220	0	470	1.9	2.3
2	40/10	1a	0.36	72	4	19	2.4	18.9
3	40/40	1a	0.65	130	16	6	2.5	108.3
4	00/40	1a	0.52	104	100	11	1.5	47.2
5	40/00	1b	0.54	107	0	266	2.2	2.0
6	40/10	1b	0.37	74	4	19	2.7	19.5
7	40/20	1b	0.31	62	8	12	1.7	25.8
8	40/30	1b	0.30	60	12	9	3.0	33.3
9	40/40	1b	0.44	88	19	8	2.9	55.0
10	00/40	1b	0.65	130	100	12	1.6	54.2
11	40/00	1c	0.58	115	0	309	1.6	1.9
12	40/10	1c	0.36	72	10	13	2.0	27.7
13	40/20	1c	0.32	64	16	10	1.5	32.0
14	40/30	1c	0.31	62	19	8	1.9	38.6
15	40/40	1c	0.40	80	36	7	3.0	57.1
16	00/40	1c	0.65	130	100	14	1.7	46.4

Copolymerization conditions: Ni = 5 μmol, temperature = 70 °C, time = 1 h, Al/Ni = 100 (molar ratio), toluene (total volume 25 mL). [a] Norbornene and styrene in feed. [b] Activity = $kg_{(polymer)}mol_{(Ni)}^{-1} h^{-1}$. [c] f_S is the content of S in the N/S copolymer determining by ^1H NMR spectrum. [d] Determined by GPC. [e] Number of polymer chains determined from yield and M_n.

3.2. Copolymerization of N and S

Copolymerizations of N with S were then conducted under the same conditions by changing S in feed from 10 to 40 mmol, with 40 mmol of N (Scheme 1).
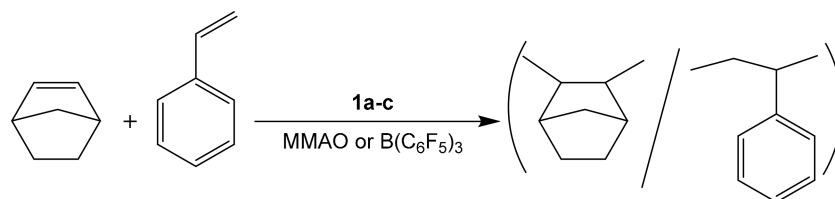
Scheme 1. N/S copolymerization with Ni catalyst.

The results are summarized in Table 1. The nickel complexes showed moderate activity for N/S copolymerization. The N/S feed ratio did not significantly affect the catalytic activity, and all the complexes showed lower activity in the copolymerizations than in homopolymerizations. The low activity in the copolymerization could be ascribed to slow cross-propagation because of the steric hindrance between these comonomers. Complex **1a**, which showed the highest activity in N polymerization, also showed the highest activity in N/S copolymerization among the complexes used (Table 1, Run 3).

The N/S copolymers were not only soluble in chloroform, but also in cyclohexane, similar to the PNB obtained by the same catalytic system. The incorporation of S in the produced copolymers was investigated by ^{1}H NMR in CDCl$_3$. A typical ^{1}H NMR spectrum of the copolymer (Run 15) is illustrated in Figure 2i. No resonances are observed from 5.0 to 6.0 ppm, which is assigned to the vinylene protons of the polymer obtained via ring-opening metathesis polymerization (ROMP) [40].
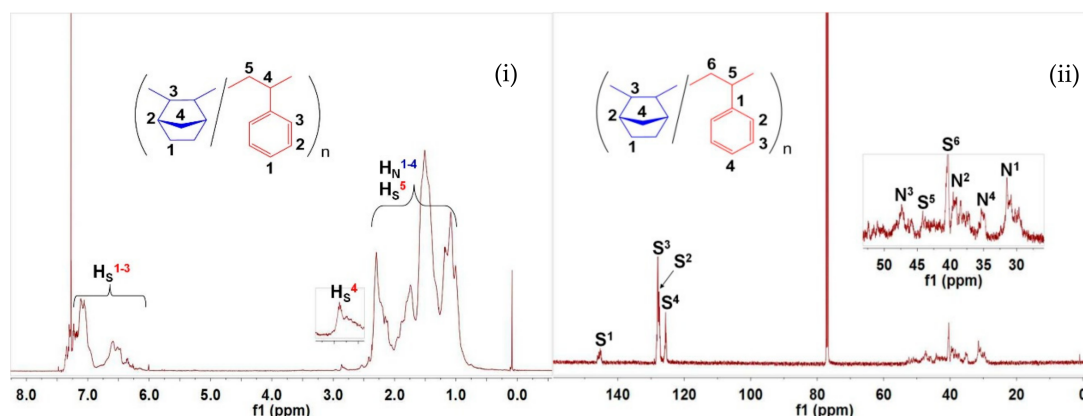

Figure 2. ^{1}H NMR (**i**) and ^{13}C NMR (**ii**) spectra of N/S copolymer obtained by Run 15 (CDCl$_3$, rt, 500 MHz).

The signals assignable to the aliphatic protons of the N and S units (H$_N^{1-4}$ and H$_S^5$) are observed in the range of 0.8–2.4 ppm. The signals attributed to the aromatic protons of the S units (H$_S^{1-3}$) are observed in the range of 6.5–7.1 ppm. Particularly, the signal of the methine proton of the S unit (H$_S^4$) adjacent to the N unit can be observed at 2.85 ppm. The ^{1}H NMR spectra of the polymers obtained under the highest styrene concentration (Table 1, Run 3, 9 and 15) are shown in Supplementary Figure S5.

A typical ^{13}C NMR spectrum of the copolymer (Run 15) is shown in Figure 2ii. According to the reported assignment of the N/S copolymer, [34] the signals of each chemical shift region were assigned as follows: 145.7 ppm for C^1, 127.3 ppm for C^2, 127.9 ppm for C^3, 125.6 for C^4, 41.5–44.2, and 40.5 ppm for C^5 and C^6 of the S segment, 47.1–52.5 ppm for C^3, 38–39.7 ppm for C^2, 34.5–37 ppm for C^4, and 29.4–31.9 ppm for C^1 of the N unit. A clear observation of the phenyl-carbons of the S units in the regions of 125–145 ppm also indicates the presence of the S units in the N/S copolymer. These results are similar to those obtained in the previously reported nickel–MAO catalytic system and confirm the random distribution of S unit in the obtained N/S copolymer [34].

The incorporation of S increased with increasing S concentration in the monomer feed ratio. The highest S content in the N/S copolymer was achieved to be 36% at 1:1 feed ratio by complex **1c** probably because of less interaction between the ligand substituent and the aromatic ring of S.

The molecular weight of N/S copolymer was measured by GPC. The increase of S concentration in feed caused the decrease in the molecular weights of the produced polymers accompanied by the increase in the number of polymer chains, which is ascribed to β-hydrogen elimination of the increased styryl propagation end [41]. Unimodal distribution ($M_w/M_n \approx 2$) indicates that the copolymerization should take place at a single active site (Supplementary Figure S6).

3.3. Effect of Polymerization Temperature on N/S Copolymerization:

The influence of reaction temperature on N/S copolymerization was studied using **1**-MMAO at the fixed feeding ratio (N/S = 4:1 in molar ratio), because the low S feed ratio gave high molecular weight N/S copolymer. The results are summarized in Table 2.

Table 2. Effects of temperature of N/S copolymerization by **1**-MMAO.

Run	Complex	Temperature (°C)	Yield (g)	Activity [a]	f_S [b] (mol%)	M_n [c] (10^3)	M_w/M_n [c]	T_g [d]
2	1a	70	0.36	72	4	19	2.4	321
17	1a	50	0.27	54	7	26	2.2	289
18	1a	30	0.14	28	9	27	2.0	267
19	1a	0	0.13	26	20	55	2.1	219
6	1b	70	0.37	74	4	19	2.7	329
20	1b	50	0.27	54	9	24	2.2	263
21	1b	30	0.20	40	12	27	2.3	252
22	1b	0	0.11	22	30	57	1.5	175
12	1c	70	0.36	72	10	13	2.0	251
23	1c	50	0.29	58	16	18	2.2	227
24	1c	30	0.24	48	21	54	1.5	212
25	1c	0	0.14	27	32	61	1.5	172

Copolymerization conditions: Ni = 5 μmol, Al/Ni = 100 (molar ratio), N/S = 4:1 (molar ratio), toluene (total volume 25 mL) time 1 h. [a] Activity = $kg_{(polymer)}mol_{(Ni)}^{-1} h^{-1}$. [b] f_S is the content of S in the N/S copolymer determining by ^{1}H NMR spectrum. [c] Determined by GPC. [d] Determined by DSC.

The copolymerization activity decreased with lowering the temperature from 70 to 0 °C. The highest activity around 70 kg polymer/(mol Ni h) for the copolymerization was achieved at 70 °C in each system. On the other hand, the S content and the M_n value monotonously increased with lowering of the polymerization temperature (Supplementary Figure S7), and the N/S copolymer with 32 mol % of S and 61,000 of M_n was obtained at 0 °C by **1c**-MMAO (Table 2, Run 25, Figure 3i). This M_n value would be the highest among the N/S copolymers reported so far [25,34,35]. The molecular weight distribution became narrow with decreasing the polymerization temperature. A decreased M_n value of the copolymers obtained with an increase in the reaction temperature is ascribed to the chain transfer at high temperature [32].

The T_g values of N/S copolymers were analyzed by DSC. The T_g value declined with an increase of S content as shown in Figure 3ii. The highest value of 329 °C (Supplementary Figure S8), and the lowest value of 172 °C, were detected for the copolymers with 4 and 32 mol % of S, respectively (Table 2, Run 6 and 25). A previous study has shown that the T_g value of the PNBs obtained with this catalyst was over 400 °C [37]. The T_g value of polystyrene is 100 °C. The single T_g value in the DSC curves reveal that N and S were uniformly distributed in the N/S copolymers obtained by the present catalysts.
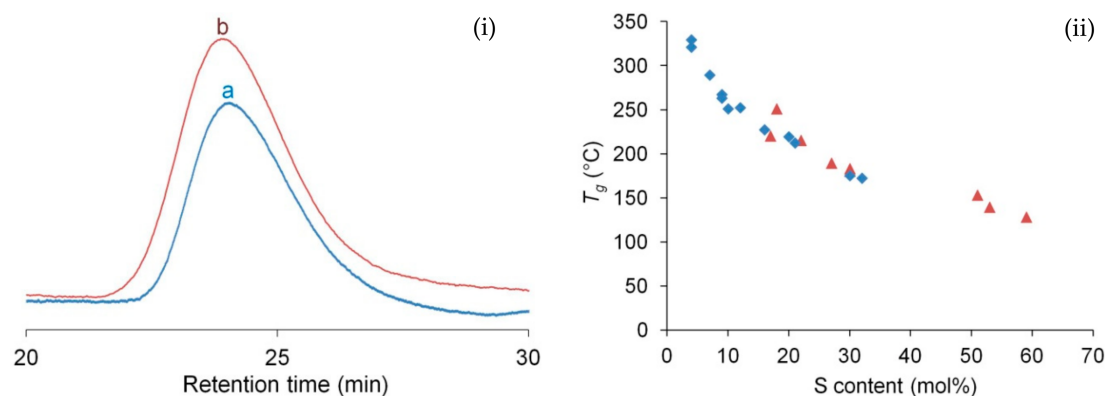
Figure 3. (**i**) GPC traces of N/S copolymers: **a**, Run 24; **b**, Run 25 (**ii**) S content versus T_g plot obtained by Ni complexes: ◆, MMAO; ▲, B(C₆F₅)₃.

3.4. N/S Copolymerization by 1-B(C₆F₅)₃:

We found the considerable effects of temperature on N/S copolymerization using the **1**-MMAO system. We observed significant effects of B(C₆F₅)₃ in E polymerization [38] and N polymerization [37] with **1a**, which were ascribed to the formation of zwitterionic nickel species [39].

Thus, the N/S copolymerization (N/S = 4:1 in molar ratio) by the **1**-B(C₆F₅)₃ system, was conducted at different temperatures (30, 50, and 70 °C) to investigate the cocatalyst effect.

The activity of the B(C₆F₅)₃ system was lower than that of the MMAO system. The incorporation of S increased with lowering the temperature, as was observed in the **1**-MMAO system. The S incorporation was almost four times higher than those of the copolymers produced by the **1**-MMAO system. The highest S incorporation was observed at 30 °C (Supplementary Figure S9), 51~59% with the M_n values (Supplementary Figure S10) of 43,000~78,000 (Table 3, Run 28, 31, and 34).

Table 3. Effects of temperature of N/S copolymers by **1**-B(C₆F₅)₃.

Run	Complex	Temperature (°C)	Yield (g)	Activity [a]	f_S [b] (mol%)	M_n [c] (10^3)	M_w/M_n [c]	T_g [d]
26	1a	70	0.126	26	17	36	1.9	220
27	1a	50	0.072	15	22	40	1.7	215
28	1a	30	0.053	11	51	43	1.9	153
29	1b	70	0.088	18	18	38	2.0	251
30	1b	50	0.067	14	30	55	1.6	183
31	1b	30	0.033	7	59	78	1.9	128
32	1c	70	0.082	17	27	38	2.5	189
33	1c	50	0.034	7	30	39	2.1	180
34	1c	30	0.030	6	53	46	2.0	139
35[e]	1a	70	0.330	66	17	103	1.4	232

Copolymerization conditions: Ni = 5 μmol, B/Ni = 4 (molar ratio), N/S = 4:1 (molar ratio), toluene (total volume 25 mL) time = 1 h. [a] Activity = kg(polymer)mol(Ni)$^{-1}$ h^{-1}. [b] f_S is the content of S in the N/S copolymer determining by ^{1}H NMR spectrum. [c] Determined by GPC. [d] Determined by DSC. [e] B(C₆F₅)₃/^{t}BuAl/BHT = 1:10:20.

In order to evaluate the effects of the cocatalysts on N/S copolymerization, the monomer reactivity ratios of **1b** were determined at 70 °C (Supplementary Table S1). The Fineman–Ross plots of **1b**-MMAO and **1b**-B(C₆F₅)₃ for N/S copolymerization are shown in Figure 4i and 4ii, respectively. The monomer reactivity ratios were determined to be r_N = 6.34 and r_S = 0.39 for **1b**-MMAO, and r_N = 0.93 and r_S = 0.13 for **1b**-B(C₆F₅)₃, indicating the better copolymerization ability of the B(C₆F₅)₃ cocatalyst. The reactivity ratios of **1c**-MMAO were also determined to evaluate the effects of the complexes (Supplementary Figure S11). The values r_N = 2.16 and r_S = 0.26 indicate the better copolymerization ability of **1c** than **1b**.
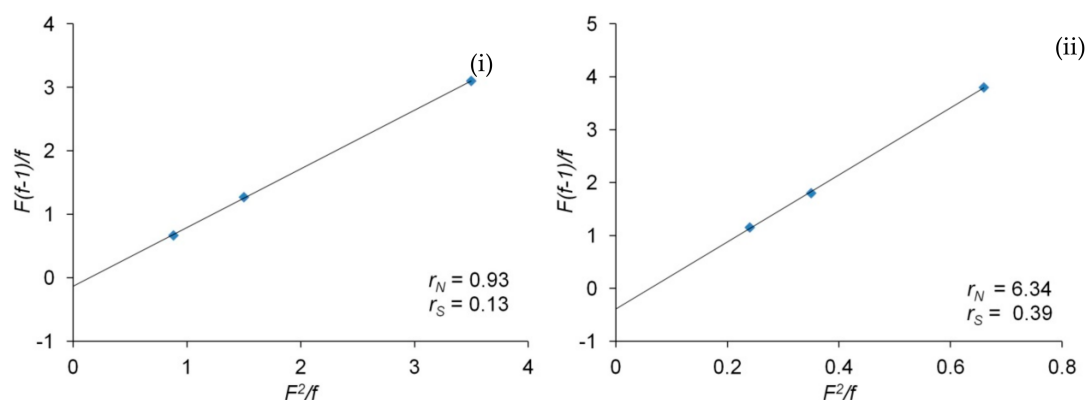
Figure 4. Fineman–Ross plots for copolymerization of N/S by **1b** with (**i**) MMAO and (**ii**) $B(C_6F_5)_3$.

The T_g values determined by DSC are shown in Table 3 and are plotted against S content in Figure 3ii. The plot is in good accordance with that of the MMAO system, but extends to the higher S content as indicated by the monomer reactivity ratios. The lowest T_g value of 128 °C (Supplementary Figure S12) was obtained by the copolymer with S content of 59 mol % and M_n of 78,000 (Table 3, Run 31). The **1**-$B(C_6F_5)_3$ system gave the copolymers with high molecular weights and high S contents, compared with the **1**-MMAO system, although the activity was low.

The lower activity would be due to the deactivation by impurities in the absence of scavenging reagents. Therefore, we conducted N/S copolymerization with **1a**-$B(C_6F_5)_3$ in the presence of the reaction mixture of $^tBu_3Al$ and 2,6-$^tBu_2$-*p*-cresol. The addition of the scavenger increased the activity, keeping the same S content and the M_n value reached 103,000 (Table 3, Run 35). The results indicate the potentiality of **1**-$B(C_6F_5)_3$ for N/S copolymerization.

3.5. Optical Property of the N/S Copolymer

The light transmittance of the N/S copolymer thin film with the thickness about 100 μm is displayed in Supplementary Figure S13 (Table 3, Run 35). The copolymer showed the transmittance above 85% in the visible light region (300–800 nm).

4. Conclusions

Copolymerizations of N and S were achieved by anilinonaphthoquinone-ligated nickel-complexes using MMAO or $B(C_6F_5)_3$ as cocatalyst. The **1**-MMAO system showed higher activity than the **1**-$B(C_6F_5)_3$ system, whereas the latter system produced the copolymers with higher molecular weight and higher styrene incorporation. The molecular weights of N/S copolymers obtained by **1**-$B(C_6F_5)_3$ were the highest among those of the copolymers reported previously using nickel-, copper-, and titanium-based catalytic systems.

Conflicts of Interest: The authors declare no conflict of interest.

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