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ORIGINAL PAPER

Copolymerization of ethylene with norbornene by using metallocene/TIBA/$B(C_6F_5)_3$ system

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ABSTRACT

Cyclic olefin copolymer is a type of high performance polyolefin material, which is prepared by using a single-site catalyst in solution polymerization. The common activator of this system is alkyl aluminoxane or organic boron/aluminum system. Among them, organic boron is mostly triphenylcarbenium tetrakis(pentafluorophenyl)borate or dimethylanilinium tetrakis(pentafluorophenyl)borate. In this study, ethylene and norbornene were copolymerized with metallocene catalyst activated with the combination of tris(pentafluorophenyl)boron and triisobutylaluminium. Compared with homopolymerization of ethylene, copolymerization shows high activity. The molecular weight of the polymer increased significantly with the increase of the insertion rate of norbornene. Fineman-Ross method was used to calculate the reactivity ratio, which showed that the reactivity ratio of norbornene was much lower than that of ethylene. The high copolymerization activity may indicate that, although norbornene has a lower coordination probability, its insertion rate is higher than ethylene. The copolymer with higher norbornene incorporation has a higher glass transition temperature, and the relationship between them is linear. **Polyolefins J (2023) 10: 71-77**

Keywords: Cyclic olefin copolymer; metallocene; norbornene; organic borate; glass transition temperature.

INTRODUCTION

In recent decades, great attention has been paid to the development of single-site catalysts represented by metallocene for olefin polymerization [1-3]. Because of the unique high efficiency of copolymerization and universality of comonomer selection of metallocene and other single-site catalyst, olefin polymer which cannot be obtained by Ziegler-Natta catalyst can be obtained by using these new generation catalysts [4]. Both the homopolymer and copolymer of cyclic olefin (COP and COC) are important examples [5-15]. The copolymerization of α-olefin and cyclic olefin is realized by coordination polymerization, and the main chain of the obtained COC contains a large number of rigid rings. Therefore, COC has the characteristics of high glass transition temperature (T_g) and non-crystallization, which makes it have excellent heat resistance, barrier,

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transparency, size stability and other properties, so it can be used in optical devices and pharmaceutical packaging. The most common COC is the copolymer of ethylene and norbornene (NBE) or tetracyclododecene (TCD), which are also components of commercial COCs. [16] The metallocene/single-site catalyst is usually used for the copolymerization of ethylene and norbornene by activation with MAO or organic boron/aluminum cocatalyst. [17-24] MAO is a very efficient cocatalyst, but it has the problem of high cost, and its high dosage will also cause the problem of high inorganic ash in the polymer. Therefore, the combination of organic boron/aluminum cocatalyst is a good choice. Among them, triphenylcarbenium tetrakis(pentafluorophenyl) borate (Ph_3C^+-$B(C_6F_5)_4^-$) [25] and dimethylanilinium tetrakis(pentafluorophenyl)borate ($PhNMe_2H^+$-$B(C_6F_5)_4^-$) [26] are most commonly used in organic boron. The simple compound, tris(pentafluorophenyl) borane ($B(C_6F_5)_3$) [27,28], is not often used. [29-31].

In the present work, copolymerization of ethylene with norbornene was conducted by using a metallocene combined with triisobutylaluminum/$B(C_6F_5)_3$. The high activity of copolymerization was observed, and the copolymer with high molecular weight and high norbornene incorporation was achieved.

EXPERIMENTAL

Materials

All experiments were carried out under a nitrogen atmosphere in a Vacuum Atmospheres drybox or using standard Schlenk techniques, unless otherwise specified. All chemicals used were of reagent grade and were purified by standard purification procedures. Toluene was distilled in the presence of sodium and benzophenone under a nitrogen atmosphere, and was stored in a Schlenk tube in the drybox over molecular sieves. Metallocene catalyst $Ph_2C(Cp)(Flu)ZrCl_2$ was purchased from APAC Pharmaceutical. Norbornene was purchased from Alfa, tris(pentafluorophenyl) borane ($B(C_6F_5)_3$) from Strem, triisobutyaluminium (TIBA) from Acros, and used as received.

Polymerization was conducted in toluene in a 250 mL glass reactor with an oil bath at 70°C. Glass reactor was purged with nitrogen and charged with an ethylene atmosphere (1 atm). Toluene, NBE solution in toluene, TIBA and the catalyst solution in toluene were introduced in this order. And then the toluene solution of tris(pentafluorophenyl)borane was injected to start the polymerization. The mixture was stirred magnetically for 20 minutes. And then the mixture was poured into EtOH (300 mL) containing HCl (10 mL). The resultant polymer was collected on a filter paper by filtration, washed thoroughly with EtOH, and was then dried in vacuo.

The molecular weight was determined by gel permeation chromatography (GPC) on a Waters Alliance GPCV2000 at 150°C with 1,2,4-trichlorobenzene as the eluent.

The glass transition temperature of the polymer was determined on TAQ 100. Approximately 2 mg of the polymer sample was heated from 25 to 200°C with a heating rate of 10°C per minute, under a nitrogen atmosphere. After keeping the temperature for 1 minute, the sample was cooled down to 25°C, and kept the temperature for 1 minute again. Then sample was heated to 200°C with a heating rate of 10°C per minute and the data was recorded.

Solution ^{13}C NMR experiments were performed on a Bruker AVANCEIII-400 MHz spectrometer with a 10 mm PASEX ^{13}C-1H/D Z-GRD probe. Sample solutions were prepared with approximately 250 mg of the polymer material dissolved in 2.5 mL of d4-o-dichrolobenzene (ODCB-d4) in a 10mm tube at 130°C. All ^{13}C NMR experiments were carried out at 125°C, 20 Hz spinning rate, 90° pulse angle, continuous Waltz-16 decoupling, 120 ppm spectral width, 5 s acquisition time, and 10 s relaxation delay.

RESULTS AND DISCUSSION

Tris(pentafluorophenyl)borane was combined with triisobutylaluminum (TIBA) to use as the cocatalyst of metallocene to copolymerize ethylene with NBE. The results are summarized in Table 1.

Under the current experimental conditions, ethylene homopolymerization gave a very low activity, which is different from the high activity of the polymerization activated by MAO. [4] Compared with the more

Table 1. Copolymerization of ethylene with norbornene by using $Ph_2C(Cp)(Flu)ZrCl_2$/TIBA/$B(C_6F_5)_3$[(a)]

Run	NBE/Et[(b)]	Yield (g)	A[(c)]	Incorpor [(d)] (mol %)	M_w[(e)] (k)	PDI[(e)]	T_g[(f)] (°C)
1	0	0.04	24	--	9.5	1.7	--
2	4.7	1.02	612	33.0	26.0	2.1	62.2
3	9.4	1.70	1020	45.0	61.1	2.0	116.6
4	14.2	1.23	738	48.3	83.1	2.2	137.3
5	18.9	1.08	648	51.0	89.0	2.2	149.7

[(a)] Catalyst $Ph_2C(Cp)(Flu)ZrCl_2$ 5 mmol, TIBA 0.5 mmol, $B(C_6F_5)_3$ 6 mmol, 70°C, 20 min, ethylene 1 atm, in toluene, total 30 mL. [(b)] molar ratio of NBE to ethylene in the liquid phase, calculated based on references [32-34], [(c)] activity in kg-polymer/mol-cat/hr. [(d)] NBE incorporation determined by using ^{13}C-NMR. [(e)] GPC data. [(f)] DSC data

commonly used organic boron, $Ph_3C^+[B(C_6F_5)_4]^-$ and $PhNMe_2H^+[B(C_6F_5)_4]^-$, $B(C_6F_5)_3$ have a worse activation efficiency for ethylene polymerization. Previous study [35] has shown that the stability of the active site formed by $B(C_6F_5)_3$ and metallocene is worse. In order to obtain better activity, a higher ratio of $B(C_6F_5)_3$ to catalyst is needed. However, the introduction of NBE significantly increased the activity, which proved the effectiveness of the system for ethylene-NBE copolymerization. However, the activity does not show a concise rule related to the feed amount of NBE. After the activity reaches a peak, the activity will decrease if the feed amount of NBE continues to increase.

The incorporation of NBE could be determined by using ^{13}C-NMR, and the incorporation of NBE was increased with the increase of NBE feed. The relationship of NBE incorporation to the molar ratio of NBE to ethylene in the liquid phase is illustrated in Figure 1.

According to the understanding of polymerization kinetics [36], the following relations can be obtained:

$$(\frac{M_2}{M_1})_P = \frac{M_2}{M_1}\frac{(1+r_2\frac{M_2}{M_1})}{(r_1+\frac{M_2}{M_1})} \quad (1)$$

where $(M_2/M_1)_P$ and M_2/M_1 are the NBE/ethylene molar ratios ([NBE]/[Et]) in the polymer and the reaction liquid phase, respectively. And r_1 and r_2 are the reactivity ratios of ethylene and NBE, respectively. Then according to the following Fineman-Ross equation, the reactivity ratios could be calculated based on the plot in Figure 2.

$$\frac{1-y}{y}\phi = r_1 - r_2\frac{\phi^2}{y} \quad (2)$$

where $y = (M_2/M_1)_P$ and $\phi = M_2/M_1$.

Results of $r_1 = 4.86$ and $r_2 = 0.017$ meant that the insertion of NBE is more different from the insertion of ethylene. However, the introduction of NBE did not decrease the polymerization activity, but increased it greatly. This may indicate that the low reactivity ratio of norbornene is only possible in the coordina-

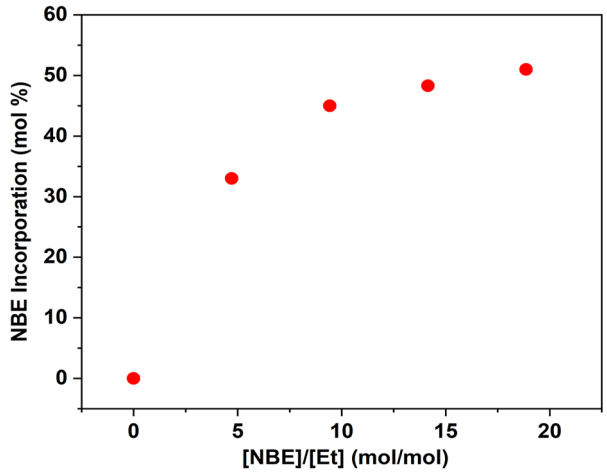

Figure 1. Copolymer composition curve.

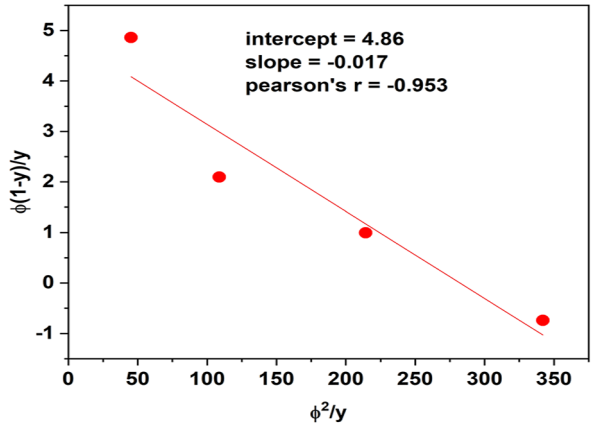

Figure 2. Fineman-Ross plot of ethylene-norbornene copolymer.

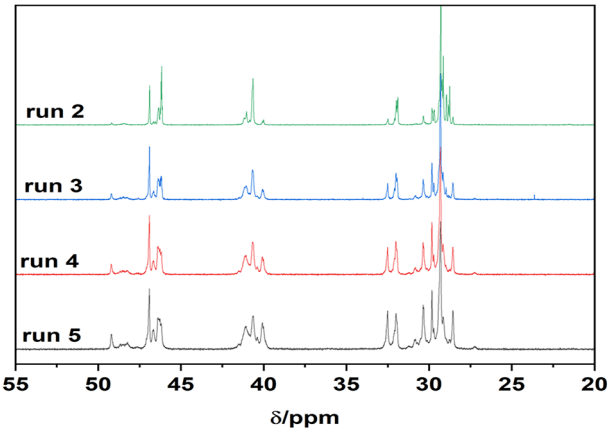

Figure 3. ^{13}C-NMR spectra of ethylene-norbornene copolymers.

tion probability. Once the coordination is successful, the insertion rate of norbornene should be higher than that of ethylene, because the cyclic structure of norbornene has a strong tendency to release the tension of the ring to obtain a thermodynamically more stable structure.

Figure 3 gives the ^{13}C-NMR spectra of the copolymers of ethylene with NBE (run 2-5). NBE incorporation could be calculated by using the reported method [6, 8, 37-40].

With the increase of NBE feed, not only the NBE incorporation increased, but also the molecular weight and glass transition temperature of the copolymer increased.

Figure 4 shows that the logarithm of the molecular weight almost linearly built up over the increase of the NBE incorporation. The molecular weight of copolymer in most catalytic systems would decrease with the

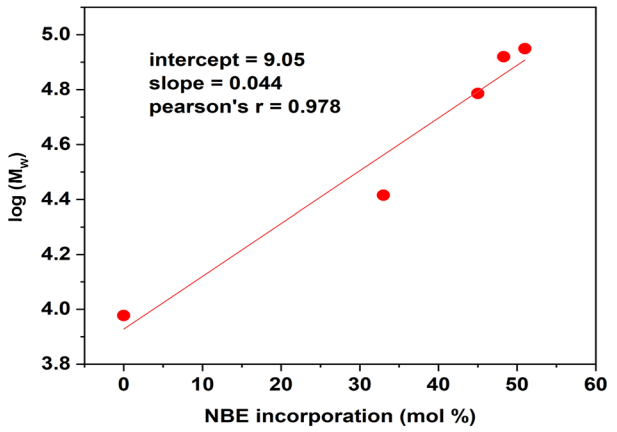

Figure 4. Relationship between the molecular weight and the NBE incorporation

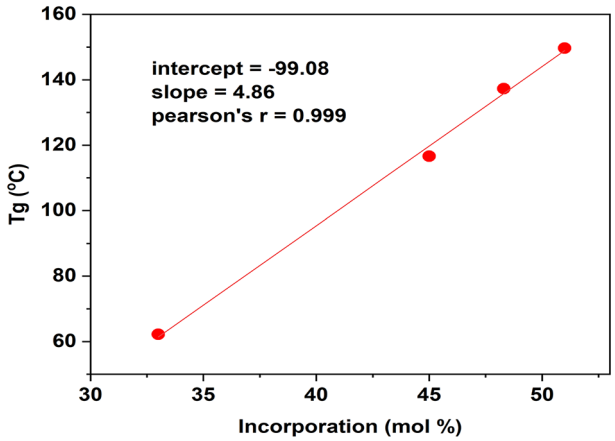

Figure 5. Relationship between the glass transition temperature and the NBE incorporation.

increase of comonomer feed, because the comonomer usually serves also as a chain transfer agent. In the present system, the increase of NBE feed does not increase the probability of the chain transfer.

Figure 5 shows that, the glass transition temperature showed a high linear correlation with the incorporation of NBE. The relationship could be expressed as following:

$$T_g = 4.86 \times I_{NB} - 99.08 \quad (3)$$

However, the parameters of this relationship do not apply to other catalyst systems. For example, the previous research gave the linear relationship with different parameters as following [36]:

$$T_g = 3.3751 \times I_{NB} - 41.4 \quad (4)$$

When the catalytic system is different, the parameters of the linear relationship are different. Polymers obtained from different catalytic systems would not give a good linear relationship. It could be possible to conclude that the catalyst system determines the comonomer distribution in the polymer chain. Different catalysts gave different comonomer distributions. Therefore, the regression parameters are not universal.

CONCLUSIONS

In this work, copolymerization of ethylene with norbornene by using a metallocene combined with

the cocatalyst of organic borate/aluminum was conducted. For the present system, copolymerization showed significantly higher activity than that of ethylene homopolymerization. The copolymerization gave a copolymer with high molecular weight, as well as the high incorporation of norbornene. The reactivity ratios of 4.86 for ethylene and 0.017 for norbornene, respectively, were obtained by using Fineman-Ross equation. The higher activity at high norbornene feed concentration may indicate the lower coordination probability but higher insertion rate. Glass transition temperature increased with increasing incorporation, and the relationship between them was linear. Nevertheless, the regression parameters were different from the previous report.

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CONFLICTS OF INTEREST STATEMENT

The authors declare that they have no conflicts of interest.

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