

Synthesis of Ethylene and Norbornene Copolymer with Metallocene Catalysts and Characteristic Analysis

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Received 10 May 2007; accepted 26 June 2007

DOI 10.1002/app.27085

Published online 13 September 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: To synthesis ethylene (E) and norbornene (NB) copolymer with high glass transition temperature and transparency, three metallocene catalysts with different symmetric structure were evaluated, respectively. The catalyst activity, NB fraction in copolymer and the transparency of copolymers produced under various conditions were investigated. It has been found that C_2 symmetric catalyst such as *rac*-[En(Ind)₂]ZrCl₂ was the best choice to produce copolymer with high NB fraction while keeping high catalyst activity. Furthermore, the effects of reaction conditions on activity of *rac*-[En(Ind)₂]ZrCl₂ and the resul-

tant copolymer structure have also been thoroughly studied. The results indicate that increasing the NB/E ratio is the effective way to increase NB content of copolymer when NB/E ratio is less than 20. However, when NB/E ratio is over 20, further increase in NB/E ratio will lead to significant lower catalyst activity and very limited increase in NB content of copolymer. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 286–291, 2008

Key words: cycloolefin copolymer; metallocene catalysts; ethylene; norbornene

INTRODUCTION

Copolymer of cyclic olefin and α -olefin (COC) is a new class of thermoplastic engineering polymer for high-quality applications. It possesses glass-like transparency, high glass transition temperature (T_g), excellent moisture barrier properties, electrical properties, biocompatibility, dimension stability, and chemical resistance, etc. COC is considered as a promising substrate material for high-density blue-laser DVD disk. Other applications include optical lenses and films, LCD flat screen components, light guide panels and fibers, medical, and pharmaceutical packaging¹.

Among COC, copolymer of ethylene (E) and norbornene (NB) (ENC) is the one of the most promising commercialized materials. This copolymer can be produced over a metallocene catalyst by an addition polymerization mechanism without ring opening reaction and succedent hydrogenation process. Although many metallocene catalysts that are effective for ethylene polymerization have no or little activity for the NB homopolymerization, the incorporation of NB into the macromolecular chain is increased significantly when the ethylene is used as a comonomer.

Some important properties of ENC are influenced by its microstructure. For example, T_g can be changed from 20 to 260°C by varying the NB content in the copolymer.^{2–5} It is also reported that the crystallinity of ENC was decreased and then disappear as NB fraction in copolymer was increased. The copolymer became amorphous when NB mole fraction was larger than about 14%.⁶ To be used as next generation optical materials, ENC need to have high NB content, and consequently higher T_g and transparency.

Copolymerization of ethylene and NB using homogeneous metallocene catalysts has been studied by many workers in the past several years.^{1–27} It remains practically important to understand how the copolymer microstructures are influenced by catalysts structure and polymerization conditions. In this article, three metallocene catalysts with different symmetric structure were used for ethylene and NB copolymerization, respectively. The effects of reaction conditions on catalyst activity and copolymer structure have been investigated. The purpose is to identify the appropriate metallocene catalyst and reaction conditions for the production of ENC with high T_g and transparency.

EXPERIMENTAL

Materials

Ethylene (99.95%) was dried by passing through columns filled with 3 Å molecular sieve and Cu catalyst. NB was dried over CaH₂ and distilled for 6 h

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Contract grant sponsor: National Natural Science Foundation of China; contract grant number: 20576115.

Contract grant sponsor: Key Project of Chinese Ministry of Education; contract grant number: 104095.

before use. Toluene was dried over a sodium/potassium alloy and distilled for 6 h before use.

All metallocene catalysts used in this work, Cp_2ZrCl_2 , $\text{rac}[\text{En}(\text{Ind})_2]\text{ZrCl}_2$, and $[\text{Ph}_2\text{C}(\text{Flu})(\text{Cp})]\text{ZrCl}_2$, were purchased from ACROS. The cocatalyst, methylaluminoxane (MAO), was provided by AKZO NOBEL in the form of 10 wt % solution in toluene.

Polymerization procedure

The ethylene and NB copolymerization were catalyzed with an three different metallocene catalysts, Cp_2ZrCl_2 , $\text{rac}[\text{En}(\text{Ind})_2]\text{ZrCl}_2$, and $[\text{Ph}_2\text{C}(\text{Flu})(\text{Cp})]\text{ZrCl}_2$, combined with MAO as the co-catalyst. The structure and symmetry of these catalysts are shown in Table I. All polymerization were carried out in a 100 mL glass flask under atmospheric pressure. Before polymerization, the reactor was evacuated and charged with nitrogen alternatively for three times. Then, ethylene, certain amounts of NB/toluene solution, and MAO/toluene suspension were added to the reactor sequentially. The polymerization was started by adding the metallocene/toluene solution. During the polymerization process, ethylene was fed to the reactor continuously to maintain the atmospheric pressure. After certain amount of time, the copolymerization was stopped by adding acidified ethanol. The reaction mixture was slowly poured into dilute HCl/ethanol solution. The precipitated polymer was filtered and washed with ethanol and then was dried under vacuum at 60°C.

Characterization of the copolymers

The microstructures of the copolymers were characterized with Varian Unity-400 nuclear magnetic resonance (NMR) instrument. ^{13}C NMR spectra of the copolymers were recorded at 120°C. The polymer samples were dissolved in deuterated *o*-dichlorobenzene with a concentration about 10%. At least 3000 scans were applied for each acquisition to obtain a good signal-to-noise ratio. The polymer chemical

shift assignments and calculations followed the analysis method of Ruchatz and Fink³. Figure 1 showed a typical ^{13}C NMR spectrum of the ENC produced in this work.

To determine molecular weight, purified copolymer was dissolved in 1,2,4-trichlorobenzene, and the flow time in Ostwald-fenske viscosimeter was measured at 150°C. The following equation was used to calculate the intrinsic viscosity:

$$[\eta] = \sqrt{2 \left[\left(\frac{t-t_0}{t_0} \right) - \ln \left(\frac{t}{t_0} \right) \right]} / C$$

Here, C is weight concentration of the copolymer solution; t and t_0 are the flow times of the copolymer solution and the pure solvent, respectively. The average molecular weight was calculated through Mark-Houwink equation with $K = 1.742 \times 10^{-4}$ and $\alpha = 0.664$.

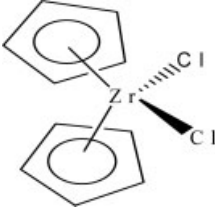
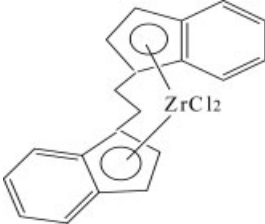
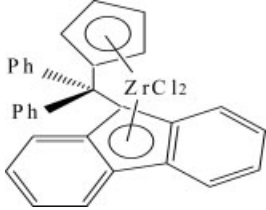
T_g of copolymers were measured through DSC analysis carried out at a heating rate of 20°C/min with a Perkin Elmer DSC-7 instrument. Melting process of copolymers was observed under Nikon Eclipse E600Pol POM.

RESULTS AND DISCUSSION

Comparison of catalysts

Results of copolymerization using catalysts with different symmetry were shown in Table II. It can be found that highest catalyst activity is achieved by C_2 symmetric catalysts $\text{rac}[\text{Et}(\text{Ind})_2]\text{ZrCl}_2$ and is barely changed as the NB/E molar ratio is increased from 2 to 10. On the other hand, activities of both C_{2v} symmetric catalysts Cp_2ZrCl_2 and C_s symmetric catalyst $[\text{Ph}_2\text{C}(\text{Flu})(\text{Cp})]\text{ZrCl}_2$ are reduced rapidly while the NB/E is increased. There are no appreciable catalyst active centers for either Cp_2ZrCl_2 or $[\text{Ph}_2\text{C}(\text{Flu})(\text{Cp})]\text{ZrCl}_2$ when the NB/E equal to 10 or 15, respectively. Highest cycloolefin incorporation ratio is achieved by $[\text{Ph}_2\text{C}(\text{Flu})(\text{Cp})]\text{ZrCl}_2$, $\text{rac}[\text{Et}(\text{Ind})_2]\text{ZrCl}_2$

TABLE I
Structure and Symmetry of Catalysts Used in this Work

Formula	Cp_2ZrCl_2	$\text{rac}[\text{En}(\text{Ind})_2]\text{ZrCl}_2$	$[\text{Ph}_2\text{C}(\text{Flu})(\text{Cp})]\text{ZrCl}_2$
Structure			
Symmetry	C_{2v}	C_2	C_s

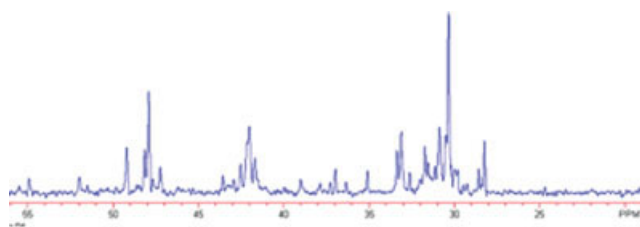


Figure 1 ^{13}C NMR spectrum of the typical ENC produced in this work. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

can produce ENC with NB mole fraction in produced copolymer more than 50 mol % if the initial molar ratio of NB to ethylene in solution was higher enough. Cp_2ZrCl_2 cannot produce ENC with NB fraction more than 40 mol %. This phenomenon is consistent with Kaminsky and Knoll's findings²⁶ that the C_s symmetric catalysts have better steric conditions for insertion of bulky NB than the C_2 and C_{2v} symmetric catalysts.

To study qualitatively the transparency, the melting and cooling processes of the resulted ENC were observed under Polarizing Optical Microscope (POM) and images were shown in Figure 2. It can be seen that the ENC produced by $\text{rac}[\text{Et}(\text{Ind})_2]\text{ZrCl}_2$ using less amount of NB (NB/E = 2) has apparent crystal spherulites similar to the ones found in the image of PE [Fig. 2(a,b)]. This is because C_2 symmetry catalyst prone to produce long E–E microblock or ethylene homopolymer at small NB/E ratio. With the same amount of NB (NB/E = 2), ENC produced using Cp_2ZrCl_2 and $[\text{Ph}_2\text{C}(\text{Flu})(\text{Cp})]\text{ZrCl}_2$ did not show any sign of crystallization [Fig. 2(c,d)]. ENC produced by $[\text{Ph}_2\text{C}(\text{Flu})(\text{Cp})]\text{ZrCl}_2$ was more transparent because of the higher NB fraction in copolymer. When the reaction time was reduced from 30 to 10 min in order to reduce the consumption of NB and obtain relative uniform NB content, the ENC pro-

duced by $\text{rac}[\text{Et}(\text{Ind})_2]\text{ZrCl}_2$ with NB = 2 still showed poor transparency [Fig. 2(e)]. However, when NB/E was increased to 15, transparency of ENC produced by $\text{rac}[\text{Et}(\text{Ind})_2]\text{ZrCl}_2$ was improved significant [Fig. 2(f)] and was even better than the ones shown in Figure 2(c,d).

On the basis of the above information, C_{2v} symmetric catalyst Cp_2ZrCl_2 performs poorly with respect to either polymerization activity or cycloolefin incorporation. If the objective is to produce ENC with high NB fraction of the copolymer for the purpose of high T_g and transparency based on the only addition of a little NB, C_s symmetric catalyst $[\text{Ph}_2\text{C}(\text{Flu})(\text{Cp})]\text{ZrCl}_2$ is the best choice among the three catalysts studied in this work. However, if the goal is to produce ENC with the high NB fraction while keeping high catalyst active, $\text{rac}[\text{Et}(\text{Ind})_2]\text{ZrCl}_2$ is the best one. In the following section, the effects of reaction conditions on $\text{rac}[\text{Et}(\text{Ind})_2]\text{ZrCl}_2$ as catalyst system have been studied farther.

Effects of temperature

The effects of reaction temperature on polymerization process and products were shown in Table III(a). As temperature is increased from 30 to 60°C, both catalyst activities and NB fraction in produced copolymer are increased. However, these results need further analysis before jumping to any conclusion. In this copolymerization system, temperature not only affects the reaction rate constant, but also affects the solubility of ethylene in toluene. Under the same pressure, the solubility of ethylene in toluene is decreased with increasing temperature. Therefore, the effective NB/E in solution is also changed in addition to the variation in temperature. The change of NB/E ratio is expected to influence both the polymerization process and products. Results in Table III(a) maybe give wrong information on the effects of temperature.

TABLE II
Copolymerization Results of Three Different Metallocene Catalysts^a

Catalyst	Run	NB/E (monomer ratio)	Activity ($10^6 \text{ g mol}^{-1} \text{ h}^{-1}$)	NB (mol %) (in copolymer)
Cp_2ZrCl_2	1	2	0.689	25.9
	2	5	0.210	34.6
	3	10	0.000	–
$\text{rac}[\text{Et}(\text{Ind})_2]\text{ZrCl}_2$	4	2	2.556	29.6
	6	5	2.559	35.0
	7	10	2.548	49.3
	8	15	2.105	53.4
$[\text{Ph}_2\text{C}(\text{Flu})(\text{Cp})]\text{ZrCl}_2$	9	2	0.930	37.2
	10	5	0.938	48.9
	11	10	0.555	56.3
	12	15	0.061	57.1

^a Conditions: $T = 70^\circ\text{C}$, Al/Zr = 1500, $P = 1 \text{ atm}$, catalyst concentration = $4 \times 10^{-5} \text{ mol/L}$, reaction time = 30 min.

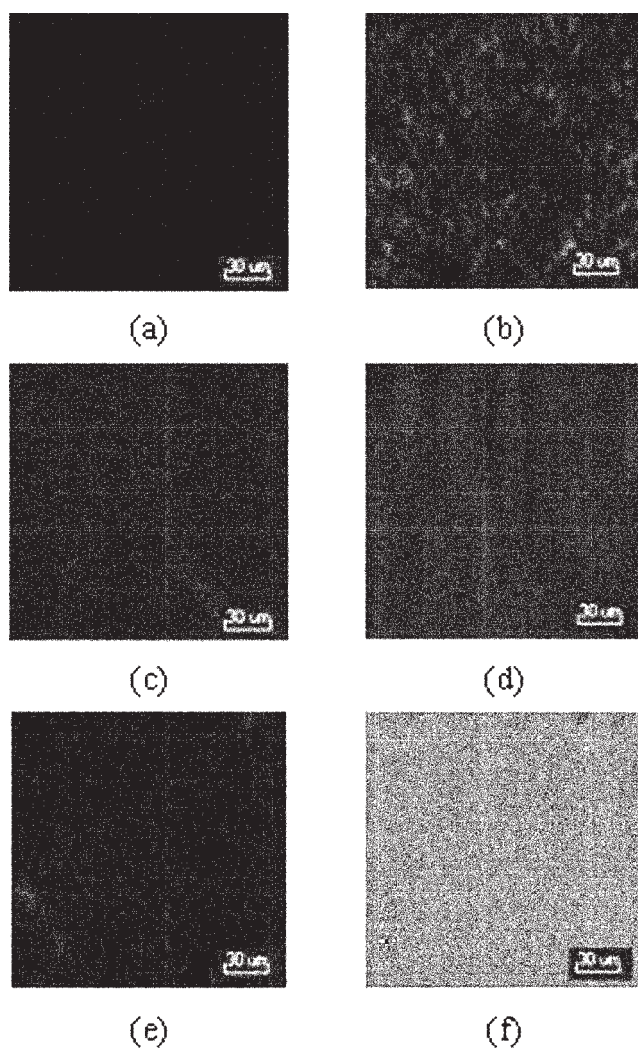


Figure 2 POM images of different samples.

To exclude the effects of variation in NB/E, solubility of ethylene at different temperature were calculated as follows²⁸:

$$C_E = P_E \times H_0 \exp\left(\frac{\Delta H_L}{RT}\right)$$

TABLE III(a)
Effects of Reaction Temperature with Constant Amount of NB^a

Temperature (°C)	NB (mL)	Activity (10 ⁶ g mol ⁻¹ h ⁻¹)	NB (mol %)
30	3.8	0.603	44.89
40	3.8	1.208	46.19
50	3.8	2.554	47.47
60	3.8	2.685	48.44
70	3.8 (NB/E = 10)	2.548	49.27

^a Conditions: catalyst concentration = 4 × 10⁻⁵ mol/L, Al/Zr = 1000, P = 1 atm, solvent = 50 mL, reaction time = 30 min.

TABLE III(b)
Effects of Reaction Temperature with Constant NB/E^a

Temperature (°C)	NB/E	Activity (10 ⁶ g mol ⁻¹ h ⁻¹)	NB (mol %)
30	10	0.637	50.99
40	10	1.555	51.76
50	10	2.234	51.02
60	10	2.986	48.68
70	10	2.548	49.27

^a Conditions: catalyst concentration = 4 × 10⁻⁵ mol/L, Al/Zr = 1500, P = 1 atm, solvent = 50 mL, reaction time = 30 min.

Here, C_E is the ethylene concentration, mol L⁻¹; P_E is the ethylene pressure, atm; H_0 , the Henry's law coefficient, is taken as 0.00175 mol L⁻¹ atm⁻¹; ΔH_L , the dissolution heat of ethylene in toluene, is equal to 2569 cal mol⁻¹; R , the ideal gas constant, is 1.989 cal mol⁻¹ K⁻¹; T is the temperature, K.

Copolymerization was carried out at different temperature with the initial amount of NB adjusted according to the corresponding solubility of ethylene to keep initial NB/E constant. The results were shown in Table III(b). It can be seen that the catalyst activity is still increased with increasing temperature in the limited range. However, different from the results in Table III(a), NB% is slightly decreased as temperature is increased, indicating that the reactivity ratio of NB is decreased with the increase in temperature. It has been reported that the bulk NB monomer is easier to be inserted to the active centers at low temperature when metallocene catalyst system is used.²⁷

Figure 3 showed that the molecular weight of ENC was decreased as temperature was increased. This can be explained by the higher chain transfer rate at higher temperature.

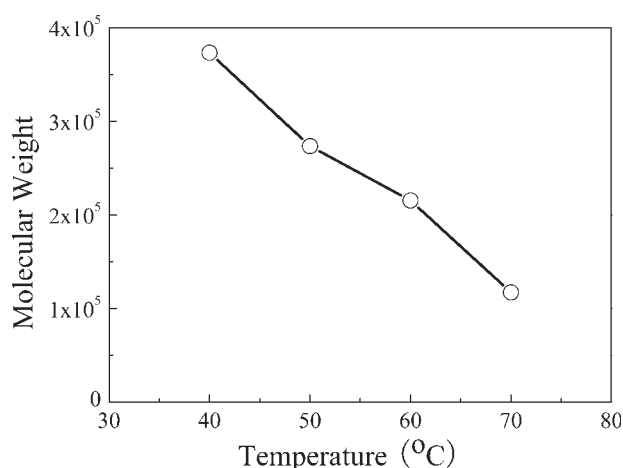


Figure 3 Molecular weight of the ENC produced at different temperature.

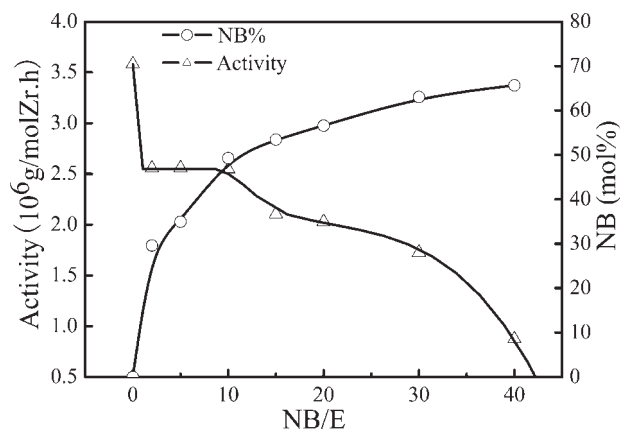


Figure 4 Effects of monomer ratio NB/E on copolymerization activity and NB fraction in produces.

Effects of NB/E

It had been shown in the above section that activity of *rac*-[Et(Ind)₂]ZrCl₂ barely changed with increasing NB/E up to 10. In Figure 4, it can be seen that catalyst activity drops dramatically when NB/E is over 15. When NB/E is equal to 40, the activity is below $10^6 \text{ g mol}^{-1} \text{ h}^{-1}$. On the other hand, NB% is increased significantly with the increase of NB/E in solution. However, as NB/E > 20, the increase in NB% will slow down. NB/E = 20 is also an important point for the molecular weight. As shown in Figure 5, molecular weight is rapidly decreased as the NB/E is increased up to 20. As NB/E is increased from 20 to 40, the molecular weight is barely changed.

Effects of catalyst concentration

Effects of catalyst concentration were shown in Table IV. It can be found that the increase in catalyst concentration has no significant effects on either catalyst activity or copolymer composition. This indi-

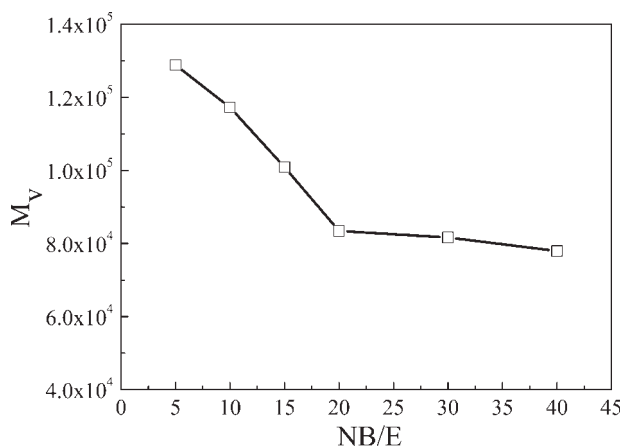


Figure 5 Molecular weight of the ENC produced under different monomer ratio.

TABLE IV
Copolymerization Results with Different Catalyst Concentration^a

Run	Catalyst concentration (mol/L)	Activity ($10^6 \text{ g mol}^{-1} \text{ h}^{-1}$)	NB (mol %)
1	2×10^{-5}	1.763	55.54
2	4×10^{-5}	1.862	53.45
3	6×10^{-5}	1.917	54.72
4	8×10^{-5}	1.886	54.28
5	10×10^{-5}	1.789	55.20

^a Conditions: $T = 70^\circ\text{C}$, Al/Zr = 1500, $P = 1 \text{ atm}$, NB/E = 15, reaction time = 30 min.

cates that the increase in active centers has no effect on the incorporation rate of either ethylene or NB into each active center. However, the increase in active center lead to lower molecular weight as termination rate is increased (Fig. 6).

Effects of Al/Zr

Another way to increase active center is to increase the amount of MAO used in the polymerization process. Table V showed the effects of Al/Zr ratio on catalyst activity and copolymer composition. It can be seen that there are no activity when Al/Zr is 500. It implies MAO also acted as a scavenger in this catalyst system. If the amount of MAO used is small, there will not be enough active centers to initiate polymerization. Polymerization occurs at Al/Zr = 800. The catalyst activity is increased with increasing Al/Zr because the number of catalyst do not change but more active center are formed because of the increase in MAO. Al/Zr has little effect on NB%. This is in agreement with the finding in last section that NB incorporation ratio of each active center is not changed with the number of active center. As shown in Figure 7, molecular weight of produced copolymer is decreased with the increase in Al/Zr ratio.

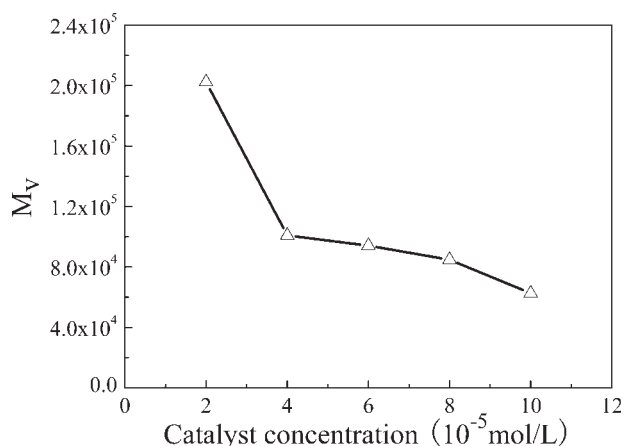


Figure 6 Molecular weight of the ENC produced at different catalyst concentration.

TABLE V
Copolymerization Results with Different Al/Zr^a

Run	Al/Zr	Activity (10 ⁶ g mol ⁻¹ h ⁻¹)	NB (mol %)
1	500	0.000	–
2	800	1.200	52.80
3	1000	1.563	52.38
4	1500	1.862	53.45
5	2000	2.268	53.18
6	3000	2.668	53.60
7	4000	3.273	52.92

^a Conditions: catalyst concentration = 4×10^{-5} mol/L, $T = 70^\circ\text{C}$, $P = 1$ atm, NB/E = 15, reaction time = 30 min.

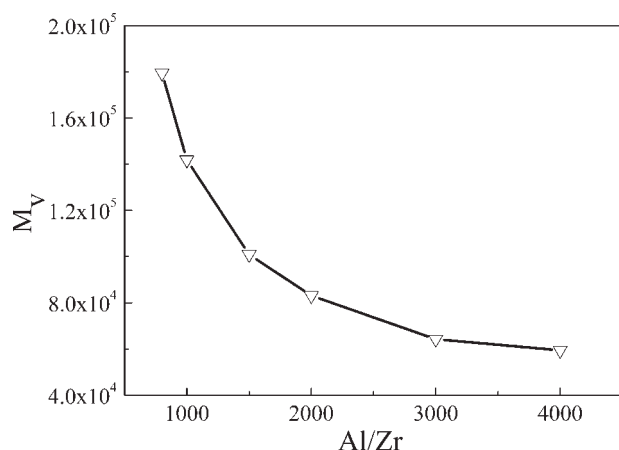


Figure 7 Molecular weight of the ENC produced at different Al/Zr.

CONCLUSIONS

Three different catalysts Cp_2ZrCl_2 , $[\text{Ph}_2\text{C}(\text{Flu})(\text{Cp})]\text{ZrCl}_2$, $\text{rac}[\text{Et}(\text{Ind})_2]\text{ZrCl}_2$, which have C_{2v} , C_s , C_2 symmetric structure, respectively, have been evaluated for preparation of ethylene and NB copolymer. It has been found that $\text{rac}[\text{Et}(\text{Ind})_2]\text{ZrCl}_2$ has the highest activity while the highest cycloolefin incorporation ratio is achieved by $[\text{Ph}_2\text{C}(\text{Flu})(\text{Cp})]\text{ZrCl}_2$. Catalyst Cp_2ZrCl_2 performs poorly with respect to both activity and cycloolefin incorporation. $\text{rac}[\text{Et}(\text{Ind})_2]\text{ZrCl}_2$ is the most effective one of the three catalysts by considering both activity and NB content in copolymer.

The ethylene and NB copolymerization processes using $\text{rac}[\text{Et}(\text{Ind})_2]\text{ZrCl}_2$ as catalyst have been extensively studied. It has been found that the only effective way to increase NB content of copolymer is to increase the NB/E ratio. However, when NB/E ratio

is over 20, further increase in NB/E will result in significant lower activity and very limited increase in NB content of obtained ENC. Increasing temperature or Al/Zr ratio can increase catalyst active, but also lead to lower molecular weight.

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