

Copolymerization of Ethylene and Norbornene via Polymethylene Bridged Dinuclear Constrained Geometry Catalysts

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Abstract: The dinuclear half-sandwich CGCs (constrained geometry catalyst) with a polymethylene bridge, $[\text{Ti}(\eta^5 : \eta^1\text{-indenyl})\text{SiMe}_2\text{NCMe}_3]_2(\text{CH}_2)_n$ [$n = 6$ (**1**) and 12 (**2**)], have been employed in the copolymerization of ethylene and norbornene (NBE). To compare the mononuclear metallocene catalysts; $\text{Ti}(\eta^5 : \eta^1\text{-2-hexylindenyl})\text{SiMe}_2\text{NCMe}_3$ (**3**), $(\text{Cp}^* \text{SiMe}_2\text{NCMe}_3)\text{Ti}$ (Dow CGC) (**4**) and *ansa*-Et(Ind)₂ZrCl₂ (**5**), were also studied for the copolymerization of ethylene and NBE. It was found that the activity increased in the order: **1** < **2** < **3** < **5** < **4**, indicating that the presence of the bridge between two the CGC units contributed to depressing the polymerization activity of the CGCs. This result strongly suggests that the implication of steric disturbance due to the presence of the bridge may play a significant role in slowing the activity. Dinuclear CGCs have been found to be very efficient for the incorporation of NBE onto the polyethylene backbone. The NBE contents in the copolymers formed ranged from 10 to 42%, depending on the polymerization conditions. Strong chemical shifts were observed at $\delta 42.0$ and 47.8 of the isotactic alternating NBE sequences, NENEN, in the copolymers with high NBE contents. In addition, a resonance at 47.1 ppm for the sequences of the isolated NBE, EENEE, was observed in the ¹³C-NMR spectra of the copolymers with low NBE contents. The absence of signals for isotactic dyad at 48.1 and 49.1 ppm illustrated there were no isotactic or microblock (NBE-NBE) sequences in the copolymers. This result indicated that the dinuclear CGCs were effective for making randomly distributed ethylene-NBE copolymers.

Keywords: dinuclear metallocene, CGC, ethylene copolymer, norbornene copolymer, microstructure.

Introduction

It is well-known that NBE and its derivatives are able to be polymerized by ring-opening metathesis polymerization (ROMP), cationic polymerization and addition polymerization.¹ The structural properties of the polymers from the ROMP and addition polymerization are wholly different. ROMP forms the polymer containing five-membered ring and vinyl group alternatively, that can be effectively applied to make the materials with high transparency.¹ On the other hand, the addition polymerization gives rise to the forma-

tion of 2,3-enchainity representing a characteristic rigid random coil conformation, which exhibits strong thermal stability, excellent dielectric properties and good optical transparency.^{2,3} One of the drawbacks of the application of NBE homopolymer is it is too rigid to be processed under the mild conditions. One of the methods to enlarge the utilization of NBE polymer is to form copolymer with the soft segment such as polyethylene to soothe its rigid property. Recently polymerization processes by using metallocene catalysts⁴⁻⁸ are known to be an excellent method to make ethylene and NBE copolymer.⁹⁻¹³ It turned out that the copolymers of ethylene and NBE are a class of attractive thermoplastic engineering polymers with a high glass tran-

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sition temperature (T_g), excellent moisture barrier properties, chemical resistance, and transparency particularly in the UV-VIS region, imparted by the NBE component.

Ethylene-NBE copolymers can be synthesized over a variety of metallocene systems such as Dow CGC,¹³⁻¹⁵ *ansa*-zirconocene,^{16,17} and half-titanocene,¹¹ through an addition polymerization. Properties of the formed copolymers are likely dependent upon several parameters such as copolymer composition, comonomer distribution within the main chain, and stereoregularity. It was found that the structural characteristics of the metallocene catalyst play the key role to produce a controlled copolymer microstructure. In this study we would like to present the results of ethylene-NBE copolymerization studies by using dinuclear CGC with specific regard to the effects of polymerization condition and copolymer microstructure.^{18,19} For comparison two mononuclear CGC systems and *ansa*-zirconocene system have been employed for the preparation of copolymers.

Experimental

General Considerations. All reactions were carried out

under dry, oxygen-free atmosphere using standard Schlenk techniques with a double manifold vacuum line. Nitrogen gas purified by passing through a column of Drierite (8 mesh). Tetrahydrofuran (THF), diethyl ether, hexanes, toluene, and pentane were distilled from sodium-benzophenone ketyl prior to use. Methylene chloride, 1,6-dibromohexane, and 1,12-dibromododecane were distilled from calcium hydride prior to use. Modified methylaluminoxane (MMAO, type 4, 6.4% wt% Al, Akzo, USA) was used without further purification. All the catalysts have been prepared according to the reported methods.^{4,15,18} ¹H- and ¹³C-NMR spectra were recorded using a Bruker DPX-300 FT-NMR spectrometer. ¹³C-NMR spectra for the ethylene-NBE copolymers were performed with proton decoupling at 100 °C either in tetrachloroethane-d₂ or in a 9 : 1 mixture of *o*-dichlorobenzene and C₆D₆ (3.0 mL). The pulse interval was 7.0 ms and acquisition time was 1.0 s. NBE contents (mol%) in the resultant copolymers were estimated by ¹³C-NMR spectra established by Tritto *et al.*¹⁷ The polymer solutions were prepared by dissolving polymers in solvent up to 10 wt%. Molecular weights were measured by Waters GPC (Alliance GPC 2000) with a polystyrene gel column at 140 °C using 1,2,4-

Table I. Results of Copolymerization of Ethylene and NBE by Using the Catalysts 1 and 2

Catalyst	T_p (°C)	NBE (mol/L)	Activity ^a	T_z (°C)	T_m (°C)	M_w ($\times 10^{-3}$)	PDI	NBE Content/mol%	
1	40	0	180		131	334	2.23		
		0.05	200		112	301	2.54		
		0.1	63		105	263	2.03		
		0.2	80	33		222	2.42		
		0.4	43	72					
		0.8	40	89					
	60	0	310			129	132.3	5.37	
		0.05	326			107	78.8	6.42	
		0.1	290			101	70.5	3.95	10.4
		0.2	260	27			65.1	5.93	23.1
		0.4	240	73					35.4
		0.8	137	94					41.5
	2	40	0	290		131	285	3.45	
			0.05	343		126	273	2.53	
0.1			210		125	192	2.44		
0.2			297	35		175	2.31		
0.4			110	71					
0.8			56	90					
60		0	397			130	103.5	2.75	
		0.05	417			121	72.5	1.86	
		0.1	343			97	47.4	4.64	12.9
		0.2	327	27			32.8	3.82	20.6
		0.4	310	59					33.8
		0.8	157	95					39.2

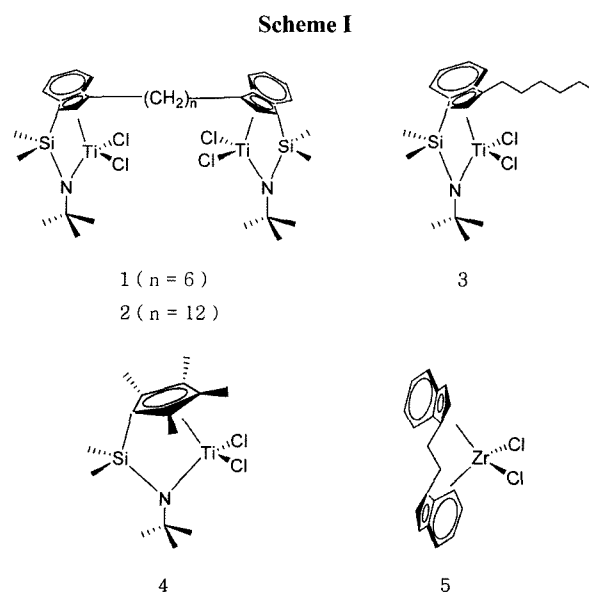
^aActivity: Kg-Polymer/mol Ti·h·atm. ^bPolymerization conditions: Ethylene, 1 atm; Toluene, 50 mL; Ti, 1×10^{-6} mol; Polymerization time, 30 min; Al/Ti, 2,000.

trichlorobenzene. The molecular weight was calculated by a standard procedure based upon the calibration with standard polystyrene samples. Differential scanning calorimeter (DSC) data were recorded by Pyris 6 DSC (Perkin-Elmer) under a nitrogen atmosphere [conditions: heating from 25 to 300 °C (20 °C/min); cooling from 300 to -55 °C (10 °C/min)].

Polymerization. Polymerization experiments were carried out in 400 mL glass reactor. The reactor was filled with the proper amount of NBE, toluene, and MMAO solution. The system was then saturated with ethylene. With a continuous flow of ethylene the polymerization was initiated by injection of catalysts and polymerized for 30 min. Polymerizations were terminated by venting ethylene and then injecting methanol (10 mL). Polymers were precipitated by pouring the reactor contents into acidic methanol (400 mL) and stirring overnight. Finally the polymer was filtered, washed with methanol, and dried at 50 °C under vacuum to constant weight.

Results and Discussion

In order to investigate the catalytic behavior of the dinuclear CGC **1** and **2**, these were delivered for the polymerization of ethylene and NBE in the presence of MMAO ([Al]/[Ti] ratio of 2,000). A series of polymerization runs have been carried out at eight compositions of monomer feed, and results are shown in Tables I and II. At the same time the mononuclear metallocene complexes *rac*-Et(Ind)₂ZrCl₂ (EBI, **5**), Me₂Si[Me₄CpN^tBu]TiCl₂ (Dow CGC, **4**), and Me₂Si[(*n*-



Hexyl)IndN^tBu]TiCl₂ (Hex-CGC, **3**) have been studied for the comparison (Scheme I).

The catalytic activity with five catalysts increased in the order of **4** > **5** > **3** > **2** > **1**, which illustrated that the dinuclear catalysts **1** and **2** represented lower activity than the mononuclear catalysts.

As shown in the Tables, this tendency has not been changed throughout ethylene/NBE copolymerization regardless of the reaction conditions. Activities of the catalyst **2**

Table II. Results of Copolymerization of Ethylene and NBE by Using the Catalysts 3, 4 and 5

Catalyst	NBE (M)	Activity ^a	<i>T_g</i> (°C)	<i>T_m</i> (°C)	<i>M_w</i> (× 10 ⁻³)	PDI	NBE Content/mol%
3	0	470		130.1	101	2.3	
	0.05	490		122.7	69	2.4	
	0.1	415	31.8	102.1	42	2.1	14.1
	0.2	373	39.8		28	2.3	24.7
	0.4	330	56.4				34.4
	0.8	197	90.5				39.7
4	0	546		133.5	103	2.7	
	0.05	703		126.2	96	2.6	
	0.1	720		125.0	81	2.5	7.6
	0.2	747	25.6		76	1.6	21.7
	0.4	986	89.6		52	2.3	29.7
	0.8	1,103	97.6				37.8
	1.20	1,203	106.7				43.9
	1.60	867	111.7				46.4
5	0	684		130.1	80	1.9	
	0.02	859	59		65	2.1	24.4
	0.4	1,020	119		42	2.1	38.4
	0.8	746	124		25	2.0	45.3

^aActivity: Kg-Polymer/mol Ti(Zr)-h-atm. ^bPolymerization conditions: Ethylene, 1 atm; Toluene, 50 mL; Ti(Zr), 1 × 10⁻⁶ mol; Polymerization time, 30 min; Tp, 60 °C; Al/Ti(Zr), 2,000.

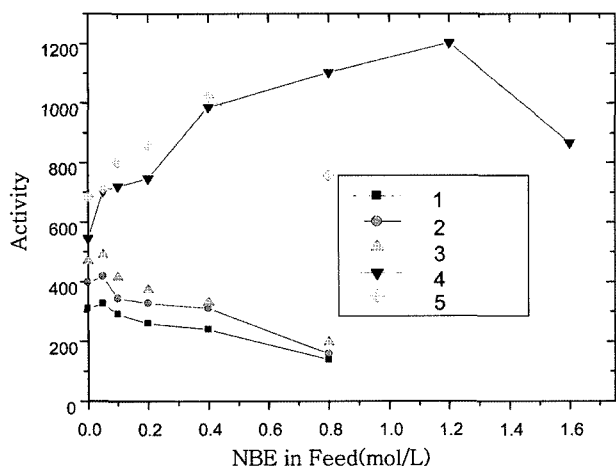


Figure 1. Correlation of activity of the catalysts with the concentration of NBE in feed at 60 °C.

with twelve methylenes as a bridge exhibit greater than those of the catalyst **1** with six methylenes. This can be explained by the implication that the steric factor may play a significant role to direct the catalytic activity of the dinuclear catalyst **1** as a consequence of coming into close contact to two active sites due to the relatively short length of six methylenes to twelve methylenes.¹⁸⁻²¹

The activities of the mononuclear catalysts seem to be in accord with the known studies basically.^{12,13} However, some important points can be noted. McKnight and Waymouth¹³ reported that the activities of the catalyst **4** were approximately 10 times more reactive than those of the CGC with indenyl group. In our experiments it turned out that the catalyst **3** with hexyl substitution at indenyl group as a η^5 -Cp derivative showed about 15 to 90% activity comparing to the activity of the catalyst **4** according to the monomer ratio in feed. For instance, with 0.8 M of NBE the activity of the catalyst **4** and **3** was 1,103 and 197 Kg-Polymer/mol-Ti·h·atm, respectively. On the other hand, with 0.05 M of NBE the activity of the catalyst **4** and **3** was 703 and 490 Kg-Polymer/mol-Ti·h·atm, respectively. Figure 1 shows the correlation of polymerization activity with the concentration of NBE in solution corresponding to the catalysts. The activity of all catalysts displayed maximum activity with the change of NBE concentration. Remarkably NBE concentration exhibiting the maximum activity was wholly affected by the structure of the employed catalyst. The catalyst **4**, Dow CGC, showed the peak activity at the concentration of 1.2 M NBE with 1,203 Kg-Polymer/mol-Ti·h·atm, which decreased with change of the NBE concentration both above and below this concentration. On the other hand, the catalyst **5** showed the maximum activity at the concentration of 0.4 M NBE with 1,020 Kg-Polymer/mol-Ti·h·atm. It should be noted that a remarkable coincidence in the concentration showing the maximum activity point of CGC's

containing η^5 -indenyl fragment regardless of mononuclear or dinuclear structure suggests clearly that the circumstances around the active site composed by the metal, nitrogen, and η^5 -ligand plays a crucial role to exhibit catalyst activity. It was reported that the activity of CGC decreased accordingly as the ratio of [ethylene]/[NBE] decreased. In terms of the general productivity pattern our results are in accord with the reported ones.^{13,18} However, at the microscopic point of view the composition of ethylene and NBE exerted a significant influence on the activity pattern of the catalyst. Even though we do not have a definite reason why the highest activity is affected by the catalyst structure, the comonomer effect,²² which was observed frequently in ethylene-propylene copolymerization, may be a good reason. Accordingly, we speculate that the different dependence of NBE concentration showing the peak activity may match to the concentration point of comonomer effect between ethylene and NBE of the corresponding catalysts.

The variation of molecular weight (Mw) and molecular weight distribution (MWD) does seem to be sensitive to not only the polymerization condition but also the catalyst structure. Dependence of Mw of copolymers upon polymerization temperature follows the general tendency that the polymerization at low temperature (40 °C) produces larger Mw. Mw's of copolymers generated at 40 °C with the dinuclear catalyst **1** ranged between 220,000 to 330,000. On the other hand, Mw's of polymers formed at 60 °C ranged from 65,000 to 132,000. Mw's of the copolymers drop steadily as the concentration of NBE increases (Table I). This outcome is typical for the ethylene-NBE copolymerization. The important feature has been found that the relation between Mw of the generated copolymers and the catalyst structure was pretty straightforward. The catalyst **1** with six methylene linkage generated the polymers with the greatest molecular weight among the five catalysts. The dinuclear CGC **2** and two mononuclear catalysts **3** and **4** were found to form a similar length of polymer. *Ansa*-metallocene was the catalyst to manufacture the shortest polymer among the five catalysts. This result may imply that twelve methylene linkages between two CGC units may be long enough to provide a full degree of freedom to each of the active site that is able to behave just like one independent catalytic site without any kind of steric interference from the other side of the active site.

It is found that two dinuclear CGC in this study are very efficient to incorporate NBE in polyethylene backbone. When comparing five catalysts **1** to **5**, it is clear that the amount of NBE incorporation was determined by not only the concentration of NBE in feed but also the catalyst employed for polymerization (Tables I and II). At the identical NBE concentration the quantity of NBE incorporation in polyethylene chain increased in the order of $5 > 1 \approx 2 \approx 3 > 4$. This consequence may demonstrate that the structure of the active site around metal is actually the most important

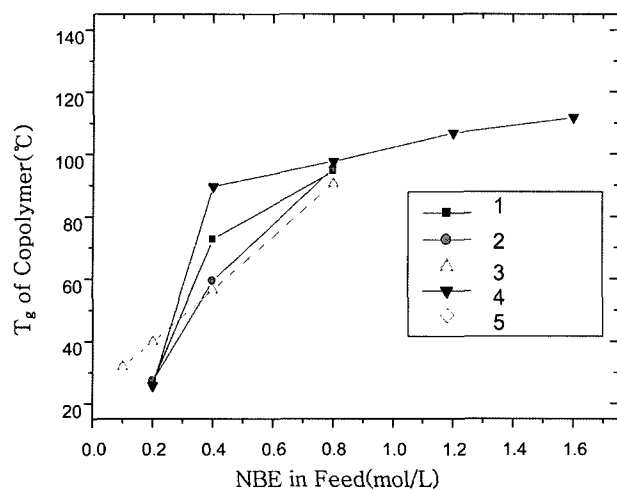


Figure 2. Variation of T_g with NBE content in copolymer.

element to incorporate NBE monomer in polymer chain. It was revealed that *ansa*-metallocene is more effective to give rise to the formation of high NBE contents copolymers.¹⁶ It was found that CGC with indenyl unit were able to form the copolymers with higher NBE contents than Dow CGC. As expected, NBE incorporation for the catalysts in this study is dependent on amount of NBE in feed and high concentration of NBE (0.8 M) needed to produce a copolymer containing 40% NBE for these catalysts, which is a similar result to the previous studies.

DSC thermograms for the copolymer showed a sole glass transition temperature (T_g) in all cases, that suggests the resultant materials possess uniform NBE incorporation as well as the formation of good copolymer. T_g 's increasing pattern according to the increase of NBE contents in copolymer is just normal. The most important feature about T_g measurement is that the nature of the catalyst appears to

have considerable effect on T_g (Figure 2). For example, copolymers with 34–40 mol% NBE generated from the catalysts having CGC structure have T_g values from 70 to 97 °C. On the other hand, copolymer with 38 mol% NBE formed from catalyst **5** shows 119.7 °C, which is substantially (at least about 20 °C) higher than abovementioned cases. This result may demonstrate another evidence to support that the structure of the catalyst precursor exerts a considerable influence on not only the apparent polymerization behavior of the catalyst system but also the microstructure of the produced copolymer.^{4,8} In spite of the some dissimilarity of T_g 's of copolymers among the catalysts T_g 's measured in this study fall within the range of values reported for the copolymers of ethylene and NBE of similar compositions. High resolution ¹³C-NMR is one of the most powerful instruments for probing copolymer composition and microstructure. Several researches have contributed to assign the complicated ¹³C-NMR spectra of ethylene-NBE copolymers. It is known that ¹³C-NMR spectra of the ethylene-NBE copolymers exhibit many resonances due to the complex microstructure including different monomer sequences, varying lengths of the NBE microblocks, meso or racemic connection of the NBE units, and pentad sensitivity. Table III represents possible microstructure and ¹³C NMR chemical shift of ethylene-NBE copolymers from the previous reports by Tritto *et al.*¹⁷

Figure 3 shows ¹³C-NMR spectra of the copolymers prepared from the dinuclear CGC **1** with different NBE concentration. As the levels of NBE incorporation escalate from 10 to 41.5% it is conceivable that the microstructure of the copolymers change gradually. At low NBE content one can observe sharp resonances of 47.1 and 41.6 ppm corresponding to the presence of the isolated NBE fragment. At high level of NBE incorporation (35.4% and 41.5%), there is a growth of the peaks at 47.8, 47.3, 42.0, and 41.9 ppm

Table III. Assignments of ¹³C Chemical Shifts (ppm) for Carbons of NBE and Ethylene Units in Ethylene - NBE Copolymers

Type	Carbon/Config	Chemical Shift/ppm	Sequences	Type	Carbon/Config	Chemical Shift/ppm	Sequences
Dyad	C2* iso	49.1	ENNE	Isolated	C1/C4	41.6	EENEE
Dyad	C3* iso	48.1	ENNE	Alternative	C7 iso, syndio	33.0	NENEN
Alternative	C2 iso	47.8	NENEN	Isolated	C7	32.9	EENEE
Alternative	C2 syndio	47.2	NENEN	Alternative	CH2 Sαβ iso	30.7	EENENEE
Isolated	C3	47.1	EENEE	Isolated	CH2 Sβγ	30.6	NEEN
Isolated	C2/C3	47.1	EENEN	Isolated	CH2 Sαδ	30.2	NEEN
Alternative	C1 iso	42.0	NENEN	Isolated	CH2 Sδδ	29.8	EEEEEEEE, NEEEEE
Alternative	C4 iso	41.9	EENEN	Dyad	C5* iso	28.1	ENNE
Alternative	C1/C4 syndio	41.6	NENEN				

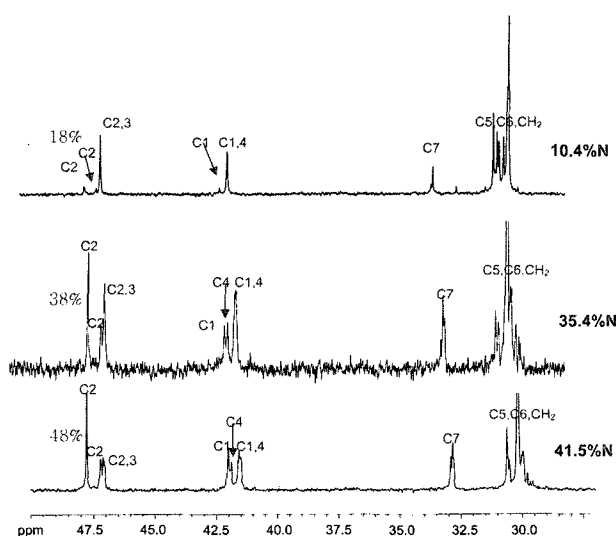


Figure 3. ^{13}C -NMR spectra of the ethylene - NBE copolymer prepared with the catalyst **1**.

and a simultaneous decrease of the peaks at 47.1 and 41.6 ppm. In addition, the growing ratio of peak intensity at 47.8 and 47.3 ppm is virtually same. At the same time, peak decreasing ratio at 47.1 and 41.6 ppm is found to be identical. These results indicate that the contents of alternative sequence of ethylene and NBE in copolymer extended as the NBE contents in copolymer increased. In case of 10.4%

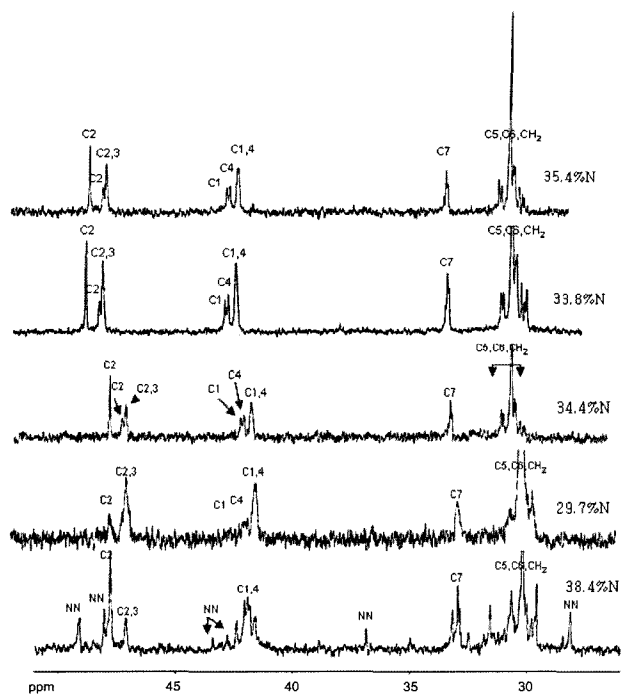


Figure 4. ^{13}C -NMR spectra of the ethylene - NBE copolymer prepared by the different catalyst system.

NBE contents polymer the ratio of alternative sequence was just 18%. The ratio of alternative sequence reached up to 48% with 41.5% NBE contents polymer. This trend of change of monomer sequence is very well accord with the previous report.^{12,13}

Figure 4 shows ^{13}C -NMR spectra of the copolymers prepared from all five catalysts **1** to **5** with NBE contents from 29.7 to 38.4%. This observation has been proceeded to figure out how the catalyst structure have an effect on the microstructure of ethylene-NBE copolymer. It is evident that ^{13}C -NMR spectra from the copolymers generated by the catalysts **1**, **2** and **3** display almost identical appearance as shown in Figure 4. The spectrum measured with the copolymer from the catalyst **4** exhibited a similar pattern to these but with the dissimilar peak intensity. On the contrary, ^{13}C -NMR spectrum of the copolymer from *ansa*-metallocene **5** was completely different from the others. We were able to observe easily the presence of NBE-NBE sequence in copolymer from the resonances at 49.1, 48.1, and 28.1 ppm. From the analysis of a series of different copolymer spectra it has been revealed that characteristic of the catalyst is the most significant factor to draw polymer microstructure. Among the five catalysts studied in this experiment *ansa*-metallocene produced ethylene-NBE copolymers with NBE microblocks. On the other hand, the catalysts with CGC fragment manufactured the copolymers with alternative block of ethylene-NBE with the high NBE contents. It is worth to point out that the dinuclear CGC **1** and **2** seemed to be more effective to incorporate NBE in polyethylene chain than the corresponding mononuclear CGC **3**. Dow CGC illustrated the greatest activity with the lowest incorporation efficiency of NBE.

Conclusions

In this study we describe the catalytic behavior of the dinuclear CGC **1** and **2** along with the mononuclear metallocene catalysts **3**, **4**, and **5** to figure out principally the properties of ethylene-NBE copolymerization. It was found that the catalytic activity with five catalysts increased in the order of $4 > 5 > 3 > 2 > 1$, which illustrated that the dinuclear catalysts **1** and **2** represented lower activity than the mononuclear catalysts. Activities of the catalyst **2** with twelve methylenes as a bridge exhibit greater than those of the catalyst **1** with six methylenes. This can be explained by the implication that the steric factor may play a significant role to direct the catalytic activity of the dinuclear catalyst **1** as a consequence of coming into close contact to two active sites due to the relatively short length of six methylenes to twelve methylenes. All the catalysts displayed maximum activity with the change of NBE concentration. The catalyst **4**, Dow CGC, showed the peak activity at the concentration of 1.2 M NBE with 1,203 Kg-Polymer/mol-Ti-h-atm. On the other hand, CGC's containing η^5 -indenyl fragment regard-

less of mononuclear or dinuclear structure showed the maximum activity at the concentration of 0.05 M NBE. The dinuclear catalyst **1** with six methylene linkage generated the largest Mw polymers among the five catalysts. It is found that two dinuclear CGC in this study are very efficient to incorporate NBE in polyethylene backbone. At the identical NBE concentration the quantity of NBE incorporation in polyethylene chain increased in the order of $5 > 1 \approx 2 \approx 3 > 4$.

As the levels of NBE incorporation escalate from 10% to 41.5% the microstructure of the copolymers change gradually. In case of 10.4% NBE contents polymer the ratio of alternative sequence was just 18%. The ratio of alternative sequence reached up to 48% with 41.5% NBE contents polymer. From the analysis of a series of different copolymer spectra it has been revealed that characteristic of the catalyst is the most significant factor to draw polymer microstructure. Among the five catalysts *ansa*-metallocene produced ethylene-NBE copolymers with NBE microblocks. On the other hand, the catalysts with CGC fragment produced the copolymers with alternative block of ethylene-NBE with the high NBE contents. The dinuclear CGC **1** and **2** is very effective to lead to form the copolymers with high incorporation of NBE in polyethylene chain.

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