A Study on the Coordination Polymerization Using C₂-Symmetric Dichloro[*rac*-ethylenebisindenyl] zirconium(IV)/Methylaluminoxane System

Dong Jin Yang, Hyun Ki Kim[*], No-hyung Park, Jun Chul Lee, and Dong Hyun Kim[†]

Korea Institute of Industrial Technology, Ansan-si, 426-910, Republic of Korea
[*]Nexene Tire, Yusan-Dong, Yangsan-Si, 626-230, Republic of Korea

C₂-Symmetric Dichloro[*rac*-ethylenebisindenyl] zirconium(IV)/Methylaluminoxane 시스템을 이용한 배위 중합에 관한 연구

양동진 · 김현기[*] · 박노형 · 이준철 · 김동현[†]

한국생산기술연구원, [*]넥센타이어

ABSTRACT：We synthesized polyethylene, poly(ethylene-*co*-1-decene), poly(ethylene-*co*-*p*-methylstyrene), and poly(ethylene-*ter*-1-decene-*ter*-*p*-methystyrene) using a *rac*-Et(Ind)₂ZrCl₂ metallocene catalyst and a methylaluminoxane cocatalyst system. The materials were characterized using nuclear magnetic spectroscopy and fourier transform infrared spectroscopy. To identify suitable reaction conditions for terpolymerization, we studied the effects of catalyst content, cocatalyst/catalyst molar ratio, polymerization time, and polymerization temperature. As the catalyst content increased, the catalytic activity and the molecular weight of the terpolymers increased. The catalytic activity sharply increased but little change was observed after a polymerization time of 30 min. The increase in the cocatalyst/catalyst molar ratio resulted in a decrease in the molecular weight of the terpolymers and an increase in the catalytic activity to some degree. The catalytic activity increased with increasing polymerization temperature, while the molecular weight of the terpolymers decreased.

요 약：*rac*-Et(Ind)₂ZrCl₂ 메탈로센 촉매와 메틸알루미늄옥산 공촉매를 이용하여 polyethylene, poly(ethylene-*co*-1-decene), poly(ethylene-*co*-*p*-methylstyrene) 및 poly(ethylene-*ter*-1-decene-*ter*-*p*-methystyrene)를 합성하였다. ¹³C NMR과 ¹H NMR 및 FT-IR을 이용하여 삼원공중합체의 특성을 분석하였다.
삼원공중합의 최적조건을 확립하기 위해 동일한 중합조건을 유지한 채 촉매량, 공촉매/촉매 몰비, 중합 시간 및 중합 온도를 변경하여 실험하였다. 촉매량이 증가할수록 삼원공중합체의 촉매활성도 및 중량평균분자량은 증가하였으나, 중합시간이 30분을 초과하자 촉매활성도는 감소하였다. 공촉매/촉매 몰비를 증가시킨 결과 중량평균분자량은 감소하였고, 촉매활성도는 어느 정도 증가하였다. 촉매활성도는 중합온도가 증가함에 따라 상승하였으나 중량평균 분자량은 감소하였다.

Keywords：metallocene catalysts, polyolefins, elastomers, cocatalyst

Ⅰ. Introduction

Research on polymerization using metallocene catalysts began with the identification of the structure of ferrocene by Wilkins and Fischer in 1952, and was further developed by Kaminsky in the 1980s. In the case of copolymerization using metallocene catalyst, preparing polymers with narrow molecular weight distribution, high stereo-regularity, and uniform comonomer incorporation is much easier than is the case when using a conventional Ziegler-Natta catalyst. That is the reason why many studies have been performed regarding coordination polymerization using metallocene catalysts.[1]

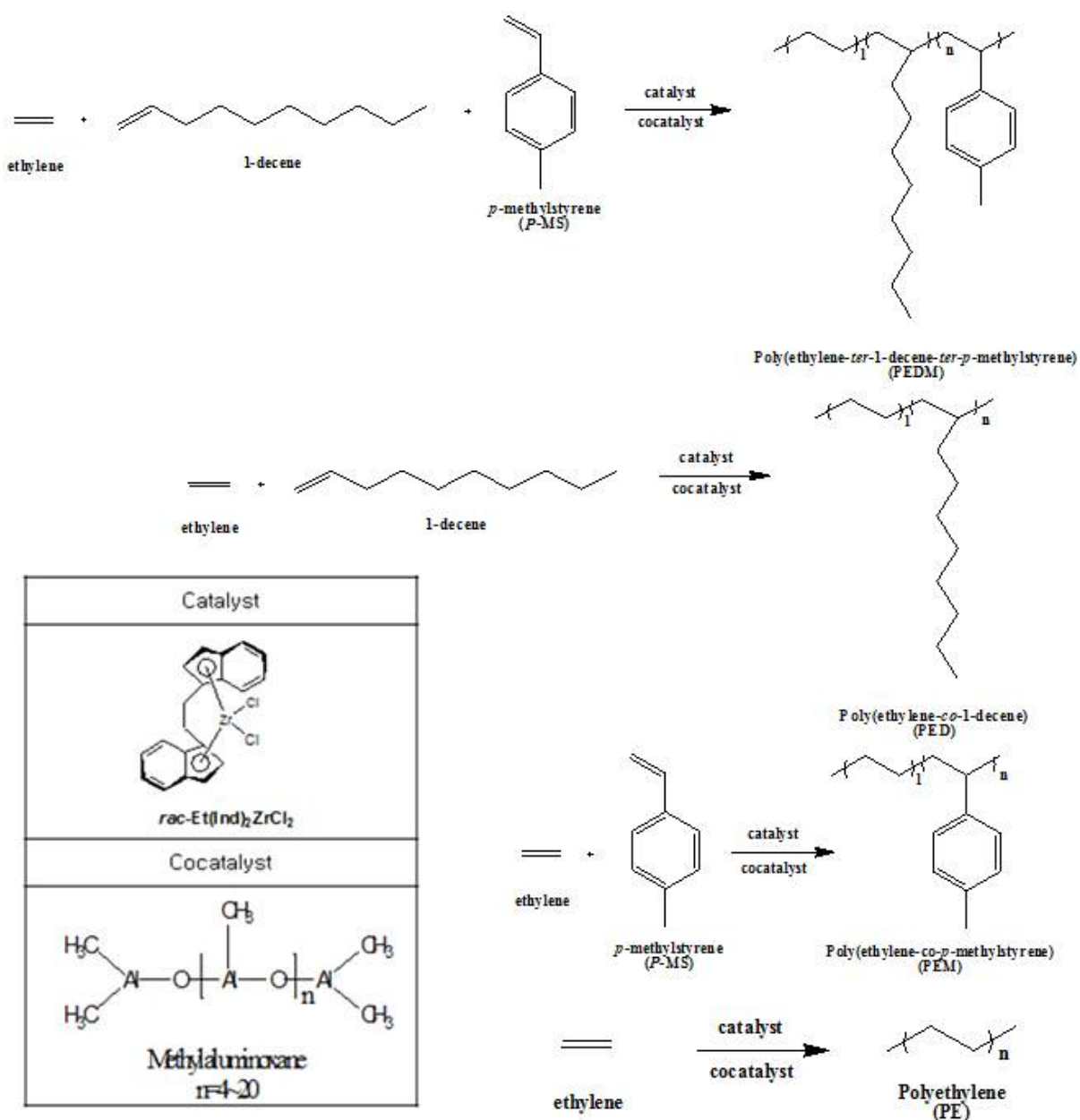† Corresponding Author. E-mail: *dhkim@kitech.re.kr*

Figure 1. Synthetic procedures for homo-, co-, and terpolymer.

However, these studies have mainly focused on the copolymerization of ethylene with high-α-olefins, diene monomers, cyclo-olefins, and styrene.[2-6] Also, other studies have been performed regarding the copolymerization of propylene with ethylene and high α-olefins.[7-9] The main reason for carrying out research on the terpolymers is to examine the influence of termonomers on the properties of EPDM-rubbers and block-terpolymers.[10,11] In particular, studies on the terpolymers with reactive groups has been limited even though it maybe possible to use the terpolymers

to develop new high-functional polyolefins.[12-15]

In this study, we prepared a polyethylene (PE), poly(ethylene-*co*-1-decene) (PED), and poly(ethylene-*co*-p-methylstyrene) (PEM), and poly(ethylene-*ter*-1-decene-*ter*-p-methylstyrene) (PEDM) using a bridged metallocene catalyst and a cocatalyst system. To optimize the coordination terpolymerization conditions, we studied the effects of the catalyst contents, cocatalyst/catalyst molar ratio, and the polymerization temperature on the catalytic activity, molecular weight, and molecular weight distribution of the terpolymer.

Ⅱ. Experimental

2.1 Materials & Specimens

All manipulations were carried out in an inert nitrogen atmosphere. We used high-purity grade ethylene gas (Dae-myung Gas Co.) after passing it through an alumina/zeolite column. 1-decene (Aldrich, 94%), n-hexane (SAMCHUN, 99.5%), and toluene (SAMCHUN, 99.5%) were purified by refluxing them over sodium, using benzophenone as an indicator, and stored in a dry box. A solution of *rac*-Et(Ind)$_2$ZrCl$_2$ (Sigma Aldrich) in toluene was also prepared. MAO (Tosho, methylaluminoxane) was used as received. *p*-methylstyrene was distilled under reduced pressure in the presence of CaH$_2$ after performing standard purification procedure.

2.2 Polymerizations

Typically, all of the polymerization reactions were carried out in a 300 mL stainless steel autoclave with a mechanical stirrer. After the autoclave was saturated with ethylene gas, the polymerization reaction was started by the injection of the required amount of catalyst solution and MAO. After several minutes, the polymer solution was poured into a diluted HCl/EtOH solution. The resultant polymer was washed with EtOH (600 mL) and dried in vacuo. After the polymerization reactions, we separated each soluble copolymer or terpolymer from insoluble by-products of the resultant polymer (some types of mixtures) using a soxhlet apparatus and n-hexane as a solvent. Through the soxhlet process, we could eliminate the insoluble polyethylene which was produced during the co- and terpolymerization. After drying the soluble fractions, we could finally obtain final PED, PEM, and PEDM which were completely soluble in common organic solvents, such as the hexane, toluene, and tetrahydrofuran.

2.3 Characterization

Fourier transformed infrared (FT-IR) analysis was performed by Thermo Scientific Co. NICOLET 6700. ^{13}C NMR spectra were obtained at 60 °C. The equipment that was used was a Bruker AVANCE 500 MHz. Sample solutions of the polymer were prepared in CDCl$_3$. The deuterated solvent was used to provide an internal lock signal.

^{1}H NMR spectra were recorded on a Bruker AVANCE 500 MHz. The NMR samples were prepared in CDCl$_3$ solvent. Using ^{1}H NMR spectra, we found the compositions of the polymers and also characterized the structures of the polymers.

The molecular weight and the molecular weight distribution of the polymers were measured using Polymer Laboratories Co. PL-GPC210 gel permeation chromatography fitted with Styragel (olesis guard column) HT-type columns. The analyses were performed at 140 °C and 1.0 mL/min with 1, 2, 4-trichlorobenzene as a solvent.

Ⅲ. Results and Discussion

3.1 Homo-, Co-, and Terpolymerization

Figure 1 shows a synthetic scheme for the preparation of PEDM, PED, PEM, and PE using *rac*-Et(Ind)$_2$ZrCl$_2$ and MAO as a catalyst and cocatalyst, respectively. Generally, the most interesting aspect of these zirconocene−MAO catalytic systems is the production of random copolymers with higher catalytic activities. The C$_2$ symmetric metallocene catalyst, *rac*-Et(Ind)$_2$ZrCl$_2$, has a relatively electron-rich indenyl ligand. This electron-rich ligand stabilizes transition metals in catalyst with cationic character, which leads to a higher catalytic activity for *rac*-Et(Ind)$_2$ZrCl$_2$ compared to that of other complexes.

Table 1 reports the results of homo-, co-, and ter-polymerization using a metallocene catalyst/cocatalyst system under the same conditions of catalyst content, cocatalyst/catalyst molar ratio, polymerization time, and polymerization temperature. The catalytic activities of PED and PEDM were higher than that of PE. The catalytic activity of PED went up 2.7 fold values more than that of PE. This was attributed to the "positive" comonomer (1-decene) effect: (1) enhanced solubility of the copolymer (PED) in comparison with that of the homopolymer (PE), which favored monomer diffusion to the active center; (2) comonomer activation of new catalyst sites by increased affinity for the metallocene catalyst; (3) increased solubility of the monomer in the liquid phase due to the presence of the comonomer, which increased its insertion rate.[17]

In the case of the terpolymer, the catalytic activity is lower than that of the copolymer (PED). This may have been due to the "negative comonomer (*p*-MS) effect." We can infer that, after the incorporation of *p*-MS into the terpolymer, its bulkiness made further insertion of ethylene and 1-decene difficult. This could also be confirmed by the very low catalytic activity of PEM, which was a copolymer of ethylene and *p*-MS.

Table 1. Summarization of homo-, co-, and ter-polymerization.

NAME [a]	Feeding			E : D : M Feed molar ratio	Composition			Catalytic activity[d]	M_w[e] (kg/mol)	M_n[e] (kg/mol)	MWD [e]
	E[b] (mol/L)	D[b] (mol/L)	M[b] (mol/L)		E[bc] (mol %)	D[bc] (mol %)	M[bc] (mol %)				
PE	0.4	0	0	1 : 0 : 0	100	0	0	1420	-	-	-
PED	0.4	0.4	0	1 : 1 : 0	79.8	20.2	0	3840	100	29	3.4
PEM	0.4	0	0.4	1 : 0 : 1	98.9	0	1.1	350	85	26	3.3
PEDM	0.4	0.4	0.4	1 : 1 : 1	65.4	33.4	1.2	2648	100	37	2.7

[a] Polymerization conditions: catalyst = 2.5 µmol (*rac*-Et(Ind)$_2$ZrCl$_2$), cocatalyst/catalyst = 3000, polymerization time = 30 min, polymerization temperature = 50 °C, and solvent = toluene.
[b] E = Ethylene, D = 1-decene, M = *p*-MS.
[c] Determined by ^{1}H-NMR spectroscopy.
[d] Catalytic activity = kg of polymer/(mol of catalyst·h).
[e] Determined by gel permeation chromatography (GPC).

Table 2. Terpolymerization of ethylene, 1-decene, and *p*-MS according to the polymerization time.

Run No.[a]	Polymerization time (min)	Catalytic Activity (kg of polymer /(mol·h))	M_w[b] (kg/mol)	M_n[b] (kg/mol)	MWD[b]
1	10	560	66	29	2.2
2	20	984	87	29	2.9
3	30	2648	96	45	2.2
4	40	2603	90	35	2.6
5	50	2680	95	28	3.3
6	60	2645	96	31	3.1

[a] Polymerization conditions: catalyst = 2.5 µmol, ethylene = 0.4 mol/L, 1-decene = 0.4 mol/L, *p*-MS = 0. 4 mol/L, catalyst = *rac*-Et(Ind)$_2$ZrCl$_2$,, cocatalyst/catalyst = 3000, and solvent = toluene.
[b] Determined by gel permeation chromatography (GPC).

3.2 Characterization

Figure 2 shows two kinds of Fourier transform infrared (FT-IR) spectra: (a) the spectrum of insoluble parts which is obtained through the soxhlet process for PEDM and (b) the spectrum of pure PE. The spectra of (a) and (b) have very similar peaks.

The C-H stretching peaks mutually appear near 2850 cm^{-1} and 2950 cm^{-1}. The CH$_2$ bending peak and out of plane C-H bending are near 1400 cm^{-1} and 720 cm^{-1}, respectively. We conclude with certainty that, through soxhlet process, we can separate the by-product (homo-polyethylene) from the terpolymer.

Figure 3 is the ^{1}H NMR spectrum of PEDM. The signatures near 7.0 ppm correspond to the aromatic peaks of *p*-MS. The peaks for the CH, CH$_2$, and CH$_3$ of ethylene or 1-decene appear in the range 0−3 ppm. The peaks for the CH$_3$ of the 1-decene and ethylene are near 0.9 ppm. The peak for the *p*-MS is at 2.3 ppm.

The peak for the CH of the 1-decene is near 1.5 ppm. Compared with the peaks for the CH$_3$ of *p*-MS, the CH$_3$ of 1-decene and ethylene occupy a relatively broad area. We can confirm the insertion of the 1-decene and *p*-MS into the terpolymer by the char-
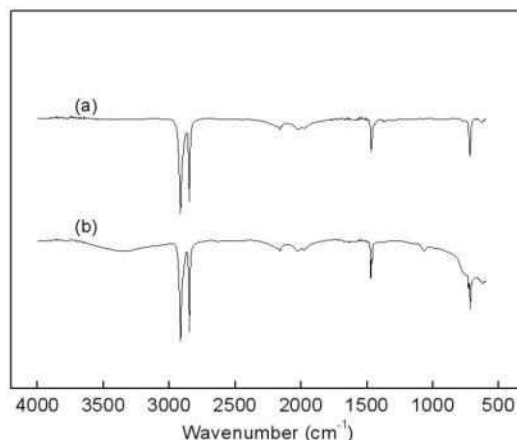

Figure 2. FT-IR spectra of (a) insoluble parts after soxhlet process for PEDM and (b) PE.
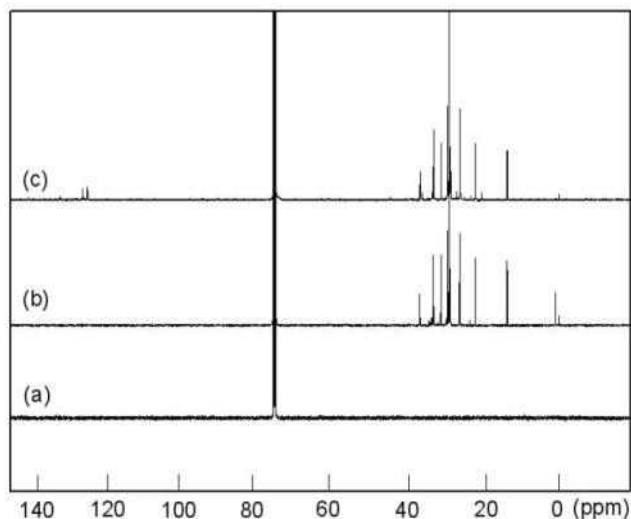
Dong Jin Yang et al. / Elastomers and Composites Vol. 48, No. 1, pp. 2~9 (March 2013)

acteristic peaks for the CH_3 and CH.

Figure 4 shows the ^{13}C NMR spectra of the PE, PED, and PEDM. In the case of PEDM in particular, ortho and meta carbon atoms are present in the benzene ring. The carbon atom at the ortho position is ortho plus meta to the substituent, and the carbon atom at the para position is meta plus para, being 129.6 ppm and 133.2 ppm, respectively. The peak for the CH_3 of p-MS is detected at 21 ppm.

It is logical to expect that the methyl group substitution at the para-position will have very little effect on the chemical shifts of methylene and methine carbons in the polymer backbone. In addition to the two chemical shifts (21.01 and 29.8 ppm), corresponding to the methyl carbon from p-MS and methylene carbons from ethylene, respectively, there are three peaks (27.74, 37.01 and 45.77 ppm) corresponding to methylene and methane carbons from p-MS units which are separated by multiple ethylene units along the polymer chain.[18]

Figure 3. ^{1}H NMR spectrum for PEDM.

3.3 Polymerization Parameters

Table 2 summarizes the catalytic activity, weight-average molecular weight, number-average molecular weight, and molecular weight distribution of the terpolymer according to the polymerization time. In these experiments, the polymerization conditions, such as the feeding ratio of the monomer/comonomer/termonomer, catalyst content, Al/Zr molar ratio, polymerization time, and polymerization temperature, are the same.

The catalytic activity sharply increases but changes little after a polymerization time of 30 min. Similar phenomena are also observed for the weight-average molecular weight of the terpolymer. At a polymerization time of 30 min, the weight-average molecular weight of the terpolymer reaches a maximum value of around 96,000.

These results are ascribed to the increase in reaction medium's viscosity which restricted the diffusion of the monomer, comonomer, and termonomer. Another reason is the decrease in the amounts of the comonomer and termonomer as single site polymerization proceeds. The ranges of the molecular weight distribution of the terpolymer are 2.2−3.3.

Table 3 shows the changes in catalytic activity, molecular weight, molecular weight distribution, T_g, and T_m of the terpolymer according to the catalyst content under the same polymerization conditions such as the Al/Zr molar ratio, polymerization time, and polymerization temperature.

As the catalyst contents increases, the T_g value of the terpolymer slightly increases while the T_m value of the terpolymer changes lightly. The ranges of the molecular weight distribution of the terpolymer are 2.1−2.5, which indicate that the effect of the catalyst content is not significant.

As shown in Figure 5, for low catalyst content such as 1.5 μmol and 2 μmol, the catalytic activities are very low. However, at a catalyst content of 2.5 μmol, the catalytic activity increases sharply. The weight-average molecular weight of PEDM increases

Table 3. Terpolymerization of ethylene, 1-decene, and p-MS as a function of catalyst content.

Run No.[a]	Catalyst Content (μmol)	Catalytic Activity (kg of polymer /(mol·h))	M_w[b] (kg/mol)	M_n[b] (kg/mol)	MWD[b]
7	1.5	187	62	24	2.5
8	2.0	300	59	23	2.5
3	2.5	2648	96	45	2.2
9	3.0	2273	100	42	2.3
10	3.5	3640	100	46	2.2
11	4.0	3245	110	52	2.1

[a] Polymerization conditions: ethylene = 0.4 mol/L, 1-decene = 0.4 mol/L, p-MS = 0.4 mol/L, catalyst = rac-Et(Ind)$_2$ZrCl$_2$, cocatalyst/catalyst = 3000, polymerization time = 30 min, and solvent = toluene.
[b] Determined by by gel permeation chromatography (GPC).

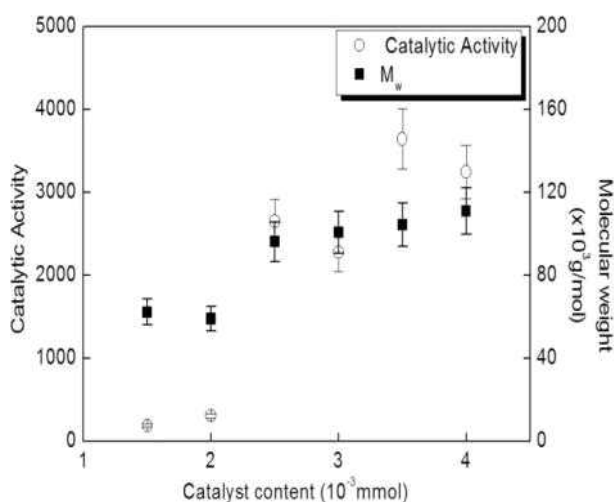**Figure 4.** ^{13}C-NMR spectra of (a) PE, (b) PED, and (c) PEDM.

Figure 5. Catalytic activity and M_w of PEDM as a function of catalyst content.

from 60,000 to 110,000 g/mol as the catalyst content increases.

Figure 6 shows the changes of the catalytic activity and weight-average molecular weight of the terpolymer according to the polymerization temperature. These factors are highly dependent on the polymerization temperature. The highest catalytic activity is obtained at the polymerization temperature of 70 °C, which reflected the increased reactivity of the monomer. Furthermore, the interaction between the cation in the catalyst and the anion in the cocatalyst increases as the polymerization temperature increases.[19]
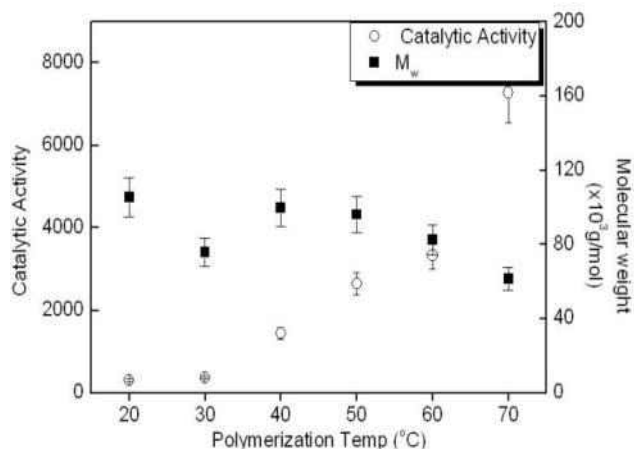
Figure 6. Catalytic activity and M_w of PEDM as a function of polymerization temperature.

However, the weight-average molecular weight of the terpolymer decreases as the polymerization temperature increases. The weight-average molecular weight of the terpolymer declines from 100,500 to 80,000 g/mol.

This result is in a agreement with the general behavior observed for ethylene/high-α-olefins copolymers under similar experimental conditions noted by Galland et al. This could be explained by the fact that during polymerization both the propagation and termination steps are affected by the reaction temperature.

The activation energy for chain-transfer reactions (termination step) is greater than that for propagation, which leads to a decrease in the molecular weight of the terpolymer at high reaction temperatures.[20]

Figure 7 shows a comparison of the changes in catalytic activities and weight-averaged molecular weight as a function of the cocatalyst/catalyst (Al/Zr) molar ratio for the same polymerization conditions such as the monomer/comonomer feeding ratio, catalyst content, polymerization time, and polymerization temperature.

During metallocene catalyzed polymerization, the cocatalyst stabilizes the cation in the transition metal, which is the center of polymerization. In addition, the cocatalyst acts as a kind of alkylating agent at the same time.

We found that the catalytic activity increases with the increasing cocatalyst/catalyst molar ratio until reaching a maximum value of 4408 at a cocatalyst/catalyst molar ratio of 4000. Further increases in the molar ratio result in the decreased catalytic activity.

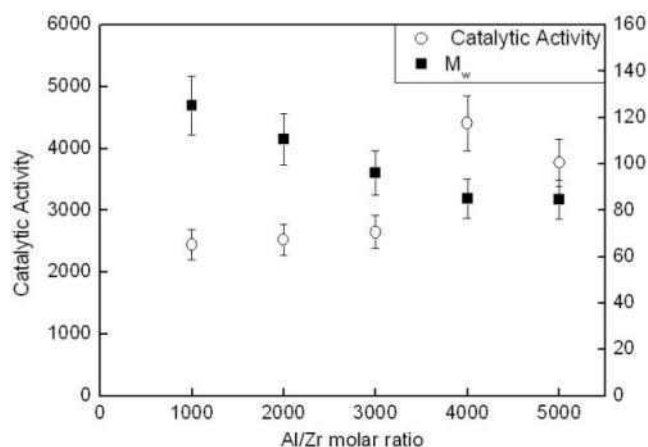This phenomenon is possibly due to the TMA (trimethylaluminium) in the reaction medium, which is one of

Figure 7. Catalytic activity and M_w of PEDM according to the cocatalyst/catalyst molar ratio.

the ingredients for the cocatalyst. TMA enhances terpolymerization by stabilizing the metallocene catalyst and simultaneously eliminating impurities such as trace of water and oxygen in the polymerization medium provided that the TMA content are proper.

However, if the TMA content is in excessive, the TMA interacts with the metallocene catalyst and forms inactive compounds on the surface of the complex, which leads to lower catalytic activity.[21]

In terms of the weight-average molecular weight of the terpolymer, a trend emerges whereby the weight-average molecular weight decreases when the Al/Zr molar ratio increases. Specially, the weight-average molecular weight of the terpolymer decreases from 125,000 to 84,000 as the Al/Zr molar ratio increases from 1000 to 5000. This result is attributed to chain transfer by alkylation of the cocatalyst.

3.4 CONCLUSIONS

We confirmed the synthesis of PE, PED, PEM, and PEDM using ^{1}H NMR, ^{13}C NMR, and FT-IR analysis.

As the catalyst contents increased, the catalytic activity and the molecular weight of the terpolymer increased simultaneously. The catalytic activity sharply increased but changed little after a polymerization time of 30 min. The catalytic activity was promoted by the increase in the cocatalyst/catalyst molar ratio until reaching maximum value at an Al/Zr molar ratio of 4000.

On the other hand, as the cocatalyst/catalyst molar ratio increased, the weight-average molecular weight of the terpolymer gradually decreased. As the polymerization temperature increased,

the weight-average molecular weight of the terpolymer decreased, whereas the catalytic activity increased.

In this study, we synthesized the terpolymer with a reactive moiety (*p*-MS) which can be easily converted into functional groups like -OH, -NH, -COOH, anhydrides, and halogens under mild conditions. We have therefore opened up the possibility of developing new high-functional elastomers in the future.

Acknowledgement

References

1. Kaminsky. W, Sinn. H. Eds, "Transition metals and organometallics as catalysts for olefin polymerization", *Springer-Verlag* (1988)

2. Shinjoon. P, Wen-Jun. W, Shiping. Z, "Continuous solution copolymerization of ethylene with propylene using a constrained geometry catalyst system", *Macromol. Chem. Phys.,* **201**, 2203 (2000)

3. Wen-jun. W, Edward K, Shiping. Z, Archie. E, "Continuous solution copolymerization of ethylene and octene-1 with constrained geometry metallocene catalyst", *J. Polym. Sci. Part A: Polym Chem.,* **37**, 2949 (1999)

4. Naofumi. N, Yukio. I, "Copolymerization of Ethylene and 1,7-Octadiene, 1,9-Decadiene with Zirconocene Catalysts" *Macromol. Chem. Phys.,* 203, 2155 (2002)

5. Kim. I, "Copolymerization of ethylene and 5-vinyl-2-norbornene by stereospecific metallocenes and epoxidation of the resulting copolymer", *React. & Funct. Polym.*, **49**, 197 (2001)

6. Kotohiro. N, Hiroya. F, Shohei. Katao, Michiya. Fujiki, Kim. H. J, Kim. D. H, Irfan. S, "Olefin Polymerization by Half-Titanocenes Containing η^2-Pyrazolato Ligands−MAO Catalyst Systems", *Macromolecules*, **44**, 1986 (2011)

7. Forlini. F, Pinci. E, Tritto. I, Sacchi. M, Piemontesi. F, "^{13}C NMR Study of the Effect of Coordinating Solvents on Zirconocene-Catalyzed Propene/1-Hexene Copolymerization", *Macromol Chem Phys.,* **203**, 645 (2002)

8. Graef. S, Wahner. U. M, Van. R, Sanderson. A. J, "Copolymerization of propylene with higher α-olefins in the presence of the syndiospecific catalyst i-Pr(Cp) (9-Flu)ZrCl2/MAO", *J. Polym. Sci. Part A: Polym Chem.,* **40**, 128 (2001)

9. Kaminsky. W, Drogemuller, "Terpolymers of ethylene, propene and 1,5-hexadiene synthesized with zirconocene/methyl-

aluminoxane", *Makromol. Chem. Rapid. Commun.,* **11**, 89 (1990)

10. Koivunmaki. J, Seppala, "Observations on the Synergistic Effect of Adding 1-Butene to Systems Polymerized with MgCl$_2$/TiCl$_4$ and Cp$_2$ZrCl$_2$ Catalysts", *J. V. Macromolecules,* **27**, 2008 (1994)

11. Gerum. W, Hohne. G. W. H, Wilke. W, Arnold. M, Wegner. T, "Hydrogenated butadiene/ethene/l -olefin terpolymers as model substances for short-chain branched polyethylene", *Macromol. Chem. Phys.,* **197**, 1693 (1996)

12. Villar. M. A. Ferreira. M. L, "Co- and terpolymerization of ethylene, propylene, and higher α -olefins with high propylene contents using metallocene catalysts", *J. Polym. Sci. Part A: Polym Chem.,* **39**, 1136 (2001)

13. Fernanda. F, Nunes E, Griselda. B. G, "^{13}Carbon Nuclear Magnetic Resonance of Ethylene–Propylene–1-hexene Terpolymers", *J. Polym. Sci. Part A: Polym Chem.,* **42**, 2474 (2004)

14. Griselda. B. G, Fernanda. F, Nunes. E, Luciano. F. da. Silva, Maria. M de Camargo F, Raul. Q, "Ethylene–propylene-α -olefin terpolymers thermal and mechanical properties", *J. Appl. Polym. Sci.,* **104**, 3827 (2007)

15. Chung. T. C, Lu. H. L, "Kinetic and Microstructure Studies of Poly (ethylene-co-p-methylstyrene) Copolymers Prepared by Metallocene Catalysts with Constrained Ligand Geometry", *J. Polym. Sci. Part A: Polym Chem.,* **36**, 1017 (1998)

16. Lu. H. L, Hong. S, Chung. T. C, "Synthesis of New Polyolefin Elastomers, Poly(ethylene-ter-propylene-ter- p-methylstyrene) and Poly(ethylene-ter-1-octene-ter-p-methylstyrene), Using Metallocene Catalysts with Constrained Ligand Geometry", *Macromolecules,* **31**, 2028 (1998)

17. Quijada. R, Narvaez. A, Rojas. R. F. Rabagliati. M. G. B, Galland. R. S, Mauler. R, Benavente. E, Perez. J. M, Perez. A. B, "Synthesis and characterization of copolymers of ethylene and 1-octadecene using the rac-Et(Ind)$_2$ZrCl$_2$/MAO catalyst system", *Macromol. Chem. Phy.,* **200**, 1306 (1999)

18. Chung T. C, Lu H. L, "Synthesis of poly(ethylene-co-p-methylstyrene) copolymers by metallocene catalysts with constrained ligand geometry", *J. Polym Sci. Part A: Polym Chem.,* **35**, 575 (1997)

19. Lee. D. H, Jung. H. K, Kim. W. S, Min. K. E, Park. L. S, Seo. K. H, Kang. I. K, Noh. S. K, "Copolymerization of Ethylene and Cycloolefin with Metallocene Catalyst: I. Effect of Catalyst", *Polymer(Korea),* **24**(4), 445 (2000)

20. Huang. J, Rempel. G. L, "Ziegler-Natta catalysts for olefin polymerization: Mechanistic insights from metallocene systems", *Prog. Polym. Sci.,* **20**, 459 (1995)

21. Lee. H. W, Park. Y. H, "Effect of Cocatalyst Type on the Characteristics of Olefin Polymerization with In-situ Supported Metallocene Catalysts", *J. Korean Ind. Eng. Chem.,* **13**(6), 570 (2002)