

Butyl Chloride as Promoter in Ethylene Polymerization by Magnesium Ethoxide-Supported Catalyst

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ABSTRACT: The effects of butyl chloride as a promoter in the ethylene polymerization were studied using a $\text{Mg}(\text{OEt})_2/\text{TiCl}_4$ /triethyl aluminum (TEA) Ziegler–Natta catalyst system, where $\text{Mg}(\text{OEt})_2$, TiCl_4 , TEA were used as support, catalyst, and activator, respectively. The influence of BC on the catalyst performance, polymerization rate, and polymer properties were investigated. This study strongly indicates that BC could act as a promoter with high performance in the ethylene polymerization. There was a remarkable increase in the catalyst yield and polymerization rate, in particularly, in the presence of hydrogen which was used for controlling the molecular weight. A reduction in the polymer molecular weight was observed in the presence of BC and hydrogen. The morphology of the polymers was evaluated through scanning electron microscopy and particle size distribution. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 2014, 131, 40189.

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INTRODUCTION

Ziegler–Natta type catalysts and polymerizations have developed considerably with the development of the new generations of catalysts and industrial processes since discovery in the early 50s. The enhancement of the catalyst and polymerization performance has been always of academic and industrial interest and various approaches have been studied. One of the efficient methods is the use of the organohalides (halocarbons) as promoters in the ethylene polymerization. It has successfully enhanced the efficiency of the catalyst and polymerization.^{1–4}

It was proven that the nature and amount of the halocarbons in the polymerization have a significant effect on the catalyst promotion, so that the catalyst activity could be increased more than two times. The promoters might influence the polymer properties including the molecular weight of the produced polymers. In addition, the other advantages of such components in the catalyst system are superior hydrogen response, and a high degree of productivity. Superior hydrogen response causes very low unsaturation in polymer and a high degree of productivity results in a very low catalyst residue. Further, this permits the utilization of a broad range of alpha-olefin comonomers, which enables the production of a wide range of densities. It also provides polymers with high bulk densities and low in fines, substantially free of agglomeration.^{5–8}

Considering possible cooperative interactions of geminal chloro groups in the catalytic system, the catalytic component which interacts with geminal chloro groups requires a specific structural arrangement to fit with and a specific chemical property to interact with. Triethyl aluminum (TEA) which prefers dimeric form with two ethyl bridge bonds and two Al Lewis acid sites of specific arrangement may be selected for the verification of the cooperative interaction with geminal chloro groups. The important chemical functions of TEA in the catalytic systems can also be counted in the selection. In normal catalytic reactions in which TEA is utilized as a catalytic system, one half order for TEA is observed because the decomposition constant of dimeric TEA into monomeric TEA is too small and dimeric TEA is involved in the catalytic reaction step. However, it can be presented that the improvement of the catalytic activity is related to the action of *in situ* generated monomeric TEA, provided that the generation of monomeric TEA from dimeric TEA is efficient in the catalytic reaction system by kinetic and/or thermodynamic interactions of other catalytic components.^{9,10}

Several halocarbons were examined for Ti-based Ziegler–Natta catalysts. Among them, butyl chloride (BC), cyclohexyl chloride, cyclopentyl chloride, and benzyl chloride have been the most effective promoters in increasing the catalyst performance.^{3–7} In addition, although some highly effective promoters were

Table I. Catalyst Analysis

Properties	Value
Surface area (m ² /g)	175.9
Pore volume (mL/g)	0.19
Average pore radius (Å)	21.1
Average particle size (μm)	12
Ti (%)	6.9
Mg (%)	18.6
Cl (%)	58.1

Table II. Effect of BC/TEA Ratio and Hydrogen on Catalyst Yield

BC/TEA (molar ratio)	H ₂ (bar)	Yield (kgPE/gCat)
0	0	34.5
0.125	0	42.5
0.25	0.125	61.9
0.5	0	51.5
0.75	0	50.5
1	0	48.5
1.25	0	41
2	0	24.2
0	3	13.7
0.25	3	34.6
0	5	4
0.25	5	9.26

reported, there were only a few reports on the details of their behavior in the polymerization and polymer properties.

In this article, BC was studied as a promoter in ethylene polymerization by the Mg(OEt)₂/TiCl₄/TEA Ziegler–Natta catalyst system. The effect of BC on the polymerization rate, catalyst hydrogen response, polymer particle size, and the molecular weights of the produced polymers were investigated in detail. Such data can be of significant interest, especially for industrial applications.

EXPERIMENTAL

Materials

Ethylene (>99.95%), nitrogen (>99.99%), and hexane (H₂O <3 ppm) were purchased from Linde (Germany), Arkan gas (Iran), and Pentane Chemistry Industries (Iran), respectively. BC (extra pure grade) was purchased from Merck (Germany).

Preparation of catalyst

The catalyst was prepared in a 1.0-L steel jacket Buchi autoclave reactor (equipped with a mechanical seal stirrer) via several steps described in detail in Refs. 11, 12.

Polymerization

Polymerization was carried out in a 1.0-L steel jacket Buchi autoclave reactor equipped with a mechanical seal stirrer (anchor form) in the slurry phase.

After running out of moisture and oxygen by nitrogen, 500 mL of hexane was added and mixed for 10 min. Afterwards,

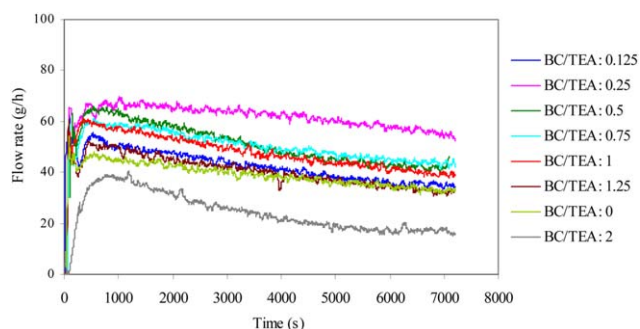


Figure 1. Effect of butyl chloride on polymerization rate. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

200 mg of TEA (in 1 mL of hexane), and a prescribed amount of BC were added to the reactor and then, the reactor was heated to 80°C. After the injection of 2 mg of the catalyst, ethylene was supplied continuously at a pressure of 8 bars during 2 h. The ethylene consumption was measured by a mass flow meter (Brooks, Holland). Meanwhile, in the polymerization with hydrogen, before ethylene was supplied, hydrogen was injected in the required amount (Table II).

After the polymerization, the unreacted gases were slowly released and the polymer was filtered and dried out.

Analysis

The amounts of titanium and magnesium elements in the prepared catalyst were measured by atomic absorption spectrophotometer (Shimadzu 6800). A precise amount of the catalyst (about 100–150 mg) was dissolved in 10 mL of 0.1M sulfuric acid solution and diluted to 100 mL with distilled water.^{13,14} The content of chloride was evaluated according to Volhard's method.¹⁴

Characterization

The surface area, pore volume, and pore radius of the catalyst were measured using BET method (NOVA2000 Quantachrome apparatus).¹⁵

The degree of crystallinity (X_c), melting, and crystallization points (T_m and T_c) of the produced polymers were studied by the DSC method.^{16,17} The measurements were performed by a Mettler Toledo 822e calorimeter at a heating or cooling rate 10°C/min under nitrogen in the range 25–200°C.

The molecular weight and molecular weight distribution of the produced polymers were measured with GPC method by PL Instrument, model PL-220. The operating conditions were set according to Ref. 18.

The morphology of the catalyst and polymer powder was depicted using scanning electron microscopy (SEM) (Cam Scan MV 2300) and their particle size was determined using the laser diffraction technique (Malvern 2000).

Catalyst yield was determined in terms of the produced polyethylene (kg) per the used catalyst (g) in the polymerization.

RESULTS AND DISCUSSION

Table I shows the BET, particle size, and elemental analyses of the used catalyst. According to the table, the catalyst had

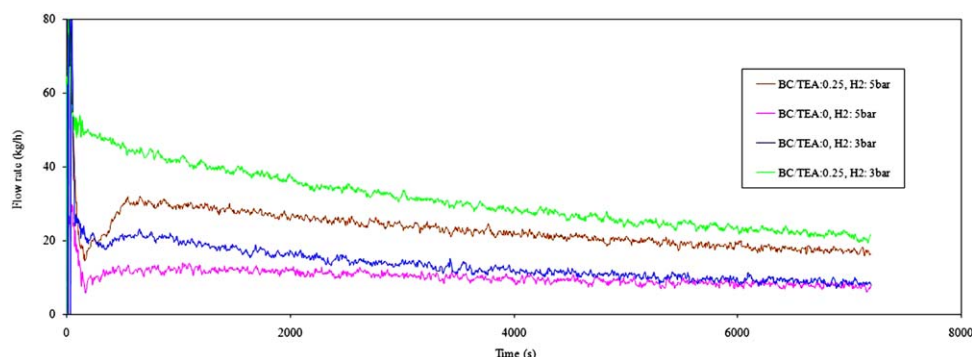


Figure 2. Effect of hydrogen on ethylene polymerization rate. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table III. Effect of Hydrogen on Molecular Weight and Molecular Weight Distribution of Produced Polymers

BC/TEA (molar ratio)	Hydrogen (bar)	Mw $\times 10^{-5}$ (g/mol)	Mn $\times 10^{-5}$ (g/mol)	Mp $\times 10^{-5}$ (g/mol)	Mz $\times 10^{-5}$ (g/mol)	MWD
0	0	3.9	0.9	9.7	18.2	3.9
0.25	0	3.2	0.9	7.2	12.4	3.3
0	3	1.3	0.2	1.5	3.1	4.7
0.25	3	1	0.1	3.4	6.8	5.2
0	5	0.7	0.1	2.6	5.3	6.4
0.25	5	0.4	0.06	2.3	5.3	6.4

remarkably high surface area (175.9 m²/g). The percentage of Ti, Mg, and Cl in the catalyst has been 6.9, 18.6, and 58.1, respectively. The catalyst had the average particle size of 12 μ m.

The effect of BC on the yield of the Mg(OEt)₂/TiCl₄/TEA Ziegler–Natta catalyst in the ethylene polymerization was investigated. Table II shows the effect of the various amounts of BC on the catalyst yield. According to the table, the yield of the catalyst enhanced with increasing the ratio of BC/TEA and following by, a decrease in the catalyst yield was observed at the high ratio of BC/TEA. Accordingly, it is concluded that the high amounts of BC poisoned the titanium-based catalyst.

As the table shows, the catalyst yield was 34.5 kgPE/gCat in the absence of BC. It increased to 61.9 kgPE/gCat at the BC/TEA molar ratio of 0.25 and then, decreased to 24.2 kgPE/gCat at

that of 2. This decrease indicates that the presence of the high amount of BC had an adverse effect on the catalyst yield.

Figure 1 exhibits the polymerization rate of ethylene at the various ratios of BC/TEA. As expected, the polymerization rate of the catalyst rose in the presence of BC. The catalyst showed the highest polymerization rate at the BC/TEA molar ratio 0.25 in which the catalyst had the maximum yield.

Hydrogen is used as a chain transfer agent for controlling molecular weight of polyolefins in the coordination polymerization with decreasing the polymer molecular weight.^{19–21} Table II exhibits the effect of hydrogen on the yield of the catalyst in the presence and absence of promoter. According to the table, the yield of the catalyst showed a decrease in the presence of hydrogen, reducing from 34.5 kgPE/gCat in the absence of hydrogen

Table IV. Particle Size Analysis

HC/TEA (molar ratio)	H ₂ (bar)	d ₁₀ (μ m)	d ₅₀ (μ m)	d ₉₀ (μ m)	Average PS (μ m)
0	0	66.6	205.8	420.3	235.6
0.25	0	79.1	214.1	429.3	251.9
0	3	31.7	100	224.4	114.3
0.25	3	51.3	155.4	381.1	220.2
0	5	14.2	44.8	100.2	63.1
0.25	5	24.0	64.6	212.5	192.1

d₁₀, d₅₀, and d₉₀ mean that 10, 50, and 90% of the particles have less than or equal to the corresponding indicated particle diameter (μ m)

Table V. Results of DSC Analysis

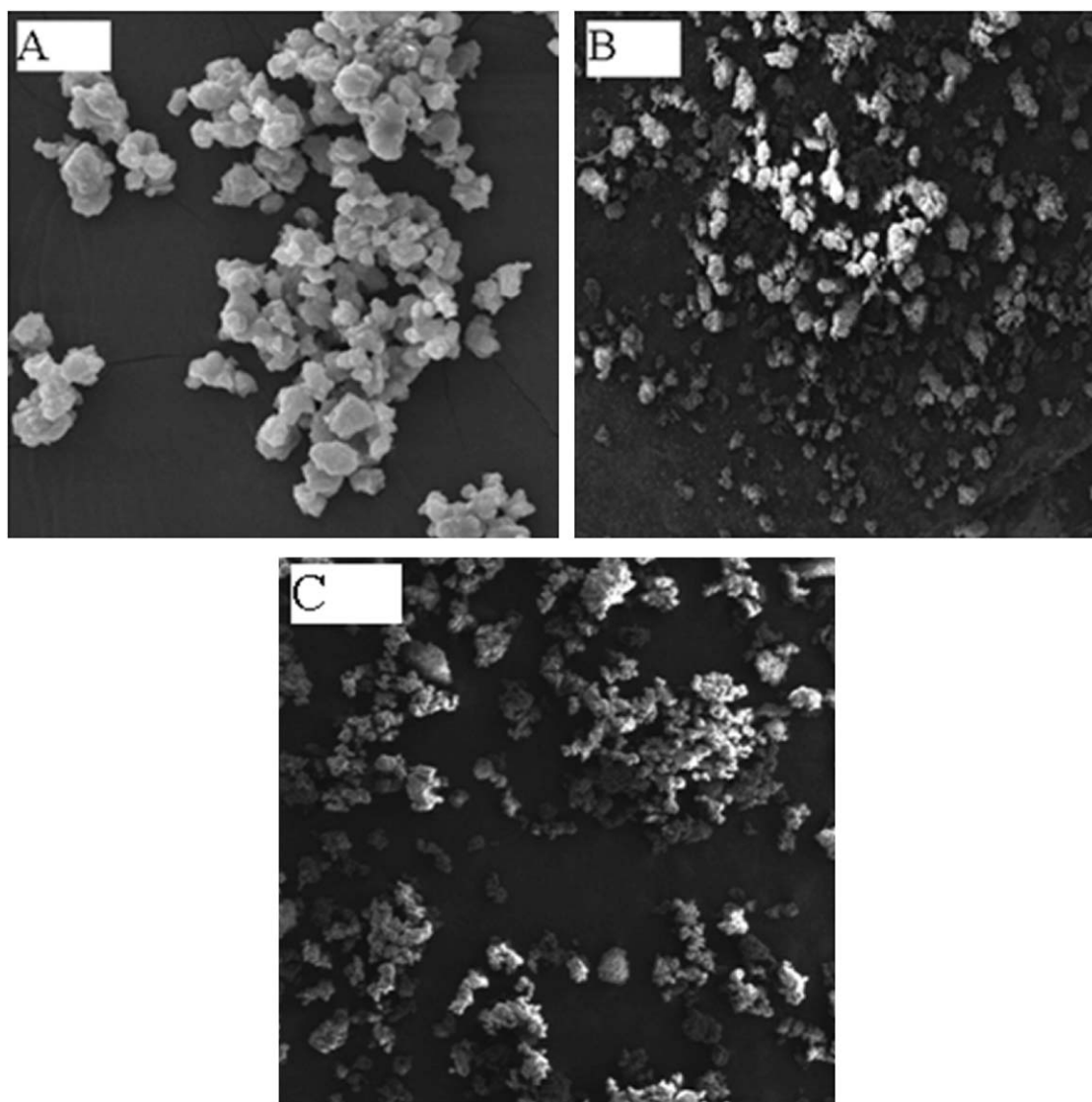
HC/ TEA	H ₂ (bar)	T _m (°C)	T _c (°C)	X _c (%)
0	0	135.7	117.9	55.8
0.25	0	136.8	118.9	57.9
0	3	134.7	118.1	65.6
0.25	3	133.6	118.6	70.2
0	5	132.3	118.3	75.8
0.25	5	131.1	117.9	83.2

to 13.7 and 4 kgPE/gCat in the presence of 3 and 5 bar of hydrogen, respectively. The main reason for such a decline in the catalyst yield was the reduction of the partial pressure of the monomer in the polymerization system by increasing the amount of hydrogen. Furthermore, the slow addition of the

monomer to the catalyst–hydrogen bond formed in the step of the chain transfer to hydrogen causes an adverse effect on the catalyst yield.^{22,23}

As seen in the table, the addition of BC to the polymerization system significantly promoted the catalyst yield. In addition, the relative promotion of the catalyst yield in the presence of hydrogen is more than the experiment with the absence of hydrogen. Since hydrogen had remarkably negative influence on the catalyst yield, the promoter can noticeably improve the catalyst performance at the presence of hydrogen. In particular, for producing some commercial products in the polyethylene industrial plants, a high amount of hydrogen is used which causes a sharp decline in the catalyst yield. In this case, the use of BC prevents the reduction in the catalyst efficiency.

Hydrogen also decreased the polymerization rate, so that the polymerization rate fell from about 70 g/h at the absence of hydrogen to about 20 and 10 g/h at the presence of 3 and 5

**Figure 3.** SEM images: (A) catalyst, (B) polymer powder, (C) polymer powder produced at the presence of butyl chloride.

bars of hydrogen, respectively (Figure 2). As the figure displays, the polymerization rate noticeably enhanced in the presence of BC.

Table III shows the GPC results of the produced polymers in the presence and absence of hydrogen, and BC in the polymerization system. As observed from the table, hydrogen had a significant effect on the molecular weight; so it decreased from about 3.9×10^5 g/mol in the absence of hydrogen to around 1.3×10^5 and 7×10^4 g/mol in the presence of 3 and 5 bars of hydrogen, respectively.

According to the table, the addition of BC caused a decrease in the molecular weight, reducing from 3.9×10^5 g/mol in the absence of BC to 3.2×10^5 g/mol in the presence of BC, when there was no hydrogen in the polymerization system. This reduction is contributed to an increase in the rate of the chain transfer agent in the presence of BC. It was proven that TEA can act as a chain transfer agent. Since the dimeric form of TEA is converted to the monomeric form in the presence of the promoter, the order of TEA increased in the polymerization system. It can be resulted in the improvement in the chain transfer agent role of TEA. For this reason, a reduction in the polymer molecular weights is observed.

Similarly, the same behavior was observed when hydrogen was used in the polymerization. Hydrogen noticeably reduced the polymer molecular weight. When BC was applied, further decrease in the molecular weight occurred. In other words, an enhancement in the catalyst hydrogen response can be obtained using less amount of hydrogen for producing polymers with a certain molecular weight in the presence of a suitable promoter in the ethylene polymerization system.

Table IV shows the particle size analysis of the produced polymers at the presence and absence of hydrogen and BC. It indicates that the polymer particle size grew in the presence of BC due to the enhancement in the catalyst yield.

According to the table, d_{10} , d_{50} , d_{90} , and average particle size of the produced polymer at the absence of hydrogen, and BC were about 67, 205, 420, and 236 μm , respectively; whereas, d_{10} , d_{50} , d_{90} , and average particle size of the produced polymer at the presence of the BC was raised to about 79, 214, 429, and 252 μm , respectively. In the presence of hydrogen, a decrease in the particle size was observed which could be contributed to the less particle size growth because of the reduction in the catalyst yield.

The values of the T_m , T_c , and X_c of the produced polymers are listed in Table V. The results show that, the melting point of the produced polymers in the presence of hydrogen and BC slightly decreased; whereas, there were not remarkable changes in the crystallization temperatures of the polymers. Meanwhile, X_c of the produced polymers at the presence of hydrogen and halo-carbon showed an increase. This increase can be attributed to the reducing in the molecular weight of the products.

Figure 3 displays the SEM images of the catalyst and the produced polymer powder. As demonstrated in the figure, the samples did not have a regular shape. It has been proven that the polymer tends to replicate the shape of the catalyst particles on

which it is produced. In other words, the catalyst particles act as template for the growth of the polymer particles.^{24,25} Since the prepared catalyst had an irregular shape, the produced polymer also showed the similar morphology.

CONCLUSIONS

The Mg(OEt)₂/TiCl₄/TEA Ziegler–Natta catalyst system showed high activity in the ethylene polymerization. The use of BC promoted the catalyst performance. A Significant enhancement in the catalyst yield, and hydrogen response was observed. It was shown that the molecular weight of the produced polymers reduced in the presence of BC. Also, there was an overall increase in the particle size when BC was used in the polymerization system. DSC results exhibited that the melting temperature of the produced polymers decreased in the presence of hydrogen; whereas there was no change in the crystallization temperature. In addition, an increase in the crystallinity degree of the produced polymers was observed at the presence of hydrogen and BC. Meanwhile, the SEM images showed that the catalyst and produced polymers did not have a regular morphology

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