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# Synthesizing UHMWPE Using Ziegler-Natta Catalyst System of $MgCl_2$(ethoxide type)/ $TiCl_4$/tri-isobutylaluminum

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**Summery:** A Ziegler-Natta catalyst of $MgCl_2$ (ethoxide type)/$TiCl_4$ has been synthesized. In order to obtain ultra high molecular weight polyethylene (UHMWPE) tri-isobutylaluminum which is less active to chain transfer was used as cocatalyst. Slurry polymerization was carried out for the polymerization of ethylene while, dilute solution viscometry was performed for the viscosity average molecular weight (Mv) measurement. The effect of [Al]/[Ti] molar ratio, temperature, monomer pressure and polymerization time on the Mv and productivity of the catalyst have been investigated. The results showed increasing [Al]/[Ti] ratio in the range of 78–117, decreased the Mv of the obtained polymer from $7.8 \times 10^6$ to $3.7 \times 10^6$ however, further increase of the ratio, resulted in decreased of by much slower rate up to $[Al]/[Ti] = 588$. The higher pressure in the range of 1–7 bars showed the higher the Mv of the polymer obtained, while increasing temperature in the range of 50 to 90 °C decreased the Mv from $9.3 \times 10^6$ to $3.7 \times 10^6$. The Mv rapidly increase with polymerization time in the first 15 minutes of the reaction, this increase was slowly up to the end of the reaction (120 min). Increasing [Al]/[Ti] ratio raised productivity of the catalyst in the range studied. Rising reaction temperature from 50 to 75 °C increased the productivity of the catalyst however, further increase in the temperature up to the 90 °C decreased activity of the catalyst. Monomer pressure in the range 1 to 7 bars yields higher productivity of the catalyst. Also by varying polymerization conditions synthesizing of UHMWPE with Mv in the range of $3 \times 10^6$ to $9 \times 10^6$ was feasible.

**Keywords:** dilute solution viscometry; slurry polymerization; UHMWPE; Ziegler-Natta catalyst

## Introduction

Many Ziegler-Natta catalysts are used for polymerization of ethylene leading to high density polymer (HDPE). A special class of HDPE is ultra high molecular weight polyethylene (UHMWPE).The polymer is high density polyethylene with a molecular weight over $1 \times 10^6$. Polymerization processes for production of UHMWPE employs is also heterogeneous Ziegler - Natta similar to the conventional HDPE.[1–5] However, polyethylene with molecular weight as high $1 \times 10^6$ was produced using metallocene catalyst as well.[3,6]

In the polymerization, polymerization method, reaction conditions such as temperature, pressure, type of catalyst, cocatalyst, and chain transfer agent can significantly influence the composition, molecular weight and its distribution, degree of branching and hence the final architecture of the polymer obtained.[1,2,7,8]

UHMWPE has desirable physical and mechanical character such as high abrasion

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resistance, high toughness, good corrosion and chemical resistance, resistance to radiation, resistance to cyclic fatigue and extremely high fiber modulus.[1,2,9–11] These properties are directly connected with the molecular structure of the polymer determined by polymerization conditions and catalyst system composition used.[7,8] Researcher in this direction showed that UHMWPE of different morphology can be synthesized by using highly active supported catalyst along with a change in polymerization conditions.[7,12,13] The polymer display poor processes ability and products of UHMWPE possess fusion defects or grain –boundaries may lead to poor mechanical performance of the finished polymer particles which cause UHMWPE eventually fails in some application.[1,14]

The aim of the present work is to study the effect of polymerization conditions on molecular weight of UHMWPE produced using the prepared heterogeneous $MgCl_2$ (ethoxide type)/$TiCl_4$/TiBA catalyst system in slurry polymerization.

## Experimental Part

Tri-isobutylaluminum (TiBA) was acquired from Schering Co Ltd (Bergkaman, Germany). Other chemical, catalyst preparation method, polymerization procedure is described elsewhere.[15,16] The viscosity average molecular weight ($M_V$) of the polymer was determined using dilute solution viscometry according to refs[15–17] while a silicon oil bath containing three viscometers was used to obtain constant temperature required.

## Result and Discussion

Several factors could affect on molecular weight of polyethylene using $MgCl_2$ (ethoxide type)/$TiCl_4$/TiBA catalytic system. $Mg(OC_2H_5)_2$ was used as starting chemical

**Table 1.**
Effect of [TiBA]:[Ti] molar ratio on productivity of the catalyst and $M_V$ of the polyethylene obtained.

| [Al]:[Ti] | g PE/mmol Ti. | $M_V \times 10^6$ |
|---|---|---|
| 78:1 | 40 | 7.8 |
| 117:1 | 714 | 5.8 |
| 157:1 | 1188 | 3.7 |
| 196:1 | 1701 | 3.8 |
| 290:1 | 2591 | – |
| 392:1 | 3598 | 3.2 |
| 486:1 | 4253 | 3.1 |
| 588:1 | 4784 | 3.8 |

Polymerization conditions; temp = 60 °C, monomer pressure = 7 bars, time = 2 hours.

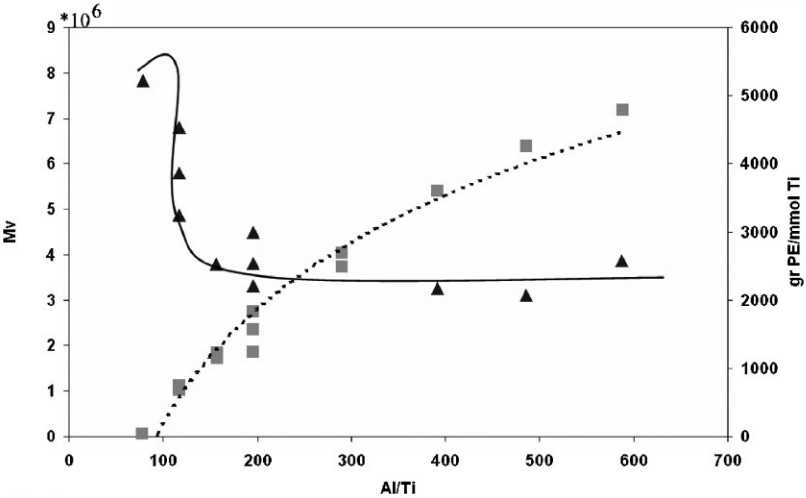

**Figure 1.**
Effect of [Al]:[Ti] on productivity of the catalyst (–□–) and Mv of the polymer obtained (-△-). Polymerization conditions as in Table 1.

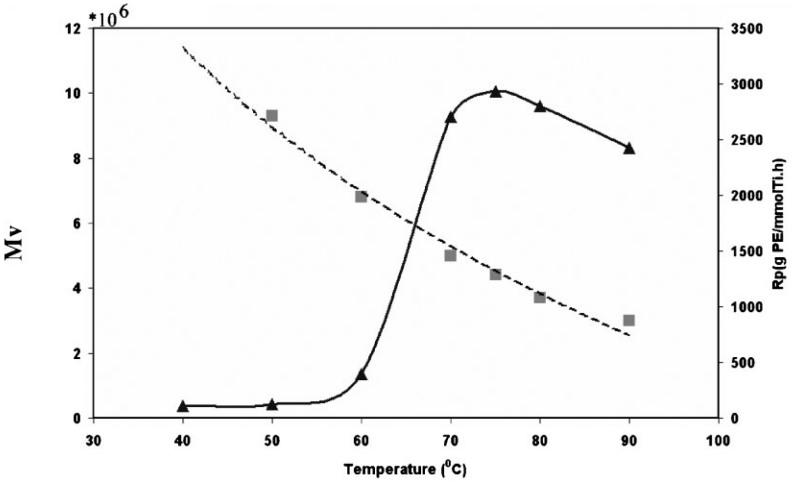

**Figure 2.**
Effect of temperature reaction on productivity (-△-) and the $M_V$ (–□–) of the polyethylene. Polymerization conditions, [Al]:[Ti] = 117:1, monomer pressure = 7 bars, polymerization time = 2 h.

which could converted to $MgCl_2$ during the catalyst preparation. $Mg(OC_2H_5)_2$ has advantage which is not hygroscopic comparing to $MgCl_2$ itself. To obtain high molecular weight polymer TiBA was used as cocatalyst which is less active for chain transfer to occur comparing to common cocatalyst used for this kind of Ziegler Natta catalyst which is tri-ethylaluminum (TEA). The effect of [Al]:[Ti] molar ratio on activity and $M_V$ was studied using the catalytic system. [Al]:[Ti] molar of 78 to 588 was used at 60°C and monomer pressure of 7 bars for 2 hours. The $M_V$ decreased with

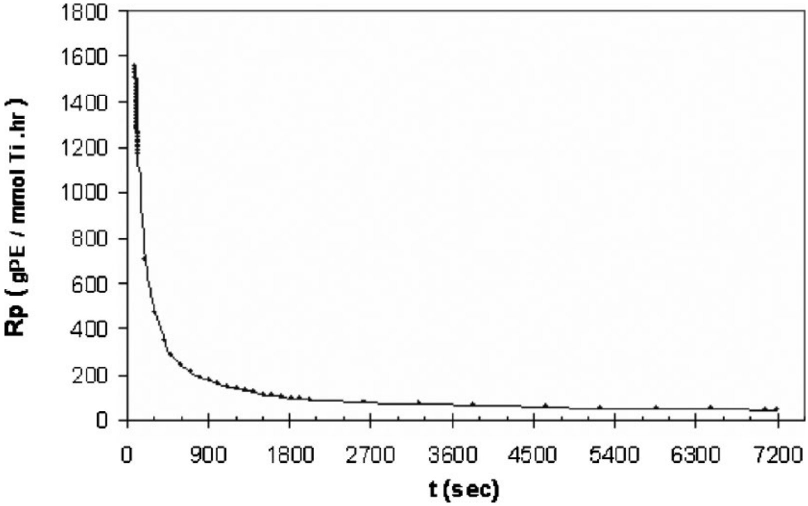

**Figure 3.**
Rate/time profile of the reaction. Polymerization conditions; temp = 40 °C, monomer pressure = 4 bars, polymerization time = 2h, [Al]:[Ti] = 117:1.

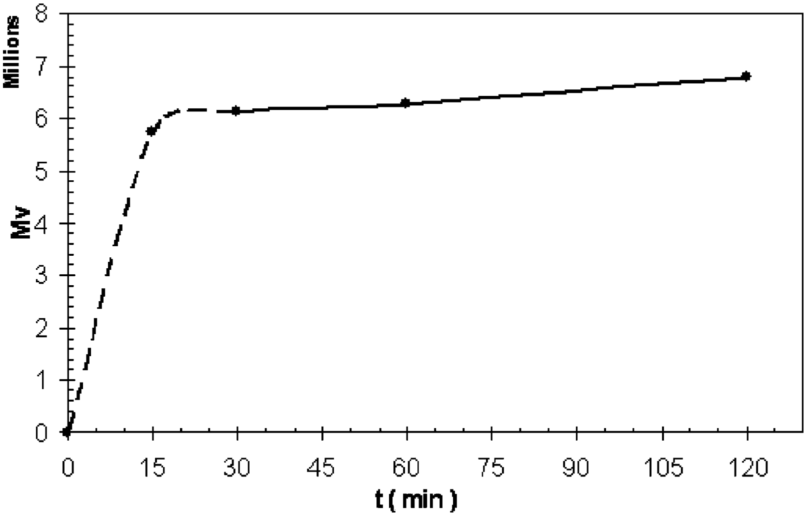

***Figure 4.***
Effect of polymerization time on the $M_V$. Polymerization conditions; Tem = 60 °C, monomer pressure = 7 bars, [Al]:[Ti] = 117:1.

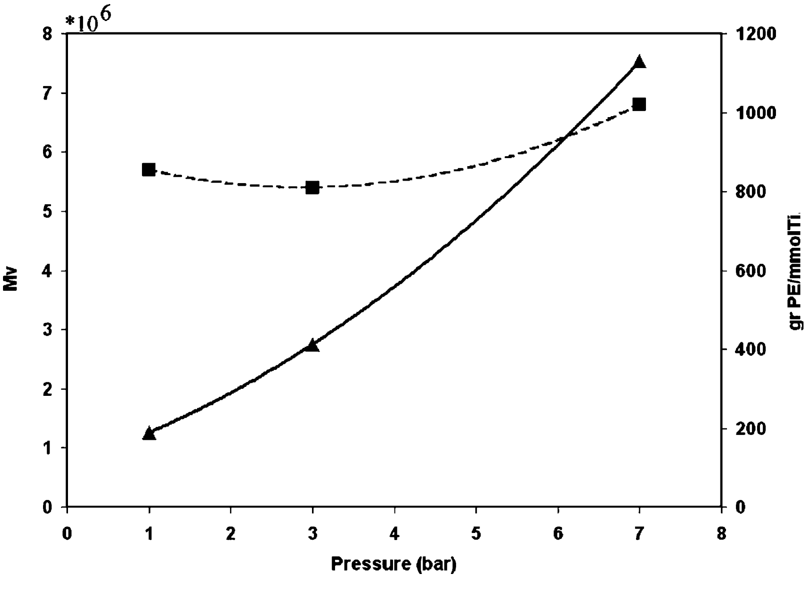

***Figure 5.***
Effect of monomer pressure on both activity (-△-) and $M_V$ (–□–) of the obtained polymer. Polymerization conditions; [Al]:[TI] = 117:1 temp = 60 °C, time = 2 h.

addition of TiBA concentration to a limiting value of about $3 \times 10^6$ (Table 1). Productivity of the catalyst in term of g PE/mmol Ti was continuously increased with increasing [Al]:[Ti] molar ratio to 588:1 which was studied. The behavior indicate of less ability of TiBA to deactivate $Ti^{IV}$ and $Ti^{III}$ active centers to less active sites of $Ti^{II}$ (Table 1 and Figure 1).

Optimum activity of the catalyst was obtained at 75 °C while the $M_V$ decreased from $9.3 \times 10^6$ to $3.0 \times 10^6$ with increasing temperature from 50 to 90 °C (Figure 2).The higher the temperature the more chain transfer to occur.[18,19]

The $M_V$ as high $9.3 \times 10^6$ was obtained at polymerization temperature of 50 °C and monomer pressure of 7 bars. The highest of the $M_V$ obtained in the study.

Rate/time profile of the catalyst was a decay type without an induction period (Figure 3) as reported.[20]

However the $M_V$ sharply increased during early stage of the polymerization (up to 15 min) following to a slow increase with polymerization time to 2 hours (Figure 4).[18]

The effect of monomer pressure of 1 to 7 bars on activity of the catalyst and the $M_V$ of the polymer were studied. Activity of the catalyst was almost exponentially increased with monomer pressure. The behavior could be due to high concentration of the monomer close to active centers and more fragmentation of the catalyst which may occur at higher monomer pressure (Figure 5).[16,21,22] The $M_V$ of the polyethylene obtained was also increased with the monomer pressure (Figure 5). The $M_V$ as high $7.8 \times 10^6$ was obtained at monomer pressure of 7 bars. The behavior is due to high concentration of monomer in polymerization media which lead more propagation to carry out.

## Conclusion

Ultra high molecular weight polyethylene may produce using Ziegler-Natta catalyst system of $MgCl_2$ (ethoxide type)/$TiCl_4$/TiBA which contain TiBA as cocatalyst. The cocatalyst has not high activity as chain transfer agent. Increasing both of TiBA concentration and polymerization temperature decreased the $M_V$, while higher monomer pressure raised the $M_V$. Activity of the catalyst was increased with monomer pressure and TiBA concentration in the range studied. In the whole range of this study the $M_V$ of higher than $3 \times 10^6$ was obtained. The highest of the $M_V$ was obtained at 50 °C and monomer pressure of 7 bars. From the study can say that temperature is more affected on the $M_V$ of the polymer obtained than monomer pressure and also TiBA concentration. Rate/time profile of the polymerization was a decay type. No optimum value of [TiBA]:[Ti] ratio was observed base on activity of the catalyst in the range studied.

It is shown that by careful selection of catalyst concentration and mole ratio of the catalyst components in slurry polymerization, UHMWPE with molecular weights from $3 \times 10^6$ to $9.3 \times 10^6$ can be obtained.

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