

Copolymerization of Ethylene/Propylene Elastomer Using High-Activity Ziegler–Natta Catalyst System of MgCl_2 (Ethoxide Type)/EB/PDMS/ TiCl_4 /PMT

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ABSTRACT: A high-activity Ziegler–Natta catalyst of TiCl_4 -supported MgCl_2 (ethoxide type) was prepared. Ethyl benzoate (EB) and polydimethylsiloxane (PDMS) were used as internal donors, while *p*-methyl toluate (MPT) and triethylaluminum (TEA) were used as the external donor and cocatalyst, respectively. Suspension copolymerization of ethylene–propylene (EPM) was carried out in *n*-heptane using the catalyst system. The relative pressures of 1.5 : 1 and 2 : 1 atmosphere of propylene-to-ethylene (P_P/P_E) gave a polymer with elastomeric properties. The relative pressure of propylene-to-ethylene higher and lower than the above values, however, gave a homopolymer or copolymer without elastomeric properties. The effect of the TEA concentration, H_2 concentration, temperature, and pressure of P_P/P_E on the yield of the polymer obtained was investigated. The effects of these factors on the glass transition temperature (T_g) and ethylene content of the polymer were studied. The content of ethylene in EPM was determined using the FTIR technique. The molar ratio of $\text{Al} : \text{MPT} : \text{Ti} = 355 : 107 : 1$ gave a polymer with an ethylene content of about 32%. However, a ratio lower than $\text{Al} : \text{MPT} : \text{Ti} = 355 : 107 : 1$ did not give a good elastomeric polymer. The highest productivity of the catalyst was obtained at a molar ratio of $\text{Al} : \text{MPT} : \text{Ti} = 355 : 107 : 1$. Increasing the temperature from 45 to 70°C caused a slight increase of Et % content and a decrease of the T_g of the copolymer obtained, while the highest productivity of the catalyst was obtained at 55°C with good elastomeric properties using an $\text{Al} : \text{MPT} : \text{Ti} = 497 : 107 : 1$ molar ratio. Increasing the pressure of propylene from 1.5 to 2.5 atm caused a sharp decrease in the T_g and ethylene content of the polymer. When the ethylene content in the copolymer was increased, the T_g value had a tendency to be closer to the polyethylene T_g . © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 84: 785–790, 2002; DOI 10.1002/app.10330

Key words: Ziegler–Natta catalyst; supported catalyst; ethylene–propylene elastomer; copolymerization; slurry polymerization

INTRODUCTION

Since the discovery of the Ziegler–Natta catalyst, catalysts have used for the polymerization and

copolymerization of α -olefins. The production of elastomeric polyolefins such as ethylene–propylene (EPM) copolymers, however, were traditionally carried out with a homogeneous Ziegler–Natta catalyst based on vanadium compounds such as VCl_4 , VOCl_2 , and vanadium triacetylacetonate.^{1–3} A large number of titanium catalyst systems for copolymerization have been used.^{2,4–6}

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It is well known that the MgCl_2 -containing Ti catalyst combined with alkylaluminum possesses very high activity in olefin polymerization. The application of the Ziegler–Natta heterogeneous catalytic system based on titanium compounds for the production of elastomeric polyolefins has recently attracted great interest,^{4–10} due, partially, to the high performance and versatility of the supported third and fourth generations of the catalytic system, which cause high activity and decrease production costs.^{11,12}

Solid components of a catalyst for the synthesis of elastomeric EPM copolymers typically amorphous, basically consisting of a Ti compound supported on a soiled component of MgCl_2 , were used.^{13–15} Examples of magnesium compounds suitable for the preparation of MgCl_2 in the final solid catalyst are MgCl_2 , $\text{Mg}(\text{OH})\text{Cl}$, $\text{MgCl}(\text{OH}_4\text{H}_9)$, and $\text{Mg}(\text{OEt})_2$.¹⁵

On the other hand, in the copolymerization of ethylene with various α -olefins over a Ti-compound catalyst, it is generally recognized that the copolymer composition strongly depends upon the catalyst systems and polymerization conditions. A solid catalyst of TiCl_4 -supported Mg compounds together with suitable electron donors give great performance for the polymerization and copolymerization of α -olefins.^{5,16–18} It may be considered, therefore, that the copolymer compositions can be controlled by changing the fractions of the active Ti^{+3} and Ti^{+2} species. These catalysts combined with Al compounds and an external donor which prevent overreduction of Ti^{+4} to Ti^{+2} showed high activity and good performance for the production of EPM.^{19–22} Ti^{+2} is only active for the polymerization of ethylene and can cause homopolymerization instead of copolymerization.²³

Catalysts based on Ti-compound-supported MgCl_2 obtained from $\text{Mg}(\text{OEt})_2$ combined with polydimethylsiloxane (PDMS) showed high activity.¹⁵ Kakugo et al.²⁴ showed that a random copolymer was produced on isotactic active centers. The centers are high in the presence of an internal donor.

EXPERIMENTAL

Materials

Polymerization-grade propylene and ethylene with high purity (purity > 99.5%) were supplied by the Arak Petrochemical Co. (Arak, Iran) and purified further by passage through columns of activated 13X- and 4A-type molecular sieves. Ni-

trogen of an extrapure grade (99.99%) was dried by passage through columns of P_2O_5 , KOH, and 4A-type molecular sieves. Heptane and hexane were supplied by the Iranian Petrochemical Co. (Tehran, Iran) and toluene (Merck) was distilled over calcium hydride and stored over 13X- and 4A-type molecular sieves. Ethyl benzoate (EB, Merck) was stored over sodium wire and 13X and 4A-type molecular sieves before use. *p*-Methyl toluate (MPT) was prepared.²⁵ Magnesium ethoxide was supplied by the Arak Petrochemical Co. and used without purification. Titanium tetrachloride (Merck) was used without further purification. Polydimethylsiloxane (Bayer, Germany) was also used without further purification. Triethylaluminum (TEA, Merck) was diluted using *n*-heptane to a 1M solution.

Catalyst Preparation

In an about 1-L glass catalyst preparation reactor equipped with a shaft motor stirrer under an atmosphere of nitrogen, diethoxymagnesium was added. Toluene, 100 mL, was added and stirred to form a suspension. TiCl_4 , 40 mL, EB, 2 mL, and PDMS, 0.7 mL, were added. The content of the reactor was heated to 90°C and stirred at this temperature for 1 h. The reaction mixture was filtered and the resultant solid was washed using 100 mL *n*-hexane twice. Toluene (50 mL) was added and the temperature was decreased to 40°C. TiCl_4 , 40 mL, was added and the mixture was heated at this temperature for further 12 h. The solid catalyst was washed 10 times using *n*-heptane at 40°C and then dried. The prepared solid catalyst was stored in a dry box under an atmosphere of nitrogen.

Polymerization Procedure

Copolymerization was carried out in a 1-L stainless-steel reactor of Buchi (bds 488), a semibatch type, equipped with a stirrer speed control, temperature control, and double feed. The reactor was purged with nitrogen. Heptane, 400 mL, was charged into the reactor and degassed at least three times. When the polymerization temperature reached the required temperature, the catalyst components were added in the following order: TEA, MPT, solid catalyst, and hydrogen (if any).

All these reagents were added as slurries, a solution in *n*-heptane, or a gas. The mixture of ethylene and propylene was separately prepared in storage with the required pressure of pro-

Table I Effect of Al : MPT : Ti Molar Ratio on Productivity of the Catalyst and Properties of Polymer Obtained

[TEA] : [MPT] : [Ti]	g EPM (mmol Ti h atm L)	T_g (°C)	Ethylene (%)
710 : 107 : 1	12,029	-15.24	—
497 : 107 : 1	9 943	-16.44	—
355 : 107 : 1	2 175	-21.84	32

pylene/ethylene. Then, the mixture of monomers was continuously fed into the reactor. The pressure inside the reactor was maintained constant. Therefore, the required amount of the monomer mixture to feed into the reactor is equal to the consumption of the monomers and was controlled by the pressure sensor. At the end of the reaction time, mainly 2 h, the monomer mixture feed was stopped and the reactor was degassed. The polymerization was terminated by draining the slurry polymer into a small volume of acidified methanol. The polymer obtained was filtered and dried at 70°C overnight.

Polymer Characterization

Determination of the glass transition temperature (T_g) was performed using a DSC PL Model STA 780. Dynamic mechanical thermal analysis (DMTA) was performed using a DMTA PL model. The ethylene content in EPM was measured according to ASTM D 3900-95 procedures²⁶ using an FTIR, BRUKER Model IFS48.

RESULTS AND DISCUSSION

Effect of TEA Concentration

The effect of the Al : Ti molar ratio on the polymerization activity, T_g , and ethylene content of the copolymer were studied. To establish the optimum activity and high content of the ethylene percent, the Ti concentration (0.035 mmol dm⁻³)

and MPT concentration (0.563 mmol dm⁻³) were kept constant and various amounts of TEA were used. Table I lists the results obtained. The relative pressure of propylene to ethylene were chosen to be 2 to 1, while the total pressure of the monomer mixture kept at 2 atmosphere. Increasing the Al : MPT : Ti molar ratio from 355 : 107 : 1 to 710 : 107 : 1 increased the productivity of the catalyst, while a further increase did not give a good copolymer. A ratio less than 355 : 107 : 1 did not give a good elastomeric polymer. At 60°C of polymerization and a molar ratio of Al : MPT : Ti = 355 : 107 : 1, the ethylene content was 32% and the T_g was -21.84°C. This ratio was chosen for further studies.

At a high concentration of TEA, overreduction of Ti⁺⁴ to Ti⁺² occurred, the species which are highly active but only active for ethylene polymerization.^{16,27,28} Decreases in the T_g of the copolymers obtained are probably due to increase of the ethylene content incorporated.²⁹

Effect of Temperature on Copolymerization Behavior

The effect of temperature on the polymerization behavior at a pressure ratio of $P_P/P_E = 2 : 1$ atm at a TEA : MPT : Ti = 355 : 107 : 1 molar ratio was investigated. The temperature range from 45 to 70°C was studied. Increasing the temperature in the range studied caused a decrease in productivity, a decrease in the T_g , and an increased ethylene content of the copolymers obtained (Table II).

Table II Effect of Temperature on Copolymer Property

Temperature (°C)	Yield g EPM (mmol Ti h atm L)	T_g (°C)	Ethylene (%)
45	3995	-8.68	—
50	3460	-17.66	28
55	2637	-20.32	31
60	2175	-21.84	32
70	1687	-23.54	36

[TEA] : [MPT] : [Ti] = 355 : 107 : 1 molar ratio, [Ti] = 0.035 mmol/lit, $P_P/P_E = 2 : 1$ atm.

Figure 1 shows the variation of the catalyst productivity with the temperature. T_g values decreased sharply as the temperature was increased from 45 to 55°C, while a further increase in temperature slightly decreased the T_g of the polymer obtained (Fig. 2). The percentage of the ethylene content in the copolymers obtained are increased almost linearly with increasing temperature (Fig. 3). The reactivity ratios of the monomer obtained for ethylene-propylene copolymerization depend on the catalyst system.²⁹ The values of the reactivity ratio for ethylene α -olefin pairs depend on the temperature of copolymerization.³ For copolymerization of ethylene/1-butene when the temperature increased from 50 to 120°C, the reactivity ratios decrease.³⁰ Several factors can contribute to the temperature effect on the reactivity ratio value, including a diffusion limitation for heavier α -olefin³¹ which can be serious at high temperature.

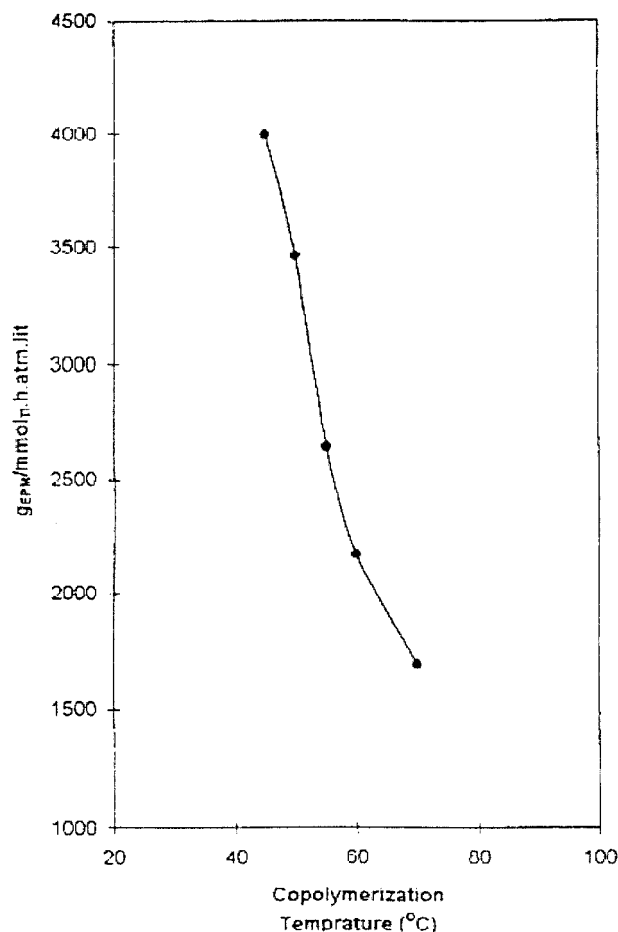


Figure 1 Plot of yield of copolymer versus copolymerization temperature. TEA : MPT : Ti = 355 : 107 : 1; [Ti] = 0.035 mmol/L; $P_P/P_E = 2 : 1$ atm.

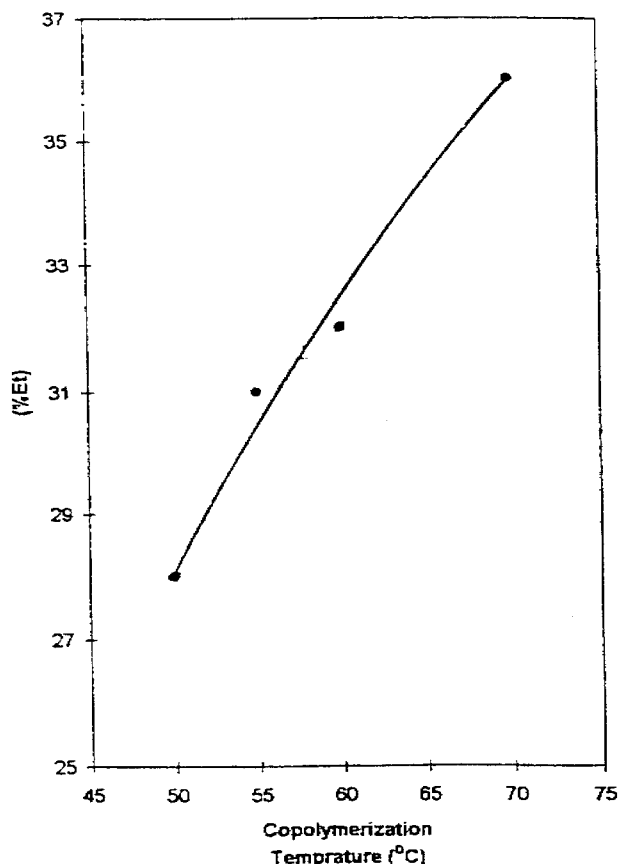


Figure 2 Plot of T_g versus copolymerization temperature. Polymerization conditions same as in Table II.

Effect of Relative Pressure on of Propylene/Ethylene

The effect of relative pressure of propylene/ethylene in the range of 1.25–5 atm on the copolymerization behavior and properties of the copolymers obtained was studied. The polymerization temperature was 60°C and a TEA : MPT : Ti = 355 : 107 : 1 molar ratio was used. Increasing the P_P/P_E ratio caused a decrease in the productivity of the catalyst, decreased T_g values of the copolymers obtained, and decreased content of the ethylene percentage in the copolymers (Table III). The results obtained in Tables I–III and the one reported in the literature³² indicate that when the ethylene content in the EPM copolymer was increased, the T_g value had a tendency to be closer to the polyethylene T_g .

CONCLUSIONS

1. The prepared catalyst system of $MgCl_2$ (ethoxide type)/EB/TiCl₄/PDMS/TEA/PMT

- has relatively high activity for the copolymerization of ethylene and propylene.
- Copolymers of various amounts of ethylene content and various T_g 's were obtained using the catalyst system at different copolymerization conditions.
 - The copolymer obtained from a TEA : PMT : Ti molar ratio of more than 710 : 107 : 1 does not show elastomeric properties. Copolymers obtained at higher ratio contained a combination of PP and PE stuck on EPM.
 - For the molar ratio of less than TEA : PMT : Ti = 355 : 107 : 1, no copolymer was obtained.
 - Relative pressures of P_P/P_E between 1.5 and 2 : 1 are suitable for the copolymerization. However, higher values give polypropylene and lower values give polyethylene.
 - The optimum temperature of copolymerization depends on the T_g and the percentage of ethylene required.

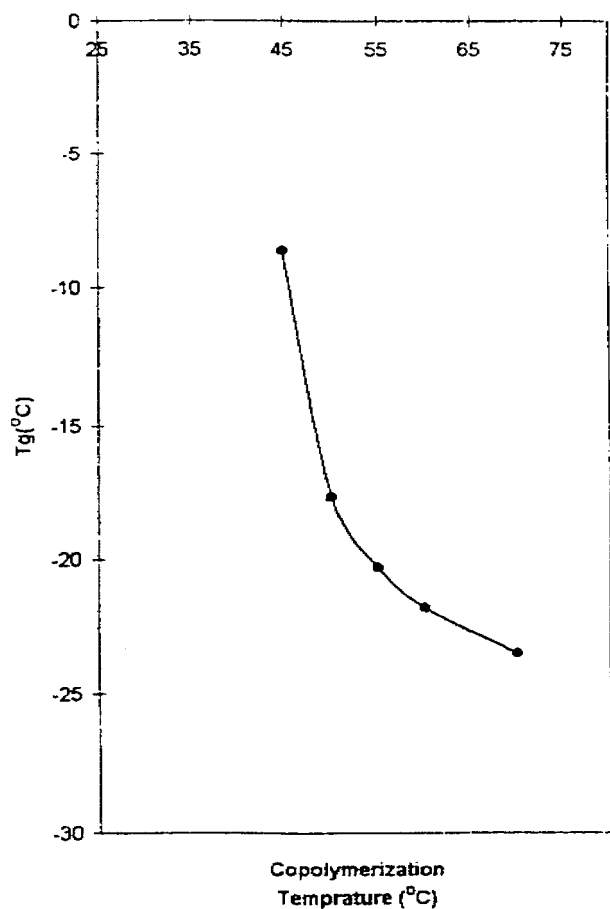


Figure 3 Plot of percentage of ethylene content versus copolymerization temperature. Polymerization condition same as in Table II.

Table III Effect of Relative Pressure of Propylene/Ethylene on Copolymer Property

Polypropylene/ Polyethylene	Yield g EPM (mmol Ti h atm L)	T_g (°C)	Ethylene (%)
1.5 : 1	755	-35.16	55
2 : 1	2175	-21.84	32
2.5 : 1	1642	-15.82	—

- Increasing the temperature of copolymerization decreased the catalyst activity.
- Increasing the temperature of copolymerization increased the ethylene content of the copolymer and decreased the T_g value. The T_g value has a tendency to be closer to the T_g of polyethylene by increasing the temperature.
- Increasing of the polyethylene content of the copolymer caused the T_g value of the copolymer to become close to the T_g of polyethylene and vice versa.

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