Copolymerization of Ethylene–Propylene Using High-Activity Bi-supported Ziegler–Natta TiCl$_4$ Catalyst

G. H. Zohuri,[1] M. M. Mortazavi,[2] R. Jamjah,[2] S. Ahmadjo[2]

[1]*Ferdowsi University of Mashhad, Iran*
[2]*Iran Polymer and Petrochemical Institute, Tehran, Iran*

ABSTRACT: Heterogeneous Ziegler–Natta TiCl$_4$ catalyst using MgCl$_2$ and SiO$_2$ as supports was prepared under controlled conditions. Mg(OEt)$_2$ was used as a starting material and was expected to convert to active MgCl$_2$ during catalyst preparation. Due to the high surface area and good morphological control, SiO$_2$ was chosen as well. Slurry copolymerization of ethylene and propylene (EPM) was carried out in dry *n*-heptane by using the catalyst system SiO$_2$/MgCl$_2$/TiCl$_4$/EB/TiBA or TEA/MPT/H$_2$ at temperatures of 40–70°C, different molar ratios of alkyl aluminum : MPT : Ti, hydrogen concentrations, and relative and total monomers pressure. Titanium content of the catalyst was 2.96% and surface area of the catalyst was 78 m^2/g. Triisobutyl aluminum (TiBA) and triethyl aluminum (TEA) were used as cocatalysts, while ethyl benzoate (EB) and methyl *p*-toluate (MPT) were used as internal and external donors, respectively. H$_2$ was used as a chain-transfer agent. Good-quality ethylene propylene rubber (EPR) of rubber was obtained at the ratio of [TiBA] : [MPT] : [Ti] = 320 : 16 : 1 and polymerization temperature was 60°C. When TiBA was used as a cocatalyst, a higher and more rubberlike copolymer was obtained. For both of the cocatalysts, an optimum ratio of Al/Ti was obtained relative to the catalyst productivity. Ethylene content of the copolymer obtained increased with increasing TiBA concentration, while inverse results were obtained by using TEA. Addition of H$_2$ increased the reactivity of the catalyst. The highest product was obtained when 150 mL H$_2$/L solvent was used. Increasing temperature from 40 to 70°C decreased the productivity of the catalyst, while irregular behavior was observed on ethylene content. Relative pressure of $P_P/P_E = 1.4 : 1$ and total pressure of 1 atm was the best condition for the copolymerization. Polymers with ethylene contents of 25–84% were obtained. Increasing ethylene content of EPR decreased T_g of the polymer obtained to a limiting value. Viscosity-average molecular weight (M_v) decreased with increasing temperature and TiBA and H$_2$ concentration. However, increasing the polymerization time increased the M_v. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 2597–2605, 2004

Key words: Ziegler–Natta catalyst; supported catalyst; TiCl$_4$ catalyst; EPR; slurry copolymerization

INTRODUCTION

The copolymerization of ethylene and higher α-olefines produced in catalytic polymerization are important commercial products. The development of catalyst systems with high efficiency is the key to rapid commercial development.[1,2] So far, numerous publications related to supported Ziegler–Natta catalysts were reported.[3–5] Some publications claimed the SiO$_2$-supported TiCl$_4$ catalyst modified by MgCl$_2$ showed very high activity for the random copolymerization of ethylene and propylene.[3,4] The combination of silica and MgCl$_2$ with the aim of preserving their advantages has attracted much industrial and academic interest.[6–11] With the catalyst SiO$_2$/MgCl$_2$/TiCl$_4$/ID (ID, internal donor), the polymerization rate increased with time, whereas with the catalyst system, MgCl$_2$/TiCl$_4$/ID, a mainly decay-type curve was obtained.[12–14] Recently, single-site metallocene catalysts were based on zirconium and titanium, which, activated with methyl aluminoxane, were used for ethylene and propylene rubber production.[15–17]

EXPERIMENTAL

The catalyst system SiO$_2$/MgCl$_2$/TiCl$_4$/EB (EB, ethyl benzoate) was prepared according to method improved at the Iran Polymer and Petrochemical Institute. SiO$_2$ (Kerman, Iran) was calcined at (500–600°C). Mg(OEt)$_2$ and SiO$_2$ were treated with excess TiCl$_4$ in the presence of EB and polydimethylsiloxane at 20–90°C for 1–3 h. The treatment was carried out twice. The prepared catalyst was dried and used as a slurry in hydrocarbon. All of the procedures were carried out under N$_2$. Surface area of the catalyst was measured by using the Brunauer Emmett Teller (BET) method, which was 78 m^2/g. Copolymerization of ethylene and propylene was carried out by using the catalyst
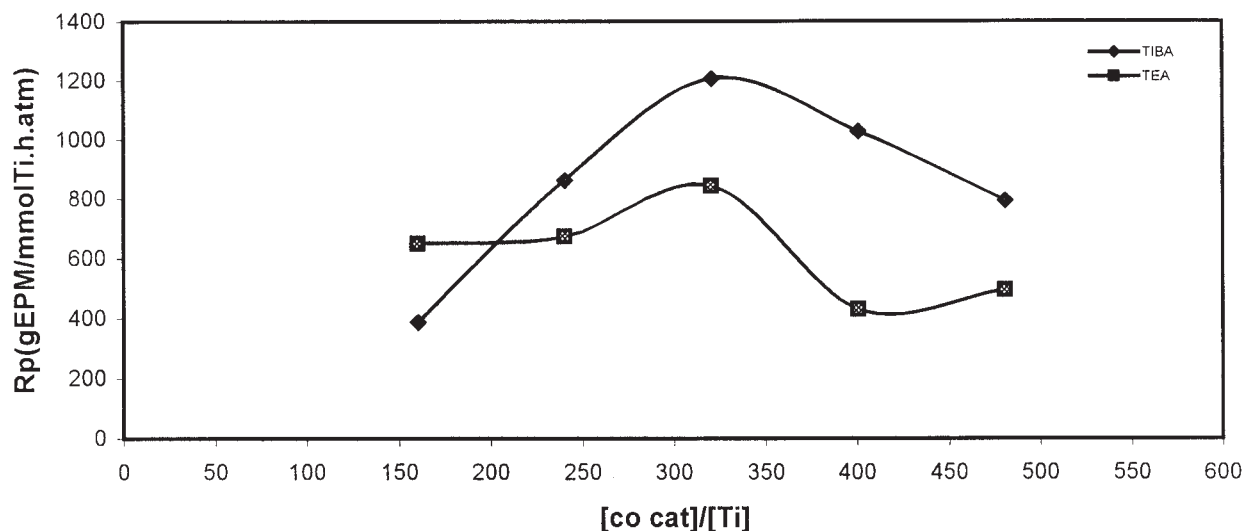
Figure 1 Effect of TiBA and TEA concentration on average rate of polymerization. Polymerization condition as in Table I.

system, whereas triethyl aluminum (TEA) and triisobutyl aluminum (TiBA; Merck, Germany) were used as cocatalysts and EB and methyl *p*-toluate (MPT) were used as internal and external donors, respectively. Copolymerization was carried out in a 1-L stainless steel reactor of Buchi bcp 280, a semibatch type, equipped with a stirrer speed control, temperature control, and double feed. The reactor was purged with N_2. Heptane, 450 mL, was charged into the reactor and degassed at least three times. When the polymerization temperature reached the required temperature, the catalyst component was added in the following order: TEA or TiBA, MPT, solid catalyst, and hydrogen (if any). The pressure inside the reactor remained constant. Therefore, the required amount of the monomers mixture to feed into the reactor is equal to the consumption of the monomers and was controlled by the pressure sensor. The polymerization was terminated by draining the slurry polymer into a

small volume of acidified methanol. The polymer was precipitated by using methanol as an antisolvent or solvent evaporation method, filtered, and dried at 70°C overnight.

POLYMER CHARACTERIZATION

Glass transition temperature (T_g), ethylene content, and M_v of the polymer obtained were studied. Et% was determined by using an IR method (FTIR, Bruker model IFS48).[18] M_v was determined by using the Mark–Houwink equation and by using decalin as a solvent.[19] The density of the polymer was determined by using a percisa balance with the densitometer facility.

RESULTS AND DISCUSSION

Effect of TEA and TiBA concentrations

To optimize the amount of TEA and TiBA needed for the copolymerization, Ti concentration (7.8×10^{-2}

TABLE I
Effect of TiBA and TEA Concentration on Polymerization Behavior

Cocatalyst	[Al]/[Ti]	EPM (g)	$\bar{R}_p \left(\dfrac{grEPM}{mmolTi\ h\ atm} \right)$	% Et	M_v
TEA	160	20.3	650	59.7	
TEA	240	21.0	672.4	48.1	
TEA	320	26.3	842.9	47.2	
TEA	400	15.2	431.1	32.4	
TEA	480	15.4	493.6	—	
TiBA	160	12.1	387.8	26.5	
TiBA	240	26.1	861.9	39.0	
TiBA	320	36.0	1206.7	42.6	75,000
TiBA	400	32.2	1028.8	42.9	70,200
TiBA	480	23.8	793.6	50.2	59,500

[Ti] = 3.12×10^{-2} mmol; temp = 60°C; time = 1 h; P_P/P_F = 1.4 : 1; P_t = 1 atm; heptane = 400 mL.
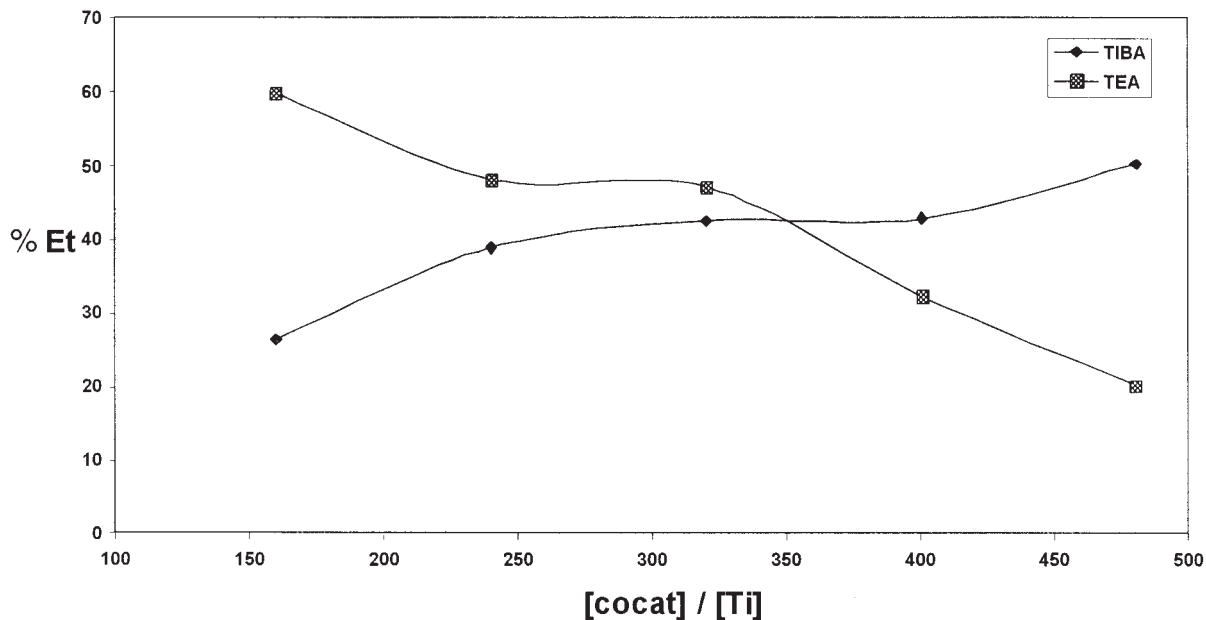
Figure 2 Effect of Al/Ti molar ratio on ethylene content of polymers obtained.

mmol/L solvent) and MPT concentration (~ 0.5 mmol) were kept constant and different ratios of Al-alkyl : Ti molar ratios were used. Figure 1 shows the polymer yield obtained against the ratio. At high concentrations of TEA and TiBA, overreduction of Ti^{4+} to Ti^{2+} occurred. The species, which are highly active, are only active for ethylene polymerization.[12,13] The polymer obtained at a high concentration of Al-alkyl, particularly TEA, does not show elastomeric properties. Table I shows the results obtained in the study. A

polymer with an ethylene content of 26.5–59.7% was obtained by using different [Al-alkyl] : [Ti] ratios. The polymerization temperature was 60°C. Upon the addition of the catalyst, the temperature rose suddenly, so its control was very difficult. The increase was not so affected by copolymerization time.

Figure 2 shows the effect of the Al/Ti molar ratio on ethylene content of the polymers obtained. Increasing TiBA concentration increased ethylene content of the polymer, whereas inverse results were obtained when
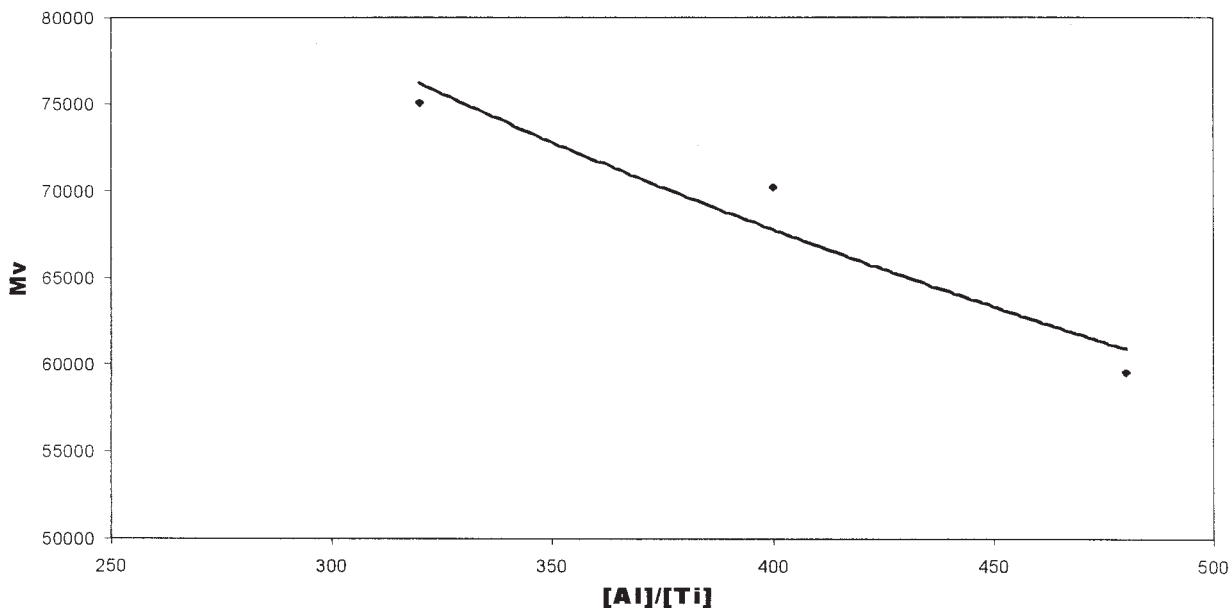

Figure 3 Effect of Al]/[Ti] on the M_v.

TABLE II
Effect of H$_2$ Concentration on Polymerization Behavior

VH$_2$/V$_{Sol}$ (mL/L)	EPM (g)	$R_p \left(\dfrac{\text{grEPM}}{\text{mmolTi h atm}} \right)$	% Et	M_v	D (g/ml)
0	36.0	1206.7	42.60	75,000	0.82
25	39.1	1253.2	—		
50	40.4	1296.2	—		
75	44.5	1426.3	46.60	50,500	0.83
100	45.0	1441	—		
150	52.9	1695.5	46.00	39200	0.84
200	45.2	1447.4	49.40		
250	37.7	1208.3	27.70	36,600	0.84

[Ti] = 3.12 × 10^{-2} mmol; [TIBA]/[Ti] = 320 : 1; temp = 60°C; time = 1 h; P_P/P_E = 1.4 : 1; P_t = 1 atm; heptane = 400 mL.

TEA was used. The behavior indicates that TEA tends to polymerize propylene more than ethylene and TiBA tends to polymerize ethylene more than propylene. The polymers obtained by using TiBA as a cocatalyst show more rubberlike behavior as well. In other words, TiBA gives more amorphous polymers than TEA. Figure 3 shows the effect of TiBA/Ti molar ratio on the M_v. The M_v sharply decreases with increasing [TiBA]/[Ti] ratio, which could be due to a high chain transfer to Al.

Effect of H$_2$ concentration

The effect of different amounts of H$_2$ on copolymerization behavior were studied (Table II). The copolymerization was carried out by using the optimum conditions obtained before (Table I). Increasing H$_2$ concentration to 150 mL/L increased productivity of the catalyst; however, a further increase of H$_2$ concentration decreased the activity (Fig. 4). The increase could be due to converting some Ti^{2+} to Ti^{3+}, the species which is active for both of the monomers used[12,13] and for activation of some dormant centers in

the catalyst.[20,21] Similar results were reported for the polymerization of propylene.[11] At very high concentrations of H$_2$, a competition on absorption of H$_2$ and monomer to active centers occurred, which reduced the concentration of the monomers close to the active centers.

Ethylene content of the copolymer increased with the addition of H$_2$, whereas, at very high concentrations of H$_2$, a decrease of Et% was observed. Figure 5 shows this behavior.

Density of the copolymer remains almost unchanged by the addition of H$_2$. M_v of the polymer was decreased from 75,000 to 39,200 with the addition of 150 mL/L solvent. However, it remained almost unchanged with the further addition of H$_2$ (Fig. 6). H$_2$ as a chain transfer agent facilitates termination of the chain growing.

Effect of temperature

Copolymerization reactions were carried out in the temperature range of 40–70°C (Table III). The copolymerization was affected by using the optimum condi-
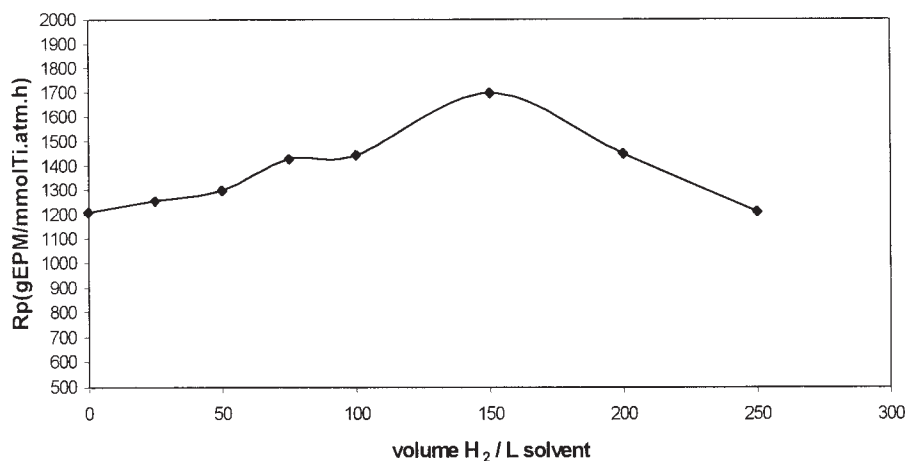

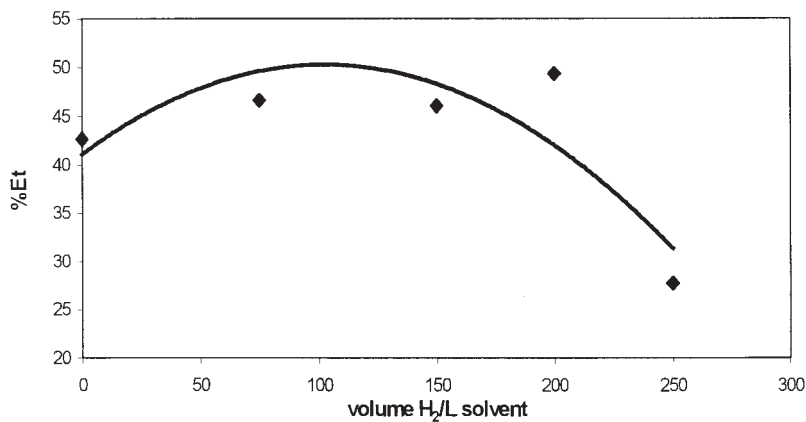**Figure 4** Effect of H$_2$ concentration on polymerization rate.

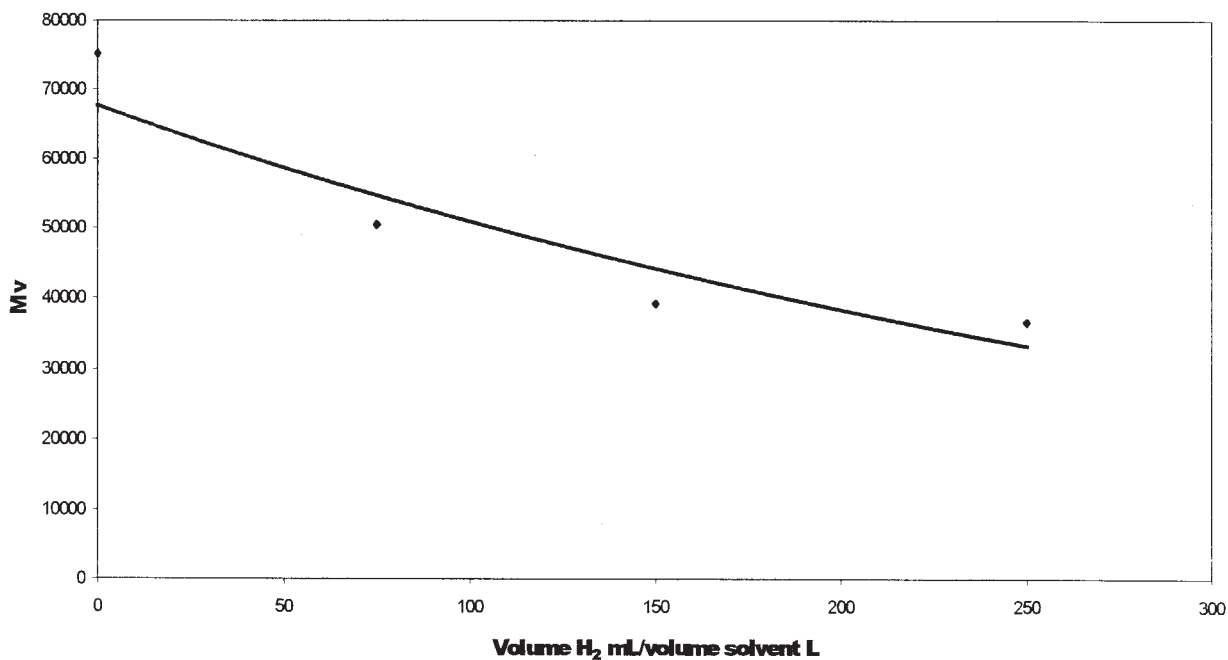**Figure 5** Effect of H$_2$ concentration on ethylene content of copolymer.

Figure 6 Effect of H$_2$ on M_v.

TABLE III
Effect of Temperature on Copolymerization Behavior

$T(°C)$	EPM (g)	$R_p\left(\dfrac{grEPM}{mmolTi\ h\ atm}\right)$	% Et	M_v
40	71.4	1994.1	63.33	106,000
45	61.8	1733.2	62.83	92,100
50	61.1	1705.9	—	60,700
55	61.7	1722.3	80.80	
60	52.9	1695.5	—	39,200
65	56.8	1585.2	—	
70	49.5	1382.4	84.20	—

[Ti] = 3.12 × 10^{-2} mmol; temp = 60°C; time = 1 h; P_P/P_E = 1.4 : 1, P_t = 1 atm, heptane = 400 mL; H$_2$ = 150 ml/L.
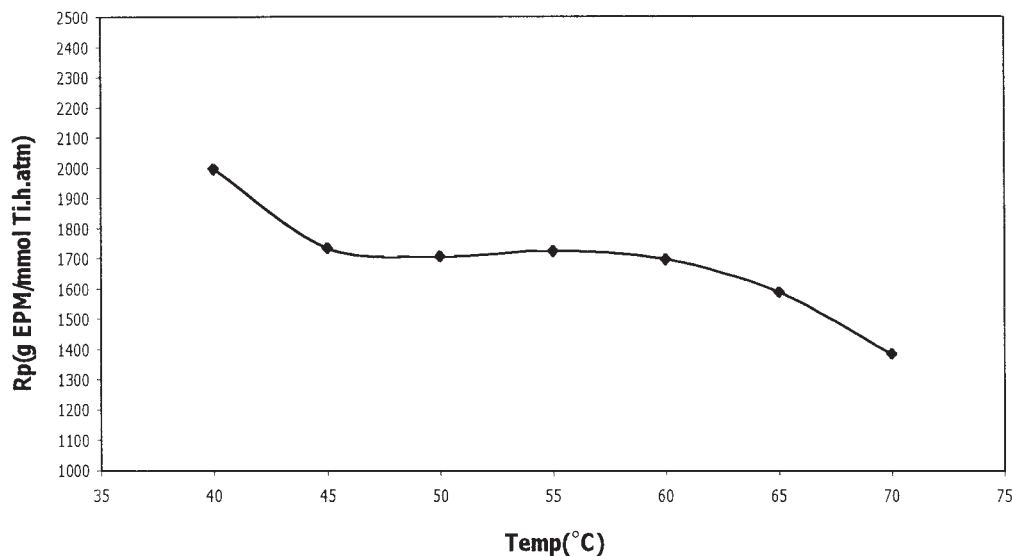
Figure 7 Effect of temperature on rate of polymerization. Polymerization condition as shown in Table III.

tion obtained before. Increasing temperature between the values studied decreased the productivity of the catalyst. Figure 7 shows the average rate of polymerization obtained against temperature. The best rubberlike polymer was obtained at 60°C. Higher and lower temperatures of the reaction results in a polymer with less rubberlike behavior. Et% of the polymer almost increased with temperature. The high temperature could decay some active centers that affected the rate of polymerization.[19] At temperatures >70°C, a similar behavior was reported for the Ziegler–Natta catalyst.[11,20]

The M_v decreases from 106,000 to 39,200 by increasing the temperature from 40 to 60°C. As shown in Figure 8, a linear decrease in the M_v with increasing

temperature was observed. The behavior indicates that termination and transfer reactions take place faster at high temperature.

Effect of monomers relative and total pressure

The effect of propylene to ethylene relative pressure of 1 : 1, 1.4 : 1, and 2 : 1 on copolymerization behavior was studied. The best elastomeric figure was obtained at the $P_P/P_E = 1.4 : 1$ relative pressure. Table IV shows the effect of relative and total monomer pressure on the copolymerization behavior. Higher and lower relative pressure from $P_P/P_E = 1.4 : 1$ atm gives more or less homopolymeric-like products.
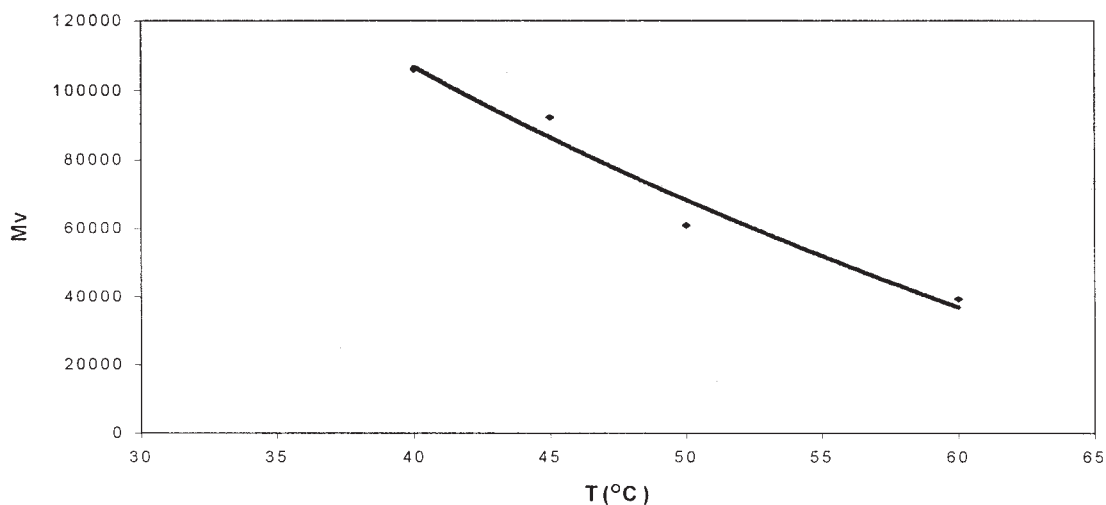

Figure 8 Effect of temperature on M_v.

TABLE IV
Effect of Total and Relative Monomers Pressure on Copolymerization Behavior

P_P/P_E	P_t	EPM (g)	$R_p\left(\dfrac{\text{grEPM}}{\text{mmolTi h atm}}\right)$	$Et\%$
1 : 1	1	78.6	2195.5	67
1.4 : 1	1	52.9	1695.5	46
2 : 1	1	22.4	626.5	—
1.4 : 1	0.5	23.4	1305	63.7
1.4 : 1	1.5	36.7	682.7	—
1.4 : 1	2	29.3	410.2	—

[Ti] = 3.12 × 10^{-2}/mmol; [H$_2$] = 150 mL/L; temp = 60°C; time = 1 h; [Al] : [PMT] : [Ti] = 320 : 16 : 1; heptane = 400 mL.

Because of the higher reactivity of ethylene monomer to react with catalyst active centers, an increase of propylene concentration decreased the productivity of the catalyst.

The effect of total monomer pressure of 0.5 to 2 atm was studied. Figure 9 shows the average rate of polymerization obtained against the pressure. As can be seen from the figure, the highest productivity can be obtained at a total pressure of +1 atm. The higher the monomer pressure, the higher the temperature of the reaction observed. Because of the high productivity of the catalyst, the expected high pressure may encapsulate the active centers or gel effect by causing a rubbery copolymer to occur. The higher productivity and the higher increase of the reaction temperature also could decay the active centers faster.[22]

Effect of polymerization time

Figure 10 shows the average rate of copolymerization versus reaction time. The profile is a decay type with a short acceleration period of about 10 min, followed by a decrease in activity to a stable period after about 40 min. The behavior was the same as for MgCl$_2$-supported catalyst, not for the bi-supported one, of course, for homopolymerization.[6,12–14,17]

Because of the rubbery form of the polymer and sudden increase in polymerization temperature upon the start of the polymerization, there are two possibilities for the unexpected behavior: encapsulation of active centers of the catalyst in rubbery polymer with a probable gel effect and the decay of some active centers due to the sudden increase of the reaction temperature.[19,20]

Polymerization time is affected on the M_v (Fig. 11). An increase of 41% in the M_v was observed when polymerization time increased from 10 to 60 min, an indication of more chain growth by polymerization time.

Effect of ethylene content on T_g

T_g of ethylene propylene rubber (EPR) decreased with increasing ethylene content of the copolymer obtained almost to a limiting value (Fig. 12). As can be seen, at Et% higher than 50%, the T_g remains almost constant, which could be due to the loss of elastomeric behavior of the copolymer.
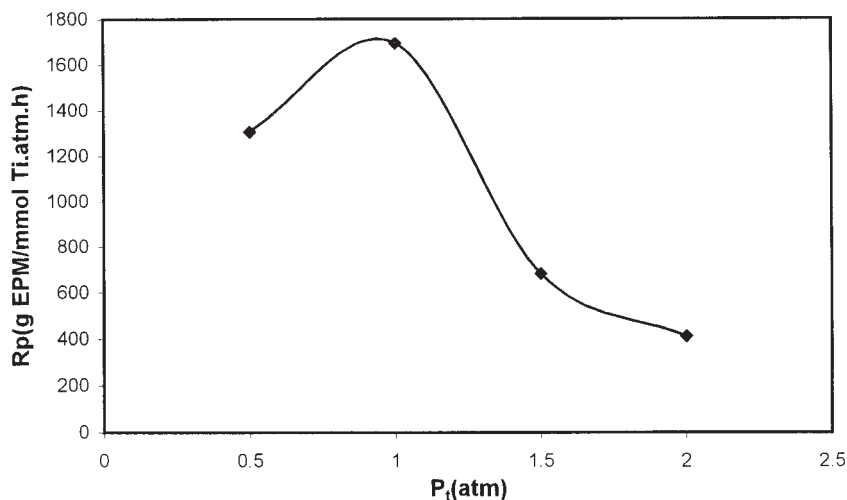

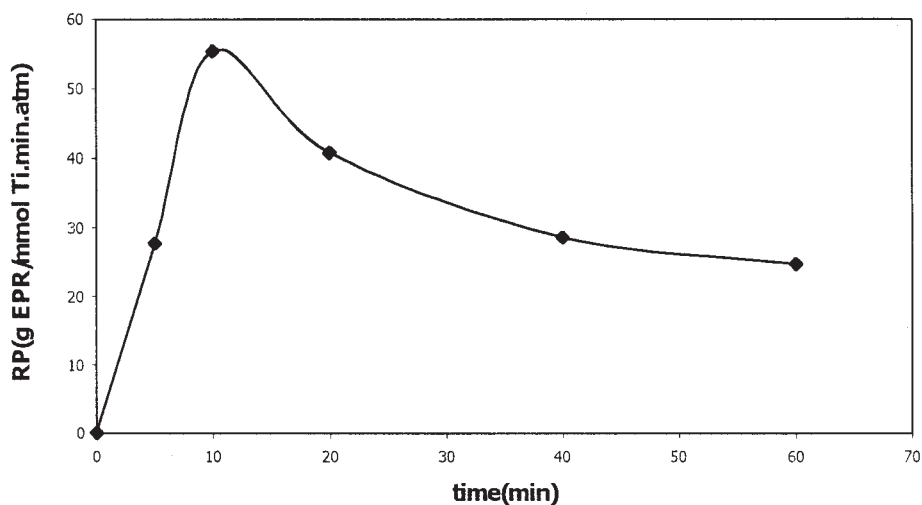**Figure 9** Effect of pressure of monomers on rate of polymerization.

Figure 10 Average rate of polymerization versus polymerization time.

CONCLUSION

1. The prepared catalyst system $SiO_2/MgCl_2/EB/TiCl_4/TiBA$ or TEA/PMT has relatively high activity for the copolymerization of ethylene and propylene.

2. There is an optimum molar ratio of Al : Ti to obtain the highest yield of copolymer. However, polymer obtained at a high concentration of TEA does not show elastomeric properties.

3. Increasing H_2 concentration up to 150 mL/L increases polymerization activity. However, a further increase of the H_2 decreases the polymer yield.

4. Ethylene contents from 27 to 84% were obtained. The value increased with increasing TiBA concentration, whereas it decreased with increasing TEA concentration. Increasing P_P/P_E relative pressure decreased Et% in the polymer.

5. Increasing Et% in the polymer decreased T_g to a limiting value.

6. TiBA as cocatalyst compared to TEA gives a higher product and better elastomeric properties.

7. Polymerization temperatures from 40 to 70°C were studied. The best elastomeric behavior was obtained at 60°C.

8. Increasing P_P/P_E relative pressure decreased the productivity of the catalyst. The best copolymer with elastomeric properties was obtained at a relative pressure of $P_P/P_E = 1.4 : 1$.

9. The M_v decreases with increasing [Al]/[Ti] ratio, temperature, and addition of H_2 concentration, whereas the M_v increased with polymerization time.

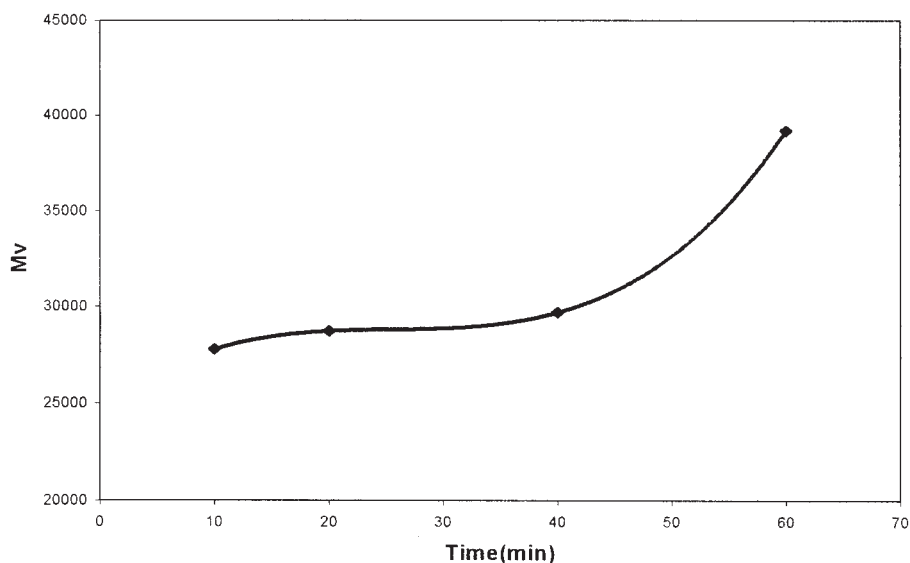10. The bi-supported catalyst has more activity than $MgCl_2$-supported catalyst.[5]

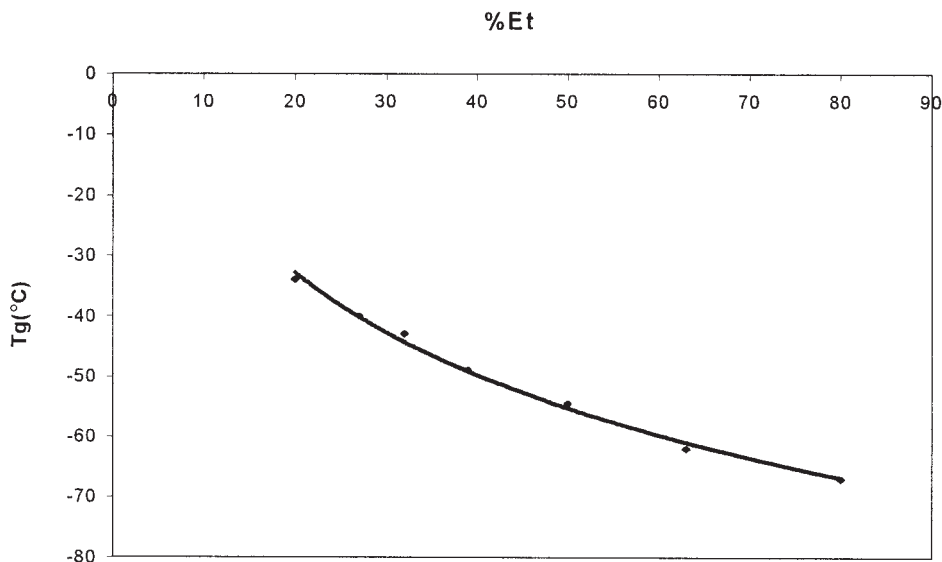**Figure 11** Effect of copolymerization time on M_v.

Figure 12 T_g against Et%.

11. The amount of Al compound needed to reach the highest activity is less for the bisupported catalyst compared with MgCl$_2$ supported one.

12. An increase of the Et% content decreases the T_g of the copolymer obtained.

References

1. Salamone, J. C. Polym Mater Encycl 1996, 3, 10, 13.
2. Krenstle, B. A.; Kissin, Y. V.; Klaner, V. J.; Stotskay, L. L. In Polymer and Copolymers of Higher α-Olefine; Hanser: Munich, 1997.
3. Banzi, V.; Loberti, G. Eur. Pat. EP0659778 (A1), 1998.
4. Kim, J. H.; Jeony, Y. T.; Woo, S. I. J Polym Sci, Part A: Polym Chem 1994, 32, 2979.
5. Zohuri, G. H.; Sadegvandi, F.; Jamjah, R.; Ahmadjo, S.; Nekoomanesh, M.; Bigdelli, E. J Appl Polym Sci 2002, Vol. 84, 785.
6. Pasquent, V.; Spitz, R. Makromol Chem 1993, 191, 3087.
7. Lu, H.; Xiao, S. Makromol Chem 2095 1993, 194.
8. Noristi, L.; Barbe, P. C.; Baruzzi, G. Makromol Chem 1991, 192, 1115.
9. Muno-Escalona, A.; Fuentes, A.; Liscano, J.; Albornoz, A. In Catalytic Olefin Polymerization; Keii; Soga, K.; Eds.; Kodansha: Tokyo, 1990; p 377.
10. Zohuri, G. H.; Ahmadjo, S.; Jamjah, R.; Nekoomanesh, M. Iran Polym J 2001, 10 (3), 149.
11. Zohuri, G. H.; Azimfar, F.; Jamjah, R.; Ahmadjo, S. J Appl Polym Sci 2003, 98, 1177.
12. Kashiwa, N.; Yoshitake, Y. Macromol Chem 1984, 185, 1133.
13. Soga, K.; Chen S. T.; Ohnishi, R. Polym Bull 1982, 8, 473.
14. Tait, P. J. T.; Zohuri, G. H.; Kells, A. M. Macromol Symp 1995, 89, 125.
15. Kaminsky, W. Macromol Symp 2001, 174, 269.
16. Schweier, G.; Brintzinger, H. Macromol Symp 2001, 173, 89.
17. Liu, S.; Meng, F.; Yu, G.; Huung, B. J Appl Polym Sci 2001, 71, 2253.
18. ASTM D 3900-95. Annu Book ASTM Stand 1996; pp 619–627.
19. Brandrup, J.; Immergut, E. H. Polymer Handbook, 3rd ed.; Wiley: New York, 1989; Vol. VII, pp 1, 7.
20. Chawick, J. C.; Miedema, A.; Sudmeijer, O. Makromol Chem 1994, 195, 167.
21. Busico, V.; Cipullo, P.; Corradini, P. Makromol Chem Rapid Commun 1992, 13, 15.
22. Zohuri, G. H. Ph.D. thesis; University of Manchester, Institute of Science and Technology, UMIST, 1993.