CHAPTER V

RESULTS AND DISCUSSION

5.1 Polymerization

From the polymerization results, we find the activities of catalyst formed to be 92 g PP/mmol Zr.hr at polymerization temperature of -20°C to 22,196 g PP/mmol Zr.hr at polymerization temperature of 50°C. Activities of the catalysts are strongly dependent on the polymerization temperature. When we plot the natural logarithm of activity versus 1/T . We get the straight line for the entire temperature range, as shown in figure 5.1, the slope is proportional to the activation energy of polymerization as described by the Arrhenius Equation (Fogler, 1992).

$$k(T) \quad = \quad A e^{(-E/RT)} \qquad \text{Arrhenius Equation}$$

In general, the activity is a function of polymerization temperature (Tp), it increases with increasing Tp, reaching a maximum, and then decreases with a further increase in temperature. This result shows that at low temperatures, the chain initiation is slow and at elevated temperatures, the catalyst deactivates rapidly.

From figure 5.1, we determined the activation energy (E_a) to be 13.25 kcal/mole (Appendix A) for the overall activation energy of polymerization. This behavior indicates a very low activation energy for initiation and there is no significant catalyst deactivation.
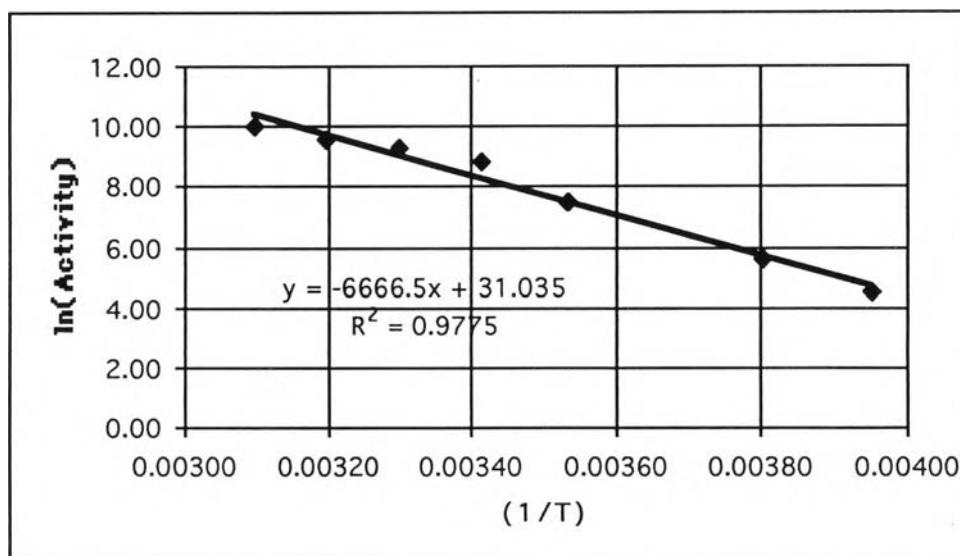
Figure 5.1 Arrhenius plot of polymerization acvtivity.

The difference between the activation energy from this study and other reported values are small. The same catalyst system by Rieger (Rieger et al., 1990) was 10 kcal/mole and that by N. Kashiwa was 15.34 kcal/mole (Kashiwa, 1989).

5.2 Characterization

5.2.1 Molecular weight and molecular weight distribution

GPC curve of polypropylene sample are shown in figure 5.2. Molecular weight distributions (M_w/M_n) of the whole polymer was relatively narrow (M_w/M_n= 2.35-2.76). The observed homogeneity of the polymer composition would be attributable to the homogeneous nature of active centres in the soluble catalyst system.

The molecular weights of the polymers synthesized were in the range 12,739-32,000 g/mole and increased significantly on lowering the polymerization temperature (M_n = 32,000 g/mole at -10°C and M_n= 12,739 g/mole at 50°C).
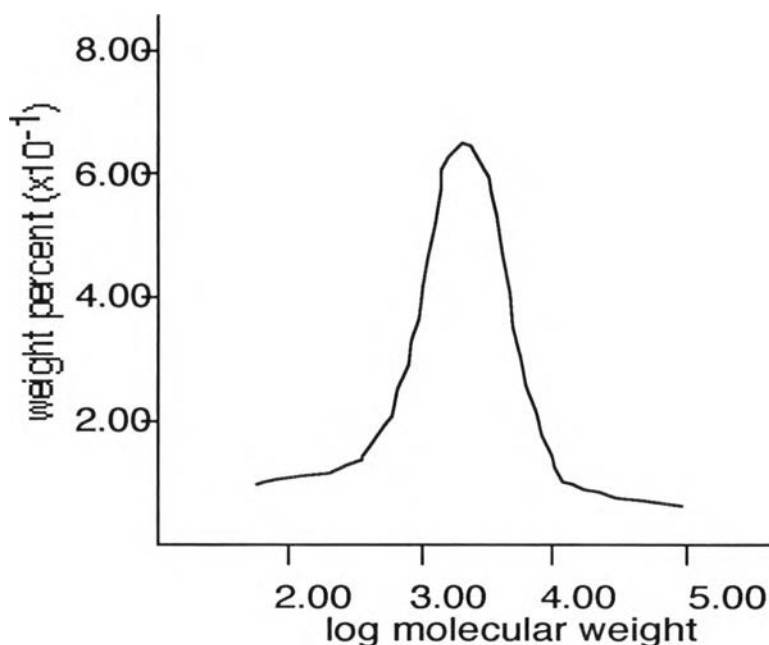

Figure 5.2 GPC curve of polypropylene.

5.2.2 Isotacticity

All of the produced polypropylene gave the IR-spectra in the region of 4,000-400 cm^{-1}, as shown in figure 5.3. The ratio of adsorbances at 995 and 970 cm^{-1} was used for isotacticity determination using the Loungo calibration curve.

The results showed that polypropylenes with high isotacticity, 92.1- 98.6 % were obtained from this zirconocene and methylaluminoxane catalyst system.

The rigid chiral metallocenes are very highly isospecific, but with low ratio of aluminum to transition metal (Zr). They can not produce highly isospecific polymers, indicating that the rigidity of the metallocene alone is insufficient to give high isospecificity.
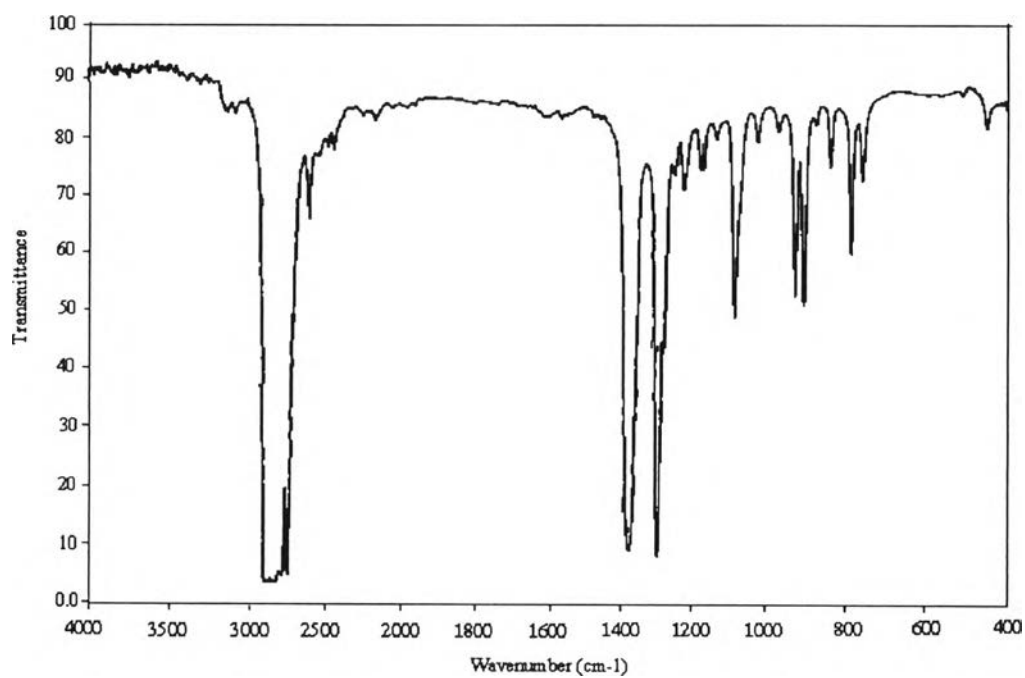
Figure 5.3 IR spectra of polypropylene sample

5.2.3 Degree of crystallinity

From x-ray diffraction, degree of crystallinity was calculated. Figure 5.4 shows x-ray diffraction pattern of polypropylene sample. It shows sharp peaks at $2\theta = 14.0°$, $16.8°$, $18.5°$ and $21.7°$ on the (110), (040), (130) and (111) reflections, respectively.

The dashed line shows the estimated position of the amorphous scattering intensity. The crystalline peaks were sharper than the amorphous diffraction. The integrated intensity of the crystal diffraction peaks divided by the integrated intensity of the sum of amorphous and crystal diffraction was equal to the *degree of crystallinity* (Kampf, G.,1986).

From x-ray diffraction pattern, degrees of crystallinity of the polypropylene samples were ranging from 52 to 66%.
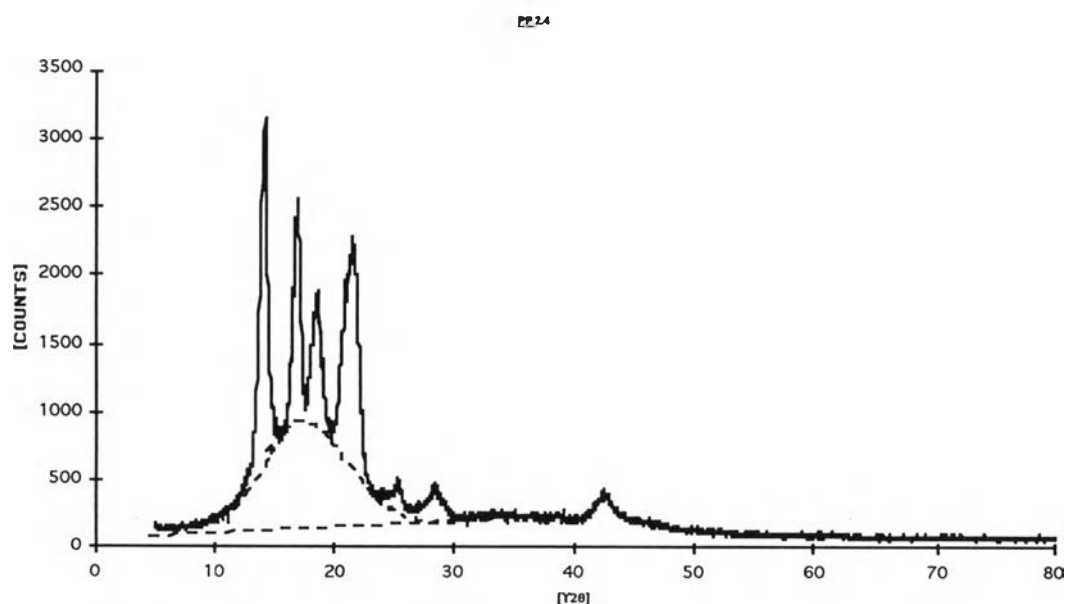

Figure 5.4 X-ray diffraction pattern of polypropylene sample.

5.2.4 Melting point

When polypropylene samples were heated from 90 to 170°C, they showed the exothermic peaks due to the melting as shown in figure 5.5. The melting points of polypropylene samples were determined from these peaks by finding the vertex.

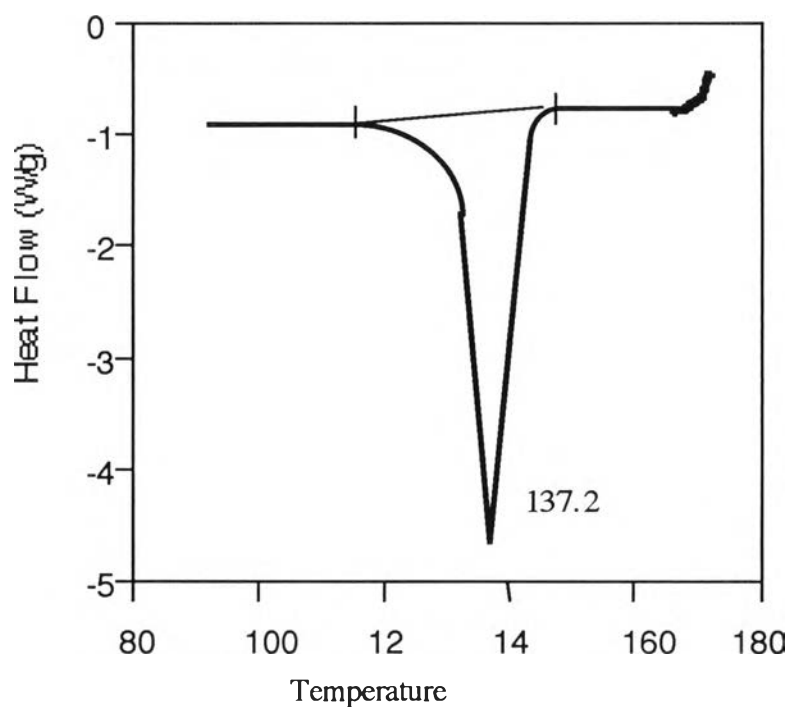The melting points of the polypropylene samples were in the range of 131.1 to 150.3 °C.

Figure 5.5 DSC Thermogram of heating polypropylene sample.

5.3   Effects of polymerization parameters

5.3.1   Effects of polymerization temperature

Table 5.1 shows the effects of polymerization temperature. From the results in table 5.1, we see that when the polymerization temperature increased, the activity greatly increased, but, molecular weight decreased. Their molecular weight distribution (MWD) from GPC, isotacticity from FT-R, melting point from DSC and degree of crystallinity from XRD also slightly decreased.

Table 5.1   Effects of polymerization temperature

Temp. (°C)	Activity*	M_w/M_n	Mn	Isotacticity (%)	Melting Point (°C)	Degree of Crystallinity
50	22196	2.35	12739	92.1	131.1	52
40	14212	2.48	16810	95.4	134.6	55
30	10738	2.48	17180	95.8	137.2	57
20	6971	2.50	17956	96.1	140.7	60
10	1832	2.50	19800	97.4	143.2	62
-10	260	2.60	32000	98.6	150.3	66
-20	92	2.76	17259	96.3	144.1	58

*(gPP/mmolZrhr)

From figure 5.6, we see that the catalyst activity depends strongly on polymerization temperature, because of higher rate of initiation and insertion reactions. At the polymerization temperature -20°C, 10 µmole of Zr was used in polymerization while at the other temperatures we used 5 µmole. The lower molecular weight from 32,000 to 17,259 g/mole could be observed.
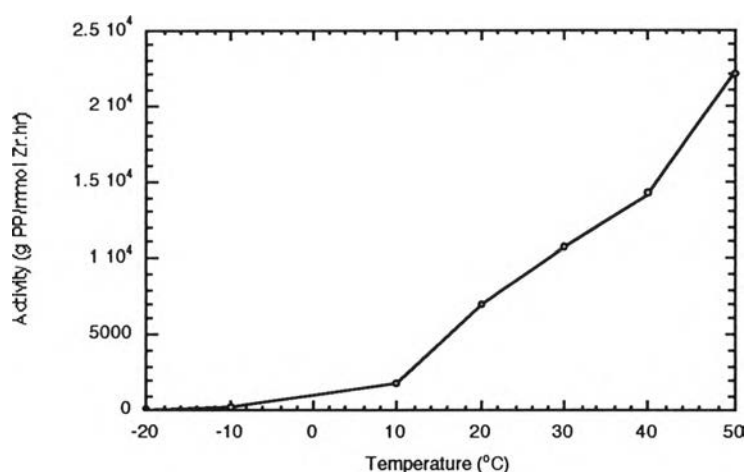
Figure 5.6 Effect of polymerization temperature on activity.

GPC curves (Figure 5.7) show the decreasing of molecular weight (MW) but also the narrowing of distribution as the polymerization temperature (Tp) increases. The results are summarized in table 5.1

Propylene conversions were in the range at 0.5 to 55.5 % (Appendix B), and $1x10^3$ to $2.43x10^5$ grams of polypropylene were produced per gram of zirconium (Appendix C).

Isotacticity of polypropylene samples decreased slightly with increasing polymerization temperature as shown in figure 5.8.

The melting point temperatures are given in table 5.1. There is a gradual and linear decrease of the melting point with increasing polymerization temperature as a result of decreasing of molecular weight, isotacticity and degree of crystallinity (Figure 5.10).
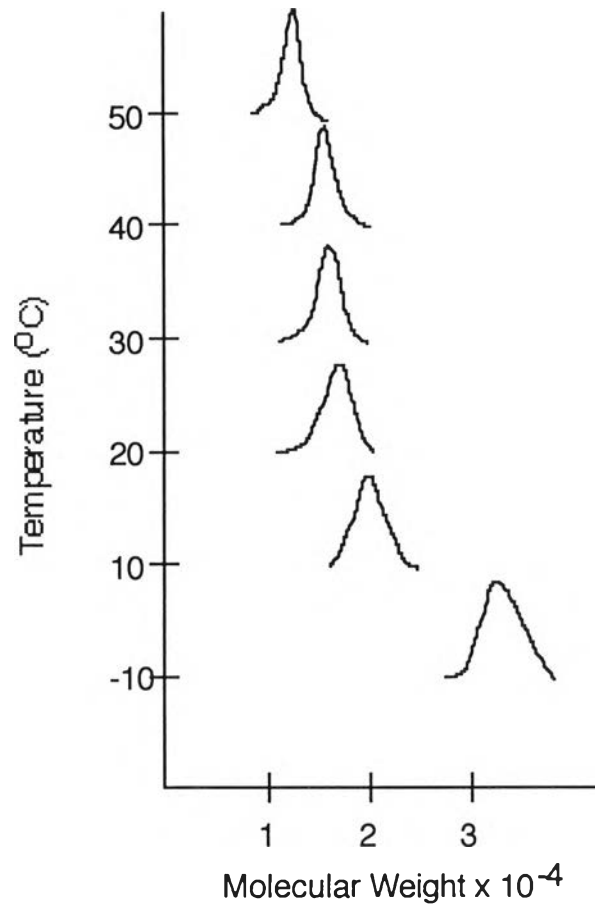
Figure 5.7 GPC curves for the whole polypropylene produced at various temperatures.
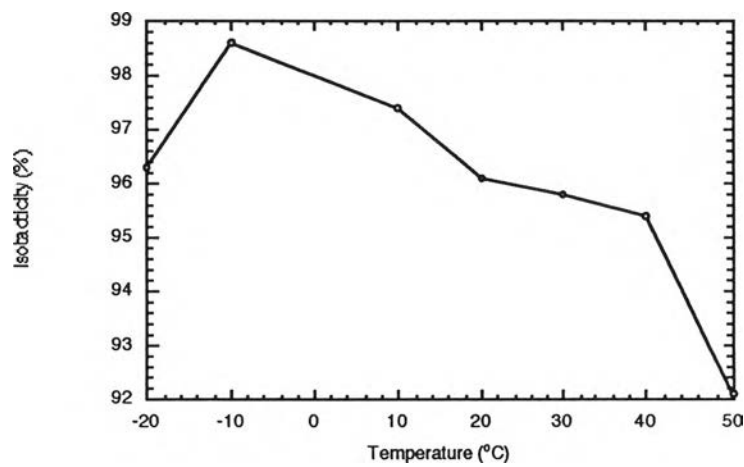

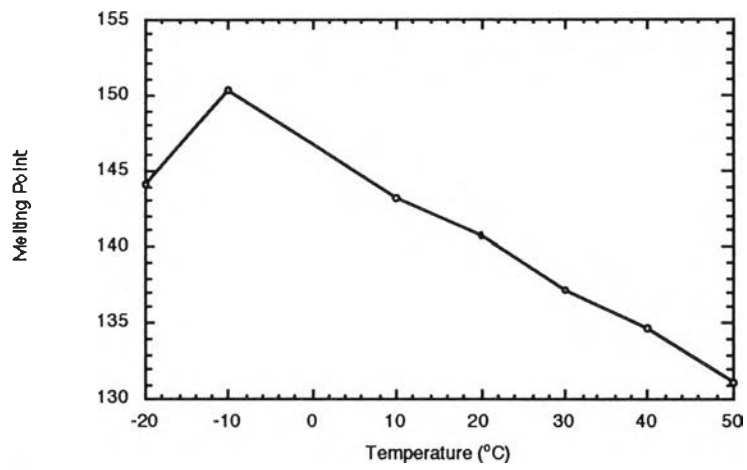**Figure 5.8** Effect of polymerization temperature on isotacticity.

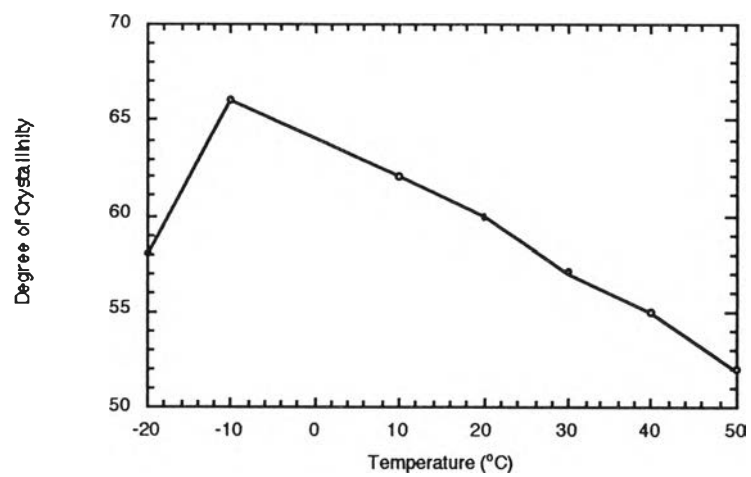**Figure 5.9** Effect of polymerization temperature on melting point.

Figure 5.10 Effect of polymerization temperature on degree of crystallinity.

5.3.2 Effects of zirconium and aluminium concentrations

The effects of changing Al and Zr concentrations were studied by keeping the ratio constant at 1,000, and just increasing the concentration as shown in table 5.2.

Table 5.2 Effects of zirconium and aluminium concentrations

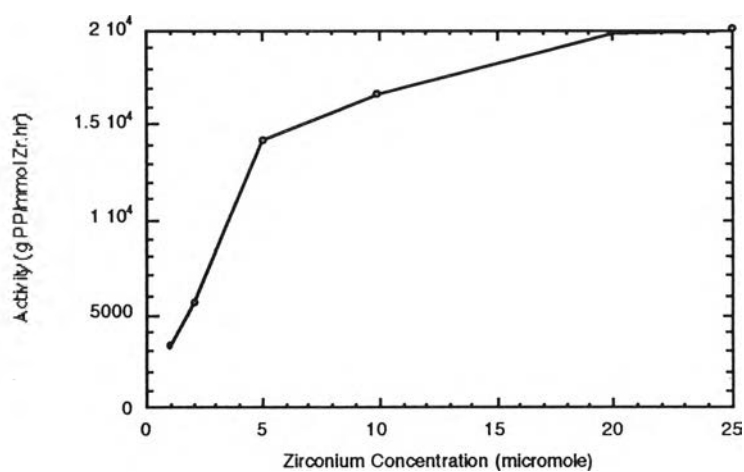| [Zr] μmole	Activity*	M_w/M_n	Mn	Isotacticity (%)	Melting Point (°C)	Degree of Crystallinity
1	3325	2.38	16951	95.6	137.2	56
2	5650	2.50	16700	94.2	135.1	55
5	14212	2.48	16810	95.4	134.6	55
10	16623	2.61	16602	96.1	132.0	57
20	19817	2.46	15820	95.8	130.3	55
25	19974	2.47	15210	94.1	128.9	54

*(gPP/mmolZr.hr)

Figure 5.11 Effect of Zr and Al concentration on activity.

Higher catalyst activity due to an increasing of zirconium and aluminium is probably due to deactivation of a smaller fraction of the total catalyst. It may also be due to increased heat generation resulting in higher activities.

At the high end, the high activity does not increase linearly because propylene availability becomes limiting. Molecular weight decreased with increasing zirconium and aluminium concentrations because of the higher number of growing polymer chains with the same overall monomer concentration. Moreover, melting point and crystallinity were also slightly decreased.

5.3.3 Effects of Al:Zr ratio

The effect of Al:Zr ratio was studied by fixing the zirconium concentration at 5 μmole at a polymerization temperature at 40°C, and increasing the aluminium concentration. The results are shown in table 5.3.

Table 5.3 Effects of Al:Zr ratio

Al:Zr	Activity*	M_w/M_n	Mn (g/mole)	Isotacticity (%)	Melting Point (°C)	Degree of Crystallinity
1000	14212	2.48	16810	95.4	134.6	55
2000	14437	2.48	16071	96.0	135.2	55
4000	14986	2.40	16522	96.2	135.3	57
5000	15372	2.36	16140	97.1	136.1	58
6000	16533	2.32	16510	97.9	136.6	60
8000	18761	2.26	16779	98.2	136.6	62
10000	19051	2.19	16638	98.6	137.1	62

*(gPP/mmolrZr)

The activity of catalyst increased by 30% approximately when the ratio of Al to Zr was increased by a factor of ten. This can be due to better activation of all the zirconium centers by the excess aluminum.
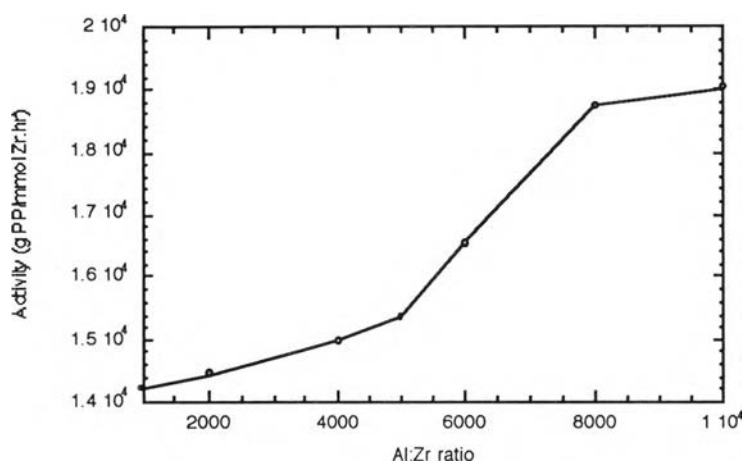

Figure 5.12 Effect of Al:Zr ratio on activity.

Isotacticity also increased from 95.4 to 98.6% with increasing Al:Zr ratio. The methylaluminoxane may function by increasing the rigidity of the chiral metallocenes by complexation (in addition to alkylation of the transition metal).

Chirality of metallocenes initiators is not due to the presence of chiral atoms which have four different substituents but results from the chirality of the whole molecule. For soluble isospecific initiators, the requirments for very high isospecificity include both chirality and structural rigidity. Neither chirality nor strucural rigidity alone is sufficient.
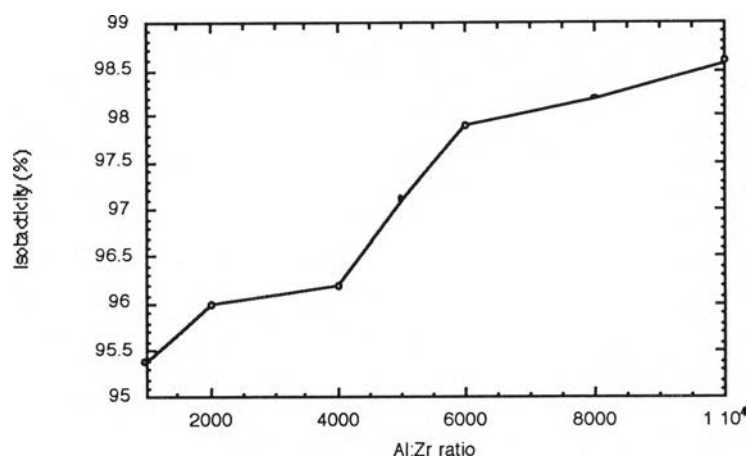
Figure 5.13 Effect of Al:Zr ratio on isotacticity.

The narrower molecular weight distribution at higher Al:Zr ratio results from larger complexes of methylaluminoxane molecules with one molecule of the catalyst and resulting in more uniform properties. Melting point which degree of crystallinity also slightly increased, with the Al:Zr ratio.

Increases in catalytic activity were obtained by both increased Zr and Al concentrations as well as their ratios. The ratios are believed to be more important parameter.

5.3.4 Effects of monomer concentration

Table 5.4 shows the effects of monomer concentration on properties of polypropylene samples which polymerized at 40°C with 5 μmole of Zr and Al:Zr ratio = 1000 in 200 ml of toluene. From the data in table 5.4 and figure 5.14 , it can be concluded that activity, melting point, and

molecular weight linearly increase with increasing propylene concentration in system. This is evidence that the chain transfer reaction with monomer is not the major termination reaction, otherwise, the molecular weight would decrease.

Table 5.4 Effects of monomer concentration

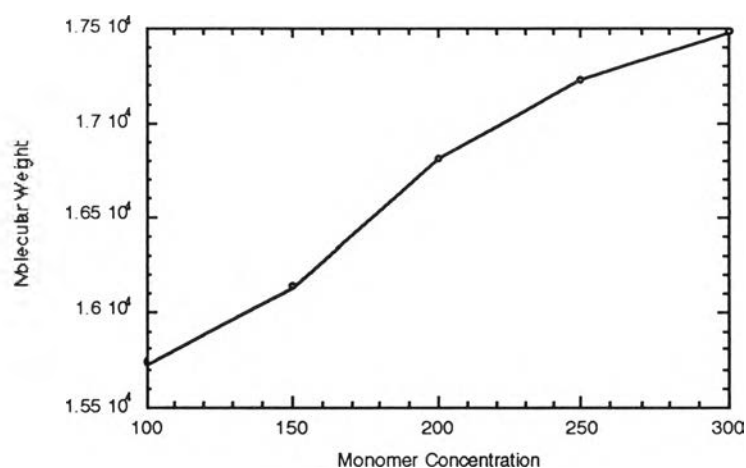| Propylene (grams)	Activity*	M_w/M_n	Mn	Isotacticity (%)	Melting Point ($^\circ$C)	Degree of Crystallinity
100	13629	2.46	15732	95.6	128.7	55
150	13808	2.45	16131	95.6	131.2	56
200	14212	2.48	16810	95.4	134.6	55
250	14300	2.49	17220	94.2	136.2	54
300	15040	2.38	17481	95.5	137.7	56

*(gPP/mmolrZr)

Figure 5.14 Effect of monomer concentration on molecular weight.