Fractionation and Crystallization of Isotactic Polypropylenes Prepared Using Homogenous Metallocene Catalyst

Ismael AMER[1]*, Touhami MOKRAN[1] & Albert VAN REENEN[2]

[1] Department of Civil and Chemical Engineering, College of Science, Engineering and Technology, University of South Africa, Private Bag X6, Florida 1710, Johannesburg, SOUTH AFRICA
[2] Department of Chemistry and Polymer Science, University of Stellenbosch, South Africa, Private Bag X1, Matieland, 7602, SOUTH AFRICA.
*Corresponding author: ismaelamer77@yahoo.co.za, Tel: +27116709382

A b s t r a c t

A series of polypropylenes were prepared using *rac*-ethylene-bis(4,5,6,7-tetrahydro-1-indenyl) zirconium dichloride (Et(H4Ind)$_2$ZrCl$_2$ (EI(4H)) as a homogeneous metallocene catalyst. The molecular weight of the polypropylene polymers was controlled using molecular hydrogen which was used as a transfer agent. To obtain materials with differing molecular weight and tacticities, polymers were fractionated with prep-TREF. Polypropylene polymers and fractions were fully characterized using various analytical techniques: differential scanning calorimetry (DSC), wide-angle X-ray diffraction (WAXD), ^{13}C nuclear magnetic resonance spectroscopy (^{13}C-NMR) and high temperature gel permeation chromatography (HT-GPC). It was found that the addition of molecular hydrogen to propylene polymerizations catalyzed using EI(4H) catalyst system resulted in a reduction in polymer molecular weight and isotacticity. Furthermore, the molecular weight, the isotacticity and the degree of crystallinity of the TREF fractions increased significantly with increasing elution temperature for all samples. Also, only the α crystal form existed in all TREF fractions of different samples.

Introduction

Metallocene catalyst systems have been around for just as long as the Ziegler-Natta systems (Auriemma *et al.*, 2001). Metallocenes are special members of a class of organometallic compounds. They are activated with methylaluminoxane (MAO) to form single-site catalyst systems that are effective for α-olefin polymerization. These catalysts produce polymers with uniform and controlled properties. Chiral metallocene catalysts possessing *C2*-symmetry have been widely studied in order to optimize, and to better understand, their ability to catalyze the stereoregular polymerization of propylene (Busico *et al.*, 1998; Soga & Shiono, 1997). Ansa *C2*-symmetric metallocene catalysts are highly isoselective in propylene polymerization and have high activity. This allows for their use in most industrial applications for the production of polypropylene homopolymers and polypropylene copolymers. Control of the molecular weight of polymers produced by *C2*-metallocene catalysts can be easily achieved by introducing hydrogen to the polymerization system or by increasing the reaction temperature. Unlike conventional Ziegler-Natta catalysts, metallocenes require only small amounts of hydrogen to significantly reduce the molecular weight of polymer produced (Lin *et al.*, 2000).

This study reports on propylene polymerization and analysis of the microstructure, molecular weight, molecular weight distribution and thermal properties of polymers produced using *rac*-ethylene-bis(4,5,6,7-tetrahydro-1-indenyl) zirconium dichloride, Et(H4Ind)$_2$ZrCl$_2$ (EI(4H)) (Figure 1) as metallocene catalyst in the absence and presence of molecular hydrogen as transfer agent. In order to establish a correlation between the molecular weight and the crystallization of these polymers, fractionation of the materials according to their crystallizability was performed by means of TREF.
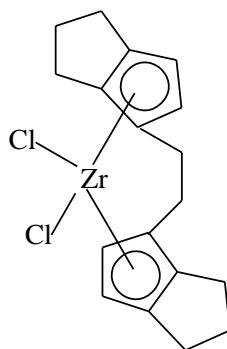
Figure 1: *rac*-Et(H4Ind)$_2$ZrCl$_2$ (EI(4H)).

Methodology

Material

Propylene was obtained from Sigma-Aldrich and used as received. High purity argon and hydrogen were obtained from Afrox (South Africa). Toluene (Sigma-Aldrich) was dried by refluxing over sodium/benzophenone and then distilling under an inert gas atmosphere. MAO was purchased from Sigma-Aldrich (10 wt % solution in toluene) and used as received. The EI(4H) catalyst used in this study was obtained from Sigma-Aldrich and used as received. Metallocene catalysts comprising group 4 metallocene complexes and MAO are air and moisture sensitive, and thus experiments must be performed under an inert atmosphere and in dry solvents.

Polymerization Procedure

All reactions were carried out under an inert gas atmosphere using standard Schlenk techniques. The polymerization reactions were carried out in a 350-mL stainless steel Parr autoclave with an inlet and a pressure gauge. Typically, the reactor was charged with MAO (10 wt % solution in toluene), catalyst (0.55 µmol in 5 mL toluene) and toluene (30 mL). The catalyst solution was stirred for 5 minutes and then the monomer was added. The reactor was pressurized with hydrogen and the content stirred for 1 hour at room temperature. The following polymerization conditions were used for all reactions: the catalyst/MAO ratio was kept at 1:2000, 4−5 g propylene was used, all reactions were carried out at room temperature, and different amounts of hydrogen were used as terminating agent to control the molecular weight. After 1 hour the reaction was quenched with 10% HCl/MeOH. The

resulting polymer was filtered off, washed several times with methanol and then dried under vacuum at 80 °C for 15 hours to yield about 2–4 g of polypropylene as a white powder.

TREF Procedure

Typically 3.0 g of polymer was introduced to a 1000 mL glass reactor containing 300 mL xylene stabilized with 0.06 wt% Irganox 1010. The polymer was dissolved at 130 °C for about 90 minutes. The hot polymer solution was mixed with preheated washed sea sand (Aldrich, as an inert support). The glass reactor was cooled from 130 °C to 20 °C at a rate of 1.5 °C/h. The solution-sand mixture was loaded into a steel elution column. Fractions of the polymer, with increasing crystallinity, were then eluted with xylene at set (increasing) temperatures. Typically fractions were isolated after elution at 7 temperatures (25, 60, 80, 90, 100, 110 and 130 °C). Subsequently the polymer fractions were recovered by removing the xylene under reduced pressure and drying at 50 °C (vacuum oven).

Characterization Techniques

Polypropylene polymers were characterized by HT–GPC (Polymer Labs PL-GPC 220, flow rate of 1 mL/min in 1,2,4 trchlorobenzene as solvent stabilized with 2,6-di-tert-butyl-4-methylphenol at 140 °C). DSC (TA instruments Q100 DSC, 2nd heating cycle at 10 °C/min used for determination of T_m, T_c determined from first cooling cycle). ^{13}C NMR spectra were recorded at 120 °C on a Varian Unity Inova NMR spectrometer equipped with an Oxford magnet (14.09 T), operating at 600 MHz, using a 5 mm inverse detection PFG probe. Samples (60–80 mg) for ^{13}C NMR analyses were dissolved at 110 °C in a 9:1 mixture of TCB and benzene-d_6 (Bz_6). WAXD analyses were performed at iThemba LABS (South Africa) on a Bruker AXS D8 ADVANCE diffractometer at room temperature with filtered CuKα radiation. All samples were scanned at 2θ angles, ranging from 6° to 50°, with a sampling width of 0.02°, where 2α is the diffraction angle.

Result and Discussion
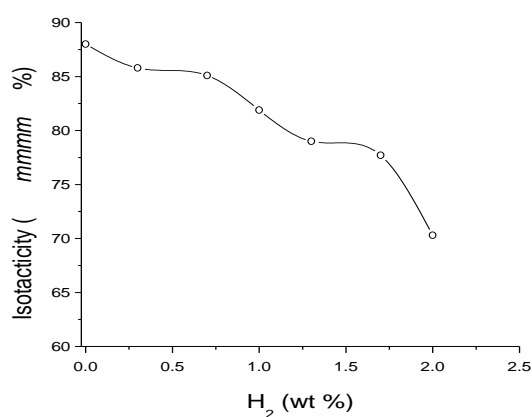
Characterization of the Non-fractionated Polypropylenes

The characteristics of the polypropylenes prepared using EI(4H) metallocene catalyst in the absence and presence of different amounts of molecular hydrogen are summarized in Table 1. The samples prepared using EI(4H) were coded as D9-D3 in Table 1. It is obvious that the use of hydrogen strongly affects polymer molecular weight. The presence of a small amount of hydrogen caused a remarkable reduction in polymer molecular weights (M_w= 24 809 g mol^{-1} in the absence of hydrogen deceased to M_w= 7 188 g mol^{-1} in the presence of 0.3 wt % of hydrogen). This decrease in the molecular weight can be explained as a result of an increase of chain termination by hydrogen.

Table 1: Results of propylene polymerization carried out with EI(4H) catalyst system using various concentrations of hydrogen at room temperature

Run	H_2 (wt %) [a]	Activity [b]	M_w [c]	PD	*mmmm* % [d]	T_m (°C)	T_c (°C)	ΔH_m [e] (J/g)	X_c [f] (%)
D9	0.0	1 785	24 809	2.0	88.0	138.0	107.7	87.4	41.8
D8	0.3	2 171	7 188	2.0	85.8	137.2	104.4	96.9	46.4
D7	0.7	2 191	5 262	1.9	85.1	135.0	102.8	101.4	48.5
D6	1.0	2 235	4 369	1.9	81.9	135.6	105.8	102.4	49.0
D5	1.3	2 287	3 290	1.8	79.0	132.0	99.8	79.4	38.0
D4	1.7	2 151	2 825	1.8	77.7	132.1	102.4	94.9	45.4
D3	2.0	2 424	2 244	1.7	70.3	127.3	95.8	81.7	39.1

[a] (g H_2/g propylene) × 100, [b] (kg PP/(mol Zr.h)), [c] determined by GPC, [d] determined by ^{13}C NMR, [e] determined by DSC, [f] ΔH_m = 209 J/g of PP 100% crystallinity (Deukkil *et al.*, 2005)

The isotacticity (measured as *mmmm* %) is affected by hydrogen. Conflicting results have been reported for different systems. Tsutsui *et al.* (1990) reported that a slight decrease in stereoregularity, from 91.7 to 89.0 % *mm* triads, for the *rac*-C_2H_4(1-Ind)$_2$ZrCl$_2$/MAO catalyst system. A stronger negative effect was found for bis(2-arylindenyl)Zr/MAO catalysts by Lin and Waymouth (1999). No effect of hydrogen on isotacticity has been found in liquid propylene at 50 °C with the *rac*-Me$_2$C(3-t-Bu-1-Ind)$_2$-ZrCl$_2$/MAO catalyst system (Moscardi *et al.*, 1999). Carville *et al.* (1997) also reported that low hydrogen levels do not influence tacticity. In the present study, the isotacticity of polypropylenes produced by EI(4H) catalyst is significantly decreased (from 88.0 % in the absence of hydrogen to 70.3 % in the presence of 2.0 wt % hydrogen), as can be seen in Figure 2 and Table 1. The decrease in the isotacticity of these polymers is due to the increase of stereo-irregular pentads, [*mmmr*], [*mmrr*] and [*mrrm*], which could be attributed to the decreasing stereoselectivity of the catalyst with an increasing the amount of hydrogen. The decrease in the isotacticity can also be attributed to the decreasing molecular weights of these polymers with increasing hydrogen, which leads to loss in the active site control over the chain propagation.

Figure 2: Dependence of the isotacticity of polypropylenes on the hydrogen content for EI(4H) catalyst.
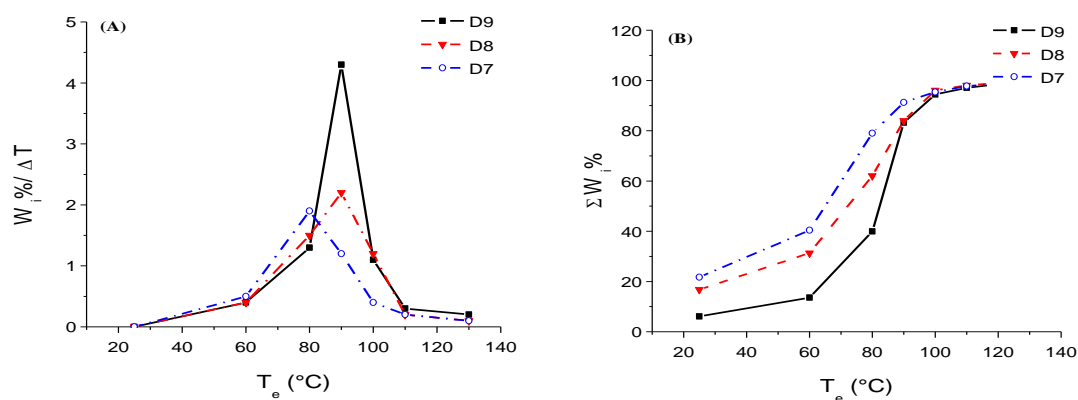
Fractionation and Characterization of Polypropylenes

TREF analyses of three different isotactic polypropylenes D9, D8 and D7 produced using EI(4H) metallocene catalyst were carried out to determine the differences in their characteristics. Table 2 summarizes the TREF fractionation data of polypropylene samples D9, D8 and D7. Their TREF curves are shown in Figure 3.

Table 2: TREF fractionation data of the TREF fractions of samples D9, D8 and D7

Runs	Fraction (T_e °C)	Wt (mg)	Wi%	ΣWi%	Wi%/ΔT
D9	25	184	6.1	6.1	–
	60	226	7.5	13.6	0.4
	80	788	26.3	39.9	1.3
	90	1 300	43.3	83.2	4.3
	100	337	11.2	94.4	1.1
	110	85	2.7	97.1	0.3
	130	89	2.9	100.0	0.2
D8	25	520	16.8	16.8	–
	60	448	14.5	31.3	0.4
	80	952	30.8	62.1	1.5
	90	676	21.9	84.0	2.2
	100	373	12.1	96.1	1.2
	110	61	2.0	98.1	0.2
	130	60	1.9	100.0	0.1
D7	25	650	21.7	21.7	–
	60	560	18.7	40.4	0.5
	80	1 160	38.6	79.0	1.9
	90	370	12.3	91.3	1.2
	100	123	4.1	95.4	0.4
	110	73	2.4	97.8	0.2
	130	65	2.2	100.0	0.1

Table 2 and the curves of the W_i%/ΔT versus the fractionation temperature in Figure 3(A) show that there is an increase in W_i%/ΔT for the first three fractions collected after the 25 °C fraction, and then a decrease for the last three fractions. The curves of D9, D8 and D7 polymers in Figure 3(A) have different distributions and shapes. On the other hands, Figure 3(B) illustrates the accumulative weight fraction percentage versus the fractionation temperatures of the three polymers D9, D8 and D7. It is clear that the curves are considerably different, which is due to the differences in the molecular weight, tacticity and molecular weight distribution of the original polymers. The weight fraction as a function of elution temperature is shown in Figure 4. The superimposed graphs provide a clear and easy way to compare the samples. It is clear from the graph that the three samples have different weight fraction distributions. It is also observed that more than 50 wt % of the original material for all samples eluted at the 80 and 90 °C fractions.

Figure 3: TREF curves of samples D9, D8 and D7: (A) Wi%/ΔT and (B) ΣWi %.
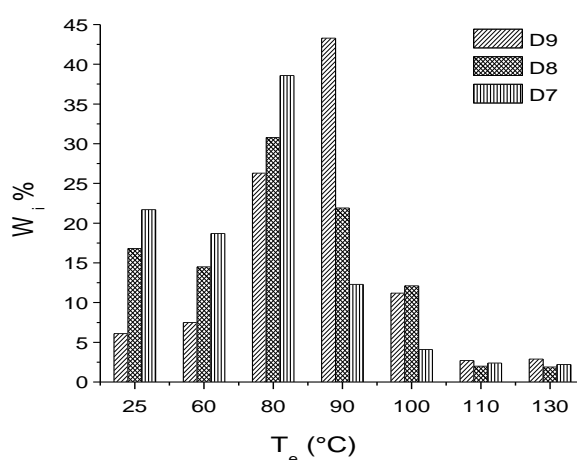
Figure 4: Distribution of weight percentage of D9, D8 and D7 fractions vs. elution temperature (°C).

The characterization results of the fractions for D9, D8 and D7 polymers are summarized in Table 3. Other researchers have clearly demonstrated that for polypropylene samples the TREF profiles qualitatively reflect the distribution of isotacticity, with isotacticity increasing almost linearly with the elution temperature (Kioka *et al*., 1994; Viville *et al*., 2001; Soares & Hamielec, 1996).

Table 3 shows that D9, D8 and D7 polymers are composed of fractions with different tacticities, ranging from rather atactic (elution temperature 25 °C) to highly isotactic (elution temperature 100 °C). An interesting outcome of this analysis is that the isotacticity of D9, D8 fractions are systematically slightly greater than those of D7 fractions, at a given elution temperature. This is spite of the tacticity of the D9, D8 parent polymers being higher than that of the D7 parent polymer (Table 1).

The degree of crystallinity of TREF fractions of samples D8 and D7 increases with elution temperature for the first four fractions and then starts to decrease for the last two fractions, while it only increases for the first three TREF fractions of sample D9 and then starts to decrease as showed in Table 3 and Figure 5.

Table 3: GPC, ^{13}C NMR and DSC Results of Fractionation Data of Samples D9, D8 and D7

Runs	Fraction (T_e °C)	M_w	PD	*mmmm* %	T_m (°C)	T_c (°C)	ΔH_m (J/g)	X_c (%)
D9	25	1 557	1.6	57.0	–	–	–	–
	60	7 438	1.6	81.0	121.1	91.6	53.6	25.7
	80	20 634	1.8	83.0	131.7	100.5	76.7	36.7
	90	28 875	1.6	87.0	137.4	104.6	79.9	38.2
	100	26 801	1.6	89.0	136.5	104.8	73.6	35.2
	110	28 481	1.6	86.0	136.4	98.1	68.8	32.9
	130	22 195	1.5	–	132.2	95.8	60.3	28.9
D8	25	1 420	1.4	56.0	–	–	–	–
	60	3 463	1.4	78.0	122.9	91.8	78.6	37.6
	80	7 042	1.5	84.0	135.7	104.1	85.0	40.7
	90	9 664	1.6	89.0	140.0	107.3	89.9	43.0
	100	9 777	1.6	91.0	141.0	109.2	95.8	45.8
	110	10 645	1.3	87.0	139.5	101.8	86.4	41.3
	130	6 930	1.2	–	133.7	98.5	81.9	39.2
D7	25	1 303	1.4	56.0	–	–	–	–
	60	3 240	1.3	77.0	125.1	96.3	77.4	37.0
	80	6 261	1.5	82.0	137.2	104.9	79.1	37.9
	90	8 478	1.5	87.0	141.4	108.9	90.5	43.3
	100	8 307	1.4	90.0	142.2	109.0	92.6	44.3
	110	7 736	1.3	85.0	140.1	102.5	84.7	40.5
	130	5 901	1.2	–	135.6	98.7	82.2	39.3
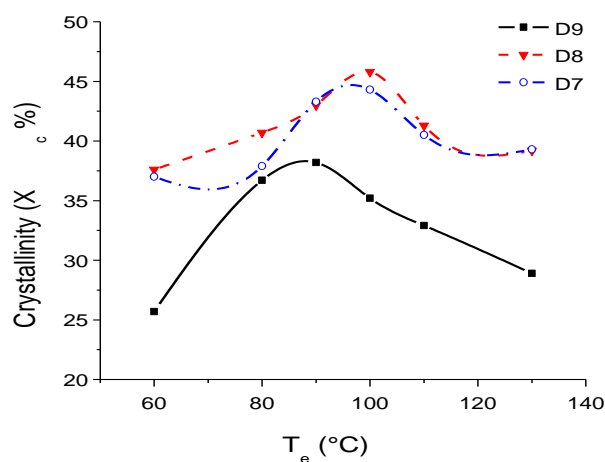
Figure 5: Degree of crystallinity of TREF fractions of samples D9, D8 and D7 versus TREF elution temperature.

The reason for the decreasing crystallinity of the last fractions is due to the significant decrease in the molecular weight and tacticity of these fractions, as evident in Table 3. Moreover, Figure 6 shows typical WAXD patterns of the α form of selected TREF fractions of sample D9, in which three strong equatorial peak of (110), (040) and (130) appear at 2θ = 14.10°, 16.90° and 18.58°.
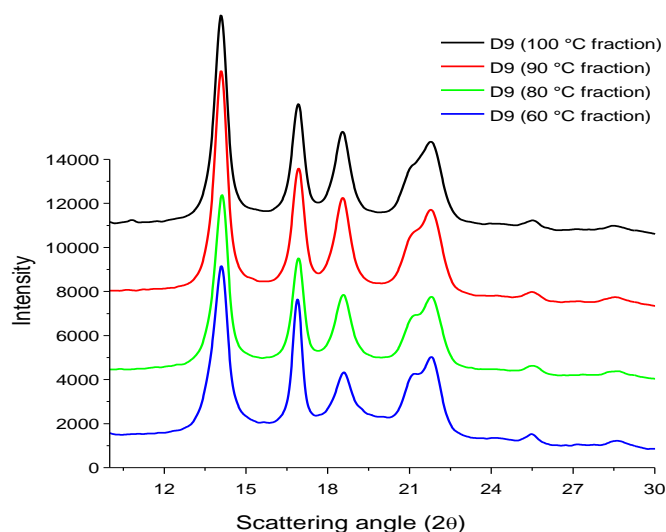
Figure 6: Typical X-ray diffraction pattern of various TREF fractions of sample D9.

Conclusion

By using metallocene catalyst system it was possible to produce polymer samples of a wide variation in tacticity and molecular weight. The addition of molecular hydrogen to propylene polymerizations catalyzed using the EI(4H) catalyst system resulted in a reduction in polymer molecular weight and isotacticity of the polypropylenes. Furthermore, Preparative TREF allowed us to produce polymer fractions of well-defined structure in terms of molecular weight and distribution, as well as tacticity. A major increase in the degree of crystallinity of the polypropylene fractions was also noticed upon increasing the elution temperature. Moreover, X-ray diffraction showed only one crystal structure (α phase) for the crystalline fractions of the polypropylene samples.

Acknowledgements

References

Auriemma, F., De Rosa, C., Boscato, T. & Corradini, P. 2001. The oriented γ form of isotactic polypropylene. *Macromolecules*. **34**(14): 4815-4826.

Busico, V., Cipullo, R., Caporaso, L., Angelini, G. & Segre, A. L. 1998. *C2*- symmetric ansa-metallocene catalysts for propene polymerization: Stereoselectivity and enantioselectivity, *Journal of Molecular Catalysis A: Chemical*. **128**(1-3): 53-64.

Carvill, A., Tritto, I., Locatelli, P. & Sacchi, M. C. 1997. Polymer microstructure as a probe into hydrogen activation effect in ansa-zirconocene / methylaluminoxane catalyzed propene polymerizations. *Macromolecules*. **30**(23): 7056-7062.

Deukkil, P., Kim, I., Yang, H., Soo, S., Kim, B. & Chang, H. 2005. Isothermal crystallization behavior of metallocene-catalyzed isotactic polypropylene. *Journal of Applied Polymer Science*. **95**(2): 231-237.

Kioka, M., Makio, H., Mizuno, A. & Kashiwa, N. 1994. Tacticity distribution of polypropylene prepared by MgCl₂-supported titanium catalyst. *Polymer*. **35**(3): 580-583.

Lin, S. & Waymouth, M. 1999. Regioirregular propene insertion in polypropenes synthesized with unbridged bis(2-aryl)indenyl zirconium dichloride catalysts: Implications on activity. *Macromolecules*. **32**(25): 8283-8290.

Lin, S., Kravchenko, R. & Waymouth, R. M. 2000. Ethylene and hydrogen effects in propylene polymerization with 2-arylindenyl zirconocenes. *Journal of Molecular Catalysis A: Chemical*. **158**(1): 423-427.

Moscardi, G., Piemontesi, F. & Resconi, L. 1999. Propene polymerization with the isospecific, highly regiospecific rac-Me2C(3-t-Bu-1-Ind)2ZrCl2/MAO catalyst. 1. Influence of hydrogen on initiation and propagation: Experimental detection and theoretical investigation of 2,1 propene insertion into the Zr-H bond. *Organometallics*. **18**(25): 5264-5275.

Soares, J. B. & Hamielec, A. E. 1996. Kinetics of propylene polymerization with a non-supported heterogeneous Ziegler-Natta catalyst - effect of hydrogen on rate of polymerization, stereoregularity, and molecular weight distribution. *Polymer*. **37**(20): 4607-4614.

Soga, K. & Shiono, T. 1997. Ziegler-Natta catalysts for olefin polymerizations. *Progress in Polymer Science*. **22**(7): 1503-1546.

Tsutsui, T., Kashiwa, N. & Mizuno, A. 1990. Effect of hydrogen on propene polymerization with ethylenebis(1-indenyl)zirconium dichloride and methylalumoxane catalyst system. *Macromolecular Rapid Communications*. **11**(11): 565-570.

Viville, P., Daoust, D., Jonas, A. M., Nysten, B., Legras, R., Dupire, M., Michel, J. & Debrasb, G. 2001. Characterization of the molecular structure of two highly isotactic polypropylenes. *Polymer*. **42**(5): 1953-1967.

Xu, J., Feng, L., Yang, S., Yang, Y. & Kong, X. 1998. Temperature rising elution fractionation of polypropylene produced by heterogeneous Ziegler Natta catalyst. *European Polymer Journal*. **34**(3-4): 431-434.

TRANSACTIONS ON SCIENCE AND TECHNOLOGY