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"Anisotactic" polypropylenes produced with a zirconocene-methylalumoxane catalyst: solid state properties and microstructure

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Summary

Propene was polymerized with ethylene bis(-1-indenyl)-dichlorozirconium ($Et(Ind)_2ZrCl_2$) and methylalumoxane (MAO) at 70°C. The polymer was fractionated by solvent extraction; there was no hexane insoluble material. The pentane insoluble, hexane soluble (C_{5i} - C_{6s}) fraction contains 67% mmmm pentads. It has x-ray crystallinity of 59% comprised of 93% γ-phase, and no NMR detectable misinsertions. However, 1,3-insertion was found in the more soluble fractions.

Introduction

Ewen (1) was the first to use $Et(Ind)_2TiCl_2$ (56% racemic, 44% meso) (2) with MAO (3) to polymerize propene at -60°C into 63% isotactic and 37% atactic products. Kaminsky et al. (4) subsequently synthesized polypropylene with an ethylene bis(4,5,6,7-tetrahydro-1-indenyl)dichlorozirconium (5) ($Et(IndH_4)_2$-$ZrCl_2$)/MAO catalyst at temperatures between -10°C and -20°C. The polymers were said to have low solubility in high boiling hydrocarbons and IR isotacticity indices between 86% and 91%. Soga (6) and Zambelli (7) found evidence for 1,3-insertions of propene using either the $Et(Ind)_2$- and the $Et(IndH_4)_2$-$ZrCl_2$ systems over the same temperature range. The polymers are said to be highly isotactic but partially soluble in boiling heptane.

On first principles, one would predict the stereorigidity of the zirconocene/MAO complex to decrease with increasing temperature. Understanding of this effect is of extreme importance for the future advances in the homogeneous stereoselective polymerization of α-olefins. We have completed a detailed investigation of the solid state properties and microstructures of polypropylenes obtained with the $Et(Ind)_2ZrCl_2$/MAO catalyst between -55°C and 80°C. The salient features of the polypropylene obtained at 70°C are presented here. The complete report will be published elsewhere.

Results and discussion

Propene at 1.5 atm was polymerized in 95 ml toluene using 8.4×10^{-7} mol $Et(Ind)_2ZrCl_2$ (9) and 1.7×10^{-3} mol of MAO (10). The polymerization was slow below 0°C but increased rapidly between 0°C and 80°C. The activity at 70°C is 7.7×10^3 kg PP ([Zr] · h · [M])$^{-1}$, where [M] is the molar concentration of propene in toluene. A previous reported drop of activity increase above 50°C (4) is attributable to a decrease of monomer solubility with the increase of temperature.

The total polymer has M_n = 12,000 and an M_n/M_w value of 2.3. All the polymer is soluble in the reaction medium. The maximum melting transition (T_m) is 107°C by DSC but the melting endotherm commences at 60°C. There are 57% of mmmm pentads according to ^{13}C-NMR.

The polymer was fractionated by Pasquon's extraction method (11), it was completely extracted by refluxing n-hexane. The properties of the fractions are summarized in Table 1.

Table 1. Properties of the polypropylene fractions.

Solvent	Acetone	Ether	Pentane	Hexane
wt% of fraction	16.4	32.0	15.3	36.2
T_m, °C	54	86	105	113
Xc, %	--	--	54.4	59.2
$C\gamma$, %	--	--	100	93
mmmm pentad, %	34.2	51.7	62.2	66.7

The polymers soluble in acetone and ether are waxy materials while the hydrocarbon fractions are obviously crystalline. However, the former polymers are by no means amorphous and therefore atactic. The acetone soluble polymer has a very broad DSC melting curve with T_m of 54°C; the curve for the ether soluble substance is less broad. These and other DSC curves will be published later (8).

X-ray diffraction patterns of the C_5 and C_6 soluble fraction were taken after heating first to 250°C and then slowly cooling down overnight under ambient pressure. The percent crystallinity (Xc) is only moderately lower than Xc of the commercial isotactic propylene. However, the patterns shown in Fig. 1B and 1C for the C_5 and the C_6 soluble fractions are predominantly that of the γ-modification; the percentage of γ-phase ($C\gamma$) are 100 and 93, respectively. These are compared with the typical α-phase pattern (12) (Fig. 1A) for polypropylene (unextracted) obtained with a $MgCl_2$ supported catalyst (13).

The melting behavior of the hexane soluble fraction was studied in detail. Dependent on the thermal history of the sample the melting point varied between 113°C and 116°C. Slow cooling (2.5 deg/min) favored the lower melting point whereas fast cooling (100 deg/min) favored the higher. The heat of fusion was found to be constant at 15.3 cal/mol. However, the polymer is not transformed to the α-modification by those thermal treatments. They were reported (14 - 16) to cause γ to α transformations for the fractions extracted from commercial polypropylene.

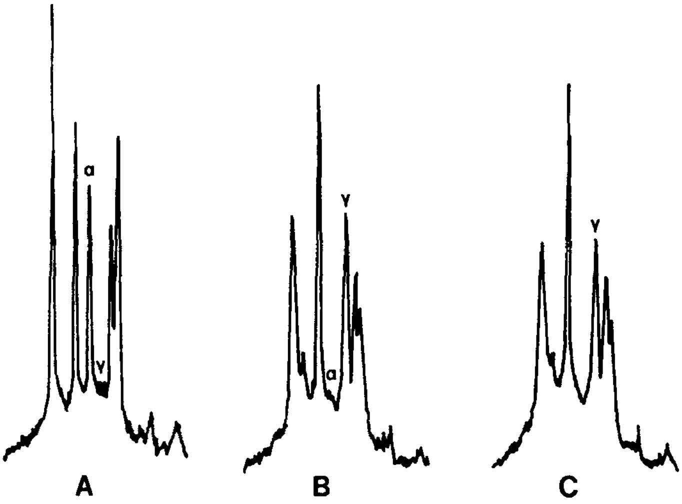


Figure 1. Powder x-ray patterns: (A) isotactic polypropylene (unextracted) obtained with a $MgCl_2$ supported $TiCl_3$ catalyst; (B) C_5 soluble fraction and (C) C_6 soluble fraction of polypropylene of this work.

The isotacticities of the fractions given in Table 1 were determined by pentad analysis of the ^{13}C-NMR spectra. The ^{13}C-NMR spectra of the acetone and of the hexane fractions are shown in Figure 2. The numbered peaks in the fraction are due to 1,3-insertions, n-propyl and vinylidene chain ends (17). Their intensities decrease with the order of extraction. Head-to-head arrangements were not found in any of the fractions.

Conclusions

Stereoregular polypropylene produced with heterogeneous titanium based δ-$TiCl_3 \cdot 0.33$ $AlCl_3$ and $MgCl_2$ supported $TiCl_3$ are ≥90%

insoluble in refluxing n-heptane which is the practical measure of isotacticity indices. These polymers have ≥97% mmmm pentads and a T_m of 170 - 175°C. Multisolvent fractionation of the heptane soluble materials (18) afforded polymers melting as low as 106 - 114°C and x-ray crystallinities of 15 - to 27% (E_i - C_{5s}). However, all the

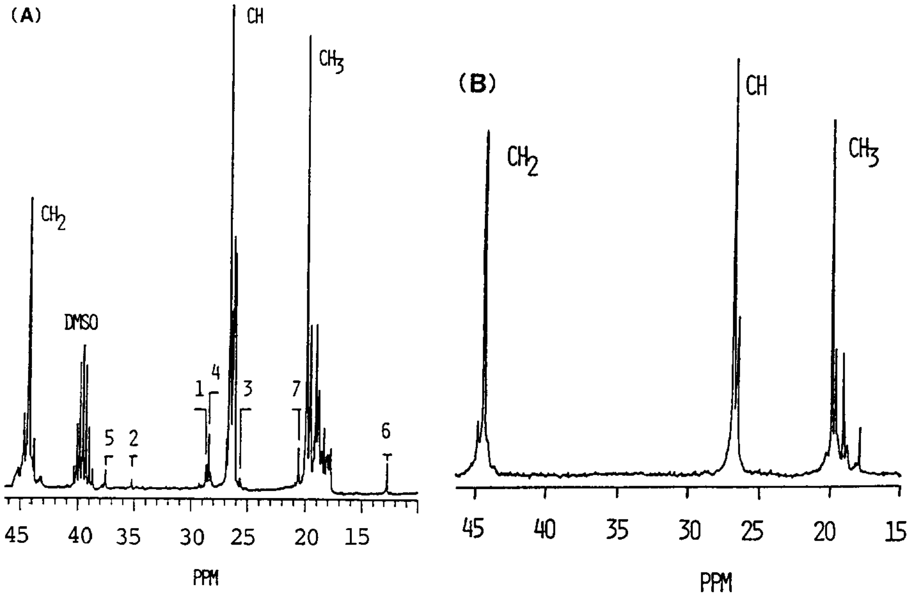
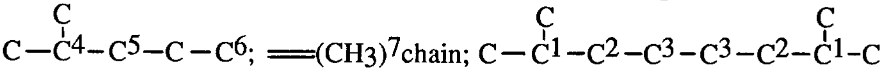


Figure 2. ^{13}C-NMR of polypropylene: (A) acetone soluble fraction; (B) C_{5i} - C_{6s} fraction. Assignments for the numbered peaks are:



$$C-\overset{C}{C^4}-C^5-C-C^6;\ =\!=(CH_3)^7\text{chain};\ C-\overset{C}{C^1}-C^2-C^3-C^3-C^2-\overset{C}{C^1}-C$$

stereoirregular materials are present in very small amounts. The γ-phase formed from these polymers by crystallization under pressure is thermally unstable, transforming γ to α-phase upon melting or even during a DSC run at either very slow or fast heating rates (16). The heterogeneous catalysts have distinct active sites differing markedly in their stereoselectivities. Truly atactic polypropylene (mm = 25%, x-ray crystallinity = 0%) is only obtained with β-$TiCl_3$/$AlEt_2Cl$ (C_{5s}, 35.5 wt%) and with VCl_3/$AlEt_2Cl$ (C_{5s}, 31 wt%) (19, 20).

The properties of the propylenes produced by the $Et(Ind)_2ZrCl_2$/MAO catalyst showed the polymers to be comprised of varying degrees of microtacticity, which can be crystallized into stable γ-modification. T_m for those samples varies from 154°C down to almost room temperature. These polymers are produced because of conformational fluctuations of the Zr complex the rate of which increases with increasing temperature. MAO acts to add stereorigidity to the Zr complex. We have coined the word "anisotactic" for these polymers to describe the gradual difference in microtactic structure for polypropylenes obtained with the soluble chiral metallocene/MAO catalyst.

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