

Gas-phase polymerization of propylene with a solid complex catalyst obtained from $\text{Et}(\text{Ind})_2\text{ZrCl}_2$ and methylaluminoxane

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Polymerization of propylene in the gas phase was carried out with a solid Zr complex catalyst obtained from ethylenebis(1-indenyl)zirconium dichloride ($\text{Et}(\text{Ind})_2\text{ZrCl}_2$) and methylaluminoxane (MAO). The resulting polymer had structurally similar features to that obtained in toluene liquid-phase polymerization with a soluble Zr catalyst composed of $\text{Et}(\text{Ind})_2\text{ZrCl}_2$ and MAO, suggesting that the solid Zr complex catalyst in the gas-phase polymerization system maintains the nature of active centres in the soluble Zr catalyst system.

(Keywords: zirconium catalyst; aluminoxane; isotactic polypropylene; gas-phase polymerization; microstructure)

INTRODUCTION

Recently, it has been shown that a soluble catalyst system composed of ethylenebis(1-indenyl)zirconium dichloride ($\text{Et}(\text{Ind})_2\text{ZrCl}_2$) or its hydrogenated derivative and methylaluminoxane (MAO) in toluene produces isotactic polypropylene (PP) having *meso-meso* sequence content comparable to commercial PP, but low melting point, probably due to the existence of irregular units in the polymer chain based on 2,1- and 1,3-insertions of propylene monomer¹⁻⁶.

Moreover, the stereo- and regiospecificity of the Zr catalyst system are found to be enhanced with the lowering of polymerization temperature^{4,5}. This behaviour may be considered to be caused by the suppression in intramolecular vibration of Zr catalyst component in toluene.

In this paper, in order to confirm the above view under the assumption that a solid catalyst system results in the suppression in intramolecular vibration of the catalyst component, a gas-phase polymerization of propylene was performed with a solid complex catalyst obtained from $\text{Et}(\text{Ind})_2\text{ZrCl}_2$ and MAO. The resulting PP was compared with PP from the corresponding soluble catalyst system.

EXPERIMENTAL

Preparation of a solid Zr complex catalyst

First, 100 ml of n-decane was charged into a 400 ml glass flask. Next, 40.3 ml of MAO toluene solution ($\text{Al}=2.48 \text{ mol l}^{-1}$) and 71.4 ml of $\text{Et}(\text{Ind})_2\text{ZrCl}_2$ toluene solution ($\text{Zr}=1.40 \text{ mmol l}^{-1}$) were added. The subject Zr catalyst was precipitated by evaporating toluene at room temperature, collected by filtration and vacuum dried. In 1 g of the obtained catalyst, there were 2.1 mg of Zr and 381 mg of Al ($\text{Al/Zr}=610$ molar ratio).

MAO and $\text{Et}(\text{Ind})_2\text{ZrCl}_2$ were prepared by the same methods as described in previous papers (refs. 7 and 5 respectively).

Polymerization

Gas-phase polymerization. In a 2 litre stainless-steel autoclave equipped with a stirrer was placed 150 g of NaCl as a disperse medium. The system was vacuum dried at 90°C, then returned to atmospheric pressure by N_2 gas and cooled to 50°C. Subsequently, 0.87 g of dried solid Zr complex catalyst was added and propylene gas was introduced into the system. Polymerization was carried out for 2 h under 5 kg cm^{-2} propylene pressure under completely dry conditions. The mixture of NaCl and the resulting polymer was poured into a large amount of water to dissolve NaCl and the powdery polymer was recovered by filtration, washed with methanol and vacuum dried at 80°C for 12 h (yield 88.0 g).

Liquid-phase polymerization. In a 500 ml glass reactor equipped with a stirrer was placed 250 ml of toluene and the system was fed with propylene gas and heated to 50°C. Subsequently, MAO toluene solution (3.05 mmol, as Al atom) and $\text{Et}(\text{Ind})_2\text{ZrCl}_2$ toluene solution (0.005 mmol) were added in this order ($\text{Al/Zr}=610$ molar ratio). Polymerization was carried out under atmospheric pressure at 50°C for 30 min and terminated by the addition of a small amount of methanol. Polymerization proceeded in solution. The whole product was poured into a large amount of methanol. The resulting powdery polymer was collected by filtration and dried in the same manner as in the gas-phase polymerization (yield 21.5 g).

Analysis of polymer

¹³C n.m.r. spectra were recorded on a JEOL GX-500 spectrometer operating at 125.8 MHz at 110°C in a solution of 0.5 ml hexachlorobutadiene and 0.1 ml benzene-d₆ containing ~150 mg of the polymer sample, using 4.2 s pulse repetition, 7500 Hz spectral width and 64 000 data points.

The molecular weight of the polymer sample was determined by g.p.c. (Water Associates, model ALC/

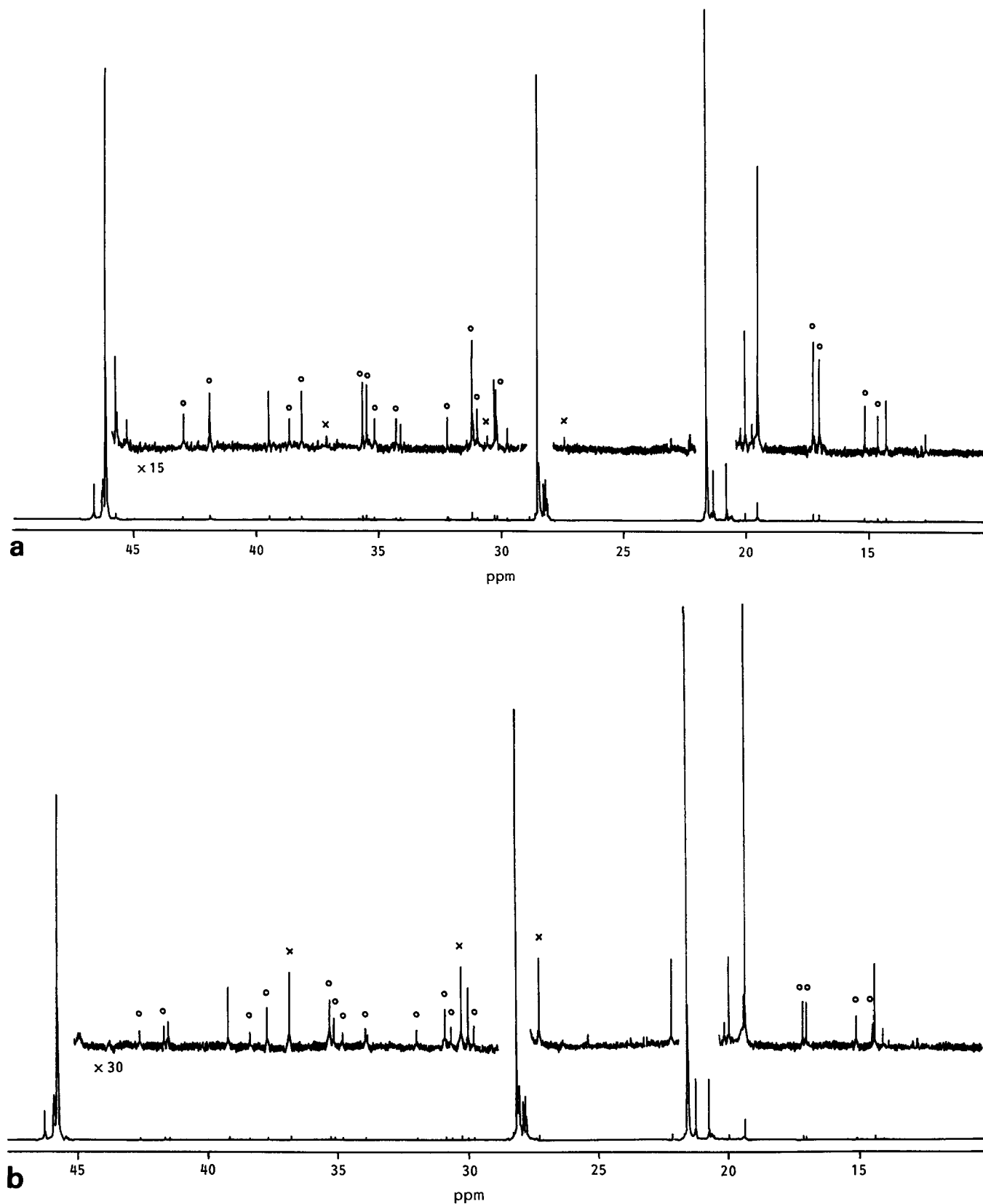


Figure 1 ^{13}C n.m.r. spectra: (a) PP obtained via gas-phase polymerization; (b) PP obtained via liquid-phase polymerization. The symbols \circ and \times indicate peaks based on 2,1- and 1,3-insertion of propylene monomer, respectively

GPC/150C) using polystyrene gel column (10^6 – 10^3 Å pore size) and *o*-dichlorobenzene as solvent at 140°C .

D.s.c. measurements were recorded on Perkin-Elmer 7 at a heating rate of $10^\circ\text{C min}^{-1}$.

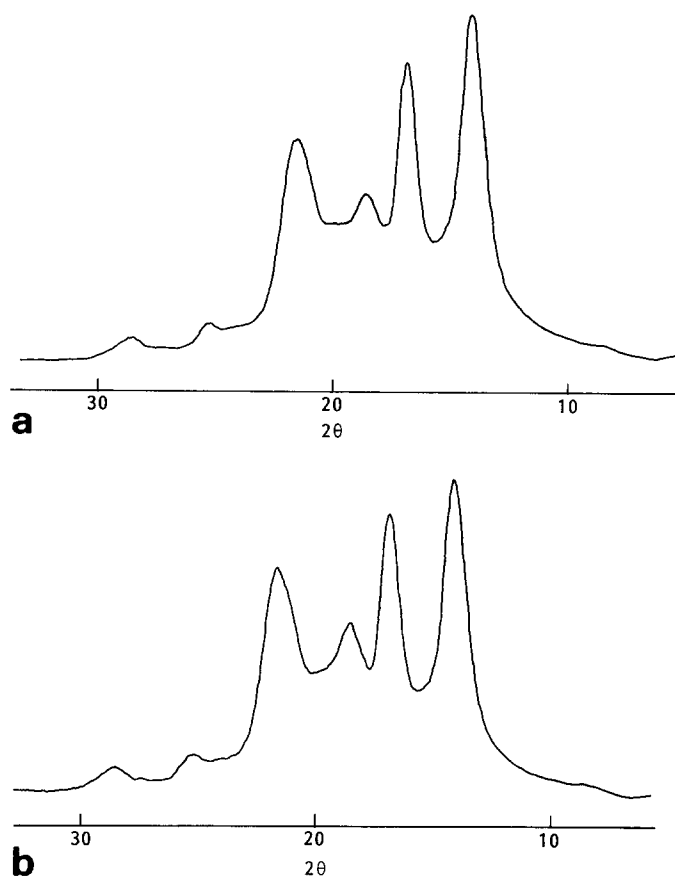
Crystallinity and long period of the polymer sample, which was prepared by rapid cooling after melting the

powdery polymer at 180°C under pressure, were measured by wide- and small-angle X-ray diffractometry, respectively (Rigaku RU-300 diffractometer, Ni-filtered $\text{Cu K}\alpha$ radiation, 50 kV, 300 mA, scanning rate 2°min^{-1}).

The lamellar thickness of the polymer was calculated from the values of crystallinity and long period.

Table 1 Results of propylene polymerization in gas and liquid phases

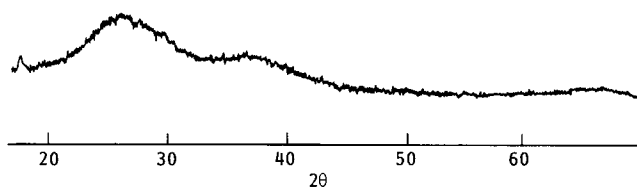
	Gas phase	Liquid phase
\bar{M}_n	9300	12500
\bar{M}_w/\bar{M}_n	2.21	1.96
T_m (°C)	122.1	121.7
mm (%)	84.2	86.3
mr (%)	10.9	9.3
rr (%)	4.9	4.4
2,1-insertion (%)	1.2	0.3
1,3-insertion (%)	0.1	0.3
Crystallinity (%)	51	52
Long period (Å)	145	140
Lamellar thickness (Å)	74	73
Crystal form	α	α

**Figure 2** X-ray diffraction spectra: (a) PP obtained via gas-phase polymerization; (b) PP obtained via liquid-phase polymerization

The X-ray diffraction spectrum of the solid Zr complex catalyst was obtained using the above wide-angle X-ray diffractometer under a N_2 atmosphere.

RESULTS AND DISCUSSION

Polymerizations of propylene in the gas phase and in toluene liquid phase were performed at 50°C with a solid Zr complex catalyst obtained from $Et(Ind)_2ZrCl_2$ and MAO and a soluble Zr catalyst composed of $Et(Ind)_2ZrCl_2$ and MAO, respectively. The ratio of MAO and Zr in both polymerizations was the same (Al/Zr = 610 molar ratio). The resulting polymers were analysed by g.p.c., ^{13}C n.m.r., d.s.c. and x.r.d. methods. The analytical data of polymers are listed in Table 1.

**Figure 3** X-ray diffraction spectrum of the solid Zr complex catalyst

The polydispersity of the polymer produced in the liquid-phase polymerization was quite narrow ($\bar{M}_w/\bar{M}_n = 1.96$) owing to homogeneity in the soluble catalyst system. In addition, the polymer produced in the gas-phase polymerization showed comparable polydispersity ($\bar{M}_w/\bar{M}_n = 2.21$), suggesting that rather uniform active centres are formed even in the solid Zr complex catalyst.

In the ^{13}C n.m.r. spectra of both polymers (Figure 1), there were a number of small irregular peaks arising from head-to-head or tail-to-tail enchainments and $-(CH_2)_4$ units, which were formed by 2,1-insertion and 1,3-insertion of propylene monomer, respectively. These peaks are not observed in PP obtained with a heterogeneous Ti catalyst system⁴⁻⁶. The polymer produced in the gas-phase polymerization had almost the same isotacticity, more 2,1-insertion units and fewer 1,3-insertion units as compared with that produced in the liquid-phase polymerization.

In Figure 2 are shown the wide-angle X-ray diffraction spectra. Both polymers showed the α -form as the crystal form of PP. From the intensity of the spectra, the crystallinity was found to be 51% for the gas-phase polymer and 52% for the liquid-phase one. Moreover, the long period and the lamellar thickness of PP were 145 and 74 Å for the former polymer and 140 and 73 Å for the latter, respectively.

As shown in Table 1, the melting point was almost the same in both polymers, probably due to the same lamellar thickness.

These data imply that the nature of active sites in the soluble Zr catalyst system remains unchanged even in the solid Zr complex catalyst of the gas-phase polymerization.

Figure 3 shows the X-ray diffraction spectrum of the solid Zr complex catalyst. In the spectrum, no peak based on crystalline component was observed, meaning that the solid Zr complex catalyst is amorphous and the active Zr centres are perhaps highly dispersed on amorphous MAO. This fact might lead to the similarity in the nature of active centres between the solid Zr complex catalyst and the soluble Zr catalyst systems.

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