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Polymerization of Propylene by Mixed Ziegler–Natta and Metallocene Catalysts

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The polymerization of propylene using a mixture of racemic metallocenes and Ziegler–Natta catalysts was investigated. The polypropylene was obtained as a mixture of a fine powder and beads, with the powder being absorbed partially on the beads. The relative amount of the powder can be controlled by the concentration of the metallocene. The compatibility between the components of the mixed catalytic systems and the effect of the components on the rate of polymerization and on the properties of the new polymers were studied. The metallocene system dramatically affects the melt viscosity, isotacticity and molecular weight of the polymers. The two catalytic systems are able to act jointly, producing different polymers, for which separate melting and crystallization temperatures are obtained. © 1998 John Wiley & Sons, Ltd.

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INTRODUCTION

Since the landmark discoveries by K. Ziegler's group in 1953 and by G. Natta's group in 1954, the Ziegler–Natta polymerization process for olefins and diolefins has come to be recognized as one of the most important and far-reaching findings ever made in polymer chemistry.[1–8] From the beginning it was known that the activity of such polymerization catalysts depended on the nature of the catalysts, the Lewis acid strength of the co-catalysts and the polarity of the solvent for homogeneous catalysts; or on the nature of the solid support for heterogeneous catalysts.[3–8] It was realized that the real importance of the acidity of the Lewis co-catalysts, and of the solvent polarity in weakly coordinating media, could be explained in terms of the formation of intermediate transition metal cations having an available coordination site for the olefin monomer.[9–14]

Besides the discovery of methylalumoxane (MAO) by Sinn and Kaminsky,[15] the major breakthrough for metallocene complexes of the early transition metals was achieved by the synthesis of stereorigid *ansa*-metallocenes by Brintzinger and co-workers.[16] The complexes have been used as stereoselective catalytic precursors for the production of isotactic polypropylene, reported by Ewen and Kaminsky in the mid-1980s.[17,18]

Over the last 17 years, in both academic and industrial laboratories major efforts have been devoted to developing these promising catalysts.[3–8] Recent scientific advances now allow a better understanding of the polymerization mechanism and the close relationship between polymer properties and metallocene structure. A clear correlation has been established between the geometry of the metallocene and polymer tacticity, molecular weight, etc.[19–24] It has also been demonstrated that the metallocenes, as olefin polymerization catalysts, are not only matching their heterogeneous counterparts in every point of producing a variety of comparable olefinic homo- and co-polymers, but they can also produce polymers that could not have been produced by other catalytic systems.

As far as the unique performance of the metallocene complexes in the polymerization of -olefins are concerned, some general conclusions can be stated: (1) metallocenes show the highest polymerization activities, as compared with $MgCl_2$-supported titanium catalysts; (2) metallocenes produce polymers with the highest stereospecificity as compared with the conventional Ziegler–Natta

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catalysts; (3) being single-site catalysts, metallocenes seem to have the highest ability to polymerize propylene, producing polypropylene chains with like structures, and of almost equal lengths, i.e. with high compositional uniformity and very narrow molecular weight distribution (MWD). In addition, metallocenes show a great ability to copolymerize various monomers, including polar ones, with uniform distribution of the co-monomers.[3–8,19–25]

The narrow MWD and low melting temperatures of the metallocene-based polyolefins may be either an advantage or a drawback, depending on the processing method and the end-product applications. Thus, commercial grades of first-generation metallocene-based polypropylene available today are intended for the production of fibers, biaxially oriented films and thin-wall injection moldings.[26–30]

Major drawbacks of the metallocene (Group IVB)-based polypropylenes, arising from low shear sensitivity of polymers with a narrow MWD, are low melt strengths, high die pressure, and a tendency to melt-fracture.[31,32] These drawbacks limit the areas of application of these materials and inhibit their introduction into the market, at present occupied by conventional Ziegler–Natta grades.

The processability of polypropylene can be improved by melt-blending of grades with different molecular weights in an extruder. This process requires prolonged mixing to achieve fine dispersion, is highly energy-consuming and is usually accompanied by polymer chains destruction.[27] An alternative method is to polymerize propylene using two successive reactors. In the first, the polymerization is carried out by the conventional Ziegler–Natta catalyst in the absence of hydrogen, in order to obtain high-molecular-weight fractions of polypropylene, while in the second the polymerization is accomplished in the presence of hydrogen to obtain fraction of lower molecular weight.[33–35] A similar option is polymerization in a single reactor, in the presence of different catalysts, under the same conditions, providing simultaneous formation of polymers with different molecular weights. Thus, has been proposed the combination of two or more homogeneous metallocene catalysts for ethylene polymerization.[35]

Here we report the synthesis and characterization of isotactic polypropylene obtained in a single reactor by mixing a conventional Ziegler–Natta catalyst (commercial T_i on $MgCl_2$) with racemic zirconium metallocene complexes. The interaction between the components of the Ziegler–Natta and the metallocene catalytic systems, the compatibility effects on the activity of the mixed systems and the properties of the polymers obtained were studied.

EXPERIMENTAL

Materials and general operations

All manipulations with air-sensitive materials were performed with rigorous exclusion of oxygen and moisture using flamed Schlenk-type glassware on a dual-manifold Schlenk line and high-vacuum (10^{-5} Torr) techniques. For storage of air-sensitive materials a nitrogen-filled Vacuum Atmospheres glovebox with a medium-capacity recirculator (1–2 ppm O_2) was used. Argon, nitrogen and propylene gases were purified by passage through an MnO oxygen-removal column and a Davison 4 Å molecular sieve column. Analytically pure solvents (diethyl ether, tetrahydrofuran, hexane, toluene) were dried by refluxing over Na/K alloy or sodium metal under argon.

Zirconium metallocenes [$C_2H_4(Ind)_2ZrCl_2$ (Ind = indenyl) and $Me_2Si(Ind)_2ZrCl_2$] were prepared according to literature procedures.[36] Methylalumoxane (Witco) was prepared from a 20% suspension in toluene by vacuum evaporation of the solvent at 25 °C/10^{-5} Torr. Ziegler–Natta catalysts (commercial T_i on $MgCl_2$) were obtained from an industrial source.

NMR spectra were recorded on Bruker AM-200 and Bruker AM-400 spectrometers. Chemical shifts for ^1H NMR and ^{13}C NMR were referenced to internal solvent resonance and are reported relative to tetramethylsilane. The NMR experiments were conducted in Teflon valve-sealed tubes (J-Young) after vacuum transfer of the liquids in a high-vacuum line. Ether solvents (THF-d_8) for NMR analysis were distilled under argon from sodium benzophenone ketyl. Hydrocarbon solvents (toluene-d_8, benzene-d_6) were distilled under argon from Na/K alloy. All solvents for vacuum-line manipulations were stored in vacuum over Na/K alloy in resealable bulbs.

All the polymerization experiments were performed in a water-cooled jacketed 4-litre stainless-steel laboratory autoclave provided with inlets for each of the gases (hydrogen, propylene and nitrogen), a mechanical mixer, thermocouple and pressure transducers. Before any experiment, the autoclave was prepared for the polymerization runs in the following manner. The reactor was purged with N_2 (70 °C, 1 h) followed by repeated (2–3 times) filling and venting at 70 °C firstly with hydrogen and then with propylene. The reactor was then cooled to room temperature before the catalysts and propylene were introduced. The Ziegler–Natta and the metallocene catalytic systems were loaded into the autoclave under a light stream of propylene (20–30 $cm^3 \cdot min^{-1}$).

Preparation of the Ziegler–Natta and metallocene catalytic systems

Preparation of the Ziegler–Natta catalytic system was performed under a nitrogen stream as follows: 80 ml of pure dried hexane was introduced into a 250-ml dropping funnel; 10 ml of a 120 $g\,l^{-1}$ solution of the triethylaluminium (TEAL) co-catalyst in hexane and a certain amount (Table 2, below) of cyclohexylmethyldimethoxysilane (external donor) were added from the dropping funnel. After 5 min precontact, 40 ml of this solution was transferred into a tailed flask, into which a weighted amount of solid Ziegler–Natta catalyst was then added, after which the catalytic system was ready to be introduced into the polymerization autoclave.

The metallocene catalytic system was prepared as follows: 40 mg of the metallocene and a certain amount of toluene (Table 1, below) were introduced into a Schlenk flask (glovebox). The mixture was exposed to an ultrasonic bath for 60 sec in order to obtain a homogeneous solution. A determined amount of the methylalumoxane [MAO,$(CH_3ALO)_n$, $n = 19$–21] co-catalyst was introduced into a second Schlenk flask, in which measured volumes of the metallocene solution and solvent (toluene or hexane) were then added. After this mixture had been exposed to an ultrasonic bath to obtain a fine dispersion, the metallocene catalytic system was ready to be inserted into the polymerization autoclave.

One-step polymerization

The Ziegler–Natta and metallocene catalytic systems were loaded successively under a light propylene stream. After both catalysts were charged and the injection port sealed off, measured amounts (see Tables) of H_2 (to cut the polypropylene chains) and propylene were introduced into the autoclave. Polymerization reactions were run for 2 h at 30–40 °C when the metallocene was used alone or at 70 °C for either the Ziegler–Natta catalyst alone or the mixed catalytic systems. The polymers obtained were dried in a vacuum oven at 70–100 °C for 1–2 h before any characterization.

Two-step polymerization

The Ziegler–Natta catalyst and half of the total quantities of hydrogen and propylene were introduced into the autoclave. After 1 h of polymerization at 70 °C, the excess of hydrogen and propylene were discharged. Then, the autoclave was cooled and the metallocene catalytic system and the rest of the propylene (i.e. the other half) (without H_2) were loaded. The polymerization process was continued at 30–40 °C for an additional hour.

Polypropylene characterization

The polymers obtained were characterized by melt flow index (MFI) (230 °C; 2.16 kg), xylene-insolubles (XI), determined as the weight percentage of the polypropylene that was insoluble in cold *o*-xylene, intrinsic viscosity ($[\eta]$) in tetralin at 135 °C (for polypropylene produced by metallocene catalysts) and zero-shear viscosity ($[\eta_0]$) (for polymers produced by the mixed Ziegler–Natta–metallocene catalytic systems). Shear viscosity of the polymer melts was measured using an ARES dynamic rheometer (Rheometric Scientific). A parallel-plates set-up was used for the tests. Frequency/temperature scan experiments were conducted in the temperature range 180–240 °C and frequency range 0.05–15 Hz. Master curves were constructed based on the results for a reference temperature of 200 °C. The viscosity data were approximated using the Carreau model.[37] Zero shear viscosity determined from the approximation was used for estimation of the molecular weight of the polymers. Melting temperatures were measured using a Perkin-Elmer differential scanning calorimeter DSC-7. Three runs (heating–cooling–heating) at a rate of 10 °C min^{-1} in the range 30–190 °C were performed for each sample of polymer. The second heating–melting peak temperature was used as the melting temperature.

RESULTS AND DISCUSSION

The catalytic polymerization of propylene to isotactic polypropylene by $C_2H_4(Ind)_2ZrCl_2$ (Ind = indenyl) **(1)** and $Me_2Si(Ind)_2ZrCl_2$ **(2)** with an excess of the co-catalyst MAO (methylalumoxane) were performed in the same experimental conditions (pressure, temperature) as for the Ziegler–Natta polymerization of propylene in an autoclave reactor to obtain comparable data. The polymeriza-

Table 1. Conditions and polymer properties of metallocene-catalyzed polymerization of propylene under high pressure

Expt	Composition of the catalytic system[a]			Process conditions			Polypropylene properties				
	Catalytic precursor	Metallo· mol × 10^4	MAO mol × 10^4	T (°C)	P (atm)	$A^b \times 10^{-3}$	XI[c] (%)	T_m[d] (°C)	ΔH_f[e] (Jg^{-1})	$[\boldsymbol{\eta}]$[f] (Pa s)	M_v[g]
1	**1**	0.239	16.8	30	13	1.8	97.3	134	55	0.53	51 000
2[h]	**1**	2.390	16.8	85	30	0.5	94.6	138	54	0.38	35 000
3	**2**	0.022	16.8	40	15	6.6	98.8	146	80	0.65	65 000
4[h]	**2**	0.178	16.8	70	30	2.8	95.9	147	74	0.49	46 000
5[i]	**2**	0.178	16.8	65	28	4.5	92.4	140	88	0.22	17 000

[a] In 10 ml toluene. [b] Activity of the catalyst (kg polypropylene mol Zr^{-1} h^{-1} atm^{-1}). [c] Fraction of polymer insoluble in cold *o*-xylene. [d] Melting temperature. [e] Enthalpy of fusion. [f] Intrinsic viscosity. [g] Calculated viscosity average molecular weight. [h] Strong self-heating of the reaction mixture. [i] Hydrogen was introduced into the autoclave.

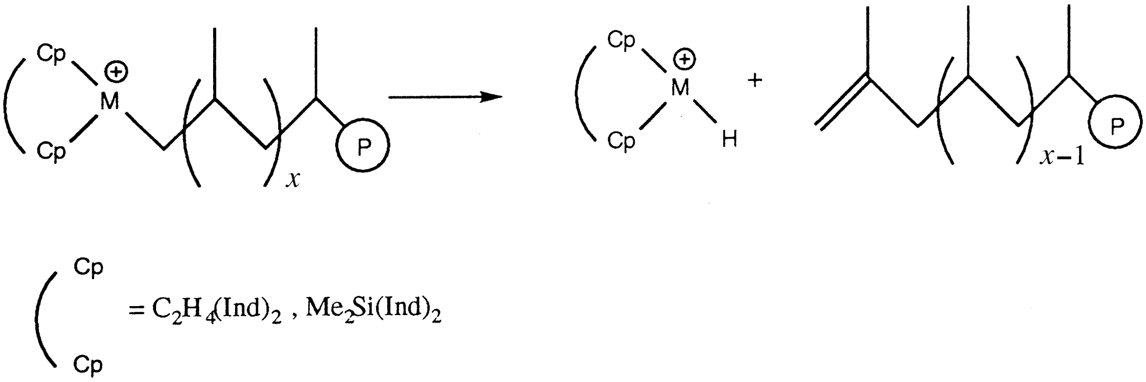
tion conditions and properties of the powdered isotactic polypropylene obtained are shown in Table 1. The polymers were obtained in the form of a fine powder, which adhered to the mixer and to the autoclave walls, reducing heat transfer through the walls and causing problems with the cooling of the reaction mixture. As a result, abrupt increases in the temperature and pressure in the reactor were observed. This effect was particularly appreciable when relatively large amounts of the metallocenes were introduced into the autoclave (Expts 2, 4 and 5). Optimal amounts of metallocenes and methylalumoxane, allowing production of sufficient amounts of polymer in controlled conditions, were found to be between 6–7 mg for metallocene **1** and 3–4 mg for metallocene **2,** with 1000–2000 mg of MAO.

Accurate MFI measurements of the polymers obtained in standard conditions (230 °C, 2.16 kg) could not be performed due to the high flowability of the melts (>500 g min^{-1}). Viscosity average molecular weight (M_v) of the polymers was estimated using the Mark–Houwink equation (Eqn [1]).

$$[\eta] = KM^{\alpha} \qquad [1]$$

Constants for equation [1] for tetralin solutions at 135 °C, $K = 0.917 \times 10^{-4}$ dl g^{-1} and $\alpha = 0.8$,[38,39] were used for the characterization of the metallocene isotactic polypropylenes. The calculated molecular weights M_v of the metallocene-catalyzed polypropylenes were in the range 33 000–53 000 for **1** and 45 000–65 000 for **2,** which are much lower than those of polypropylenes produced by the heterogeneous Ziegler–Natta system under the same conditions (see below).

Interestingly, increasing concentration of the metallocenes leads to lower intrinsic viscosities (Expts 1 and 2; 3 and 4), i.e. to a decrease in molecular weights. This is the result of self-heating of the reaction mixture and an increase of the polymerization temperature, which enhances the β-hydrogen elimination pathway (Eqn [2]). The same trend, of decreasing molecular weight of the polymers, is observed when hydrogen is being added to the system (compare Expts 4 and 5 in Table 1).[3–8] Furthermore, increasing the metallocene concentration leads to a decrease in the xylene-insoluble fractions. Assuming the effect is being determined mainly by isotacticity, but not by xylene-soluble low-molecular-weight fractions, this could be due to the higher Zr/Al ratio, arguing



$= C_2H_4(Ind)_2$, $Me_2Si(Ind)_2$

[2]

that the lower the ratio the better are the isotacticities.[19–24]

It is noteworthy that melting temperatures T_m of the metallocene polymers are in the range from 134 to 147 °C, while the Ziegler–Natta catalysts produce polypropylenes with T_m in the range 164–167 °C (Fig. 1**a**–**d**). The polymers produced by **2** have higher crystallinity (as estimated from the enthalpy of fusion, ΔH_f), and melting temperatures than those obtained with **1.**

Experimental conditions for the polymerization of propylene promoted by the mixed Ziegler–Natta and metallocene catalytic systems, and the polymers' properties, are shown in Table 2. For comparison, results of propylene polymerization promoted by the Ziegler–Natta catalyst alone are also given (Expt 6).

The polypropylenes prepared by the mixed catalytic systems were obtained as a mixture of fine powder and beads. Relative amounts of the powder fraction diminished with a decrease in the metallocene content in the catalytic mixture. Analysis of Table 2 allows us to estimate compatibility between different components of both catalytic systems and their influence on the catalytic polymerization process and the polymer properties. Interestingly, all the components of each catalytic system have to be present. Thus, for example, methylalumoxane, instead of TEAL, does not act as a co-catalyst with the Ziegler–Natta catalyst in the conditions studied, and no polymer is produced (Expt 7).

It is noteworthy that the mechanical, viscoelastic and optical properties of the polymers obtained using the mixed catalytic system in the one-step process are different from those of polymers synthesized separately by each catalytic system (Ziegler–Natta, metallocene) and then melt-blended (the differences among blend, extruder

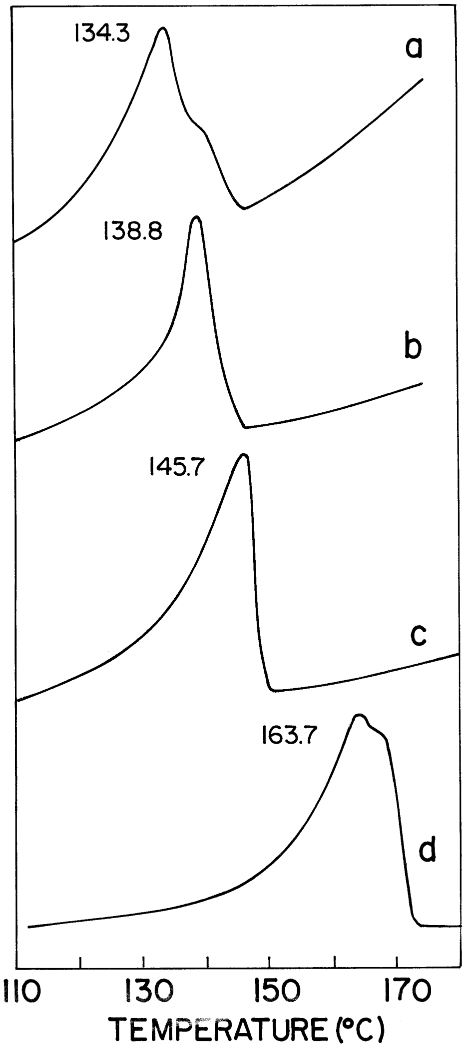


Figure 1 DSC heating curves for metallocene-obtained polypropylene in Expts 1 (**a**), 2 (**b**) and 3 (**c**); polypropylene obtained using Ziegler–Natta catalyst in Expt 6 (**d**).

Table 2. Results of propylene polymerization promoted by Ziegler–Natta catalyst and mixed Ziegler–Natta–metallocene catalytic systems in the one-step process

	Composition of the catalytic system					Polypropylene properties				
Expt	Ziegler-Natta mol × 10^4	TEAL[a] mol	Donor[b] mol × 10^4	Catalytic precursor	Metallocene mol × 10^4	MAO mol × 10^4	MFI[c] g/10	XI[d] (%)	$[\boldsymbol{\eta}_0]$[e] (Pa s)	M_v[f]
6	0.34	0.011	3.2	—	0.0	0.0	7.8	94.7	4610	215 000
7	0.29	0.0	3.2	—	0.0	8.4	—	—	—	—
8	0.51	0.011	3.2	**1**	0.17	0.0	6.0	94.9	9550	265 000
9	0.21	0.011	3.2	**1**	0.11	22.3	24.0	79.5	1430	150 000
10	0.69	0.011	3.2	**1**	0.0	16.8	22.2	89.0	260	100 000
11	0.59	0.011	16.0	**1**	0.17	4.2	5.1	96.5	11 000	275 000
12	0.57	0.011	16.0	**1**	0.17	20.0	13.0	91.5	6300	230 000
13	0.22	0.011	3.2	**2**	0.05	8.4	10.4	89.1	2550	182 000
14	0.22	0.011	4.8	**2**	0.05	8.4	10.6	92.9	2500	180 000
15	0.24	0.011	3.2	**2**	0.12	16.8	>500	84.1	150	80 000

Polymerization conditions: $T = 70$ °C, $P = 30$ atm. [a] 1.05 M solution in hexane. [b] 0.32 M solution in hexane. [c] Melt flow index. [d] Fraction of polymer insoluble in cold *o*-xylene. [e] Zero-shear viscosity. [f] Calculated viscosity average molecular weight.

and reactor mixtures of polymers for polypropylene prepared by metallocene and Ziegler–Natta catalysts will be reported separately).

Introduction of the metallocene catalyst alone (without MAO) together with the Ziegler–Natta system hardly changes the properties of the polymer formed (Expts 6 and 8). However, addition of MAO to the Ziegler–Natta system (without the metallocene), or increasing its content in the mixed catalytic system, leads to an increase in the MFI and to a decrease in zero-shear viscosity of the polymer, i.e. to a decrease in molecular weight (compare Expts 6 and 10 or 11 and 12). This effect is due to the known ability of the co-catalyst MAO to break down the growing polymer chains resulting in the formation of polypropylene with lower molecular weight.[19–24,40] While MAO is not a good starting co-catalyst for the Ziegler–Natta system (Expt 7), it is capable of cutting the polymer chains from the Ziegler–Natta system by a chain-transfer mechanism, allowing these chains to interact with the metallocene and thus producing a second domain in the polymer (see below).

Also, addition of MAO to the Ziegler–Natta catalytic system causes a decrease in the XI (compare Expts 6 and 10). The effect of MAO on the isotacticity of the polypropylene is presumably due to the reversible complexation of the methylalumoxane (Lewis acid) with the external donor (Lewis base).[3] Because of such complexation, the latter is unable to deactivate the less stereospecific polymerization centers of the heterogeneous Ziegler–Natta catalyst,[3–8,41,42] and the isotacticity of the polypropylene decreases. This effect is corroborated by the fact that decreasing the MAO concentration (Expts 11 and 12) in the mixed Ziegler–Natta and metallocene catalytic systems or increasing the external donor concentration (Expts 13 and 14) results in an increase in the isotacticity of the polypropylenes obtained.

Zero-shear viscosity of melts was used for estimation of the molecular weights of the polymers obtained with mixed Ziegler–Natta and metallocene catalytic systems. Values of the Mark–Houwink constants (Eqn [1]) for the melts at 200 °C were determined experimentally by testing three polypropylene grades with known average molecular weights: 580 000, 340 000 and 250 000. Zero-shear viscosity values of 84 500, 12 300 and 4500 Pa s respectively, were obtained. The calculated constants $\alpha = 3.5$ (in agreement with the theoretical value)[43] and $K = 10^{-5}$ dl·g^{-1}, determined for this Ziegler–Natta polypropylene, were used for the characterization of the polymers

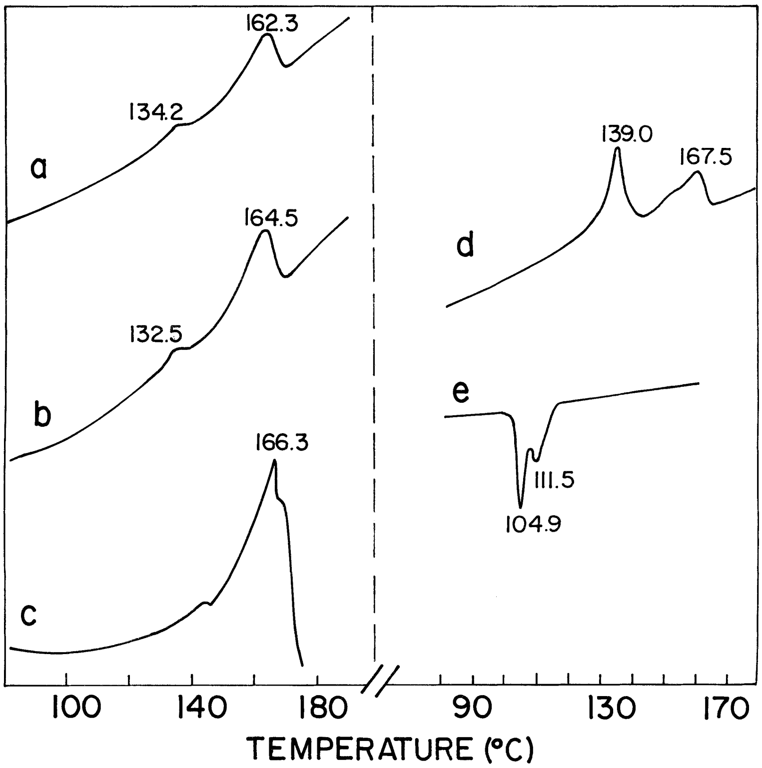


Figure 2 DSC heating curves for polypropylene prepared using mixed Ziegler–Natta and metallocene catalytic systems in Expts 9 (**a**), 12 (**b**), 14 (**c**) and 15 (**d**). DSC cooling curve for the polymer obtained in Expt 15 (**e**).

obtained using the mixed catalytic systems. Molecular weights of the polymers were calculated using these constants and are presented in Table 2.

The results of the DSC measurements of the polymers obtained (Fig. 1 and Fig. 2) allow us to estimate the combined action of both catalytic systems during the propylene polymerization process. DSC first heating thermograms of the polymers produced using the mixed catalytic system in the one-step process (Fig. 2 traces **a**–**d**) show a strong endothermic peak at about 162 °C partially overlapping with a low-intensity endothermic peak at about 140 °C, which is absent in the DSC heating thermograms of polypropylene obtained using heterogeneous Ziegler–Natta systems alone (Fig. 1 trace **d**). The DSC cooling curve of the polymer shows two exothermic peaks (Fig. 2 trace **c**). The endothermic and exothermic peaks indicate the co-existence of two domains with two crystalline phases. The strong endothermic peaks at higher temperature can be attributed to the melting of the polymer fraction produced by the Ziegler–Natta catalyst, whereas the low-temperature peaks can be attributed to melting of the polymer produced by the metallocene system.

Apparently, the two catalytic systems, when mixed, are able to act jointly, producing individual polymer fractions. Each fraction melts on heating and crystallizes on cooling at specific temperatures and snows its own separate melting and crystallization peaks.

The ratio of the two different polymeric domains (as indicated by DSC) can be tailored by mixing a large portion of the metallocene (keeping the metallocene: MAO ratio constant) with the Ziegler–Natta system, producing, as expected, polypropylene with higher MFI and lower molecular weight (Expt 15; Fig. 2 traces **d** and **e**).

The separation of the melting peaks diminishes on the second heating, while the high-temperature peak shifts towards lower temperatures. Hence, there is an interaction and some degree of miscibility between the crystalline phases of the two polymer fractions. These fractions are probably being intimately mixed because, while the two catalytic systems act jointly, the polymer produced by the metallocene catalyst is at least partly absorbed on the growing Ziegler–Natta polypropylene beds.

The polymerization of propylene by the mixed catalytic systems in a two-step process shows similar separation of the melting peaks and similar polymer properties to the polymers obtained in the one-step polymerization.

CONCLUSION

Ziegler–Natta and metallocene systems can jointly polymerize propylene, producing intimately mixed polymer fractions. The results obtained in this study indicate that the metallocene catalyst produces polymer, partly adsorbed on the growing particles of the Ziegler–Natta polypropylene, allowing intimate mixing. Polypropylene produced by the mixed catalytic system can be 'tailored' by adding different components (MAO, external donor) to the Ziegler–Natta systems or by changing the concentration of the metallocene system. Mechanical, viscoelastic, optical and thermal properties for each of the polymers obtained will be presented in a separate publication.

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