Propylene Polymerization Using Combined Syndio- and Isospecific Metallocene Catalysts Supported on Silica/MAO

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ABSTRACT: Syndiotactic and isotactic polypropylene were produced using the metallocene compounds $Ph_2C(Flu)(Cp)ZrCl_2$ and $SiMe_2(2\text{-Me},4\text{-Ph-Ind})_2ZrCl_2$ in homogeneous system and supported on silica/MAO. These catalysts were evaluated either isolated or as a binary system. In the latter case, the iso- and syndiospecific metallocene complexes were immobilized together during the preparation of the supported catalyst. In a further experimental set, the syndio- and isospecific isolated heterogeneous catalysts were mixed at the moment of propylene polymerization. The polypropylenes obtained were evaluated using differential scanning calorimetry. The catalytic activities were also investigated. At all the studied polymerization temperatures, the results showed that the binary catalyst produced polypropylenes with lower melting temperatures in comparison with those obtained when the mixture of isolated supported syndio- and isospecific catalysts was employed. Moreover, the activation energies for the polymerization of all catalysts systems were calculated, resulting in a lower value for the binary system when compared to that employing the catalyst mixture and to both the isolated supported metallocene catalysts. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 628–637, 2006

Key words: syndiotactic; isotactic; polypropylene; metallocene; catalyst mixture; reactor blend

INTRODUCTION

Since its first production, polypropylene (PP) has been widely used on account of its low cost and versatile properties. This polymer is a thermoplastic material that can be obtained in different microstructures. The isotactic form was successfully synthesized in 1958 using Ziegler–Natta (ZN) catalyst.[1,2] Two years later, the syndiotactic form of PP was recognized as a by-product obtained in the same synthesis but this isolated polymer contained considerable amount of both stereo- and regio-irregular defects.

The discovery of stereospecific metallocene-based catalysts allowed the production of the highly stereo- and regio-regular syndiotactic form (s-PP) by Ewen et al.[3] After that, s-PP gained more interest in terms of industrial applications. Since then, s-PPs have been extensively explored in areas such as films, injection molding, and melt-spun fibers.[4]

Another interesting difference between metallocene and ZN polypropylenes is the distribution of stereo defects. In metallocene PPs the distribution of stereo defects is homogeneous, but in ZN PPs the formation of stereoblocks takes place. This characteristic makes PP synthesized with metallocene catalysts to have shorter average isotactic sequences than ZN PPs with the same average stereo defect, also possessing no "atactic" blocks in their chains.[5] It is well known that the resulting physical properties are strongly dependent on the polymers' morphology and on the extent of its crystallization.

Metallocene isotactic polypropylene (i-PP) has physical and mechanical properties that come from the narrow molecular weight distribution and from the absence of low tacticity, and low molecular weight polymer fraction. Isotactic polypropylenes produced with metallocene catalysts differ in their chain microstructure because of the presence of different amounts of regiodefect units, depending on the structure of the metallocene precursor.[6,7] These isopolypropylenes have different properties and, in some cases, could be considered as different products. They can be used in many applications traditionally covered by Ziegler–Natta-based isotactic polypropylene, such as films, fibers etc., where narrow molecular weight distribution and transparency are important.

Polyolefins produced by metallocene catalysts have some advantages such as improved optical, barrier, and mechanical properties, as long as puncture and impact resistance.[6,7] These properties make them ideal

TABLE I
Propylene Polymerization with the Syndiospecific Catalyst (Homogeneous System, Cat 1)

Polymerization temperature (°C)	Yield (g)	A	T_m (°C)	ΔH_m (J/g)	X_c (%)
20	82.25	53.4	135	8	5
40	60.37	67.4	—	—	—
60	76.72	133.7	—	—	—
80	92.49	239.0	—	—	—
90	99.94	314.0	—	—	—

100 mL of toluene; 0.005 mmol of catalyst; 5.8 mL of MAO 10% p/v (Al/Zr 2000); A (catalic activity): kg PP/mmolZr.mol P.h; T_m: melting temperature; ΔH_m: melting enthalpy; X_c: crystallinity degree; -: amorphous polypropylene.

for the use as ultrathin films in the food packaging industry. Articles with high clarity, processed through injection molding or thermoforming, can also be obtained. Their improved sound damping properties, fracture behavior, and so forth are opening avenues in automotive applications. Also, elastomeric PP can be substituted for high impact polystyrene, plasticized poly(vinyl chloride), and other traditional thermoplastic elastomers (TPEs) because of the reasons mentioned earlier.[6]

Recently, the physical, mechanical, and rheological properties of polypropylene blends produced by the use of mixture of catalysts have been more and more studied. The aim of these researches was the direct production of a reactor blend, to combine the desirable properties of each component, to achieve new properties, and also to decrease or maybe to eliminate their poor properties.

In the present study, the metallocene catalysts $Ph_2C(Flu)(Cp)ZrCl_2$ and $SiMe_2(2\text{-}Me,4\text{-}Ph\text{-}Ind)_2ZrCl_2$ were investigated both in homogeneous and on silica/MAO supported systems for propylene polymerization. These catalysts were also employed in a binary system and as catalyst mixture to produce a polypropylene reactor blend. The aim was to find out whether there is an interaction between both metallocene complexes in the polymerization of propylene.

EXPERIMENTAL

Chemicals

All operations were carried out in a dry nitrogen atmosphere. Propylene and nitrogen were purified by sequential passage through columns containing 4 Å molecular sieve and copper catalyst to remove moisture and oxygen, respectively. Toluene was refluxed over metallic sodium/benzophenone and was distilled under a nitrogen atmosphere prior to use. $Ph_2C(Flu)(Cp)ZrCl_2$ and $SiMe_2(2\text{-}Me,4\text{-}Ph\text{-}Ind)_2ZrCl_2$ was brought from Boulder Scientific Company; commercial silica gel (309 m^2/g surface area, Sylopol 948),

was donated by Grace Davison; MAO (10 wt % solution in toluene) was purchased from Witco GmbH, Germany, and were used without further purification.

Catalysts preparation

Homogeneous systems

Homogeneous solutions of $Ph_2C(Flu)(Cp)ZrCl_2$ (Cat 1) and $SiMe_2(2\text{-}Me,4\text{-}Ph\text{-}Ind)_2ZrCl_2$ (Cat 2) in toluene were prepared and 0.005 mmol Zr was directly employed in the propylene polymerization reactions.

Heterogeneous system

- Silica pretreatment with MAO

Silica gel was heated to 400°C for 4 h, under a nitrogen atmosphere. After that, silica was pretreated with MAO (5 mmol Al/g silica) at room temperature in toluene. The solid material was separated and washed three times with toluene at 90°C.

- Immobilization of metallocene catalyst on silica/MAO
- Cat 1S—$Ph_2C(Flu)(Cp)ZrCl_2$ solution in toluene was made to react with MAO-pretreated silica (0.05 mmol Zr/g silica) in a Schlenk flask under vigorous stirring for 4 h. After the metallocene immobilization, the heterogeneous catalyst was washed three times with 30 mL of toluene each time, at room temperature, and dried until no weight loss was observed.
- Cat 2S—$SiMe_2(2\text{-}Me,4\text{-}Ph\text{-}Ind)_2ZrCl_2$ was immobilized on MAO-pretreated silica (0.05 mmol Zr/g silica) by the same procedure described for catalyst 1S.
- Cat 1/2S—A mixture of $Ph_2C(Flu)(Cp)ZrCl_2$ (0.025 mmol Zr/g silica) and $SiMe_2(2\text{-}Me,4\text{-}Ph\text{-}Ind)_2ZrCl_2$ (0.025 mmol Zr/g silica) solutions, both in toluene, was made to react with MAO-pretreated silica under vigorous stirring at room temperature for 4 h.

TABLE II
Propylene Polymerization with the Syndiospecific Catalyst (Heterogeneous System, Cat 1S)

Polymerization temperature (°C)	Yield (g)	A	T_m (°C)	ΔH_m (J/g)	X_c (%)
20	9.12	5.9	141	39	24
40	27.81	31.1	120/132	28	17
60	45.74	79.7	118	21	12
80	40.14	103.7	86/93	16	10
90	31.05	97.4	—	—	—

100 mL of toluene; 0.1 g of heterogeneous catalyst; 5.8 mL of MAO 10% p/v; A (catalic activity): kg PP/mmolZr.mol P.h; T_m: melting temperature; ΔH_m: melting enthalpy; X_c: crystallinity degree; -: amorphous polypropylene.
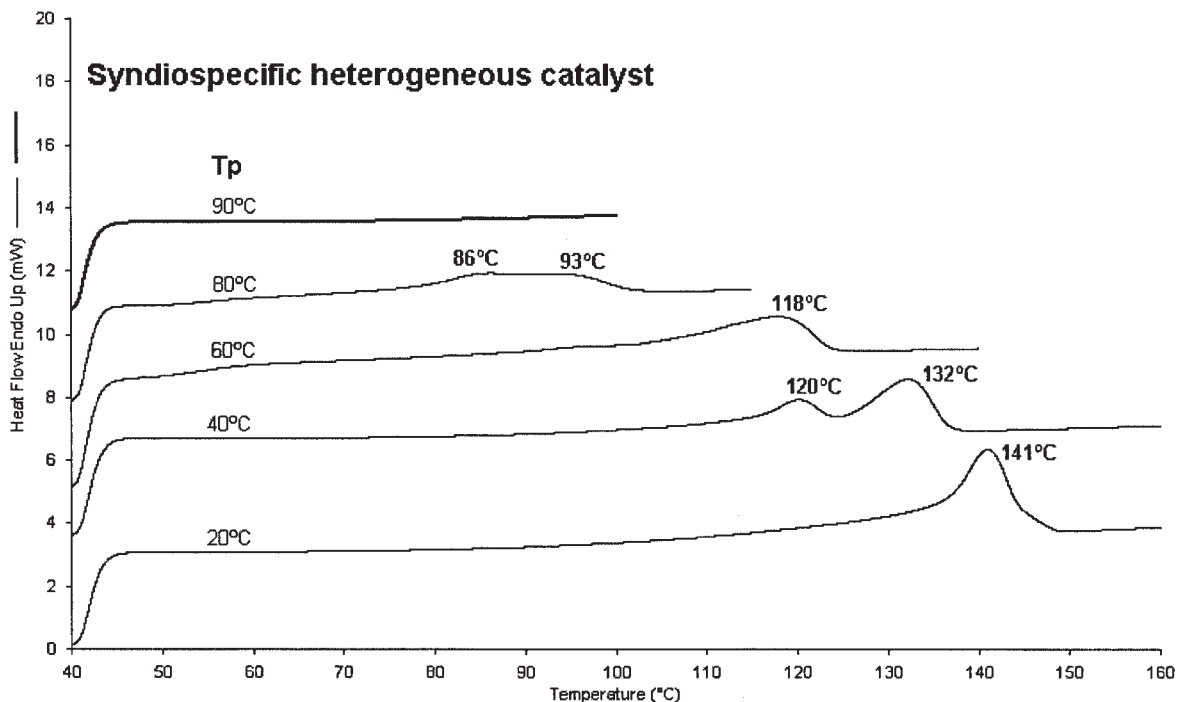
Figure 1 Melting endotherms of syndiotactic polypropylene produced with Cat 1S at different polymerization temperatures (T_p).

After the immobilization reaction the supported catalyst was washed in the same way.
- In relation to the heterogeneous catalysts, the values of catalytic activities were calculated using the amount of zirconocene employed during its preparation (0.05 mmol Zr/g silica).

Propylene polymerization

Polymerization reactions were performed in a 0.5-L double-walled round bottom glass autoclave equipped with vacuum pump and thermostatic bath. The stirring speed was 600 rpm. At 0.2 bar of nitrogen
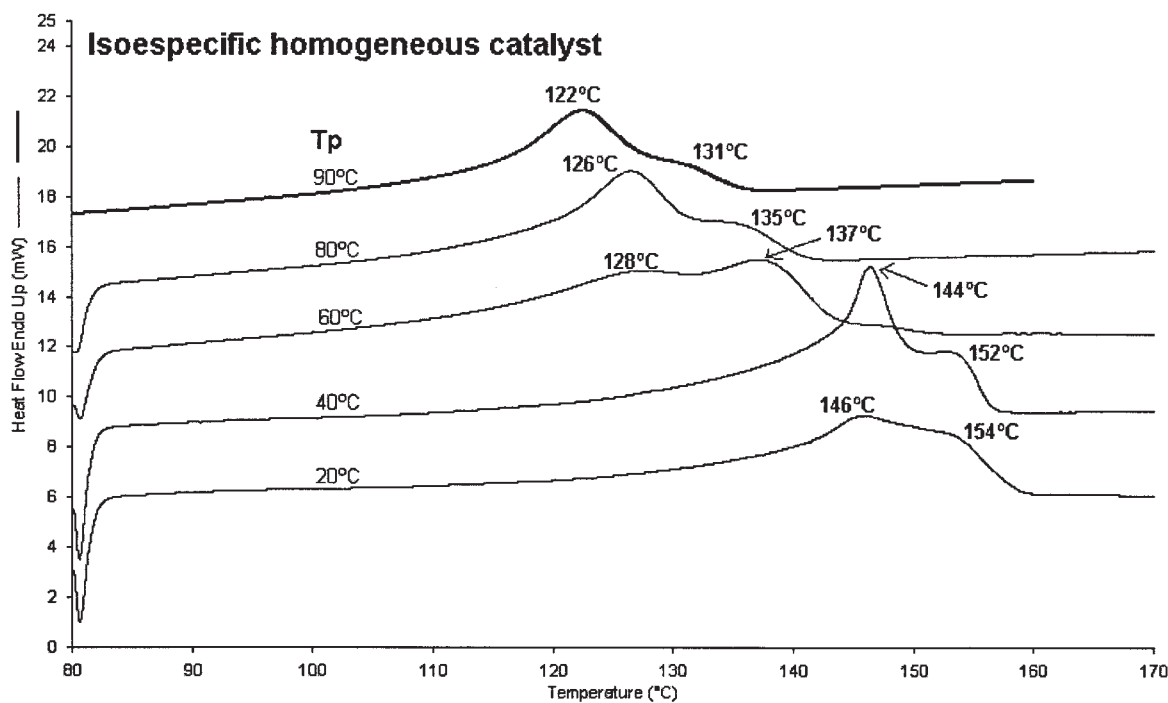

Figure 2 Melting endotherms of isotactic polypropylene obtained with Cat 2 at different polymerization temperatures (T_p).

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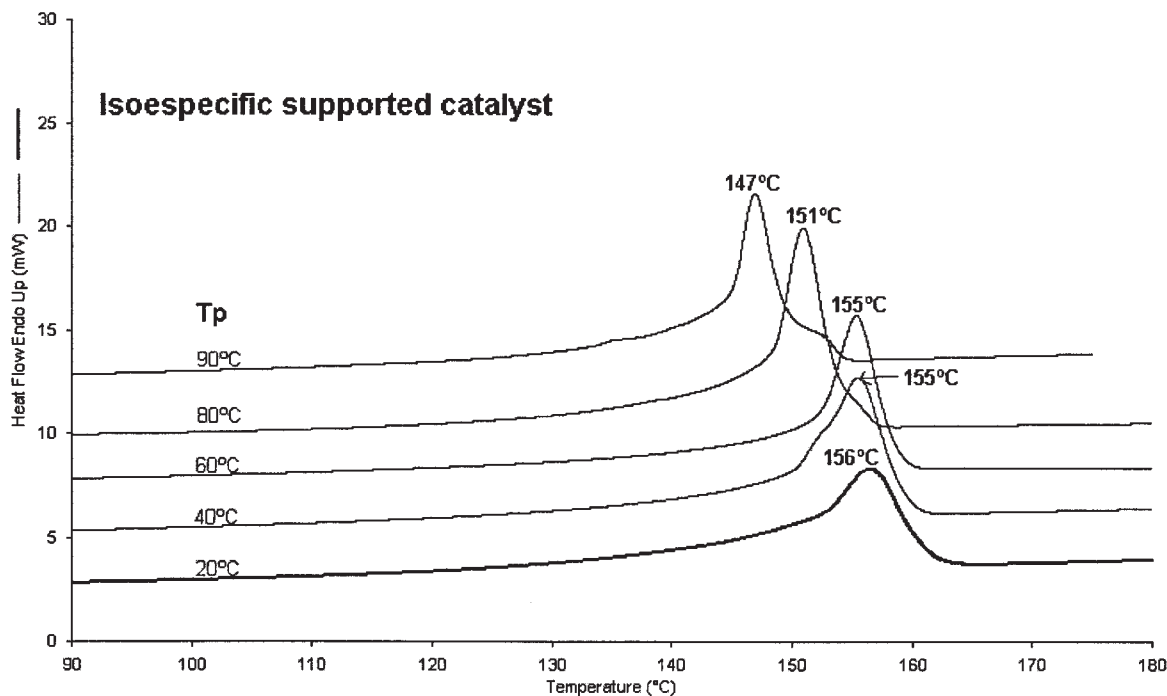
Figure 3 Melting endotherms of isotactic polypropylene obtained with Cat 2S at different polymerization temperatures (T_p).

flow, the diluent (toluene) was transferred to the reactor. After that, part of the MAO was introduced in the reactor, and the other part was kept in contact with the catalyst suspension of the heterogeneous system (containing Cat 1S or Cat 2S or Cat 1/2S or a mixture of Cat 1S and Cat 2S in toluene), or with the catalyst solution (homogeneous system) for about 10 min. The nitrogen in the reactor was purged and the toluene was saturated with 2 bar of propylene monomer. For some reactions the monomer pressure was increased until 4 bar immediately after catalyst addition. Afterwards, the catalyst was introduced in the reactor,
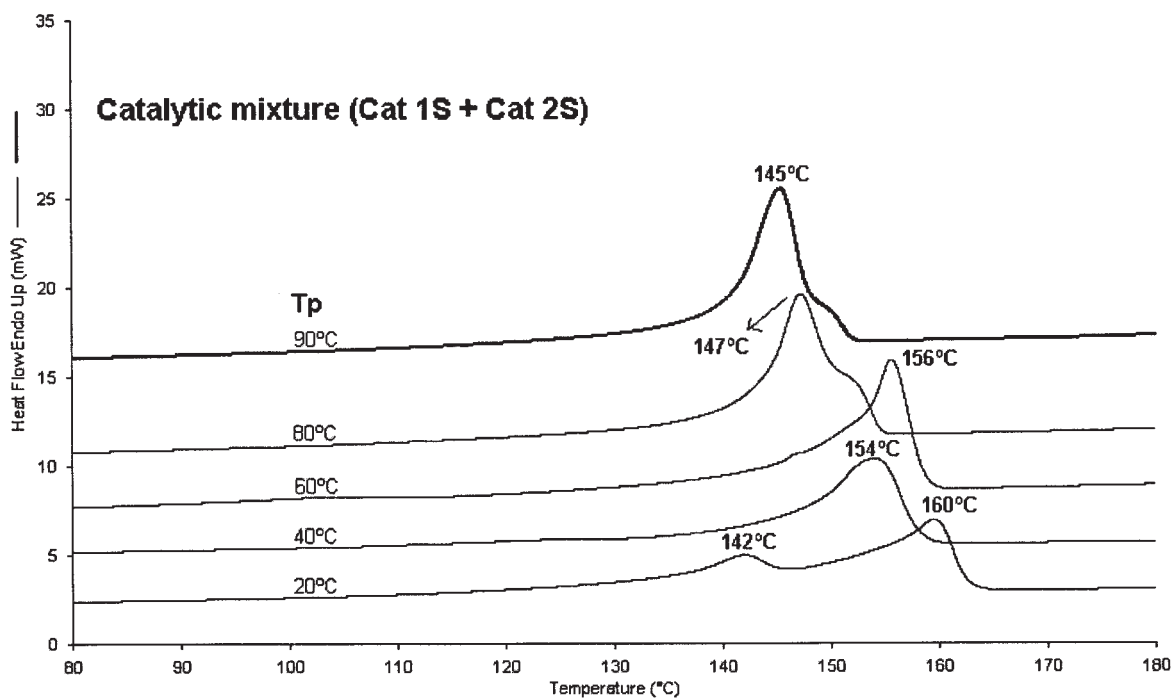

Figure 4 Melting endotherms of polypropylene obtained with Cat 1S + Cat 2S at different polymerization temperatures (T_p).
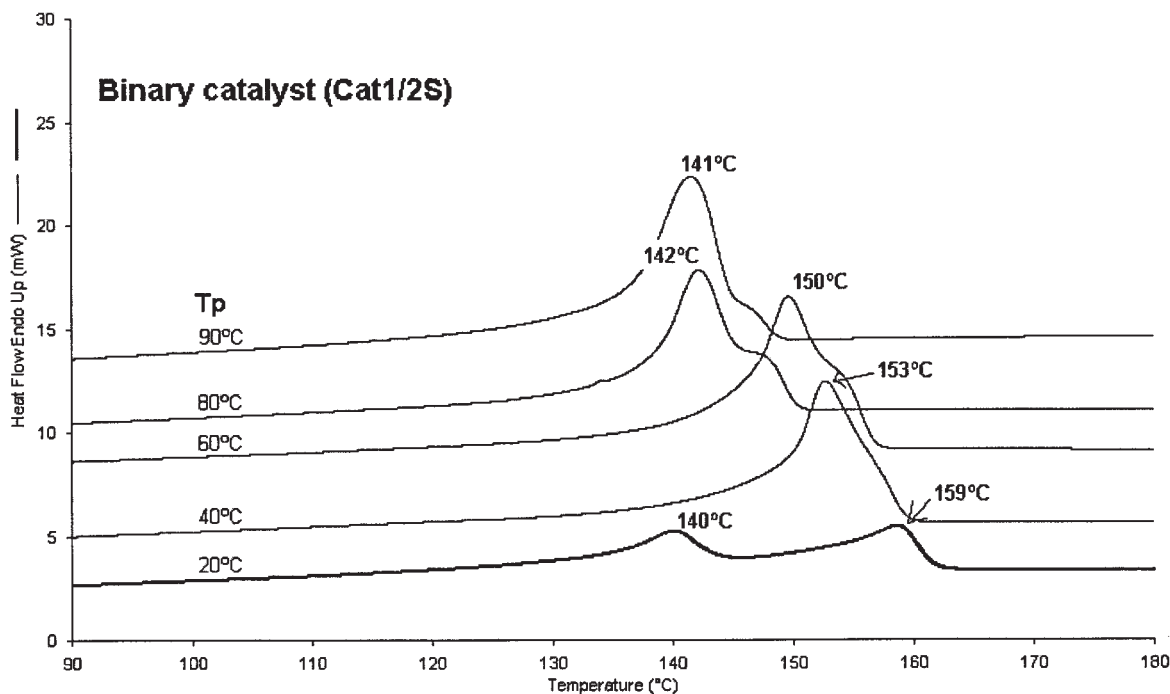
Figure 5 Melting endotherms of polypropylene obtained with Cat 1/2S at different polymerization temperatures (T_p).

starting the polymerization. The consumption of monomer was followed using a hot-wire flow meter (model 5850D) from Brooks Instrument connected to a personal computer through an A/D converter. The polymerization was ended after 1 h, by stopping the stirring, followed by degassing the reactor and by the addition of a solution of 5% hydrochloric acid in ethanol. The polymer was then washed with ethanol and distilled water, filtered, and dried by vacuum at 60°C.

Polymer characterization

The melting temperature was measured using a PerkinElmer Differential Calorimeter DSC-7. Three runs (heating, cooling and 2nd heating) were performed, using a heating rate of 10°C/min in the range of 40–190°C. The observed peak at the second heating was taken as the melting temperature. The crystallinity degree (%) was calculated using the following melting enthalpies: $\Delta H_m^{100\%}$ (iso-PP) = 195 (J/g); $\Delta H_m^{100\%}$ (synd-PP) = 166 (J/g).[8]

RESULTS AND DISCUSSION

Tables I and II show the results of propylene polymerization with the metallocene catalyst $Ph_2C(Flu)(Cp)ZrCl_2$ in homogeneous (Cat 1) and in heterogeneous systems (Cat 1S), respectively. According to these results, the catalytic activity increased with the increase of polymerization temperature up to 80°C, in both systems, especially with the heterogeneous syndiospecific cat-

alyst. The activity for the supported catalyst was around the half of the one obtained with the homogeneous counterpart at polymerization temperatures between 40 and 80°C. It was also observed that only the syndiotactic polypropylene obtained with the homogeneous catalyst at 20°C presented crystallinity. Besides, by supporting this syndiospecific catalyst on silica/MAO, using higher polymerization temperatures (40–80°C), it was possible to obtain crystalline PP. These phenomena clearly show that, even at high temperature (80°C), the metallocene catalyst has its stereo or regiospecificity increased, when fixed on silica support. Crystallinity degree of the s-PP obtained at 20°C increased significantly when the syndiospecific catalyst was supported on silica/MAO.

Figures 1–5 illustrate five sets of DSC melting endotherms of the PPs produced. Each set corresponds to one kind of catalyst. These endothermic events were recorded after crystallization from the melt state, starting at 40°C. The melting temperature of s-PP obtained with the heterogeneous catalyst decreased with the increase of polymerization temperature. Some of the syndiotactic polypropylene obtained with the heterogeneous catalyst prepared in this study (Cat 1S) showed double-melting endotherms. According to Supaphol and Spruiell the low temperature melting endotherm was found to be associated with the melting of the primary crystallites, while the high temperature melting endotherm was attributed to the melting of recrystallized crystallites.[9]

TABLE III
Propylene Polymerization with the Isospecific
Metallocene Catalyst (Homogeneous System, Cat 2)

Polymerization temperature (°C)	Yield (g)	A	T_m (°C)	ΔH_m (J/g)	X_c (%)
20	94.97	30.8	146/154	68	35
40	97.72	54.6	144/152	70	36
60	197.15	171.8	128/137	60	31
80	207.39	267.9	126/135	56	29
90	211.88	332.5	122/131	50	26

400 mL of toluene; 0.025 mmol of catalyst; 2.9 mL of MAO 10% p/v (Al/Zr 2000); A (catalic activity): kg PP/mmolZr.mol P.h; T_m: melting temperature; ΔH_m: melting enthalpy; X_c: crystallinity degree.

TABLE V
Results of Propylene Polymerization by using the
Catalytic Mixture Cat 1S and Cat 2S

Polymerization temperature (°C)	Yield (g)	A	T_m (°C)	ΔH_m (J/g)
20	26.57	4.3	142/160	67
40	56.89	15.9	154	70
60	83.81	36.5	156	75
80	103.48	66.8	147	79
90	100.17	78.6	145	75

400 mL of toluene; 0.05 g of Cat IS and 0.05 g of Cat 2S; 5.8 mL of MAO 10% p/v; A (catalytic activity): kg PP/mmolZr.mol P.h; T_m: melting temperature; ΔH_m: melting enthalpy.

Tables III and IV show the results of propylene polymerization by the use of isospecific metallocene catalyst SiMe$_2$(2-Me,4-Ph-Ind)$_2$ZrCl$_2$ in homogeneous (Cat 2) and in heterogeneous (Cat 2S) systems, respectively.These results show that the catalytic activity has also significantly increased with the increase of polymerization temperature for both homogeneous and heterogeneous isospecific metallocene catalysts. Furthermore, it seems that the activity for the obtained supported isospecific catalyst was <50% when compared with the performance of the homogeneous system.The Results also showed that both the syndiospecific and isospecific metallocene catalysts, using the supported systems obtained, presented similar values of activity.

Isotactic polypropylene obtained with the supported catalyst (Cat 2S) showed higher melting temperatures when compared with those synthesized with the homogeneous one (Cat 2). According to the melting endotherms of isotactic polypropylene obtained with Cat 2S, it was observed that by increasing the polymerization temperature the values of T_m started to decrease at temperatures above 80°C. On the other hand, when the isospecific homogeneous catalyst (Cat 2) was employed, the T_m of PPs produced started to decrease slowly at reaction temperature of

40°C and to a higher extent at reaction temperature of 60°C. These results clearly indicate that the support hinders the formation of stereo/regiodefects on PP microstructure.

The behavior in propylene polymerization by using a mixture of isospecific (Cat 1S) and syndiospecific (Cat 2S) supported catalysts made at the moment of polymerization reaction is shown in Table V. On the other hand, the performance in propylene polymerization of the binary supported catalyst Cat 1/2S, consisting of both metallocene complexes supported on the same silica particles, is shown in Table VI.

Similar to the isolated catalytic systems, it was also observed that the activities of both in situ mixture and binary Cat 1/2S increased with the increase in the polymerization temperature. Higher values of activities were obtained when Cat 1/2S was used in comparison with the catalyst mixture (Cat 1S + Cat 2S). This decrease in performance maybe due to the less manipulation of catalysts by using the binary system directly.

When the heterogeneous catalysts (Cat 1S and Cat 2S) were mixed in the reactor medium, the PP produced at temperatures up to 40°C showed values of melting enthalpies in the same range of those obtained when the isospecific supported catalyst was employed. Moreover, comparing Figures 3 and 5, it can

TABLE IV
Propylene Polymerization with the Isospecific
Metallocene Catalyst (Heterogeneous System, Cat 2S)

Polymerization temperature (°C)	Yield (g)	A	T_m (°C)	ΔH_m (J/g)	X_c (%)
20	16.22	5.3	156	80	41
40	65.29	36.5	155	80	41
60	50.33	43.9	155	63	32
80	80.66	104.2	151	91	47
90	69.27	108.7	147	76	39

400 mL of toluene; 0.05 g of supported catalyst; 2.9 mL of MAO 10% p/v; A (catalic activity): kg PP/mmolZr.mol P.h; T_m: melting temperature; ΔH_m: melting enthalpy; X_c: crystallinity degree.

TABLE VI
Results of Propylene Polymerization by using the
Heterogeneous Binary Catalyst Cat 1/2S

Polymerization temperature (°C)	Yield (g)	A	T_m (°C)	ΔH_m (J/g)
20	74.83	12.1	159	57
40	78.69	22.0	153	87
60	118.98	51.8	150	82
80	153.60	99.2	142	76
90	144.48	113.4	141	76

400 mL of toluene; 0.1 g of Cat 1/2S; 5.8 mL of MAO 10% p/v; A (catalytic activity): kg PP/mmolzr.mol P.h; T_m: melting temperature; ΔH_m: melting enthalpy.
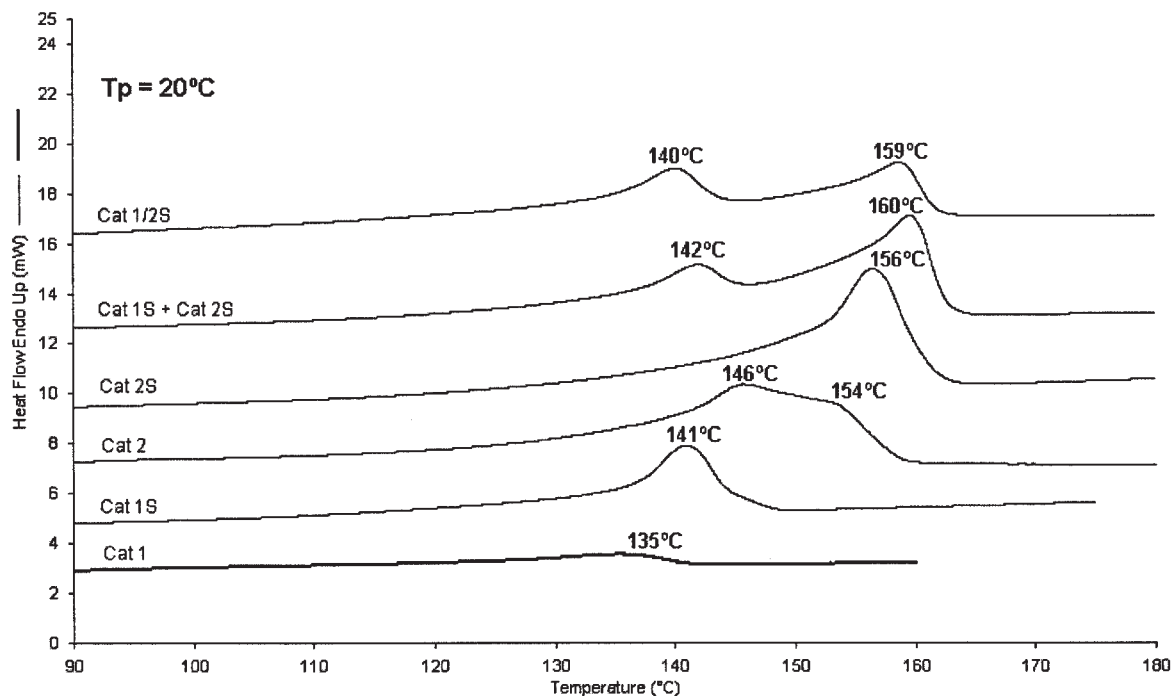
Figure 6   Melting endotherms of PPs obtained at 20°C.

be inferred that the polypropylenes produced with Cat 1/2S showed lower values of T_m, specially at higher polymerization temperatures, in relation to the values obtained when Cat 2S was employed. These results indicate that the chain transfer reactions between iso- and syndiotactic growing chains could be the reason for the interruption on the development of the original crystal structure, decreasing the polymer chain, especially at higher temperatures. On the other hand, with Cat 1S + Cat 2S this effect was practically not noticed. This also indicates that when the metallocene compounds were heterogeneized, most of the chain transfer reactions occur between growing chains, which are closely fixed on the same support, in comparison with those on separated catalyst particles.

To evaluate the influence of the different catalysts prepared in this study on the melting temperatures, five sets of DSC melting endotherms of PPs obtained at different polymerization temperatures (20, 40, 60, 80, and 90°C, respectively), were displayed in Figures 6–10.

The melting curves illustrated earlier showed that two distinct melting endothermic events only occurred in the PPs synthesized at 20°C, for the mixed as long as for the binary systems, one of them related to s-PP (at 141°C) and the other related to i-PP (at 159°C).According to Figure 6, it was observed that the endotherms obtained at 20°C for the polypropylenes produced with both Cat 1S + Cat 2S and Cat 1/2S showed a significant shift to higher values of T_m, as for the peak corresponding to the isotactic PP fraction is

considered. Probably, the small spherulites of syndiotactic PP act as nucleator for the growing isotactic PP chains.[10]

Moreover, observing the DSC curves of PP obtained at 40°C (Fig. 7), it also seems that the endotherms corresponding to the isotactic PP produced by the binary catalyst was narrower and appeared at lower temperature, when compared with that of the PP synthesized with the catalyst mixture. Although the PP obtained by the isolated supported syndiospecific catalyst (Cat 1S) presented clearly two different melting temperatures, due to the phenomenon of recrystallization described by Marigo et al.,[11] none of the polymers synthesized by the catalysts comprising both stereospecific metallocenes (Cat 1S + Cat 2S or Cat 1/2S), have shown the typical endotherm of s-PP. This may be attributed to an increase of stereo and regioerrors in the polymer chains obtained in the presence of two different metallocene structures, specially on the same support.

It is possible that at higher polymerization temperature there are more chain transfer reactions, and both the iso- and syndiotactic sequences have incorporated some stereoblocks, as illustrated in Figure 11. The same effect was observed in the polymers obtained at 60, 80, and 90°C, that is, the melting temperatures of the PP obtained with the binary system are lower than those obtained with the isolated supported isoespecific catalyst and those obtained with the heterogeneous catalyst mixture.
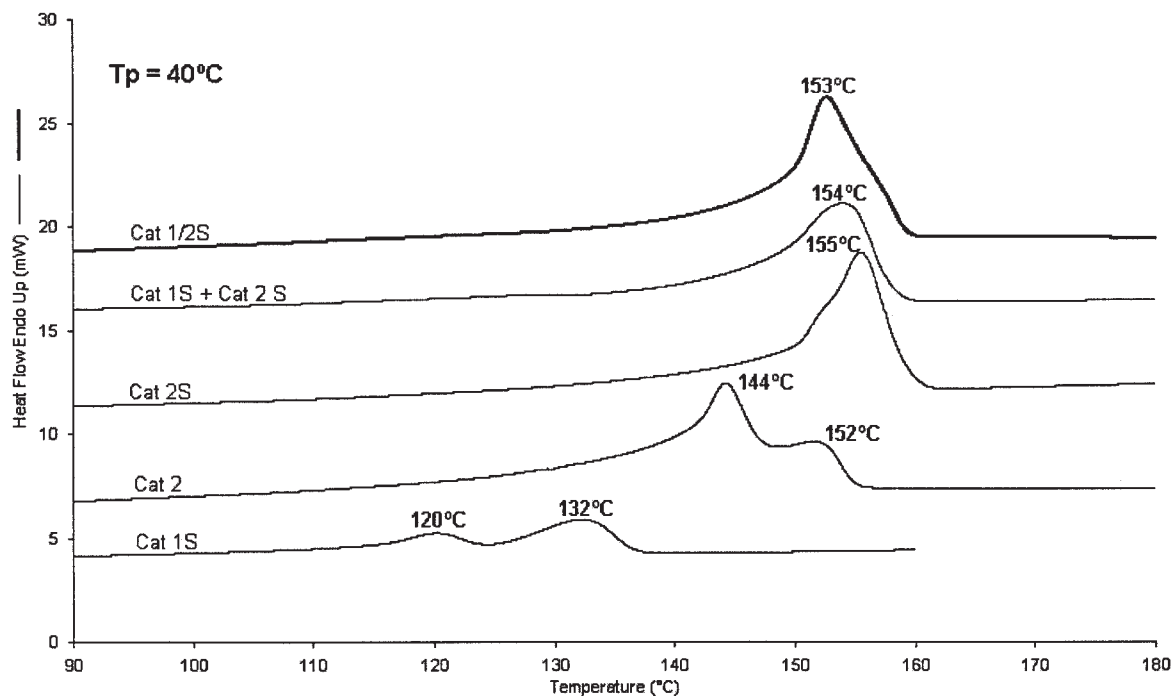
Figure 7 Melting endotherms of PPs obtained at 40°C.

Table VII shows the values of activation energy (E_a) calculated from Arrhenius equation (eq. (1)).

$$K = A - e^{-Ea/RT} \tag{1}$$

where K is the polymerization rate constant (L/(mol/ s)); A is the frequence factor; R = 8.314 J/(mol/K); T is the temperature (K). According to the results showed on Table VII, the activation energy increases when both the homogeneous syndiospecific (Cat 1) and the isospecific (Cat 2) catalysts are supported on silica/ MAO, this enhancement being greater for the syndio-specific catalyst. Moreover, the activation energy for the reaction with the catalyst mixture was, as ex-
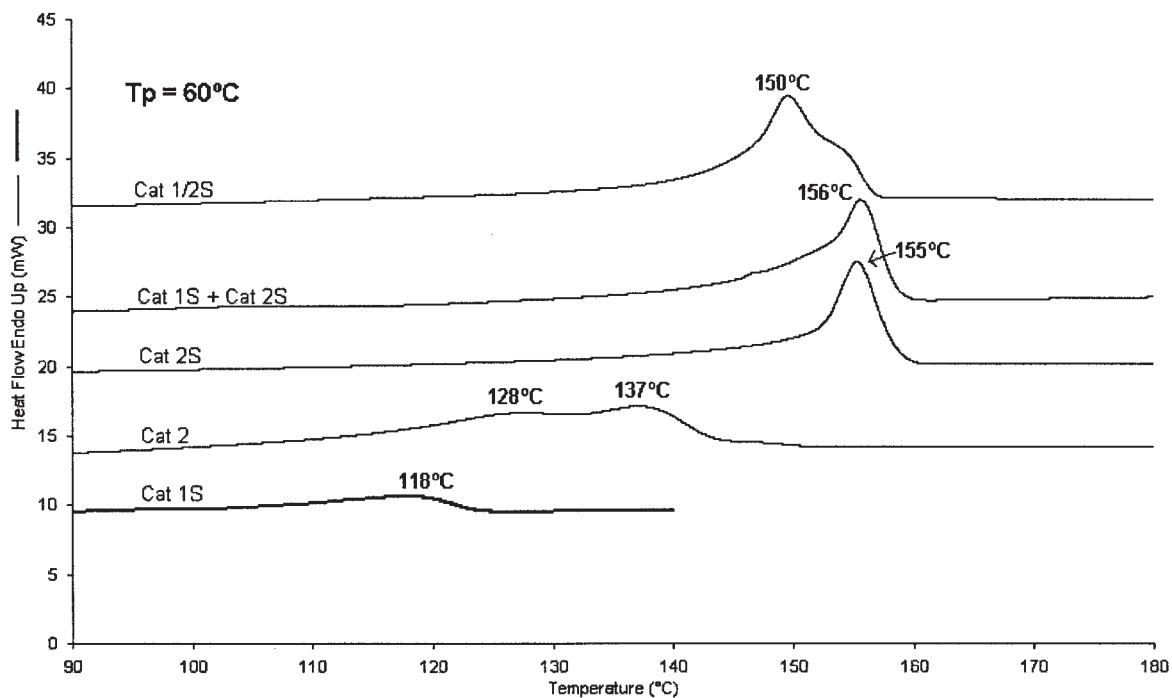

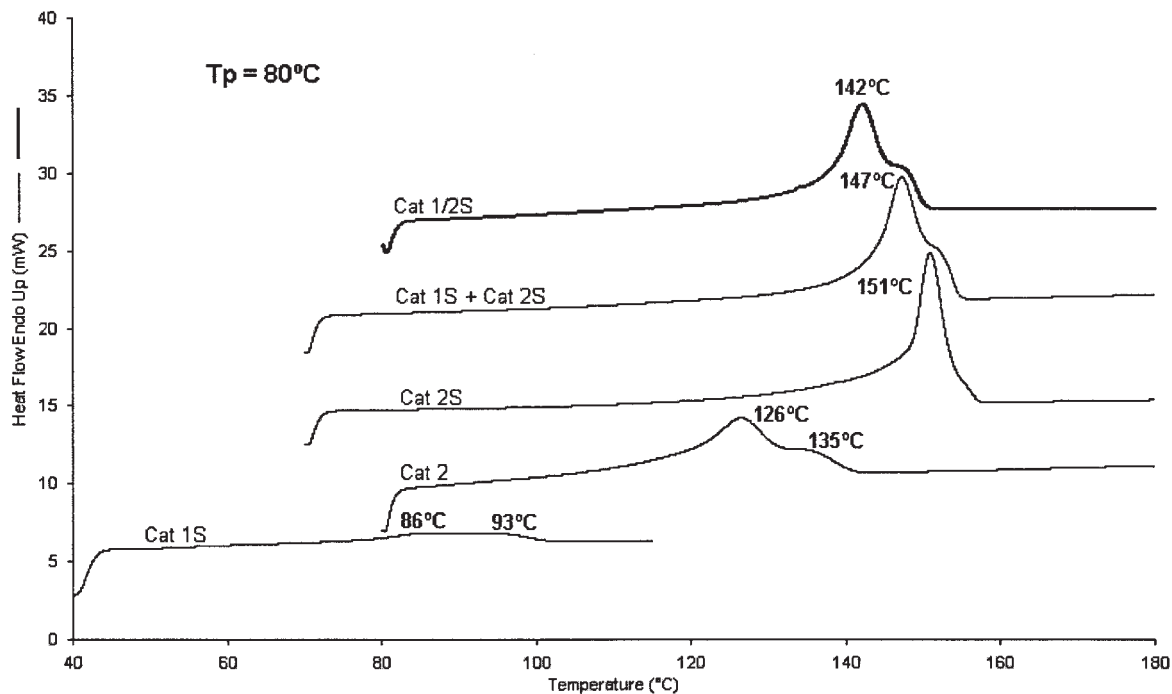**Figure 8** Melting endotherms of PPs obtained at 60°C.

Figure 9   Melting endotherms of PPs obtained at 80°C.

pected, in the same range as that with both supported catalysts. On the other hand, the polymerization with the binary system showed the lowest value of Ea among all obtained supported systems. This shows that a synergetic effect between both metallocene cat-

alysts has occurred, which means that the activated complex in the binary system has lower energy level than that of the isolated supported catalysts. In other words, an interaction between the active sites on the same support has indeed occurred.
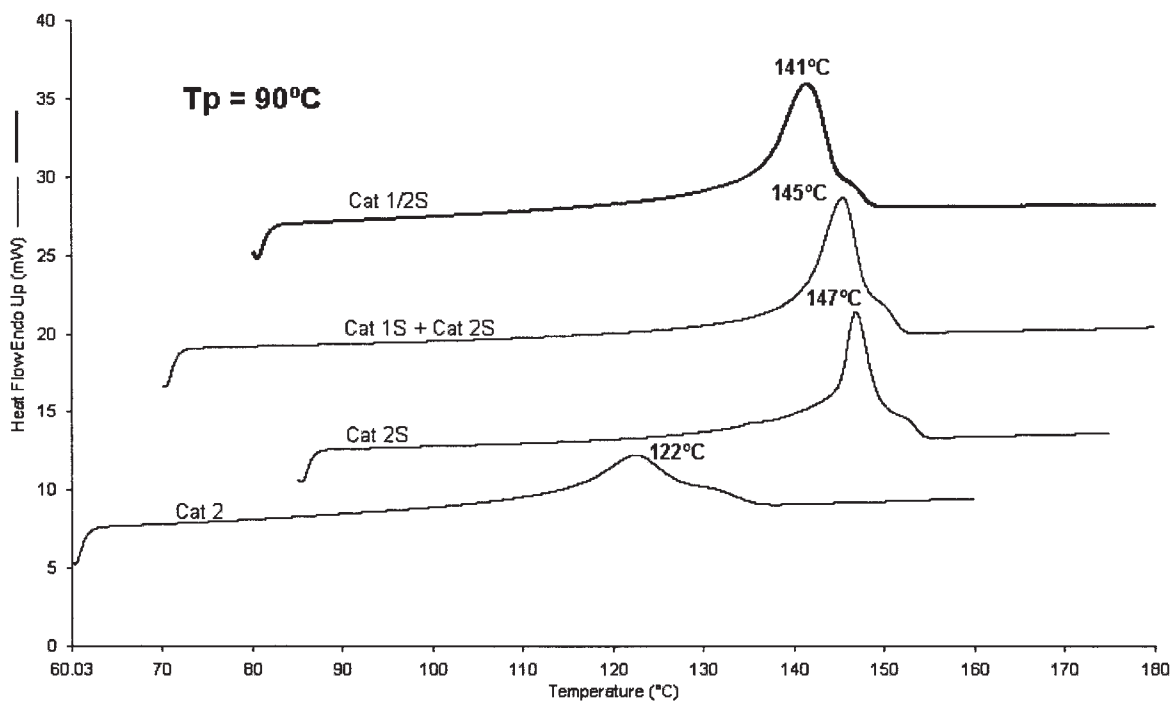

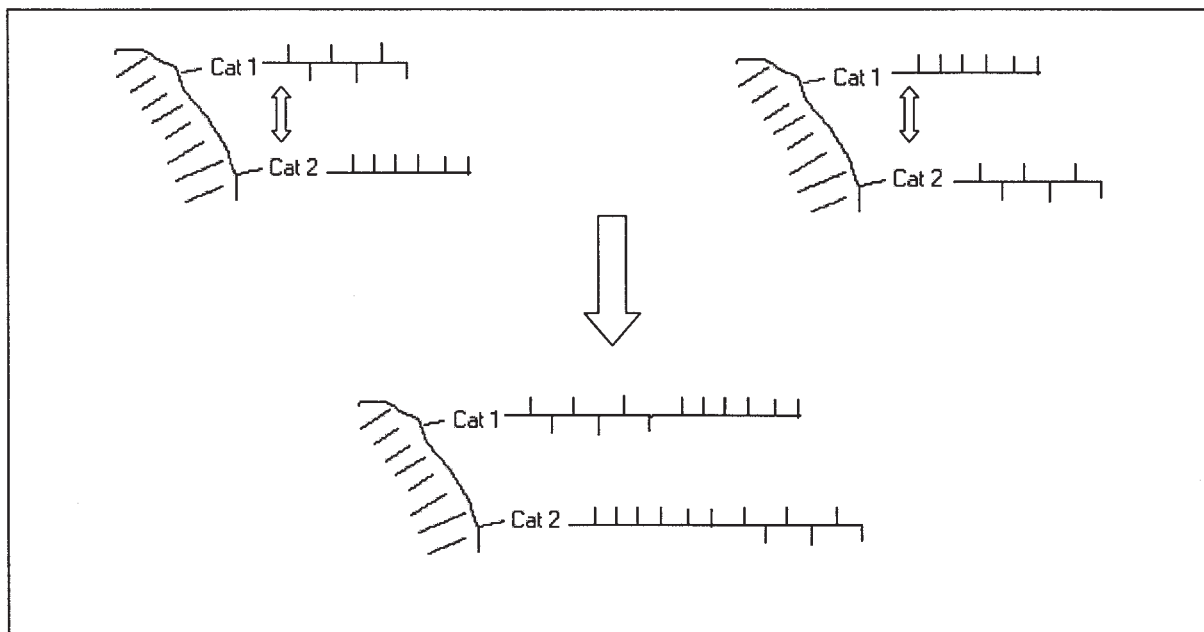**Figure 10**   Melting endotherms of PPs obtained at 90°C.

Figure 11 Proposed model for the formation of stereblocks.

CONCLUSIONS

The melting temperatures of the polypropylenes obtained with the syndio- and isospecific supported binary metallocene on silica/MAO at all the employed polymerization temperatures were lower than those of the polymers synthesized with the isolated supported systems and also with the catalyst mixture. This means that the stereo and regiodefects in both iso- and syndiotactic propylene sequences have increased in the binary system. Moreover, a synergetic effect between both metallocene complexes on the support surface has been detected in the polymerization of propylene.

TABLE VII
Activation Energies for the Different Catalytic Systems Evaluated

Catalytic systems	E_a (J/mol)
Cat 1	0.3386
Cat 1S	0.5122
Cat 2	0.4584
Cat 2S	0.5242
Cat 1S + Cat 25	0.5297
Cat 1/2S	0.4304

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