The Effect of the Mixed External Donors on the Sequence Length Distribution of Polypropylene

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ABSTRACT: The effects of different mixed external donors on the crystallization behavior and sequence length distribution of polypropylene prepared by MgCl$_2$-supported TiCl$_4$ Ziegler–Natta catalyst were studied through successive self-nucleation and annealing (SSA) technique. The SSA results show that the crystallization ability and the relative contents of long isotactic sequence length gradually increase with the increase of the relative component of Donor-1 (cyclohexylmethyldimethoxysilane, dicyclohexyl(dimethoxy)silane, and dipiperidinedimethoxysilane) in the different mixed external donors when the ratio of the mixed external donors/Ti (Si/Ti) is unchanged. The thickness distribution of lamellar also becomes broader, indicating the sequence length distribution of polypropylene gets broader. The crystallization ability and the relative contents of long isotactic sequence length of polypropylene prepared by the mixed cyclohexylmethyldimethoxysilane and n-propyltriethoxysilane (C—N) external donors are lowest. However, the effect of the mixed dicyclohexyl(dimethoxy)silane and n-propyltriethoxysilane (H—N) and the mixed dipiperidinedimethoxysilane and n-propyltriethoxysilane (Py—N) external donors on the crystallization ability and sequence length of polypropylene are more significantly. Especially, the relative content of long isotactic sequence length increases sharply from 0.2 to 27.5% in the polypropylene chain of sample prepared by the mixed Py—N external donors when the proportion of Donor 1 is running up to 90%. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 129: 1026–1035, 2013

INTRODUCTION

Polypropylene (PP) can be divided into i-PP, s-PP, and a-PP according to the stereochemical regularity.[1] Isotactic PP has been widely used for its good mechanical properties, thermal properties, and chemical stability because of the regularity of molecular chain. The properties of i-PP are highly related to crystallization properties, which are closely related to the regularity of molecular chain. Currently, the high isotactic PPs are mostly prepared in industry by the fourth-generation Ziegler–Natta catalyst which is the MgCl$_2$-supported TiCl$_4$ with diester as internal donor, such as diisobutyl phtalate. The isotacticity of these i-PP resins determined by boiling heptanes extraction method or NMR is about 96–99%, and the rest is a-PP or s-PP.[2–4] For i-PP, the methyl groups of its molecular chain are not all perfectly in the same side in fact, as well as there are a small amount of "mistake inserted" monomers, leading to the formation of syndiotactic or atactic structure as shown in Figure 1. The length between every two "mistake inserted" monomers is called isotactic sequence

length. The crystallization properties of i-PP are not only related to the overall isotacticity, but also related to isotactic sequence length of PP.

In general, during the propylene polymerization by the fourth-generation Ziegler–Natta catalyst, external donors are necessary, which can not only improve PP isotacticity significantly, but also has an important impact on polymerization activity, the molecular weight distribution (MWD) and microstructure of polymer.[5–20] There are several reports about the effect of external donor on the sequence length distribution of PP in the polymer chains. Echevskaya et al.[21] investigated the effect of an external donor phenyltriethoxysilane (PES) on the microstructure of ethylene–propylene copolymers, and found that the addition of PES caused an increase in the average sequence length of ethylene and propylene determined by ^{13}C-NMR. Sacchi et al.[22] characterized the effects of different alkoxysilane external donors (Ph(EtO)$_3$Si, Me(EtO)$_3$Si, and Ph$_2$(EtO)$_2$Si) on the average sequence lengths of all the fractions after propylene/
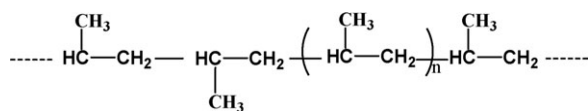
Figure 1. Schematic diagram for *i*-PP chain structure.

1-butene copolymer were fractionated by ^{13}C-NMR. The results showed that different external donors would promote the propylene sequence length growth of the copolymers and affect the copolymer microstructure by changing the types of the alkoxysilane external donors. Xu et al.[23,24] investigated the influence of external donor diphenyldimethoxysilane (DDS) on the tacticity distribution and the composition distribution of PP and propylene/butene copolymers by temperature-rising elution fractionation (TREF), and found that the addition of external donor DDS could reduce the weight percentage of the fractions eluted at lower temperature and increase the weight percentage of fractions having high isotacticity. Garoff et al.[25] made a study of the effect of different ratio of the external donor/Ti (Si/Ti) on the isotacticity and the lengths of isotactic sequence by stepwise isothermal segregation technique, and found that there was an increase in isotacticity with the rise of the amount of the donor, resulting in an increase of the lengths of isotactic sequence and the shorter isotactic sequences were reduced. Ma et al.[26] investigated the influence of external donors phenyltrimethoxysilane, PES, and DDS on the propylene polymerization by the MgCl$_2$-supported Ziegler–Natta catalysts, and the results indicated that the external donors not only led to an increase in the isotactic index, but also affected the morphology of resultant polymer particles. Lou et al.[27] studied the effect of different external donors $CH_3CH_2CH_2CH_2OCH_3$ and $(CH_3)_2CHCH_2$—OCH_3, and DDS on the propylene polymerization activity and isotacticity index of PP. They first reported that the mixture of the ethers and DDS could increase the propylene polymerization activity and isotacticity index compared to those of the systems only with silane as external donor. Harding and van Reenen[28] studied the PP prepared with a Ziegler–Natta catalyst using two different external donors DDS and methylphenyldimethoxysilane (MPDMS) by TREF fraction technique, and the TREF results showed that the DDS external donor exerted greater influence at the active sites and the microstructure on physical properties than MPDMS did. Kang et al.[29] studied the effect of different mole ratio of the cocatalyst triethylaluminum (TEA)/external donor DCPDMS (Al/Si) on the stereo-defect distribution of *i*-pp by TREF, ^{13}C-NMR, and successive self-nucleation and annealing (SSA) techniques. The results from TREF and ^{13}C-NMR showed that as the Al/Si ratio increased gradually from 30 to 36, the amounts of fractions with different isotacticities changed gradually, and the intra- and intermolecular distribution of stereo-defects became more uniform. The SSA results also showed that as the Al/Si ratio increased, the relative height of the high melting peak decreased gradually, whereas the relative height of the lower peak increased.

SSA technology was designed and first reported by Muller et al.[30] in 1997, which is based on the self-nucleation and annealing steps sequentially to a polymer sample originally devised by Fillon et al.,[31] and has been widely used to analyze the chain structures of semi-crystallized polymers such as polyethylene and PP.[32–44] As SSA can enhance the microstructure fractionation during crystallization and encourage annealing of the unmelted crystals at each stage of the process and the lamellae of crystallization polymer may have enough time to diffuse and grow in the annealing step, the SSA technology can carry on selective thermal fractionation according to the crystallization sequence length of polymer. Generally, it is believed that lamellae thickness is related to the isotactic sequence distribution of polymer. There is a good correspondence between the SSA and the TREF techniques.[39] The results of SSA are coincident with the results of high-resolution ^{13}C-NMR, TREF, and xylene solvent fractionation, but SSA can provide important quantitative information about the lamellar thickness distribution.[29,32] With the increase of separation temperature, the component separated by TREF shows higher melting temperature and longer crystalline sequence length after SSA treatment. In addition, ^{13}C-NMR result also shows that isotacticity and isotactic sequence length of PP increase.[29,45,46] Therefore, the crystalline sequence is directly related to the isotactic sequence in PP chain.[47]

Accurate characterization of the microstructure and sequence length distribution of PP is important to the structure–property relationship research of PP. There are a variety of testing methods used to study the molecular chain microstructure of polyolefin.[48,49] Compared with ^{13}C-NMR and TREF fractionation, SSA can provide important quantitative information about the lamellar thickness distribution and is more time saving than TREF. To our knowledge, there is no report yet about the effect of mixed silane external donors on the crystallization behavior and the isotactic sequence length distribution of PP prepared by MgCl$_2$-supported TiCl$_4$ Ziegler–Natta catalyst. This article mainly studied the effect of the different mixed external donors on the sequence length distribution of PP prepared by Ziegler–Natta catalysts using SSA technology. The SSA results show that the crystallization ability and the relative contents of long isotactic sequence length gradually increase with the rise of the relative component of Donor-1 in the different mixed external donors, and the thickness distribution of lamellar also becomes broader. For different kinds of the mixed external donors, the crystallization ability and the relative contents of long isotactic sequence length of PP prepared by the mixed C—N or C—T external donors are lowest. However, the effect of the mixed H—N and Py—N external donors on the crystallization ability and sequence length of PP are more significantly. Most of all, the relative content of long isotactic sequence length increases sharply from 0.2 to 27.5% in the PP chain of sample prepared by the mixed Py—N external donors when the proportion of Donor 1 is running up to 90%.

EXPERIMENTAL

Materials

MgCl$_2$-supported Ziegler–Natta catalyst (CS-1, Ti content of 3.38%) is provided by Xiangyang Chemical Factory (China). The cocatalyst TEA is purchased from Aldrich (USA). The external donors cyclohexylmethyldimethoxysilane (Donor-C), *n*-propyltriethoxysilane (Donor-N), and tetroethoxysilane (Donor-

Table I. Molecular Weight and the MWD of PP

Samples	Si/Ti[a]	M_n	M_w/M_n	I.I(%)[b]
C-N-1[c]	1.0	27,870	8.53	96.0
C-N-5[c]	1.0	25,140	8.57	96.2
C-N-9[c]	1.0	21,260	8.63	96.2
C-T-1[d]	1.0	26,270	8.72	96.5
C-T-5[d]	1.0	27,650	8.69	96.2
C-T-9[d]	1.0	20,650	8.75	96.4
H-N-1[e]	1.0	28,240	8.51	96.1
H-N-5[e]	1.0	26,360	8.54	95.9
H-N-9[e]	1.0	26,730	8.61	96.8
Py-N-1[f]	1.0	28,340	8.37	96.5
Py-N-5[f]	1.0	30,380	8.41	96.2
Py-N-9[f]	1.0	32,800	8.47	96.3

[a] The molar ratio of external donor and catalyst.
[b] The isotactic index (I.I.) were tested by extraction with boiling n-heptane for 6 h.
[c] Ziegler–Natta catalyst, 0.1 MPa propylene, Donor-C, and Donor-N.
[d] Ziegler–Natta catalyst, 0.1 MPa propylene, Donor-C, and Donor-T.
[e] Ziegler–Natta catalyst, 0.1 MPa propylene, Donor-H, and Donor-N.
[f] Ziegler–Natta catalyst, 0.1 MPa propylene, Donor-Py, and Donor-N.

T) are purchased from Aldrich (USA); dicyclohexyl(dimethoxy)-silane (Donor-H) and dipiperidinedimethoxysilane (Donor-Py) are synthesized according to the literature[50] and configured in hexane solution before use. Propylene (polymerization grade) was provided by Yanshan Petrochemical (China). Hexane solvent was refluxed with metal sodium and benzophenone for 24 h and then was distilled out before use.

Propylene Slurry Polymerization

All the operations which are sensitive to water and oxygen are standard Schleck operations. Polymerizations were carried out as follows. In a typical experiment, a 500-mL flask was equipped with a magnetic stirrer and O₂ was removed; then, 100 mL of n-hexane solution and 5.4 mmol of n-hexane solutions of TEA, 20 mg of n-hexane slurry of Ziegler–Natta catalyst, and different volumes of 0.025 mmol/mL of the mixed external donors were added to the flask, respectively. After adding the reagents, propylene gas was charged into the flask reactor and the reaction pressure was kept under 0.1 MPa. After 1 h at 50°C, the reaction was terminated with acidic ethanol and filtered. The product was washed with ethanol several times, and then dried overnight under vacuum at 60°C. The molecular weight (M_n) and the MWD of all samples are listed in Table I.

Characterization

All differential scanning calorimetry (DSC) measurements were performed with a Mettler 822e DSC in a nitrogen atmosphere. Samples about 2–4 mg in aluminum pans were first melted by heating from 50 up to 200°C at a rate of 50°/min and were held for 5 min to erasure the previous thermal history, then cooled down to 50°C at a rate of 10°C/min, held at 50°C for 5 min, and then finally heated again to 200°C at a rate of 10°C/min. The melting temperature T_m and the enthalpy of fusion ΔH_m were determined from the second melting. The degree of

crystallinity was calculated according to the following formula[51,52]:

$$\chi_c = \frac{\Delta H_m}{\Delta H_m^0}$$

where ΔH_m is the fusion enthalpy obtained from DSC curve, ΔH_m^0 is the fusion heat of a perfectly crystallization PP, that is, 209.0 J/g.[53]

SSA fractionation was performed as follows: Samples were first held at 200°C for 5 min under nitrogen atmosphere and then decreased to 50°C at 20°C/min to create a standard thermal history. The self-seeding temperature (T_s), which is high enough to melt almost all the crystals but low enough to leave "small" crystal fragments that can act as self-nuclei, was suggested by Muller et al. to be the minimum temperature in domain II which was one of the self-nucleation temperature ranges divided by Fillon.[31] Therefore, single-step self-nucleation experiments have been performed to determine the melting domains of PP components in all samples and after the effect of SSA parameters on the crystallization properties of PP were detailedly researched; the first T_s was chosen as 164°C, the fraction window adopted here was 5°C, and the annealing time was 15 min in this study.[54] Pijpers et al.[55] recently introduced the high-speed calorimetry concept that the increment in heating rate can be compensated by reducing the sample mass. Hence, a higher scanning rate of 20°C/min was employed to reduce the fractionation time, and a smaller sample mass of 2.5 mg was used as compensation. The temperature range for thermal fractionation was from 144 to 164°C in all samples. After completion of the fractionation process, the sample was heated at 10°C/min from 50 to 200°C, and a multiple melting endotherm was obtained. The schematic diagram of SSA is shown in Figure 2

^{13}C-NMR spectra of polymers were tested in DMX 300M (Bruker, USA). Polymer solution was prepared with 80 mg of polymer in 0.5 mL of deuterated o-dichlorobenzene at 383 K. The o-dichlorobenzene solvent was used to provide the internal lock signal with its highest peak at 133.22 ppm as the standard reference. Experimental conditions were as follows: number of
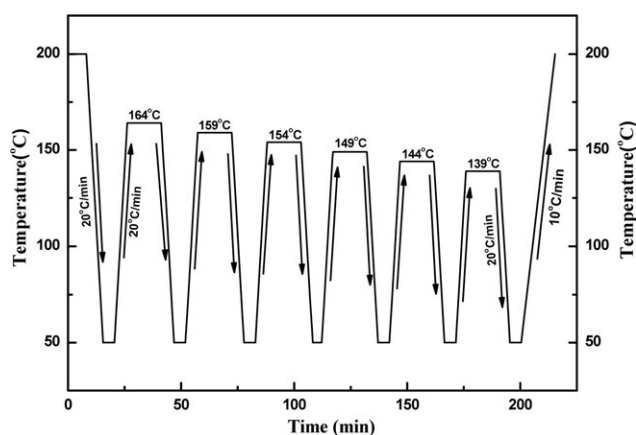
Figure 2. Schematic representation of the applied thermal program during SSA.

Table II. Thermal Characterization of DSC of all PP Samples

Samples	Donor-1	Donor-2	Donor-1 (mol %)	I.I. (%)	T_m^a (°C)	ΔH_m^b (J/g)	T_c^c (°C)	ΔH_c^d (J/g)	X_c^e (%)
C-N-1	C	NPTES	10	96.0	158.9	70.3	113.9	−73.8	33.6
C-N-5	C	NPTES	50	96.2	159.4	72.4	114.8	−73.7	34.6
C-N-9	C	NPTES	90	96.2	159.8	88.6	114.2	−89.1	42.4
C-T-1	C	TEOS	10	96.5	158.8	69.7	114.0	−68.2	33.3
C-T-5	C	TEOS	50	96.2	159.5	80.8	114.4	−84.7	38.7
C-T-9	C	TEOS	90	96.4	159.5	83.6	113.8	−82.0	40.0
H-N-1	H	NPTES	10	96.1	160.3	81.3	113.8	−82.9	38.9
H-N-5	H	NPTES	50	95.9	161.2	82.6	116.1	−84.4	39.5
H-N-9	H	NPTES	90	96.8	162.6	87.7	113.5	−89.2	42.0
Py-N-1	Py	NPTES	10	96.5	160.6	80.1	114.1	−87.8	38.3
Py-N-5	Py	NPTES	50	96.2	161.6	85.3	115.5	−83.4	40.8
Py-N-9	Py	NPTES	90	96.3	163.9	87.3	119.5	−86.8	41.8

[a]Melting temperature as determined from the peak maximum value in the endothermic curves of DSC, [b]The value of the endothermic enthalpy as determined from DSC, [c]Crystallization temperature as determined from the peak maximum value in the exothermic curves of DSC, [d]The value of the exothermic enthalpy as determined from DSC, [e]The degree of crystallization calculated from the value of the endothermic enthalpy.

pulses, more than 10,000; pulse angle, 30; spectrum width, 25,000 Hz; and relaxation delay, 7 s. All spectra were completely proton decoupled.

The molecular weights (M_n and M_w) and the MWD of the PP were determined by a PL-GPC 220 high-temperature gel permeation chromatography (Polymer Laboratories Ltd, UK) at 413.15 K, using 1,2,4-trichlorobenzene as solvent with the injection volume of 100 mL and the flow rate of 1.0 mL/min. Calibration was made by polystyrene as the standard sample.

RESULTS AND DISCUSSION

In our other experiments, we have found that the external donor has an important impact on propylene polymerization. When Donor-C, Donor-H, and Donor-Py were used for propylene

Figure 3. The SSA melting curve of PP samples prepared by the C—N-mixed external donors. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

polymerization, the isotacticity of the obtained PP is above 96%. Although *n*-propyltriethoxysilane (Donor-N) and tetroethoxysilane (Donor-T) were used as external donors, the isotacticity of PP samples is only about 90–92%. Donor-C was selected to mix with Donor-N, Donor-T separately to form the C—N-mixed external donors and the C—T-mixed external donors. On the other hand, Donor-H and Donor-Py were mixed with Donor-N separately to form the H—N-mixed external donors and the Py—N-mixed external donors. The effects of the different mixed external donors on the crystallization behavior and the isotactic sequence length distribution of PP were investigated when the Si/Ti ratio was constant.

The Thermal Behavior of PP

The thermal behavior of all PP samples was studied by DSC, and the results are summarized in Table II. The enthalpy of fusion ΔH_m, the degree of crystallinity, the crystallization temperature, and the crystallization enthalpy are the tendencies to gradually increase with the increase of the relative component of the external donor Donor-1 (Donor-C, Donor-H, and Donor-Py) in the different mixed external donors. This is mainly because when the increase of the external donor Donor-1, the regularity of PP chains is higher, and hence the enthalpy of fusion ΔH_m and the degree of crystallinity increase. For each kind of the mixed external donor systems, the enthalpy of fusion ΔH_m and the degree of crystallinity of PP prepared, respectively, by the C—N- and C—T-mixed external donors change larger with the increase of the relative component of Donor-C, indicating that the content of Donor-C in the mixed external donors has an important impact on the crystallization and melting behavior of PP. Although the enthalpy of fusion ΔH_m and the degree of crystallinity of PP prepared, respectively, by the H—N- and Py—N-mixed external donors are higher than those of PP prepared, respectively, by the C—N- and C—T-mixed external donors, the changes are smaller with the increase of the relative component of the external donor Donor-1.
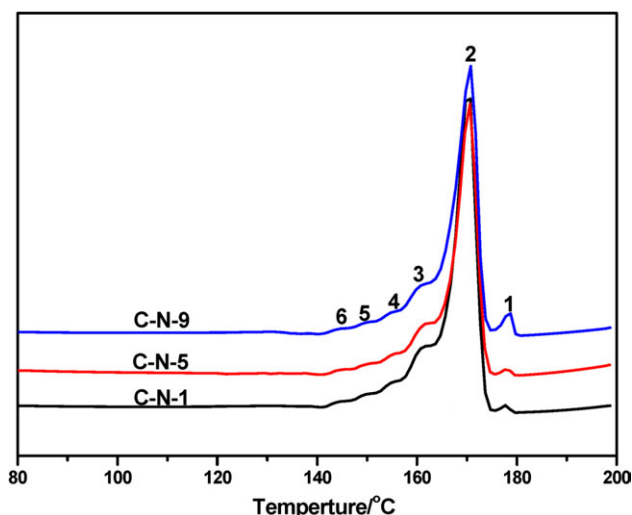
Table III. SSA Results of Propylene Samples Prepared by the Mixed External Donors

Samples	I.I. (%)	$T_s{}^a$ (°C)	$\Delta H_m{}^b$ (J/g)	$T_{m1}{}^c$ (°C)	T_{m2} (°C)	T_{m3} (°C)	T_{m4} (°C)	T_{m5} (°C)	T_{m6} (°C)
C-N-1	96.0	164	74.7	178.0	170.3	160.9	154.7	149.7	144.2
C-N-5	96.2	164	80.0	178.1	170.4	161.2	154.4	150.2	144.6
C-N-9	96.2	164	91.5	178.5	170.8	160.1	154.9	149.7	144.2
C-T-1	96.5	164	80.0	178.4	170.5	160.2	154.5	149.3	144.4
C-T-5	96.2	164	84.4	178.5	170.8	160.1	154.9	149.7	144.2
C-T-9	96.4	164	91.8	178.9	171.0	160.5	154.9	149.9	144.8
H-N-1	96.1	164	94.9	178.9	171.0	160.3	155.0	149.3	144.8
H-N-5	95.9	164	96.9	179.3	171.2	160.1	154.9	149.8	144.6
H-N-9	96.8	164	105.9	179.8	171.3	160.5	155.1	150.4	143.7
Py-N-1	96.5	164	89.5	178.3	170.7	160.4	154.8	149.2	144.7
Py-N-5	96.2	164	96.7	178.3	171.2	160.1	154.7	149.4	144.3
Py-N-9	96.3	164	109.1	178.4	171.1	159.7	154.6	149.8	144.2

[a]The optimal annealing temperature T_s of each sample, [b]The value of the endothermic enthalpy as determined from SSA curve, [c]The melting temperature as determined from the peak value in the SSA curves.

The Effect of the Mixed External Donors on Isotactic Sequence Length Distribution of PP

The melting curves of the PP samples prepared by the mixed C—N external donors after SSA treatment are shown in Figure 3. Each peak of the melting point and the enthalpy of fusion ΔH_m of each sample are listed in Table III. As shown in Figure 3, there are six melting peaks on the melting curves after SSA fractionation. Though the PP isotacticities determined by boiling heptane of the three samples C-N-1, C-N-5, and C-N-9 are almost the same (Table I), the melting temperature of peak 1 gradually increased from 178.0 to 178.5°C, and the total melting enthalpy of 81.6 J/g gradually increased to 91.5 J/g, which shows that the crystallinity of the PP increases with the increase of the Donor-C content in the C—N-mixed external donors.

To quantitatively evaluate the variations of each melting peak, the relative content (i.e., the integral area percentages on the SSA melting curve) of each peak was calculated using Peakfit

4.12 software. The calculated relative contents of all peaks of all samples are summarized in Table IV. Figure 4 shows the SSA melting curves and the fitted peaks of sample C-N-1 by Peakfit 4.12 software. The SSA melting curve of sample C-N-1 comprises peak 1 on the highest temperature region (>175°C), two peaks (peaks 2 and 3) on higher temperature region (155–175°C), and three minor peaks (peaks 4–6) at low temperature region (<155°C). To discuss conveniently, the peaks are classified into three groups in our study. The peak 1 located at the highest temperature region is behalf of the long isotactic sequence length, the peaks 2 and 3 on higher temperature region stand for the *meso*-isotactic sequence lengths, and the other three minor peaks (peaks 4–6) at low temperature region are correspond to form the short isotactic sequence lengths.

As shown in Table IV and Figure 4, the relative contents of peak 1 of PP samples prepared by the C—N-mixed external donors increase gradually from 0.3 to 3.6%, showing that the long

Table IV. The Relative Contents of all Peaks on the SSA Curve of Polypropylene

Samples	I.I. (%)	T_s (°C)	ΔH_m (J/g)	$n_1{}^a$ (%)	n_2 (%)	n_3 (%)	n_4 (%)	n_5 (%)	n_6 (%)
C-N-1	96.0	164	74.7	0.3	65.5	16.3	9.5	5.4	3.0
C-N-5	96.2	164	80.0	0.7	59.4	17.0	12.9	6.3	3.7
C-N-9	96.2	164	91.5	3.6	50.6	20.3	10.8	8.9	5.8
C-T-1	96.5	164	80.0	0.9	62.4	16.5	10.6	6.2	3.5
C-T-5	96.2	164	84.4	2.1	52.4	19.7	11.0	8.9	5.8
C-T-9	96.4	164	91.8	3.4	53.5	16.1	12.8	8.4	5.9
H-N-1	96.1	164	94.9	1.8	54.8	17.2	12.7	7.6	5.9
H-N-5	95.9	164	96.9	8.2	47.8	20.1	9.9	8.6	5.4
H-N-9	96.8	164	105.9	14.9	42.7	19.7	10.1	7.7	4.9
Py-N-1	96.5	164	89.5	0.2	66.0	17.5	8.7	5.0	2.7
Py-N-5	96.2	164	96.7	6.1	52.6	19.0	11.8	6.5	4.0
Py-N-9	96.3	164	109.1	27.5	35.3	18.2	9.6	6.3	3.2

[a]The relative content of peak 1 on the SSA curve of polypropylene calculated using Peakfit 4.12 software.
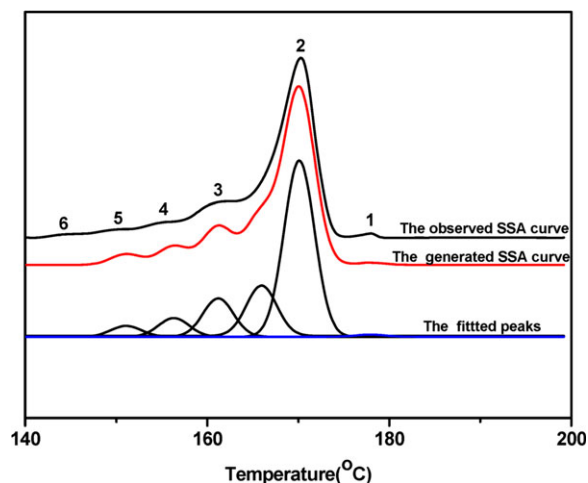
Figure 4. Plots of SSA melting curve of the C-N-1 sample and its fitted curves by Peakfit 4.12 software where the peakfit variance r^2 of the fitted peaks is 0.9963. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

isotactic sequence length of PP increases gradually. Meanwhile, the relative contents of peaks 2 and 3 decrease gradually from 81.8 to 71.0%, indicating that the *meso*-isotactic sequence lengths of PP decrease gradually. The relative contents of the peaks at low temperature region increase from 17.8 to 25.5%, exhibiting that the short isotactic sequence lengths also gradually increase. The above results reveal the long regulatory sequence length of PP chain increases with the increase of the content of Donor-C in the C—N-mixed external donors. This indicates that the change of the Donor-C content in the C—N-mixed external donors can influence the sequence length distribution of PP and the microstructure of the PP chain when the donor/Ti is unchanged.

The Effect of the Mixed External Donors on Lamellar Thickness Distribution of PP

As the SSA melting peaks of the fractionated samples are related to the melting of different lamellar thicknesses, crystallites

formed and annealed at each self-nucleation temperature were employed.[34,39] The Thomson–Gibbs equation can be used to establish a correlation between temperature and lamellar thickness, which has been used by several authors who have applied SSA fractionation.[30,39] The lamellar thickness could be estimated from the SSA results with the Thomson–Gibbs equation as follows.[25,29,38,53,54,56]:

$$T_m = T_m^0 \left(1 - \frac{2\sigma}{\Delta H_0 L_i}\right)$$

where the equilibrium melting temperature $T_m^0 = 460$ K (estimated values between 459 and 467 K),[57,58] $\Delta H_0 = 184 \times 10^6$ J/m^3, the surface energy $\sigma = 0.0496$ J/m^2, and L_i is the lamellar thickness.[59]

The lamellae thicknesses of all samples after SSA thermal fractionation are calculated and listed in Table V. L_1 is the lamellae thickness of peak 1 of PP after SSA treatment. As summarized in Table V, with the increase of Donor-C content in the C—N-mixed external donors, the lamellae thickness L_1 of the long isotactic sequence length of PP gradually increases from 28.02 to 29.70 nm. The lamellae thicknesses L_2 and L_3 of the *meso*-isotactic sequence length of PP change a little. The effect on lamellae thicknesses L_4–L_6 of the short isotactic sequence length of PP is small. These results indicate that the increase of the Donor-C content in the C—N-mixed external donors is conducive to increasing the long isotactic sequence length of PP.

Moreover, for further analysis, the statistical parameters describing the lamellar thickness, the arithmetic average L_n, weighted average L_w, and the broadness index I, are calculated using the following equations.[60]

$$L_n = \frac{n_1 L_1 + n_2 L_2 + n_3 L_3 + n_4 L_4 + \cdots n_j L_j}{n_1 + n_2 + n_3 + n_4 + \cdots + n_j} = \sum f_i L_i$$

$$L_w = \frac{n_1 L_1^2 + n_2 L_2^2 + n_3 L_3^2 + n_4 L_4^2 + \cdots n_j L_j^2}{n_1 L_1 + n_2 L_2 + n_3 L_3 + n_4 L_4 + \cdots + n_j L_j} = \frac{\sum f_i L_i^2}{\sum f_i L_i}$$

$$I = \frac{L_w}{L_n}$$

Table V. The Lamellar Thicknesses of PP Samples After SSA Thermal Fractionation

Samples	I.I. (%)	L_1(nm)	L_2 (nm)	L_3 (nm)	L_4 (nm)	L_5 (nm)	L_6 (nm)
C-N-1	96.0	28.02	14.98	9.56	7.71	6.68	5.81
C-N-5	96.2	28.34	15.08	9.67	7. 64	6.77	5.87
C-N-9	96.2	29.70	15.45	9.27	7.76	6.68	5.81
C-T-1	96.5	29.35	15.17	9.31	7.67	6.60	5.84
C-T-5	96.2	29.70	15.45	9.27	7.76	6.68	5.81
C-T-9	96.4	31.19	14.72	9.41	7.76	6.71	5.90
H-N-1	96.1	31.19	15.65	9.56	7.79	6.60	5.90
H-N-5	95.9	32.85	15.85	9.27	7.76	6.69	5.87
H-N-9	96.8	35.18	15.95	9.41	7.81	6.80	5.75
Py-N-1	96.5	29.01	15.36	9.38	7.74	6.59	5.88
Py-N-5	96.2	29.01	15.85	9.27	7.71	6.62	5.83
Py-N-9	96.3	29.35	15.75	9.13	7.69	6.69	5.81

Table VI. Lamellar Thickness Statistical Parameters of PP Prepared by the Mixed External Donors

Samples	L_w (nm)	L_n (nm)	$I = L_w/L_n$
C-N-1	13.62	12.73	1.071
C-N-5	13.49	12.45	1.083
C-N-9	14.54	12.53	1.160
C-T-1	13.87	12.69	1.092
C-T-5	14.03	12.34	1.137
C-T-9	14.31	12.35	1.159
H-N-1	14.28	12.61	1.132
H-N-5	17.2	13.78	1.248
H-N-9	20.78	15.51	1.340
Py-N-1	13.93	12.99	1.073
Py-N-5	15.71	13.45	1.169
Py-N-9	21.01	16.62	1.264

where n_i is the normalized peak area, and the L_i is the lamellar thickness for each fraction. The results of all samples are summarized in Table VI. As summarized in Table VI, the L_w of sample C-N-1 to sample C-N-9 increases gradually, indicating an increase of the amount of thick lamellar. Moreover, the broadness index I increase from 1.071 to 1.160 slightly, indicating the thickness distribution of lamellar becomes broader.

As it is studied previously, the average isotacticities of samples prepared by the C—N-mixed external donors are similar. However, the SSA results suggest clearly that the isotactic sequence length distributions of all samples are totally different. The differences among the C—N samples can be, respectively, observed from the differences of the melting peaks areas and the lamellar thickness. It is found that with the increase of Donor-C ratio from 10 to 90% in the C—N-mixed external donors, the amount of the long isotactic sequence length and the short isotactic sequence length increase gradually, whereas the amounts of the *meso*-isotactic sequence length decrease gradually, indicating that the sequence length distribution of PP becomes broader.

Correlation Between SSA and ^{13}C-NMR Results on Sequence Length Distribution of PP

To investigate the correspondence between the SSA and the ^{13}C-NMR techniques of the effect of the donor 1 in the mixed external donors on the variation of the isotactic sequence distribution, the high-resolution ^{13}C-NMR was performed to the three PP samples prepared by the C—N-mixed external donors. The results obtained are summarized in Table VII. Moreover, to further analyze deeply, the statistical parameters describing the

Table VIII. The Statistical Triad Sequence Length of PP

Samples	$\bar{n}$	$\overline{n_m}$	$\overline{n_r}$	$\overline{n_m}/\overline{n_r}$
C-N-1	23.47	45.34	2.02	22.46
C-N-5	34.72	49.00	1.46	33.68
C-N-9	39.92	53.49	1.38	37.27

sequence lengths of can be calculated using the following equations,[61] and the values are listed in Table VIII.

$$\bar{n} = \frac{1}{[rr] + 1/2[mr]}$$

$$\overline{n_m} = \frac{[mm] + 1/2[mr]}{1/2[mr]}$$

$$\overline{n_r} = \frac{[rr] + 1/2[mr]}{1/2[mr]}$$

where $\bar{n}$ is the number average PP sequence length, $\overline{n_m}$ is the number average PP isotactic sequence length, and $\overline{n_r}$ is the number average PP atactic sequence length.

As summarized in Table VII, with the ratio of Donor-C in the C—N-mixed external donors gradual increase from 10 to 90%, the content of the regular triads "mm" increases gradually from 93.55 to 95.36%, meanwhile, the amount of "mr" and "rr" decreases. As listed in Table VIII, all the number average PP sequence lengths also have an increasing trend with the increase the ratio of Donor-C in the C—N-mixed external donors. The number average PP isotactic sequence length $\overline{n_m}$ increases rapidly from 45.34 to 53.49 and the $\overline{n_m}/\overline{n_r}$ also increases gradually from 22.46 to 37.27, and the number average PP atactic sequence length decrease from 2.02 to 1.38. As the main defects in the homo-PP chains are the stereo-defects of the arrangements of the side methyl groups of "mistake inserted" monomers. As the variation of the average isotacticity for the C—N samples is very small (Table I), namely, the total amount of stereo-defects of the samples nearly remains constant. As a result, the above results indicate that the sequence length distribution of PP in the microstructure chain becomes more uniform. The occurrence opportunity of the stereoregular insertion of the propylene monomer increases with the increase of Donor-C ratio from 10 to 90%, and then increases the isotactic sequence length of PP. Hence, the results of high-resolution ^{13}C-NMR are coincident with the results of SSA when they are used to study the isotactic sequence distribution of PP.

The Effect of the Different Mixed External Donors on Isotactic Sequence Length Distribution of PP

The SSA melting curves of PP samples prepared, respectively, by the C—T- and H—N-, and Py—N-mixed external donors are
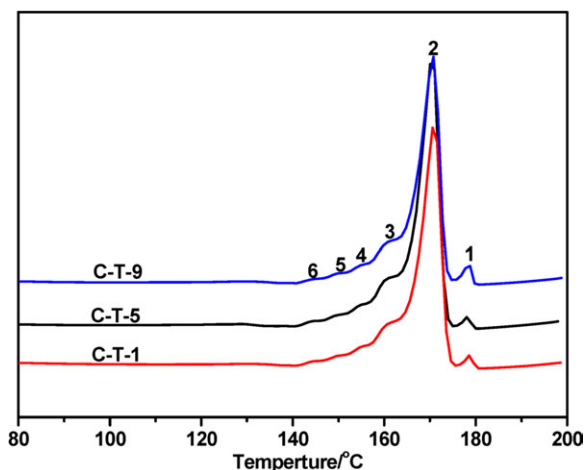
Table VII. The ^{13}C-NMR Results of the Stereosequence Distribution of Isotactic PP Samples Prepared by the C—N-Mixed External Donors

Samples[a]	mm[b]	mrmr	mmrr	mrmm+rmrr	mrmr	rr	rrrr	rrrm	mrrm
C-N-1	93.55	4.22	2.92	0.32	0.98	2.15	1.39	0.39	0.37
C-N-5	95.04	3.96	2.78	0.56	0.62	0.90	0.18	0.49	0.23
C-N-9	95.36	3.63	2.51	0.86	0.56	0.69	0.09	0.41	0.19

[a]The C—N samples without any treatment were tested by high-resolution ^{13}C-NMR, [b]The triad mm consists of the pentads mmmm, mmmr, and rmmr.

Figure 5. The SSA melting curve of PP samples prepared by the C—T-mixed external donors.

Figure 7. The SSA melting curve of PP samples prepared by the Py—N-mixed external donors. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

shown in Figures 5–7. As shown in Figures 5–7, the effects of the C—T-, H—N-, and Py—N-mixed external donors on the PP microstructure are similar to the C—N-mixed external donors. There are also six melting peaks on the melting curve of PP samples prepared, respectively, by the C—T-, H—N-, and Py—N-mixed external donors after the SSA fractionation. The areas of high-temperature melting peaks gradually increase with the increase of the external donor Donor-1 (Donor-C, Donor-H, and Donor-Py, respectively). As summarized in Table III, the melting temperature of peak 1 of the long isotactic sequence length and the total melting enthalpy of all PP samples gradually increase, showing that the crystallization ability and the degree of crystallinity of the PP increase with the rise of the Donor-1 (Donor-C, Donor-H, and Donor-Py, respectively) content of the mixed donors.

Table IV lists that the relative contents of peak 1 of the long isotactic sequence length of all samples prepared by the C—T-, H—N-, and Py—N-mixed external donors increase obviously
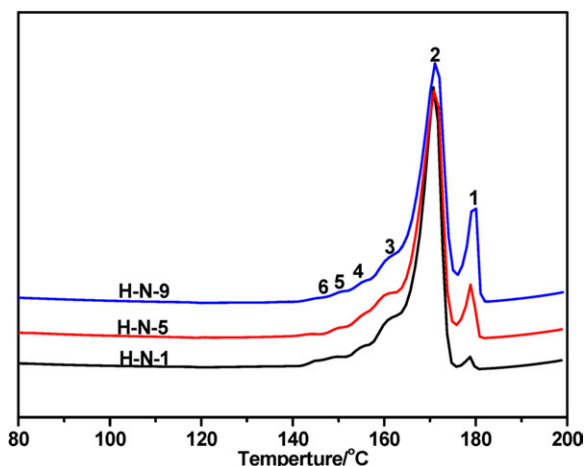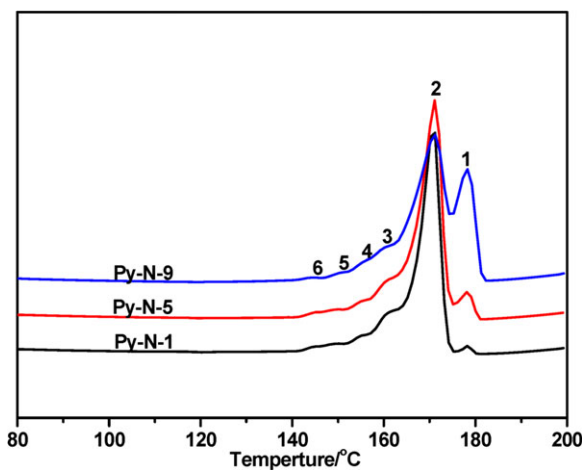
with the increase of content of the Donor-1, especially for PP samples prepared by the Py—N-mixed external donors, the relative content of peak 1 increases sharply from 0.2 to 27.5%, revealing that the long isotactic sequence length increases clearly. The relative contents of the medium isotactic sequence decrease in some sort, but the relative contents of the short isotactic sequence change unobviously. With the increase of content of the Donor-1, the lamellae thicknesses L_1 and L_2 of the higher isotactic composition of PP gradually increase as summarized in Table V, and the broadness index I also increases as listed in Table VI, indicating that the thickness distribution of lamellar becomes broader.

For the different kinds of the mixed external donors, Tables II and III lists that the crystallization ability of the PP is weak and the degree of crystallinity of the PP is lower, and Figure 8 shows that the isotactic sequence length distribution of PP prepared by the mixed external donors is small when Donor-1 of the four
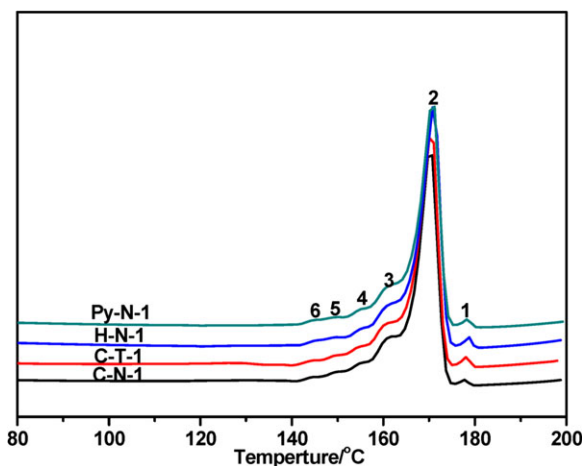

Figure 6. The SSA melting curve of PP samples prepared by the H—N-mixed external donors. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 8. The SSA melting curve of the PP samples prepared by Donor-1 is 10% in the different kinds of the mixed external donors. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

mixed external donors is relatively low (10%). When the content of Donor-1 in the mixed external donors is 50%, Table IV and Figure 9 show that the relative contents of peak 1 of all samples prepared by the four mixed external donors are moderate different, and the relative contents of peak 1 of sample prepared by the H─N-mixed external donors are higher than that of other samples. The results of the lamellae thickness also reveal that the PP sample prepared by the H─N-mixed external donors has more isotactic component in PP chain, which is also coincident with the results of the broadness index I. When the ratio of Donor-1 in the four mixed external donors is running up to 90%, Table IV and Figure 10 show that the relative content of peak 1 of sample Py-N-9 reaches 27.5%, which is significantly different with that of samples prepared by the other kinds of the mixed external donors. The results of the lamellae thickness also reveal that the PP sample prepared by the Py─N-mixed external donors has the maximum isotactic component in PP chain, evidencing the isotactic sequence length of PP prepared by the Py─N-mixed external donors is longest.

CONCLUSIONS

In this study, the PP samples were prepared by Ziegler–Natta catalyst with different mixed external donors. The crystallization behavior and sequence length distribution of PP were studied by SSA technology for the first time.

The SSA experimental results showed that the mixed external donors have an important effect on the sequence length distribution of PP when the ratio of the mixed external donors/Ti (Si/Ti) is unchanged. The crystallization ability and the relative contents of long isotactic sequence length gradually increase with the rise of the relative component of Donor-1 in the mixed external donors, and the thickness distribution of lamellar also becomes broader.

For different kinds of the mixed external donors, the crystallization ability and the relative contents of long isotactic sequence length of PP prepared by the mixed C─N or C─T external donors are lowest, whereas the effect of the mixed H─N and
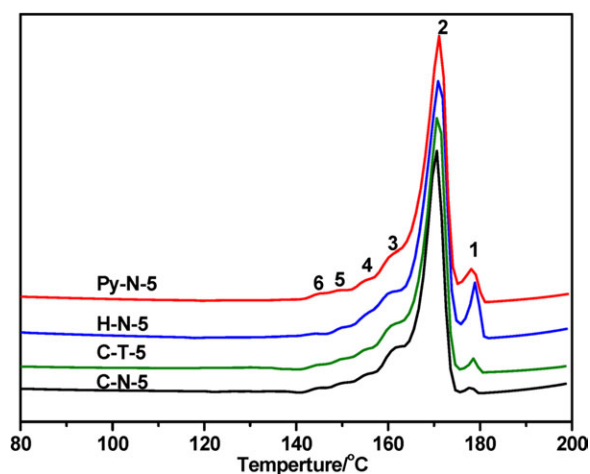

Figure 9. The SSA melting curve of the PP samples prepared by Donor-1 is 50% in the different kinds of the mixed external donors. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
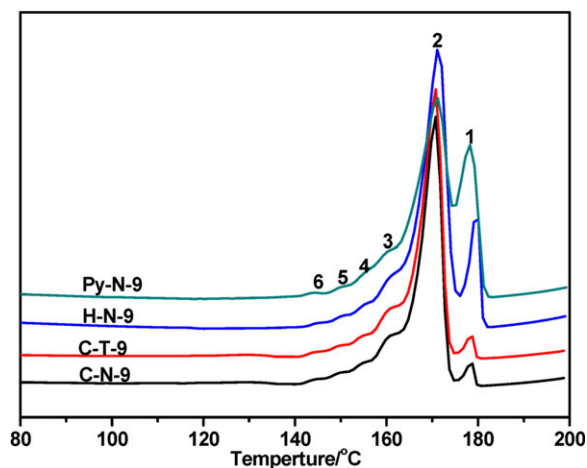

Figure 10. The SSA melting curve of the PP samples prepared with Donor-1 is 90% in the different kinds of the mixed external donors. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Py─N external donors is more significantly. Especially, the relative content of long isotactic sequence length increases sharply from 0.2 to 27.5% in the PP chain of sample prepared by the mixed Py─N external donors when the proportion of Donor 1 is running up to 90%.

ACKNOWLEDGMENTS

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