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View Article Online
DOI: 10.1039/C6RA13819E

RSC Advances

ARTICLE

Microstructure of polypropylene and active center in Ziegler-Natta catalyst: Effect of novel salicylate internal donor

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Qian Zhou,[a] Tao Zheng,[a] Huayi Li,*[,b] Zhi Luo,[a] Ailian Wang,[a] Liaoyun Zhang,*[,a] and Youliang Hu[b]

Abstract: Five salicylates with different size of hydrocarbon substituents were firstly synthesized and employed as ecofriendly internal donors of Ziegler-Natta catalyst for propylene polymerization. The influences of these salicylates and traditional industrial internal donor diisobutyl phthalate on the microstructure of polypropylene and active center in Ziegler-Natta catalyst were both studied. It was found that the catalyst activities of catalyst containing salicylate internal donors with proper volume were higher than that catalyst containing diisobutyl phthalate internal donor. GPC results showed that the molecular weights of polypropylene prepared by salicylate internal donors were all lower than that prepared by diisobutyl phthalate, which indicated that polypropylene chains produced by salicylate internal donors were easier to transfer than that prepared by diisobutyl phthalate internal donor. Deconvolution of GPC curves exhibited that as increasing the volume of salicylate internal donor, some of active center for low molecular weight transferred into active center for high molecular weight. The results of ^{13}C-NMR and SSA both suggested that the salicylate internal donor with appropriate size volume in catalyst was beneficial to increasing isotactic sequence length, isotacticity index and regular triads ''mm'' of polypropylene, while further increasing the volume of salicylate internal donor in catalyst would lead to the polypropylene chain containing more stereo-defects. Moreover, the active centers with different stereospecificity parameter p_{iso} in catalyst could explain the trend of stereo-defects in polypropylene chain when different internal donors were used. In addition, it was found that the isotactic sequence length and isotacticity index of polypropylene prepared by isobutyl 2-benzyloxy-3,5-isopropyl benzoate were close to that produced by diisobutyl phthalate internal donor. Meanwhile, the lamella thickness distribution of polypropylene produced by salicylate internal donor was broad, which might have potential application as expanded polypropylene materials.

Introduction

Driven by the continuous developments in catalyst technology and polymerization process, polypropylene has owned many excellent properties and becomes one of the most widely used thermoplastic resins.[1-3] At present, the forth Ziegler-Natta catalyst is one of the most widely used catalyst system for propylene polymerization,[4] which always contains $MgCl_2$-supported $TiCl_4$, internal donor, triethyl aluminium (TEA) and external donor.[5] Since internal donors are applied to Ziegler–Natta catalyst system, it has become a key component for improving comprehensive property of polypropylene[6-8]. Many kinds of compounds[9-14] are used as internal donors of Ziegler–Natta catalyst for research. Now phthalate[3] is the most widely used internal donor for the industrial production of polypropylene. However, it is found that phthalates is harmful to human body, moreover, European Union and the United States both have restricted the use of phthalates in certain plastics. Our group also uses aliphatic diester as ecofriendly internal donor[15] and obtains catalysts with high catalytic activity and polypropylene with high isotacticity. However, the synthesis of aliphatic diester is hard to be industrialized. Salicylic acid is known for its ability to ease aches and pains, which is a composition of aspirin. [16] Moreover, some salicylates are often used in cosmetics as a fragrance additive and UV light absorber. However, it is not found any reports about salicylate as internal donor for polypropylene polymerization. In addition, it was found that internal donor could strongly impact on the active center of Ziegler-Natta catalyst and the microstructure of polypropylene[15, 17, 18], which determine the property and industrial application of polypropylene. Successive self-nucleating and annealing (SSA) thermal fractionation[19, 20] can give lamella thickness and lamella thickness distribution of polypropylene, which are related to the isotactic sequence length and isotactic sequence distribution of polypropylene. In addition, ^{13}C-NMR [21, 22]can be used not only to measure the stereo-defect distribution of polypropylene, but also to analyze the stereoselectivity of active center in Ziegler-Natta catalyst. Based on the results of ^{13}C-NMR and DSC, a DSC curve model[23] could be used to analyze the active center with different stereoselectivity in Ziegler-Natta catalyst. In our study, five salicylates with different size of hydrocarbon substituents are firstly synthesized and employed as ecofriendly internal donors of Ziegler-Natta catalyst for propylene polymerization. It was found that the

[a] College of Chemistry and Chemical Engineering, University of Chinese Academy of Sciences, Beijing 100049, China. E-mail: zhangly@ucas.ac.cn.
[b] Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Engineering Plastics, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China. E-mail: lihuayi@ucas.ac.cn.

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DOI: 10.1039/C6RA13819E

catalyst activity of catalyst containing SID internal donors with proper volume was higher than that catalyst containing DIBP internal donor. Deconvolution of GPC curves indicating that as increasing the volume of SID internal donor, some of active center for low molecular weight transferred into active center for high molecular weight. The results of ^{13}C-NMR and SSA both suggested that the SID internal donor with appropriate size volume in catalyst was beneficial to increasing isotactic sequence length, isotacticity index and regular triads ''mm'' of polypropylene, while further increasing the volume of SID internal donor in catalyst would lead to the polypropylene chain containing more stereo-defects. DSC curve model was used to study the stereospecificity parameter p_{iso} of active center in catalyst, which could be used to explain the trend of isotactic sequence length of polypropylene prepared by different internal donors. In addition, it was found that the isotactic sequence length and isotacticity index of polypropylene prepared by SID-4 were very close to that produced by DIBP internal donor.

Experimental

Materials

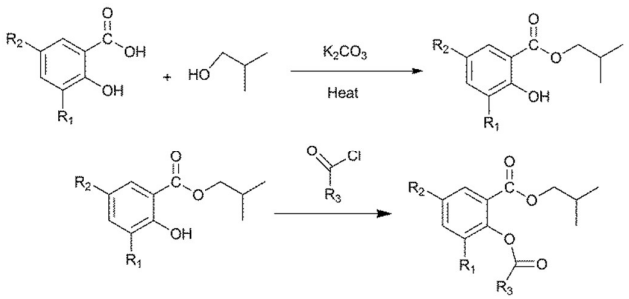
Salicylic acid, 3-methyl salicylic acid, 3,5- isopropyl salicylic acid, 3,5-tert-butylation salicylic acid, benzoyl chloride, trimethylacetyl chloride, sodium bicarbonate, chloroform, propylene, hydrogen, triethylaluminium (TEA), diisopropyldimethoxysilane (Donor-P) and diisobutyl phthalate (DIBP) were purchased from Aladdin as a reagent grade and used without further purification.

Synthesis of salicylate internal donor

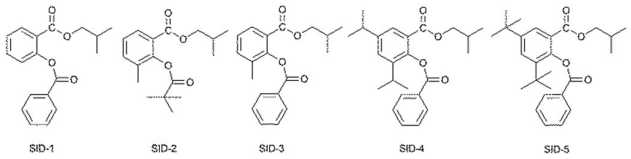
The synthesis method for the five salicylate internal donors was according to literature.[24] The purity of salicylate used for propylene bulk polymerization was above 98%. The synthetic route of salicylate and the structures of five salicylates were shown in Scheme 1 and Scheme 2, respectively. As a typical example, the synthesis process of isobutyl 2-benzyloxybenzoate (SID-1) was carried out as follows:

A 100 ml flask was placed with 40 ml isobutanol, 0.3 mol salicylic acid, 0.5 ml concentrated sulfuric acid. The mixture was stirred at 120 ^{o}C for 5 h. When water no longer appeared in water separator, the heater was turned off. After the formation of isobutyl salicylate was confirmed by gas chromatography, isobutyl salicylate was purified by decompressing distillation. 0.05 mol isobutyl salicylate, 0.08 mol benzoyl chloride, 0.005 mol bismuth(III) oxychloride were stirred at 40 ^{o}C for 6 h. After isobutyl 2-benzyloxybenzoate was confirmed by gas chromatography, the mixture was stirred with aqueous sodium hydrogen carbonate. Organic phase were extracted from water phase, then a transparent and oily liquid 2-benzyloxybenzoate was obtained by decompressing distillation.

The synthesis processes of the other salicylates including isobutyl 2-benzyloxy-3-methyl benzoate (SID-2), isobutyl 2-trimethyloxy-3-methyl benzoate (SID-3), isobutyl 2-benzyloxy-3,5-isopropyl benzoate (SID-4) and isobutyl 2-benzyloxy-3,5-tert-butyl benzoate (SID-5) were similar to that of SID-1. ^{1}H NMR (DMSO) δ (ppm): SID-1: 0.81 (d, 6H), 1.73(m, 1H), 3.92 (d, 2H), 7.25 (t, 2H), 7.60 (m, 3H), 7.72 (d, 1H), 8.07 (d, 1H), 8.19 (d, 2H); SID-2: 0.82 (d, 6H), 1.21(s, 9H), 1.92 (m, 1H), 2.13 (s, 3H), 4.01 (d, 2H), 7.08 (t, 1H), 7.38 (d, 1H), 7.80 (d, 1H); SID-3: 0.85 (d, 6H), 1.80(m, 1H), 3.95 (d, 2H), 7.42 (d, 2H), 7.60 (t, 3H), 7.75 (d, 1H), 8.25 (d, 2H) ; SID-4: 0.85 (d, 6H), 1.14(d, 12H), 1.91 (m, 1H), 2.81 (m, 1H), 2.99 (m, 1H), 3.96 (d, 2H), 7.47 (s, 1H), 7.53 (t, 2H),7.66 (m, 2H) 8.16(d, 2H); SID-5: 0.88 (d, 6H), 1.39(s, 18H), 1.78 (m, 1H), 3.90 (d, 2H), 7.54 (t, 2H), 7.63 (t, 1H),7.93 (s, 2H) 8.25(d, 2H);



Scheme 1 Synthetic route of salicylate internal donors



Scheme 2 Structures of salicylate internal donors with different substituent groups

Preparation of catalyst

The Ziegler-Natta catalysts with salicylate as internal donor were prepared in a reactor under dry nitrogen condition. 5 g magnesium ethoxide and 150 mL dry toluene were added to glass reactor under nitrogen condition at room temperature. Then 50 mL $TiCl_4$ was added to reactor by funnel in half an hour at 5 ºC. 2 ml salicylate internal donor was injected to reactor after dripping $TiCl_4$. The mixture was stirred at 110 ºC for 2 h. After reaction, the supernatant was removed and the residue was washed by toluene. Precipitated solid was treated again with a mixture of 150 ml toluene and 50 ml titanium tetrachloride at 110 ºC for 2 h. After discarding supernatant, the residue was washed with toluene and hexane, respectively. A solid catalyst was obtained.

Propylene bulk polymerization

Firstly, 800 g propylene gas and 0.3 MPa hydrogen gas were charged with a reactor. The C(H_2)/C(propylene) ratio was 2.59 mmol/mol. Then 20 mg Ziegler-Natta catalyst, 12 mmol TEA in n-hexane solution and 0.39 mmol Donor-P were added to the system. The reactor was heated to 70 ^{o}C and stirred at 300 r/min for an hour. Then propylene was exhausted and polypropylene was obtained as white powder.

UV–Vis spectra

The content of Ti in catalyst was measured by UV–Vis spectra (UV-1800). Firstly, catalyst was dissolved in a dilute sulfuric acid solution. Then titanium was converted to $[TiO(H_2O_2]SO_4$ by the addition of H_2O_2. Spectrophotometer was used to record UV–Vis spectra of the resultant solution of complexes of catalyst.

Gas chromatography

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The ester content of the catalysts was determined on gas chromatograph (clarus 580), manufactured by PE in the US.

Differential scanning calorimetry

Mettler 822e differential scanning calorimeter was used to measure the thermal properties of polypropylene. 2～4 mg polypropylene was put in an aluminium pan. For erasure of thermal history, the pan with polypropylene was heated from 50 °C to 200 °C, the heating rate was 50 °C/min, and it was held at 200 °C for 5 min in nitrogen atmosphere. Then polypropylene in pan was cooled to 50 °C and held at 50 °C for 5 min. Finally, polypropylene was heated to 200 °C at 10 °C/min.

Gel permeation chromatography

PL-GPC 220 high-temperature gel permeation chromatography (Polymer Laboratories Ltd) was used to measure molecular weights (M_n and M_w) and the polydispersity index (*PI*) of polypropylene. The measuring temperature was 413.15 K. 1,2,4-trichlorobenzene was solvent of polypropylene. The injection volume was 100 ml and the flow rate was 1.0 ml/min. Calibration was made by linear polystyrene as the standard sample.

Successive self-nucleation and annealing

Successive self-nucleation and annealing (SSA) technology has been widely used to analyze lamellar thickness and isotactic sequence length of polymer[25]. The method included several heating and cooling steps, which finished by DSC. (1) heating polypropylene to 200 °C at 50 °C/min and then held for 5 min; this step was for erasure of crystalline thermal history of polypropylene; (2) Cooling polypropylene to 50 °C at 20 °C/min and held for 5 min; (3) Then heating polypropylene from 50 °C to a partial melting temperature denoted T_s at 20 °C/min; (4) kept polypropylene at T_s for 10 min; (5)Then cooling polypropylene from T_s to 50 °C at 20 °C/min; (6) Repeat step 'c' to 'e' at increasingly a new lower T_s, which were varied from 164 to 144 °C at 5 °C intervals for a total five self-nucleation/ annealing steps. (7) Finally, heating polypropylene from 50 °C to 200 °C at 10 °C/min. Then the multiple melting curve (SSA curve) was obtained. Pijpers gave the method of looking for the optimum T_s temperatures of polypropylene in literature.[26]

Nuclear magnetic resonance spectroscopy

DMX 300M (Bruker) was used to test ^{13}C-NMR spectra of polypropylene. 80 mg~100 mg polypropylene was dissolved 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 132.700 ppm. The number of pulses was more than 5,000; Pulse angle was 30; Spectrum width was 25,000 Hz, and relaxation delay was 7 s. All spectra were completely proton decoupled.

Results and discussion

Components and catalytic activity of Ziegler-Natta catalyst

Five salicylates with different hydrocarbyl substituents on phenyl group were firstly prepared, as Scheme 2 showed. Then the five salicylates (SID) and di-butyl phthalate (DIBP) were used as internal donors to prepare six Ziegler-Natta catalysts, as Table 1 listed, which also displayed the Ti content and ester content in Ziegler-Natta catalyst. As shown in Table 1, the Ti contents and ester contents in SID catalysts were both lower than that in DIBP catalyst, indicated that the Ti and ester contents in catalyst could be affected by types of internal donors. Besides, comparing Cat-1, Cat-3 and Cat-4, the ester content of catalysts increased from Cat-1 to Cat-4, while their Ti content decreased from Cat-1 to Cat-4. It was reported that ester could coordinate with Mg atoms on the (110) facets of $MgCl_2$ crystallites[27], which could block the surface sites on $MgCl_2$ support and lead to Ti hardly coordinating with support. Therefore, the trend of relative content of Ti and ester was contrary. Previous research found that the increase of ester content in catalyst was beneficial to improving catalyst activity of Ziegler-Natta catalyst[28]. Table 1 showed that catalyst activity increased from 6.6×10^5 gPP/g.Ti to 24.1×10^5 gPP/g.Ti, as the ester content of catalyst increased from 1.1% to 2.2%. The trend of catalyst activity and ester content in catalyst also matched previous conclusion. In addition, it was found that catalyst activities of SID catalyst (except for SID-1) were much higher than that of DIBP catalyst, which indicated that SID internal donor with proper volume were more beneficial to improving the catalyst activity than DIBP internal donor in catalyst.

Table 1 Components and catalytic activity of Ziegler-Natta catalysts containing different internal donor

Samples	Donor	Catalytic Activity ($\times10^5$ g PP/ g.Ti)	Ti [a] (wt %)	Ester [b] (wt %)
Cat-1	SID-1	6.6	2.5	1.1
Cat-2	SID-2	13.7	1.7	1.9
Cat-3	SID-3	10.3	1.8	1.7
Cat-4	SID-4	24.1	0.9	2.2
Cat-5	SID-5	23.7	0.7	1.9
Cat-D	DIBP	8.3	2.7	6.8

[a] the weight percent of Ti in catalyst.
[b] the weight percent of ester in catalyst.

Molecular Weight and Polydispersity Index of Polypropylene

Table 2 Molecular weight and polydispersity index of polypropylene prepared by different internal donor

Donor	$M_n\times10^{-4}$ (g/mol)	$M_w\times10^{-4}$ (g/mol)	M_w/M_n
SID-1	4.53	26.39	5.82
SID-2	5.13	26.45	5.15
SID-3	4.25	27.24	6.40
SID-4	4.99	27.38	5.48
SID-5	3.83	27.55	7.19
DIBP	7.54	43.26	5.74

Table 2 listed the molecular weight and polydispersity index of polypropylene prepared by different internal donors. It was shown that the polydispersity index of polypropylene prepared by SID internal donor ranged from 5.15 to 7.19, which was similar with that prepared by DIBP internal donor. Table 2 also showed that the molecular weights of polypropylene prepared by SID internal donors were all lower than that prepared by DIBP, which indicated that polypropylene chain produced by SID internal donor was easier to transfer than that prepared by DIBP internal donor. Furthermore,

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it was also found that the weight-average molecular weight M_w of polypropylene successively increased from SID-1 to SID-5. In order to deeply analyze the trend of molecular weight of polypropylene prepared by different internal donors, GPC curves were deconvoluted by Schulz–Flory distribution functions.

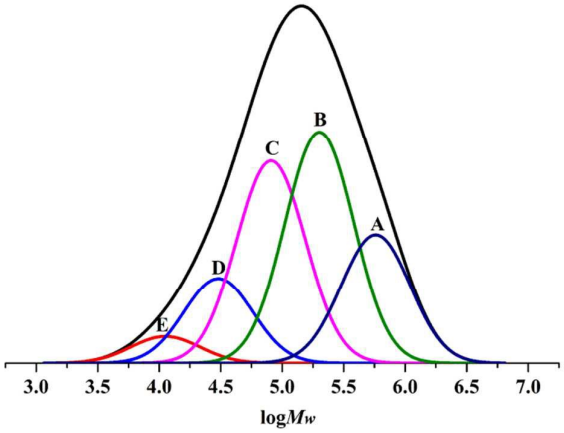

Fig. 1 Resolution of GPC curves into five Flory components for polypropylene

Active centers based on the molecular weight of polypropylene

The M_w/M_n ratio of polypropylene prepared by single active center catalyst was narrow (2~3), and the wider distribution of molecular weight indicated the catalyst containing multiple active centers. Judging by the polydispersity index of polypropylene, catalysts with SID and DIBP internal donors both contained several types of active centers. Fig. 1 showed that GPC curves of polypropylene prepared by SID and DIBP internal donors were both deconvoluted into five kinds of Flory compounds with small polydispersity index, which could correspond to different active centers in catalyst, as literatures did[29]. Compared the active centers in catalyst with different SID internal donors, it was found that each type of active center in different SID catalyst produced polypropylene with similar molecular weight, however, the relative content of each kind of active center in five SID catalysts changed regularly. The relative contents of C_A^* and C_B^* increased from Cat-1 to Cat-5, while the relative contents of C_C^*, C_D^* and C_E^* all decreased from Cat-1 to Cat-5. It was indicated that as increasing the volume of SID internal donor in catalyst some of C_C^*, C_D^* and C_E^* transferred into C_A^* and C_B^*. In addition, it was found that the molecular weight of polypropylene prepared by each kind of active center in DIBP catalyst were obviously different with that in SID catalyst, which indicated that the active centers in SID catalyst were different with that in DIBP catalyst. The molecular weight of polypropylene mainly depended on hydrogen response, owning that chain transfer to hydrogen was more sensitive than the chain transfer to monomer or to TEA[27]. And the sensitivity of chain transfer to hydrogen was primarily dependent on regioselectivity of active center, which had great relationship with proportion of secondary (2,1-) monomer insertion[30]. Taking into account of the same addition amount of hydrogen for SID and DIBP systems, the different molecular weight of polypropylene prepared by active center in SID and DIBP catalysts was ascribed to the different internal donor in catalyst. Although it was reported that some of ester internal donor could be removed by TEA, internal donor that strongly coordinated with support could not be removed[31], which could influence on the active center in catalyst. It was suggested that the different type of internal donor remained in catalyst might have different impacts on regioselectivity of active center in Ziegler-Natta catalyst, which led to SID and DIBP catalysts producing polypropylene with different molecular weight.

The stereo-defect in polypropylene chain

The stereo-defect of molecular chain could significantly impact on the thermal and mechanical properties of polypropylene, therefore, detailed characterization of the stereo-defect in molecular chain was important to obtain polypropylene with better properties. The fraction of heptane-insoluble crystalline polypropylene was defined as the isotactic index (I.I.) of polypropylene, which could be used to roughly analyze the stereo-defect in polypropylene chain. Table 4 showed the isotactic index of polypropylene prepared by different internal donors, it was found that the isotactic index of polypropylene increased from 96.3% to 98.6% as internal donor successively changing from SID-1 to SID-4, which indicated that the volume of SID internal donor could impact on the stereoregularity of polypropylene. In addition, the isotactic index of polypropylene produced by SID-4 was close to that prepared by DIBP internal donor. In order to obtain more information of stereo-defect in molecular chain, successive self-nucleation and annealing (SSA) and nuclear magnetic resonance spectroscopy (^{13}C-NMR) were both used to study the microstructure of polypropylene. [32, 33]

Table 3 Results of GPC Deconvolution by Flory Components

Samples	C_A^*		C_B^*		C_C^*		C_D^*		C_E^*	
	Fr[a]	M_w[b]	Fr	M_w	Fr	M_w	Fr	M_w	Fr	M_w
Cat-1	16.3	56.4	33.9	19.7	32.3	8.2	12.9	2.9	4.4	0.9
Cat-2	18.1	56.5	35.0	19.8	31.1	8.0	11.6	3.0	3.9	1.2
Cat-3	18.3	57.9	35.7	19.8	30.7	7.7	11.4	2.9	3.6	1.1
Cat-4	19.0	57.6	35.9	19.2	30.1	8.1	11.3	3.3	3.5	1.2
Cat-5	19.8	58.4	37.9	18.5	29.3	7.3	10.2	2.5	2.7	0.7
Cat-D	8.2	138.9	30.7	51.2	38.8	17.9	18.0	6.7	4.3	2.1

[a] Fr was the weight percentage of the fraction produced by a certain active center in catalyst.
[b] Weight average molecular weight, in 10^4 g/mol.

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Table 4 SSA Results of Polypropylene Prepared by different internal donors

Donor	ΔH_m [a] (J/g)	*I.I.*[b] (%)	T_{m1} [c] (°C)	T_{m2} (°C)	T_{m3} (°C)	T_{m4} (°C)	T_{m5} (°C)
SID-1	104.2	96.3	175.9	170.2	165.8	160.6	154.8
SID-2	99.1	96.9	175.9	169.4	165.1	160.3	154.7
SID-3	109.9	98.0	176.0	169.9	165.6	160.5	155.0
SID-4	118.1	98.6	176.3	169.9	165.5	160.3	153.5
SID-5	106.2	97.7	176.1	169.8	165.2	160.0	154.0
DIBP	121.0	98.5	171.4	166.0	160.2	--	--

[a] the isotactic index (I.I.) was tested by extraction with boiling n-heptane for 6 h.
[b] The value of the endothermic enthalpy was determined from SSA curve.
[c] The melting temperature was determined from the peak value in the SSA curves.

As an effective method in features of microstructure of polypropylene, SSA could give lamellar thicknesses and thickness distribution of polypropylene, which could be connected with the isotactic sequence length of polymer. The melting curves of polypropylene prepared by different internal donor after SSA thermal fractionation were shown in Fig. 2 and the melting enthalpy ΔH_m of each polypropylene were listed in Table 4. Comparing the melting enthalpy ΔH_m of polypropylene prepared by SID-1, SID-3 and SID-4, it was found that the melting enthalpy ΔH_m of polypropylene increased from SID-1 to SID-4, while the melting enthalpy ΔH_m of polypropylene prepared by SID-5 was lower than those prepared by SID-4, which reflected the trend of crystallinity degree of polypropylene.

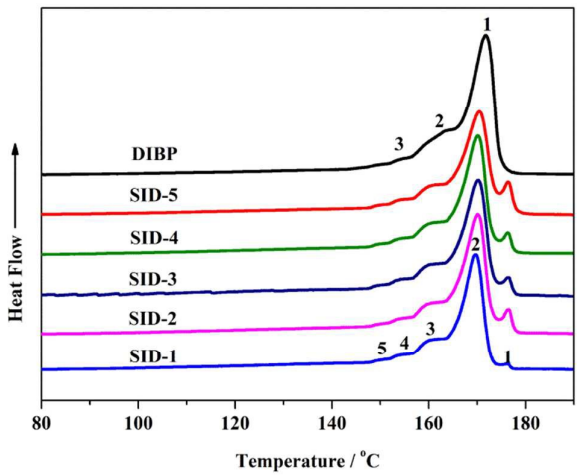

Fig. 2 SSA melting curves of polypropylene samples prepared by different internal donor

Each melting peak of polypropylene in SSA melting curves was related to different thickness of lamellar crystallites, which formed and annealed at each self-nucleation temperature.[34] Thomson–Gibbs equation[35] could give the information about the thickness of lamellar of polypropylene:

$$T_m = T_m^0(1 - 2\sigma/\Delta H_0 L_i)$$

equilibrium melting temperature T_m^0 = 460 K [36], ΔH_0 = 184×10^6 J/m^3, the surface energy σ=0.0496 J/m^2 and L_i is the lamellar thickness.[37]

The lamellar thicknesses of polypropylene after SSA thermal fractionation were calculated and listed in Table 5. It was showed that polypropylene prepared by SID internal donor had five kinds of lamellar thicknesses but polypropylene prepared by DIBP internal donor owned only three kinds of lamellar thicknesses, which indicated that the distribution of lamellar thickness in polypropylene produced by SID internal donor might be different with that prepared by DIBP internal donor. It was also found that all of SID internal donor produced polypropylene with similar lamellar thickness, which differed from those prepared by DIBP internal donor, revealing that the type of internal donor could affect the thickness of each kind of lamellae in polypropylene.

Table 5. The lamellar thicknesses of polypropylene prepared by different internal donor

Donor	L_1	L_2	L_3	L_4	L_5
SID-1	22.65	13.81	11.78	9.45	7.74
SID-2	22.65	13.57	11.52	9.34	7.71
SID-3	22.68	13.66	11.71	9.42	7.82
SID-4	22.79	13.66	11.67	9.34	7.44
SID-5	22.71	13.62	11.56	9.23	7.55
DIBP	16.04	11.89	9.30	--	--

Moreover, it was found that the isotactic sequence length of polypropylene was closely related with lamellar thickness. The following equations[38] were used to calculated average lamellar thickness, thickness distribution (arithmetic average L_n, weighted average L_w and broadness index *I)* and average isotactic sequence length(arithmetic average MSL_n, weighted average MSL_w). n_i is the content of each fraction on SSA curve, and the L_i is the thickness of lamella for each fraction, L_{helix}=0.65 nm.

$$L_n = \frac{n_1L_1 + n_2L_2 + n_3L_3 + n_4L_4 + \cdots n_jL_j}{n_1 + n_2 + n_3 + n_4 + \cdots n_j} = \sum f_iL_i$$

$$L_w = \frac{n_1L_1^2 + n_2L_2^2 + n_3L_3^2 + n_4L_4^2 + \cdots + n_jL_j^2}{n_1L_1 + n_2L_2 + n_3L_3 + n_4L_4 + \cdots + n_jL_j} = \frac{\sum f_iL_i^2}{\sum f_iL_i}$$

$$I = L_w/L_n \qquad MSL = 3L/L_{helix}$$

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Table 6 Lamellar thickness statistical parameters and isotactic sequence length of polypropylene prepared by different internal donor

Donor	L_n(nm)	L_w(nm)	MSL_n	MSL_w	I
SID-1	12.36	13.27	57.04	61.25	1.074
SID-2	12.77	13.37	58.93	61.71	1.057
SID-3	12.62	13.39	58.24	61.80	1.061
SID-4	12.96	13.52	59.82	62.40	1.056
SID-5	12.66	13.48	58.43	62.22	1.065
DIBP	13.11	13.76	60.50	63.09	1.043

Comparing the average isotactic sequence length MSL_n of polypropylene prepared by different internal donors in Table 6, the isotactic sequence length MSL_n of polypropylene prepared by SID internal donor ranged from 57.04 to 59.82, which were close to that produced by DIBP internal donor. Meanwhile, the distribution of lamella thickness I of polypropylene prepared by SID internal donors ranged from 1.056 to 1.074, which was broader than that prepared by DIBP internal donor. It was suggested that SID internal donor in catalyst was more conducive to produce polypropylene with broad distribution of lamella thickness than DIBP. In addition, comparing SID-4 and DIBP, it was found that the average lamella thickness of polypropylene prepared by SID-4 was similar with than produced by DIBP, but the thickness and thickness distribution of each lamella in polypropylene for SID-4 and DIBP internal donor were different.

Table 7 Meso sequence length calculated from ^{13}C-NMR and the results of ^{13}C-NMR

Donor	mm	mr	rr	*MSL*
SID-1	85.46	7.81	6.66	15.56
SID-2	88.08	6.11	5.81	22.97
SID-3	89.61	5.25	5.15	19.16
SID-4	90.98	3.74	4.47	28.58
SID-5	88.88	5.50	5.63	22.76
DIBP	91.67	3.82	4.51	30.66

Nuclear magnetic resonance spectroscopy (^{13}C-NMR) was always used to study macrostructure of polypropylene[39]. The methyl regions results from the 300 MHz ^{13}C-NMR spectrum of the polypropylene were listed in Table 7. It was found that the content of the regular triads ''mm'' of polypropylene prepared by SID-1~SID-4 internal donor increased gradually from 85.46% to 90.98%, while the amount of ''mr'' decreased from 7.81% to 3.74% and the amount of ''rr'' also decreased from 6.66% to 4.47%. In addition, comparing polypropylene prepared by SID-4 and DIBP internal donor, the content of the regular triads ''mm'' of polypropylene prepared by SID-4 internal donor were slightly lower than that prepared by DIBP internal donor. It suggested that both type and volume of internal donors could impact on the regular triads "mm" of polypropylene. ^{13}C-NMR results could also be used to analyze the average meso sequence length of polypropylene. Average isotactic sequence length calculated from ^{13}C-NMR result was defined as *MSL*, which could be calculated by the following equation[40]:

$$MSL = \frac{mmmm + 3 \times \frac{1}{2} \times mrrr + 2rmmr + \frac{1}{2}rmrm + \frac{1}{2}rmrr}{\frac{1}{2}mmmr + rmmr + \frac{1}{2}rmrm + \frac{1}{2}rmrr}$$

Table 7 showed the average isotactic sequence length *MSL* calculated from the results of ^{13}C-NMR. Comparing polypropylene prepared by SID-1, SID-3, SID-4, it was found that the average meso sequence length *MSL* calculated from ^{13}C-NMR increased from SID-1 to SID-4, however, SID-5 give polypropylene with lower meso sequence length than SID-4, which was in good coincident with the trend of MSL_n calculated from SSA. Moreover, the trend of the average isotactic sequence length was also similar with the rule of isotacticity index and regular triads ''mm'' of polypropylene prepared by different SID internal donors, which was suggested that the appropriate size of volume of SID internal donor in catalyst would benefit to decrease the content of stereo-defect in polypropylene chain, while further increasing the volume of SID internal donor in catalyst might lead to polypropylene chain containing more stereo-defect. It was supposed that SID internal donor with different volume might have different effect on the stereoselectivity of catalyst, which led to produce polypropylene with different stereo-defect.

The thermal properties of polypropylene

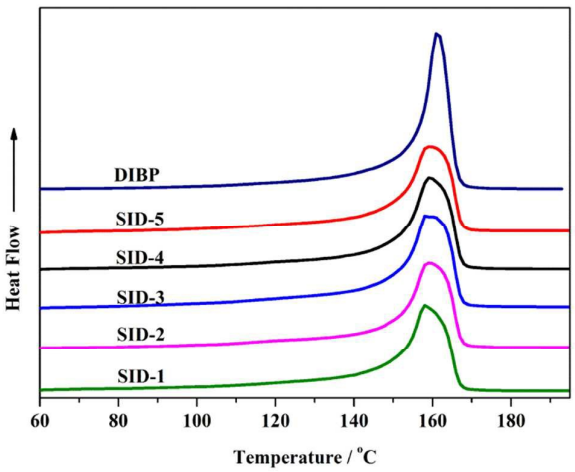

Fig. 3 DSC curves of polypropylene prepared by different internal donor

Fig. 2 showed that the SSA curves of polypropylene prepared by SID internal donor were all broader and had more peaks than that prepared by DIBP internal donor, which represented more kinds and broader distribution of lamellar thickness of polypropylene prepared by SID internal donor. Therefore, it was assumed that SID internal donor might produce polypropylene with broad DSC curves. Fig. 3 displayed that the DSC curves prepared by SID internal donor were indeed broader than DIBP. Many researchers found that the broad melting curve of polymer was beneficial to expand the crystallization temperature range for expanded polypropylene, which was conducive to the control of foaming of polypropylene[41]. Hence, that polypropylene produced by SID internal donor might be possibly used as the material for expanded polypropylene.

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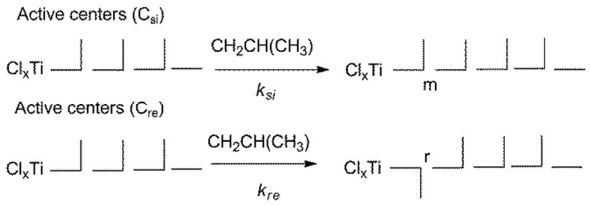
Active center with different stereoselectivity



Scheme 3 Active Centers (C_{si}) and Active Centers (C_{re})

It was reported that there were multiple active centers with different stereoselectivity in heterogeneous Ziegler-Natta catalysts[42], which could produce polypropylene chain with varying distribution of stereo-defects. The results of ^{13}C-NMR and SSA had confirmed that internal donor could significantly impact on the relative content and distribution of stereo-defect in molecular chain of polypropylene. It was supposed that different internal donors in catalyst might have different influence on stereoselectivity of active center in Ziegler-Natta catalyst. Combining the results of ^{13}C-NMR and DSC, a modeling of DSC melting curve[23] could be used to analyze the stereoselectivity of active center in Ziegler-Natta catalyst. If all of active center in catalyst was perfectly isospecific, which mean that the probability of meso linking of adjacent propylene monomer units was highest (stereospecificity parameter p_{iso} was the highest and defined as 1), polypropylene prepared by the active center would own very narrow DSC curve and the T_m of the DSC curve would be highest (T_m^o); "mmmm" value of polymer would be close to 1. Therefore, there were certain relationships between T_m, "mmmm" value and stereospecificity parameter p_{iso}, which had been reported by Kissin[42]. Fig. 4 was the fitting straight of T_m from DSC curve and "mmmm" value from ^{13}C-NMR. It was found that the highest melting temperature T_m^o was 171.2 °C, which was obtained by extrapolating "mmmm" value to 1 in the straight. And the highest melting temperature T_m^o could be used to calculate the stereospecificity parameter p_{iso} of active center[43]. Fig.5 was the modeling of DSC curve of polypropylene prepared by SID catalyst. It was showed that there were four fitting curves to fit the DSC melting curve of polypropylene, which corresponded to four active centers with different stereospecificity parameter p_{iso}. Combining melting temperature of the fitting curve from Fig. 5 with T_m^o from Fig. 4, the stereospecificity parameter p_{iso} of each active center could be obtained [43]. The stereospecificity parameter p_{iso} and the relative content of active center I_{stereo} and II_{stereo} for different catalyst were listed in Table 8, which corresponded T_{m1} and T_{m2} in DSC curve model and had high stereoselectivity in catalyst. Comparing active center I_{stereo} and II_{stereo} for Cat-1, Cat-3 and Cat-4, relative content of active I_{stereo} and II_{stereo} both increased from Cat-1 to Cat-4, while Cat-5 contained lower content of active center I_{stereo} and II_{stereo} than Cat-4. Meanwhile, the trend of stereospecificity parameter p_{iso1} and p_{iso2} were both similar with the rule of the relative content of active center I_{stereo} and II_{stereo}. It was indicated that the stereoselectivity of catalyst increased as increasing the volume of SID internal donor in catalyst, but SID internal donor with excessive large volume could decrease the stereoselectivity of catalyst. It was reported that Ti active center attached to the surface of (110) facets of $MgCl_2$ crystallites by the coordination of Cl^- on $TiCl_4$ with Mg on $MgCl_2$[44]. Meanwhile, ester internal donor could also coordinate with Mg, which would lead to disperse Ti on surface of $MgCl_2$ crystallites well and decrease the space of Ti active center[27]. It was also confirmed that although some of ester internal donor could be exchanged by external donor during polymerization, the ester internal donor remained in catalyst could significantly impact on the active center of catalyst[31]. Therefore, it was speculated that as increasing the volume of SID internal donor remained in catalyst, the space of active center around internal donor became smaller, which was favor of improving the stereoselectivity of catalyst. However, the excessive large volume of SID internal donor would result in excessive small space of active center, which might be harmful to meso-insertion of propylene units in the polymer chain. Therefore, the stereoselectivity of catalyst decreased. In addition, the structure of SID and DIBP was different, which might lead to the different stereoselectivity of SID and DIBP catalyst.

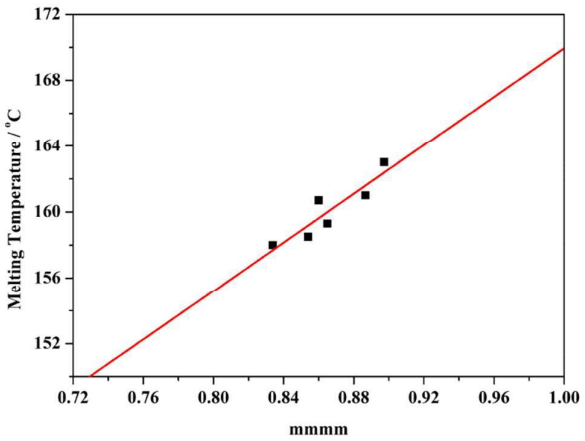


Table 8 Stereospecificity parameter p_{iso} and activation energy ΔE_{act} *(si/re)* of active center calculated from DSC model

Samples	I_{stereo}			II_{stereo}		
	p_{iso1}(°C)	$\Delta E_{act}(si/re)_1$	Yield(%)	p_{iso2}(°C)	$\Delta E_{act2}(si/re)_2$	Yield(%)
Cat-1	99.09	-3.14	30.2	98.62	-2.86	56.2
Cat-2	99.21	-3.23	31.8	98.66	-2.88	58.0
Cat-3	99.26	-3.28	32.2	98.77	-2.93	58.2
Cat-4	99.27	-3.29	33.9	98.81	-2.95	60.5
Cat-5	99.23	-3.25	32.5	98.76	-2.93	59.6
Cat-D	99.49	-3.45	25.6	99.06	-3.12	64.8

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Fig. 4 The fitting straight of T_m from DSC curve and "mmmm" value from ^{13}C-NMR

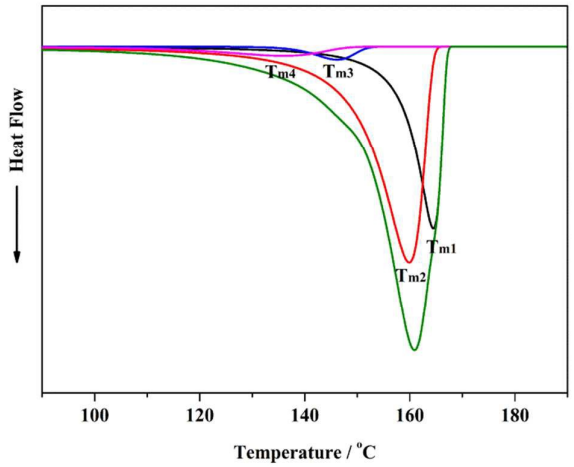

Fig. 5 Resolution and fitting of DSC curves for four components

In addition, stereospecificity parameter p_{iso}, defined as $k_{si}/(k_{si}+k_{re})$ in kinetics, can be used to analyze the activation energy $\Delta E_{act}(si/re)$, as the following equation: $\Delta E_{act}(si/re)=R\cdot T\cdot\ln(k_{si}/k_{re})=R\cdot T\cdot\ln[(1-p_{iso})/p_{iso}]$ [23]. Table 8 showed that the law of $\Delta E_{act(si/re)1}$ *and* $\Delta E_{act(si/re)2}$ values for active center in SID catalyst was both contrary to the trend of isotactic sequence length (from SSA and ^{13}C-NMR), regular triads ''mm'' (from ^{13}C-NMR) and isotacticity index of polypropylene. This trend further confirmed that internal donor in catalyst could impact on the stereoselectivity of active center in Ziegler-Natta catalyst, which led to the changing of the activation energy $\Delta E_{act(si/re)}$ and further influence on the distribution and content of stereo-defects of propylene during polymerization; finally it showed as the general trend of isotactic sequence length and thermal property of polypropylene for different internal donor.

Conclusions

Five salicylates with different size of hydrocarbon substituents on phenyl group were firstly synthesized and employed as ecofriendly internal donors of Ziegler-Natta catalyst for propylene polymerization. The effect of these salicylates and traditional industrial internal donor DIBP on the microstructure of polypropylenes were studied by GPC, SSA and NMR. Meanwhile, the active center in catalyst was studied by deconvolution of GPC curves and DSC model. GPC results showed that the molecular weights of polypropylene prepared by SID internal donors were all lower than that prepared by DIBP, which indicated that polypropylene chain produced by SID internal donor was easier to transfer than that prepared by DIBP internal donor. Deconvolution of GPC curves showed that as increasing the volume of SID internal donor, the relative contents of active center for high molecular weight increased, while the relative contents of active center for low molecular weight decreased. The isotactic sequence length from ^{13}C-NMR and SSA both gradually increased from SID-1 to SID-4, while SID-5 gave polypropylene with lower meso sequence length than SID-4, which was similar with the trend of isotacticity index and regular triads ''mm'' of polypropylene. The general trend of stereo-defect in polypropylene chain was explained by the stereoselectivity of active center in catalyst for different internal donors, indicating that appropriately increasing the volume of SID internal donor could benefit to improve the stereoselectivity of catalyst, but excessive large volume of SID internal donor would reduce stereoselectivity of catalyst. In addition, it was found that the catalyst activities of catalyst containing SID internal donors with proper volume were higher than that catalyst containing DIBP internal donor. And the isotactic sequence length and isotacticity index of polypropylene prepared by isobutyl 2-benzyloxy-3,5-isopropyl benzoate were close to that produced by DIBP internal donor.

Acknowledgements

The authors express thanks for the supports of the science and education integration innovation project of Molecular Science of Chinese Academy of Sciences.

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Volume of eofriendly salicylate internal donor for propylene polymerization has important impact on catalyst active center and microstructure of polypropylene.

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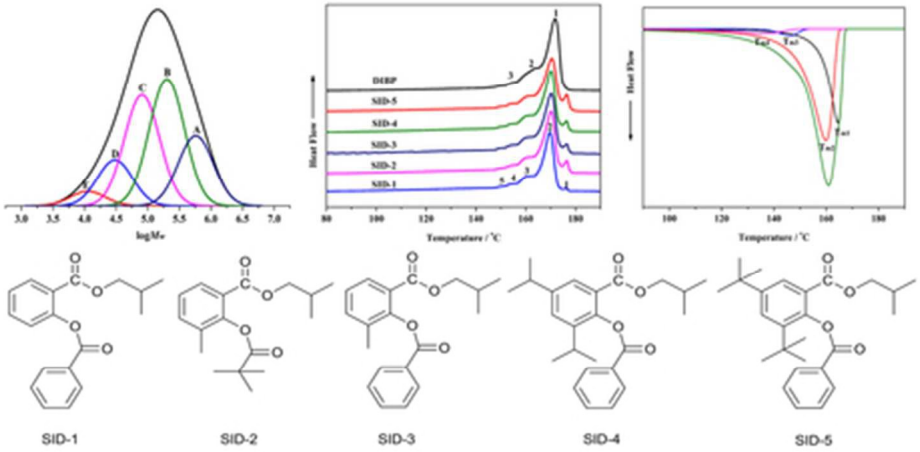

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