

Tuning the short chain branch distribution of ethylene and 1-hexene copolymers by SiO₂-supported silyl chromate catalyst with different Al-alkyl co-catalysts

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ABSTRACT

SiO₂-supported silyl chromate catalyst is an important industrial catalyst for production of high grade HDPE pipe materials. The control of the short chain branch (SCB) distribution using this catalyst system is still a great challenge. In this work, ethylene and 1-hexene copolymers were synthesized using SiO₂-supported silyl chromate catalyst combined with triisobutylaluminium (TIBA), triethylaluminium (TEA) and mixed TIBA/TEA at molar ratio 1:1 (TIBA/TEA/1:1) as three different Al-alkyl co-catalysts. The temperature rising elution fractionation (TREF) and successive self-nucleation and annealing (SSA, by DSC) methods were combined to analyze the short chain branch distribution (SCBD) of these ethylene/1-hexene copolymers. The results showed that different types of co-catalyst had a great influence on SCBD of ethylene/1-hexene copolymers. The copolymer produced with TIBA showed better SCBD than the copolymer produced with TEA, and the copolymer produced with TIBA/TEA/1:1 showed a SCBD in between those with TIBA and TEA. **Polyolefins J (2014) 1: 93-105**

Keywords: ethylene/1-hexene copolymerization; Al-alkyl co-catalyst; polymerization kinetics; SiO₂-supported silyl chromate catalyst; short chain branch distribution;

INTRODUCTION

Nowadays chromium-based catalysts including SiO₂-supported inorganic chromium oxide catalyst (Phillips catalyst) and SiO₂-supported organic silyl chromate catalyst (S-2 catalyst) are widely used as important industrial catalysts to manufacture polyethylene products for various applications such as containers, automobile parts, packing films and pipe materials, which produce nearly 40% polyethylene resins in the

world market [1], mainly high density polyethylene (HDPE). These two catalysts have their own unique features on ethylene polymerization behavior and polyethylene products.

In more than 50 years, many publications, including several important literature reviews by Hogan [2, 3], McDaniel [4-6], Zecchina et al. [7], and Liu et al. [8], have been published on ethylene polymerization, performance and polymerization mechanism using Phillips catalyst and the structures of the resulting

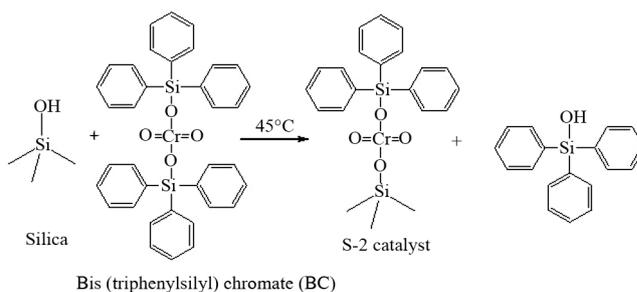
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polymer, etc. However, S-2 catalyst has not been fully investigated, especially on the effects of different Al-alkyl co-catalysts (such as TIBA and TEA) during the past several decades. Traditionally, S-2 catalyst is directly synthesized from bis(triphenylsilyl)chromate (BC) supported on thermal-treated silica gel by wet impregnation method as shown in Scheme 1. It is well known that the catalytic activity is obviously increased when BC is supported on silica gel and its treatment with Al-alkyl [9]. Gaspar et al. have found that S-2 catalyst shows lower polymerization activity than Phillips catalyst due to S-2 catalyst with less Cr⁶⁺ and Cr²⁺ active species in their calcined and reduced states, respectively [10, 11]. However, S-2 catalyst using Al-alkyl co-catalyst could produce polyethylene with broader molecular weight distribution (MWD) on both ends of high and low molecular weight segments than that of Phillips catalyst without using a co-catalyst [12].

On the other hand, the structure of the HDPE materials produced by ethylene/ α -olefin copolymerization with chromium-based catalysts has also been studied intensively by many researchers. The molecular weight (MW), MWD and short chain branch distribution (SCBD) of ethylene/ α -olefin copolymers are regarded to be the most important key factors to influence the property of HDPE materials. The MW and MWD have been fully investigated initially by many researchers such as Kennedy et al. [13] and Jordens et al. [14]. Most researchers recognize that many mechanical properties of HDPE material are greatly influenced by MW and MWD. The relatively high MW and broad MWD are required for high grade HDPE materials. Then, the SCBD has become of great concern because of its vital role on the long term mechanical properties of HDPE pipe materials [15-19]. More and more publications have focused on the SCBD of ethylene/ α -olefin copolymers by many researchers such as Soares et al. [20], Hubert et al. [21, 22], Deslauriers et al. and McDaniel et al. [23, 24]. In summarizing their experiments and previous literature in order to confirm the important effect of SCBD of ethylene/ α -olefin copolymers on the long term mechanical properties of HDPE pipe materials they have concluded that the more short chain branches (SCB) on the high MW segments and less inserted on low MW segments would be a helpful approach to achieve high performance HDPE pipe materials [25]. This concept is now widely accepted

in both academic circle and industry. Therefore, it is important and valuable to regulate the MWD and SCBD in HDPE. Recently, we just reported that a hybrid inorganic and organic Cr-based catalyst could produce ethylene and 1-hexene copolymer with better SCBD through modification of the catalyst active center [26]. However, up to now, the effects of Al-alkyl co-catalysts in tuning the SCBD of the product for Cr-based catalysts are rarely reported.

Some effective methods were found to be able to analyze the SCBD of ethylene/ α -olefin copolymers for HDPE materials. The most effective and quantitative method for SCBD characterization of HDPE was size exclusion chromatography-Fourier transform infrared spectroscopy (SEC+FTIR) which was reported by Deslauriers et al. and McDaniel et al. [23, 24]. However, it has still been a great challenge to use SEC+FTIR method to characterize SCBD in HDPE samples because usually there is a very low concentration of SCB in HDPE samples with relatively low comonomer content incorporated especially in their high MW fractions. Some indirect methods such as temperature rising elution fractionation cross ¹³C-NMR (TREF+¹³C-NMR) [27, 28] or TREF cross FTIR [15] etc. could be alternative methods for SCBD characterization of HDPE samples. In these methods, the copolymers are separated to several fractions on the basis of crystallinity and then analyzed for subsequent characterization [29]. However, most characterizations for the SCBD of ethylene/ α -olefin copolymers by those methods are based on crystallinity such as successive self-nucleation annealing (SSA) [30], step crystallization (SC) [31], TREF+SSA [32] and TREF+SC [33, 34] which are mainly focused on low density polyethylene (LDPE) or linear low density polyethylene (LLDPE) polymers [35-43] with high comonomer incorporated and seldom considered for HDPE materials with less comonomers inserted. In our previous work [26, 44], TREF+SSA was



Scheme 1. Preparation of S-2 catalyst.

used to characterize HDPE pipe materials. Although ^{13}C -NMR was considered as a quantitative and direct method to characterize SCBD of HDPE samples, it was time consuming with high cost. On the other hand, SSA could effectively and qualitatively describe the relative comonomer content and its SCBD in HDPE pipe materials with low cost.

Herein it could be summarized that it is still a great challenge to tune the SCBD of the HDPE pipe materials. As mentioned above, although some researchers reported that modifying the catalyst active center could alter the SCBD of HDPE, there has not yet been any report on how the Al-alkyl co-catalyst could regulate the SCBD in HDPE used as pipe materials. In this work, three different co-catalysts (TIBA, TEA and TIBA/TEA/1:1) were used with SiO_2 -supported silyl chromate S-2 catalyst to produce ethylene/ α -olefin copolymers. These copolymers were characterized by HT-GPC, DSC, TREF+SSA methods.

EXPERIMENTAL

Raw materials

The high purity nitrogen ($\text{N}_2 \geq 99.999\%$) used in the catalyst preparation was further purified by passing through one column of 4\AA molecular sieves (purchased from Sinopharm Chemical Reagent Co., Ltd.) for dehydration and one column of silver molecular sieves (28 wt% of silver (I) oxide on alumina, purchased from Sigma-Aldrich) for deoxidation. The gases for ethylene/1-hexene copolymerization including high purity nitrogen and ethylene monomer were directly purified by commercial gas purification equipment, which was purchased from Dalian Samat Chemicals Co., Ltd. Each gas was purified by passing through two large columns filled with different molecular sieves for dehydration and deoxidation. All the solvents including n-hexane (AR grade) and n-heptane (AR grade), which were also purchased from Sinopharm Chemical Reagent Co., Ltd., were first purified by 4\AA molecular sieves and subsequently purged through distillation in the presence of sodium metal slices and diphenyl ketone as indicator until the indicator showed pure blue before use or for storage in a stainless-steel storage tank under purified nitrogen. Bis(triphenylsilyl) chromate (BC, total purity $\text{BC} \geq 95\%$) and silica gel (Grace Davison 955, surface

270.4 m^2/g , pore volume 1.65 cm^3/g and average pore size 24.5 nm) were donated from Qilu Branch Co., SINOPEC. Triisobutylaluminium (TIBA, 1.0M in heptane) and triethylaluminium (TEA, 1.0M in heptane) were purchased from Alfa Aesar. 1-Hexene (total purity 97%) as comonomer was purchased from J&K Chemical Co. 1-Hexene was also purged through distillation in the presence of sodium and diphenyl ketone until the indicator showed pure blue and transferred into storage tank under purified nitrogen before use.

Catalyst preparation

A 10 gram silica gel was treated at 600°C . By using 150 mL purified n-hexane as solvent, chromium precursor BC was supported on treated silica gel support, continuously stirred for 6 h in a flask at 45°C under the nitrogen atmosphere till complete reaction to prepare an S-2 catalyst. The chromium loading (based on mass of Cr) was 0.25 wt%. Finally, the S-2 catalyst was dried at 80°C under the nitrogen atmosphere for 5 h to remove the solvent and transferred into a glove box for storage before use.

Ethylene/1-hexene copolymerization

The flow chart of ethylene/1-hexene copolymerization is shown in Figure 1. In this work, the semi-batch slurry polymerization mode was utilized for ethylene/1-hexene copolymerization. A 0.5 L volume stainless-steel reactor equipped with a mechanical stirrer, a manometer, a thermocouple, an external heating and cooling jackets and a device for breaking catalyst bottle within the reactor was used for the polymerization. About 200 mg catalyst was previously weighted and sealed into a small ampoule bottle in the glove box and then fixed in the interior of the reactor. The reactor was vacuumed and purged by nitrogen keeping at 90°C by a silicone oil bath with thermostat for 1.5 h. Then 200 mL n-heptane was pressed from the storage tank into the reactor at ethylene pressure of about 0.12 MPa and a certain amount of 1-hexene was pressed into the reactor (6 mL, i.e. the volume ratio of 1-hexene and the solvent of 3 vol%) and a certain amount of co-catalyst, such as TIBA, TEA and TIBA/TEA/1:1 (Al/Cr molar ratio = 20) was also injected into the reactor with mechanically stirring. Thereafter, the temperature of the reactor was adjusted to a certain polymerization temperature and then the entire reactor

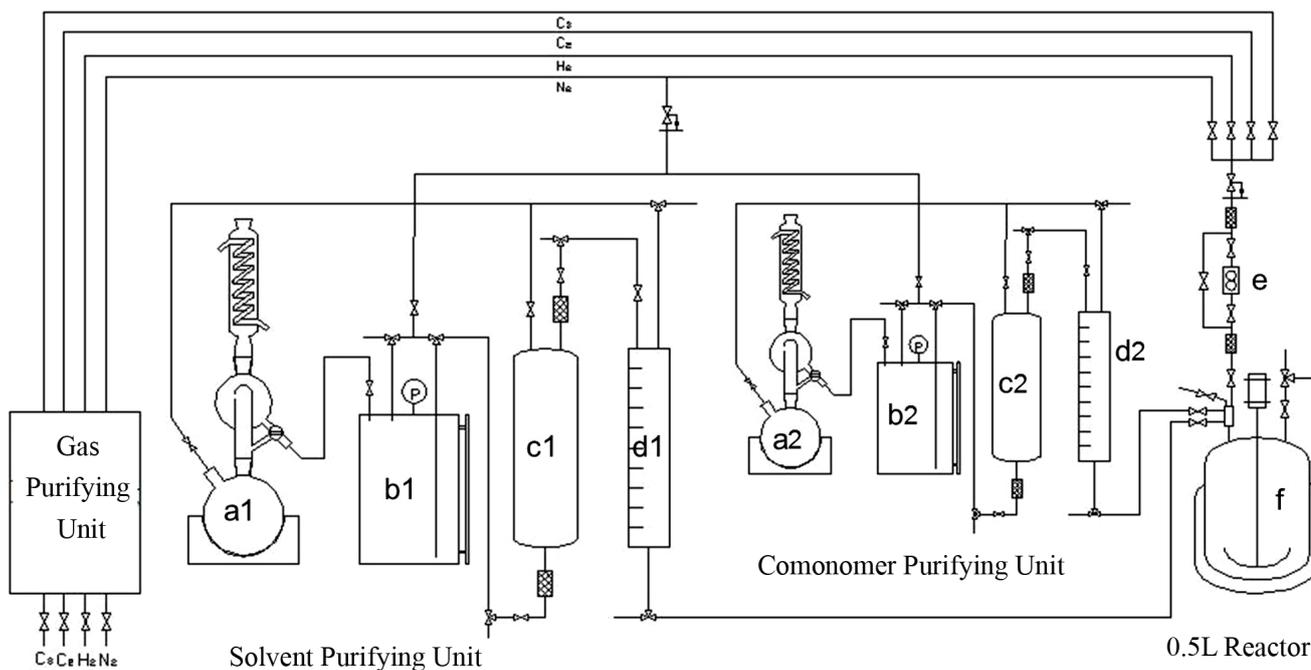


Figure 1. Flow chart of ethylene/1-hexene polymerization system. a1/a2: solvent/comonomer reflux unit, b1/b2: solvent/comonomer storage tank, c1/c2: solvent/comonomer refining column, d1/d2: solvent/comonomer measuring tank, e: mass flowmeter for ethylene monomer and f: polymerization reactor.

was kept at that temperature under the ethylene pressure of about 0.12 MPa. Until the solution was saturated at a certain higher ethylene pressure, the polymerization was initiated by breaking the catalyst bottle to carry out at that polymerization temperature as mentioned above for 1 h. The instantaneous consumption of monomeric ethylene was recorded by an on-line mass flow meter (BrooksSAL5851). Finally, the polymerization was terminated by adding 200 mL ethanol/HCl solution and the polymers were collected. All the obtained polymers as mentioned above were washed again with ethanol, filtered from the solution and dried under vacuum at 60°C for at least 6 h.

Characterization of polymers

Gel permeation chromatography (GPC)

The MW and MWD of polymers were measured by high temperature GPC (HT-GPC, Agilent PL-220) with PL-Mixed B gel column at 150°C and the flow rate of 1.0 mL/min. 1,2,4-Trichlorobenzene (TCB) and polystyrene (PS) were used as solvent and standard sample, respectively.

Differential scanning calorimetry (DSC)

About 6 mg polyethylene sample was weighed and then heated to 150°C at the rate of 10°C/min for 5

min to remove thermal history, then cooled down to 50°C at 10°C/min and finally heated to 150°C at 10°C/min by DSC analyzer (TA, DSC Q200) to record the second heating curve and melting temperature (T_m). The enthalpy of fusion (ΔH_f) of each sample was calculated by this DSC curve.

TREF+SSA

In this work, a home-made TREF system was used to fractionate the samples, which were mainly composed of a silicone oil bath with a Huber thermostat (POLYTSTAT CC3±0.02°C), a 850 mL column type fractionation column filled with quartz sand (AR), a pump (KNF Lab, STEPDOS 08 S) and a rotary evaporator (EYELA). About 1.5 g sample was heated and fully dissolved in about 150 mL xylene in a three-necked flask with stirring for at least 2 h, quickly transferred into the fractionation column with pre-heated quartz sand which was emerged into a silicone oil bath with thermostat. The sample was kept dissolved at 135°C for 1 h and then cooled down to 30°C at 5°C/h. After cooling, the temperature was raised to the selected temperature and kept for at least 1 h for dissolution of the corresponding fraction. Hereafter during the elution step, the fraction at this selected temperature was collected in a collection bottle in elution solution pressed out from fractionation column

by pump under nitrogen atmosphere. Before the next fraction was collected, the pure xylene was added into the fractionation column and then temperature was raised step-by-step continuously. The whole process including heating and cooling steps was operated under nitrogen atmosphere. In this work, the solvent of each fraction of samples was eliminated by rotary evaporator, and the polymer of each fraction was deposited with isopropyl alcohol and finally vacuumed at 60°C for 12 h.

About 6 mg fraction of PE sample was heated to 160°C at 50°C/min and kept at this temperature for 5 min to remove thermal history. It was then cooled down to 0°C for 3 min to create an initial “standard” thermal history, and heated to 125°C at 25°C/min for 5 min, which was the first selected self-seeding and annealing temperature denoted as T_s . Again the sample was cooled down to 0°C and the crystals which could not melt at T_s would self-nucleate during the cooling step. Thereafter, the sample was re-heated to the second T_s that was 5°C lower than the previous T_s ($\Delta T = 5^\circ\text{C}$) at 25°C/min for 5 min. At this T_s , parts of melted crystals were nucleated by the unmelted crystals under isothermal crystallization. The rest of unmelted crystals was annealed and crystallized in the next cooling step down to 0°C. This process was repeated until the last T_s (80°C) reached, and the sample was cooled down to 0°C again. Finally the thermally treated samples were heated from 0°C to 160°C at 25°C/min and the corresponding endothermic curves were recorded by a TA DSC analyzer (DSC Q200). According to literature the SSA method is introduced as a common approach [42, 43, 45] which is usually applied to characterize the lamella thickness distribution of polymer.

RESULT AND DISCUSSION

In industry, the traditional SiO_2 -supported silyl chromate S-2 catalyst is an important catalyst for commercial production of HDPE products. However, it still has some unsatisfactory aspects such as low activity and undesirable SCBD, etc.. Thus, further modification of this important industrial catalyst is needed. Recently, we just reported that a hybrid inorganic chromium oxide (Phillips catalyst) and organic silyl chromate catalyst (S-2 catalyst) could produce ethylene and 1-hexene copolymer with higher

activity and better SCBD than the S-2 catalyst through modification of the types of active center [26]. As it is well known, the Al-alkyl co-catalyst is also one of the key factors governing the copolymerization behavior and the microstructure of the copolymer. However, up to now, the effects of Al-alkyl co-catalysts in tuning the SCBD of the copolymer obtained from S-2 catalyst have not been reported yet. In this work, the influences of different Al-alkyl co-catalysts on the ethylene/1-hexene copolymerization of the S-2 catalyst would be investigated in terms of the kinetics and the characterization of copolymers especially the SCBD characterization by TREF+SSA etc. methods.

The copolymerization mechanism in relation to the nature of co-catalysts

Co-catalyst is an important factor in polymerization mechanism, which could influence the activity of catalyst and modify the polymers as well. In this work, TIBA, TEA and TIBA/TEA/1:1 were used with S-2 catalyst in subsequent ethylene/1-hexene copolymerization reactions. Firstly, the amount of co-catalyst was one factor considered in this copolymerization. With the increase of Al/Cr molar ratio, the activity of S-2 catalyst with Al-alkyl co-catalysts increased to a maximum value and then decreased. The roles of co-catalyst are known to be able to reduce the active precursor, alkylate the active site to initiate the first polymer chain and remove the poisons such as oxygen, moisture or by-products [6]. But a very high dosage of co-catalyst could lead to deactivation of the active site through over-reduction and also enhancement of the chain transfer reaction to co-catalyst, which was not beneficial for increasing the activity of the catalyst. In this work, Al/Cr=20 was used as the proper dosage of co-catalyst in the subsequent investigation. Secondly, from our previous work [26] and some literature report [1], there were some main effects of 1-hexene such as comonomer, chain transfer reagent and reduction reagent for reducing the surface silyl chromate Cr^{6+} species. So the added amount of 1-hexene was the other factor considered in the ethylene/1-hexene copolymerization. A minute amount of 1-hexene could not affect the copolymerization behavior of the catalyst and the microstructures of its polymer, and a very large amount of 1-hexene might not be beneficial for the reduction of surface chromate species. It could very much facilitate the other two aspects of 1-hexene

as comonomer and chain transfer reagent. In this work, 1-hexene of 3 vol% was used in the subsequent investigation.

The kinetic curves of ethylene/1-hexene copolymerization of the S-2 catalyst with different co-catalysts are shown in Figure 2. It has been found that the kinetic curves of copolymerization with these co-catalysts were similar, which were composed of two types of polymerization behavior in the S-2 catalyst. One was promoted to fast active site formation followed by fast decay and the other led to slow active site formation followed by a slow decay. Similar kinetic results of ethylene homopolymerization were reported by Zhang et al. [26] and Xia et al. [46]. Based on the similarity of kinetic results between Xia's and ours, it was inferred that there might exist two kinds of Cr active sites in the ethylene/1-hexene copolymerization with the S-2 catalyst system: a fast formation and fast decay type and another slow formation and slow decay type, which might be derived from the reduction of the surface silyl chromate Cr^{6+} precursors by ethylene monomer and Al-alkyl co-catalyst and 1-hexene comonomer. Because of the difference in reducibility of the three different Al-alkyl co-catalysts, the activity of copolymerization could be different. The activity of copolymerization with TIBA is higher than the activity of copolymerization with TEA, and the activity of copolymerization with TIBA/TEA/1:1 is in between the two co-catalysts as shown in Table 1.

In order to further investigate the influence of co-catalysts on the copolymerization, the obtained polymers were systematically characterized using HT-GPC and DSC methods. The results are shown in Table 1, Figure 3 and Figure 4. Comparing the HT-GPC results of their copolymers in Figure 3, it was found that the MWD of TEA sample was broader than that from TIBA sample. The TIBA was inclined to create high molecular weight segment and TEA was inclined to create low molecular weight segment, whereas the TIBA/TEA/1:1 co-catalyst could produce a bimodal copolymer. This might have been due to stronger

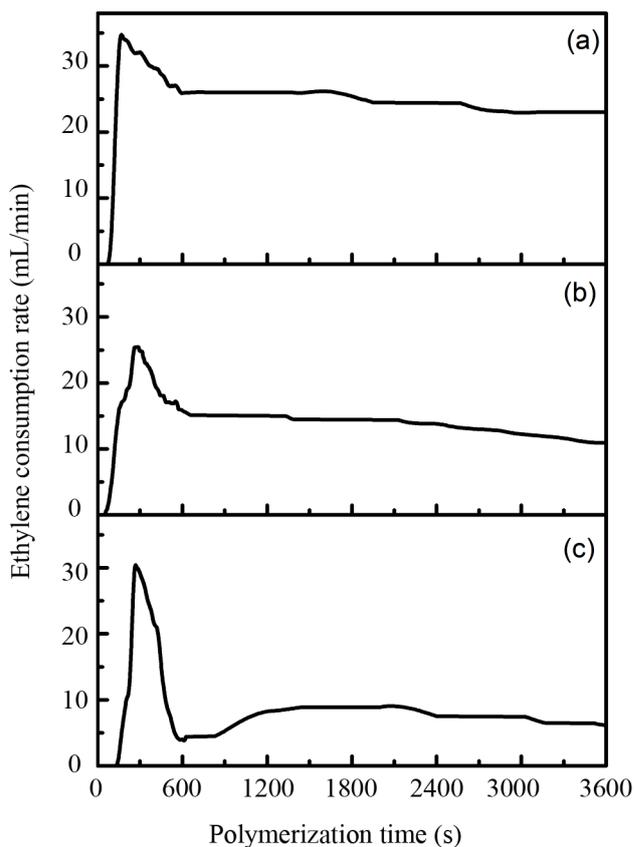


Figure 2. The kinetic curves of copolymerization of S-2 catalyst with different co-catalysts. (a) TIBA (b) TIBA/TEA/1:1 and (c) TEA.

effect of TEA on chain transfer compared with that of TIBA. Through the comparison made on the activity and MWD of three co-catalysts, it was suggested that TIBA/TEA/1:1 co-catalyst showed well-balanced properties. It had higher activity than TEA co-catalyst, and its polymer had higher average MW and broader MWD than that from TIBA co-catalyst. From the DSC curves of these three copolymers as shown in Figure 4 and the data from Table 1 we have found that their T_m are almost identical, but the ΔH_f of TIBA is larger than TEA sample, and that of TIBA/TEA/1:1 sample is in between the two other samples. It means that the content of the comonomer of TEA is higher than TIBA and that of TIBA/TEA/1:1 sample is in between the two.

Table 1. Copolymerization activities of S-2 catalyst with different co-catalysts and the characterization of their polymers

No.	Sample	Activity (kgPE/molCr.h)	T_m ($^{\circ}\text{C}$) ^(b)	ΔH_f (J/g) ^(b)	M_w ($\times 10^5$) ^(c)	PDI ^(d)
1	TIBA	246	132.1	188.8	4.37	21.3
2	TIBA/TEA/1:1 ^(a)	178	132.1	184.1	5.23	28.5
3	TEA	162	131.9	181.6	4.48	29.8

Conditions: catalyst 200 mg, ethylene 0.4 MPa, n-heptane 200 mL, 1-hexene 3.0mL, Al/Cr ratio=20, 90 $^{\circ}\text{C}$, 1 h (a) TIBA/TEA/1:1 was mixed TIBA/TEA as 1:1 mole ratio; (b) T_m and ΔH_f by DSC thermograms; (c) M_w estimated by HT-GPC in TCB; (d) PDI (M_w/M_n)

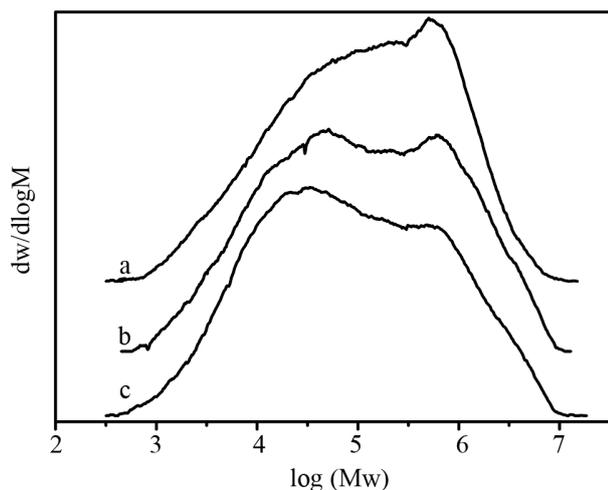


Figure 3. The HT-GPC curves of TIBA, TIBA/TEA/1:1 and TEA samples. (a) TIBA, (b) TIBA/TEA/1:1 and (c) TEA.

In order to further investigate the difference between TIBA, TIBA/TEA/1:1 and TEA co-catalysts the various aspects of copolymerization behavior and the microstructures of their copolymers were taken into consideration. The results showed that catalysts with TIBA, TEA and TIBA/TEA/1:1 showed many differences in such aspects as activity, kinetic curve and ΔH_f and MWD of their copolymers as shown in Table 1, Figures 3 and 4. Herein after the above comparison, the difference of SCBD between these three co-catalysts has remained unclear. Further comparison of the SCBD of their three copolymers is still needed.

Comparing SCBD in three copolymers

By comparing S-2 catalyst performance in ethylene/1-hexene copolymerization with that of three different co-catalysts and the MWD of the final copolymers, the SCBD of each respective copolymer was further investigated. The SCBD was the most important structural property for the copolymers because it could greatly influence the long term performance of HDPE pipe materials. The SCBD of the three copolymers obtained from TIBA, TIBA/TEA/1:1 and TEA co-catalysts were compared by TREF+SSA method. In our previous work [34], we used a similar method namely “TREF+SC” to compare qualitatively the SCBD of two commercial HDPE pipe materials obtained from an identical SiO_2 -supported silyl chromate S-2 catalyst through the lamella thickness distributions of their copolymers. This method was demonstrated to be an effective and indirect process for the qualitative

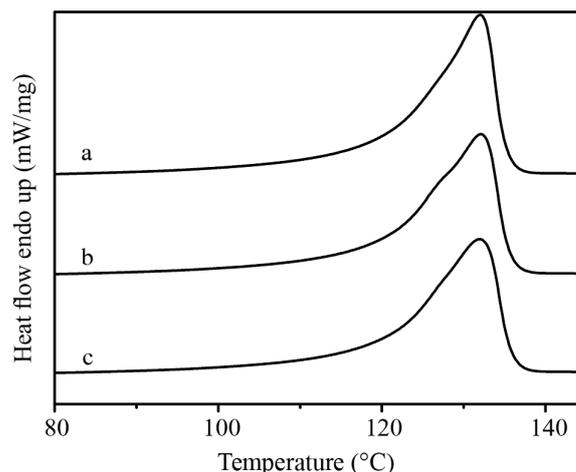


Figure 4. The DSC curves of TIBA, TIBA/TEA/1:1 and TEA samples. (a) TIBA, (b) TIBA/TEA/1:1 and (c) TEA.

SCBD characterization of HDPE with lower cost and less time consumption. Herein, the SSA method as a similar characterization method was used to substitute SC method, which was more efficient than SC method because of its less time consumption.

First, the preparative TREF method was applied to physically fractionate the ethylene/1-hexene copolymers into several fractions based on crystallinity. The weight distributions of TREF fractions of TIBA, TIBA/TEA/1:1 and TEA samples are shown in Figure 5. It is found that all three curves are narrow as typical HDPE samples with very small amount of low and high temperature fractions. In our previous work [34], two important conclusions were made: first, the low temperature fraction corresponded to low average molecular weight segment, and the high temperature fraction corresponded to high average molecular weight segment. Second, the relatively higher SCB content on the highest MW segment and the relatively lower SCB content on the lowest MW segment were much more beneficial for the long term performance of high grade HDPE used as pipe materials. This conclusion was also consistent with Krishnaswamy's results [25].

Thereafter, the SSA method was used to characterize the SCBD of those six TREF fractions of each sample indirectly. The difference between the SSA curves of high temperature fractions of three samples such as 103~108°C, 108~115°C and 115~124°C fractions in Figure 6 was too small to be clearly distinguished, which showed a strong single peak with a broad shoulder. The further peak fitting and calculation methods were needed in order to achieve more accurate results. The

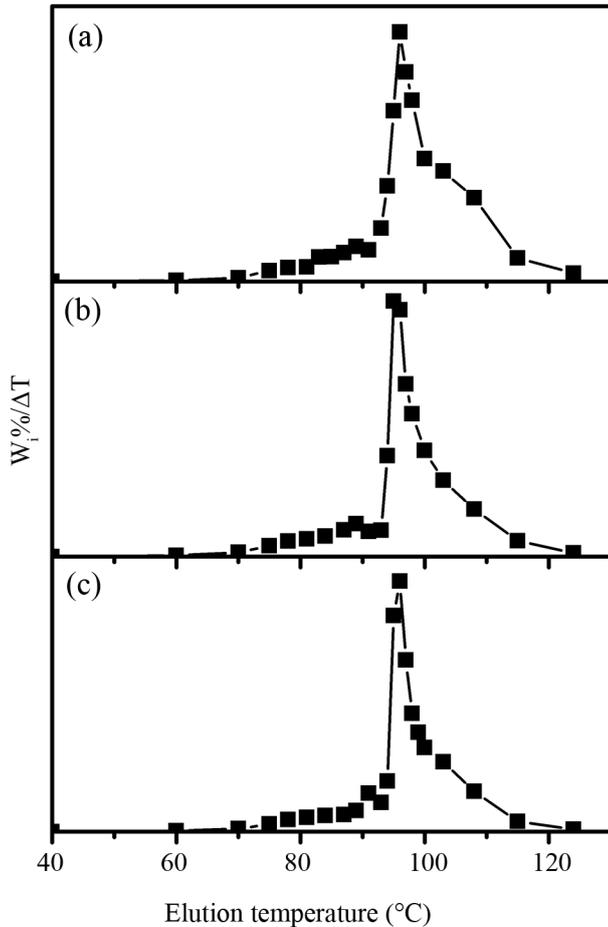
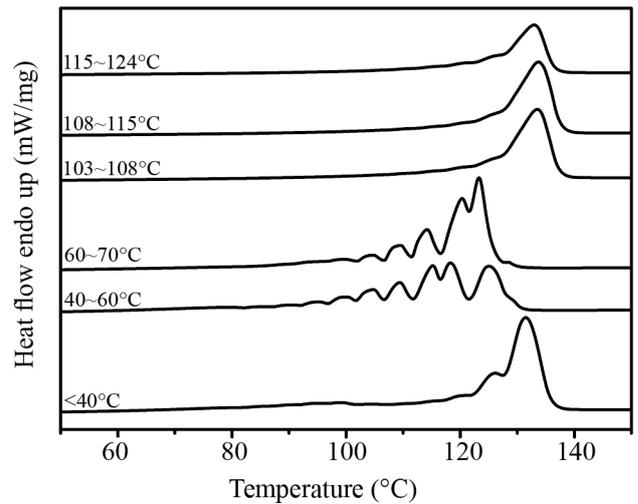


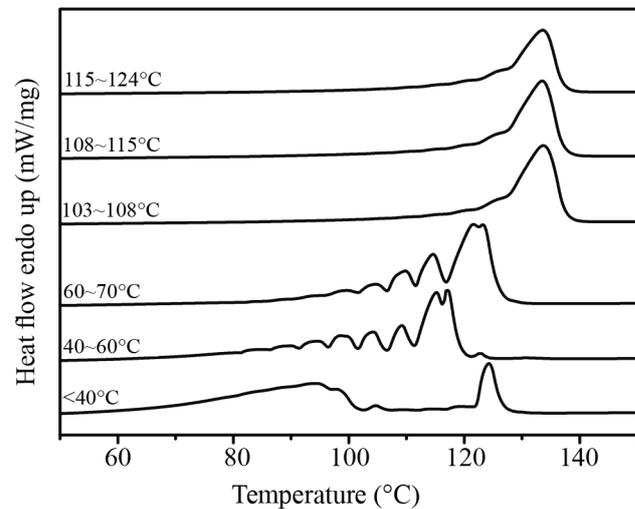
Figure 5. Weight distribution curves of fractions of TIBA, TIBA/TEA/1:1 and TEA samples after TREF. (a) TIBA, (b) TIBA/TEA/1:1 and (c) TEA.

main difference appeared on low temperature fraction group, especially that of $<40^{\circ}\text{C}$ fraction. It was clear that the DSC-SSA curves of $<40^{\circ}\text{C}$ fractions obtained from TEA co-catalyst showed much more multiple peaks accentuated at lower temperature, the peaks of SSA curves of $<40^{\circ}\text{C}$ fractions obtained from TIBA co-catalyst were mainly at higher temperature, and the multiple peaks of SSA curves of $<40^{\circ}\text{C}$ fractions obtained from TIBA/TEA/1:1 co-catalyst existed at both lower and higher temperatures. This result suggested that the copolymer obtained from TEA co-catalyst had much more thinner lamella in $<40^{\circ}\text{C}$ fraction than those obtained from TIBA and TIBA/TEA/1:1 co-catalysts, meaning that the co-monomer content distribution of TEA with higher 1-hexene incorporated at low crystalline temperature and also low molecular weight segment.

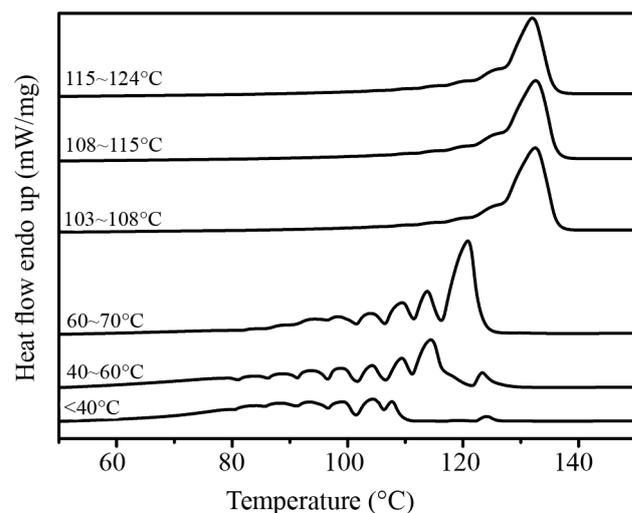
In order to accurately compare the SCBD of these three samples through the lamella thickness distribution, it was necessary to calculate the lamella



(a)

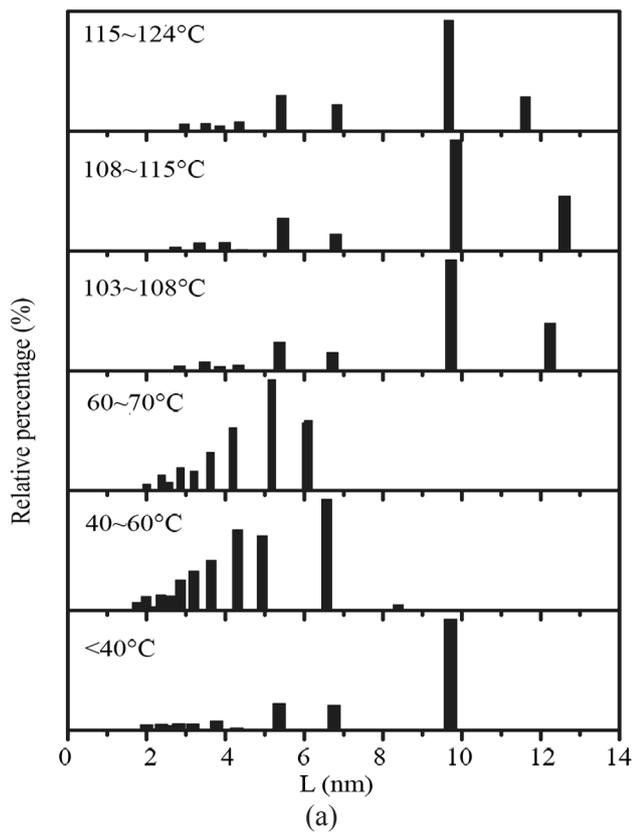


(b)



(c)

Figure 6. SSA curves of different fractions of TIBA, TIBA/TEA/1:1 and TEA samples. (a) TIBA, (b) TIBA/TEA/1:1 and (c) TEA.



thickness of each selected fraction of three samples by multiple peaks fitting and identify their distribution. Because the content of SCB in TREF fractions could influence the lamella thickness of each fraction, and the more incorporated comonomer led to thinner lamella thickness. Herein the modified Thomas Gibbs equation (as shown in Equation 1) was applied to establish a correlation between temperatures and simulate lamella thickness (L).

$$L = \frac{2\sigma T_{mp}^0 \Delta z}{\Delta h (T_{mp}^0 - T_{mp})} \quad (\text{Equation 1})$$

where T_{mp}^0 = the melting point of linear polyethylene (418 K) [43], T_{mp} = the melting point of each endo thermal peak in the SSA curve of each fraction of the three copolymers after peak fitting, σ = the value of lamellar surface free energy (5.0 kJ.mol⁻¹), Δh = the enthalpy of fusion of each C₂H₄ group (8.2 kJ.mol⁻¹) and Δz = the length of C₂H₄ unit (0.254 nm)[47].

By calculation of lamella thickness for each selected fraction of copolymer samples obtained

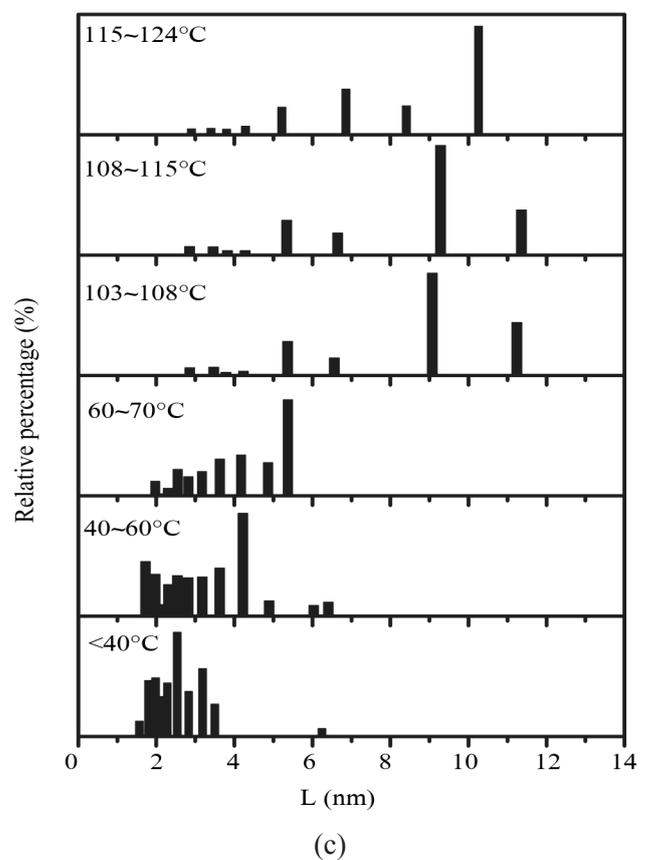
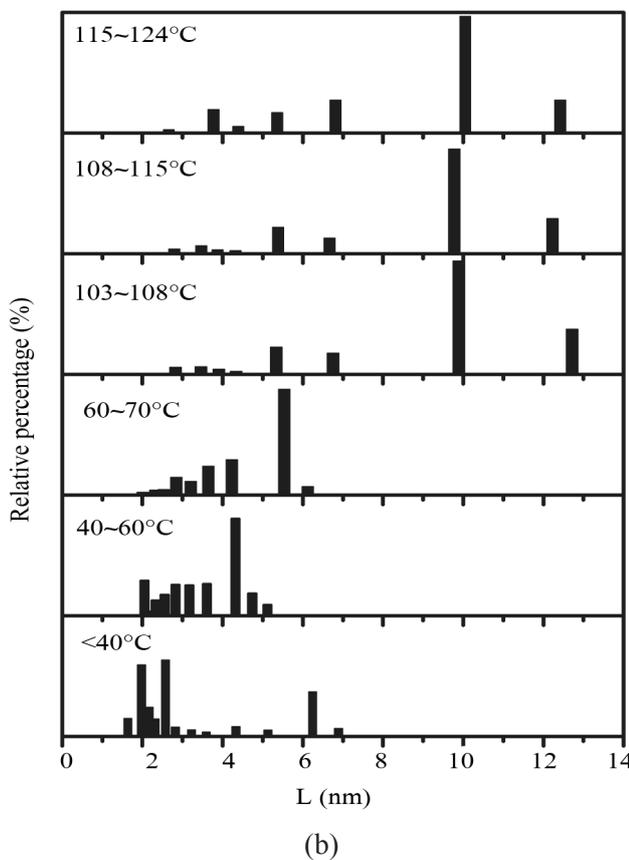


Figure 7. Lamella thickness distribution of different fractions of TIBA, TIBA/TEA/1:1 and TEA samples. (a) TIBA, (b) TIBA/TEA/1:1 and (c) TEA.

from TIBA, TIBA/TEA/1:1 and TEA, the results of lamella thickness distribution are shown in Figure 7. Firstly, through the comparison of the lamella thickness distribution of the three copolymer samples at highest temperature fraction (115~124°C fraction, corresponding to the highest MW segment of the copolymer), it may be suggested that the lamella thickness of copolymer obtained from TEA co-catalyst is similar and slightly thinner than those obtained from TIBA and TIBA/TEA/1:1 co-catalysts. This result indicates that the corresponding relative SCB content of copolymers in the highest MW segment obtained from TEA co-catalyst are slightly higher than those obtained from TIBA and TIBA/TEA/1:1 co-catalysts. Secondly, in the lowest temperature fraction (<40°C fraction, corresponding to the lowest MW segment), the copolymers obtained from TEA co-catalyst show much thinner lamella (corresponding to much higher relative SCB content) than those obtained from TIBA co-catalyst, and the value of thinner lamella of the copolymer obtained from TIBA/TEA/1:1 co-catalyst lies in between the two. Hence the copolymers obtained from TIBA co-catalyst should have the thickest lamella (corresponding to the least relative SCB content) in lowest MW segment of the three copolymers. The result is consistent and much more apparent with the previous results of directly comparing their DSC-SSA curves of low temperature fractions. Then, through the comparison of the lamella thickness distribution, it may be suggested that the thickest lamella of each temperature fraction of copolymers obtained from TEA co-catalyst should be thinner than those of copolymers obtained from TIBA co-catalyst, which means that the relative SCB content of copolymers obtained from TEA co-catalyst should be higher than that from TIBA co-catalyst. This result is consistent with the comonomer content of three samples analyzed by DSC as discussed above. Finally, considering the relative SCB content in both the lowest and highest temperature fractions of the three copolymers, it is suggested that the SCBD of copolymer obtained from TIBA co-catalyst is the best one among the three copolymers. This may be because its copolymer shows similar relative SCB content in the highest MW segment as those obtained from TEA and TIBA/TEA/1:1 co-catalysts. In contrast, it has the least relative SCB content in the lowest MW segment of the three copolymers.

Herein the comparison of SCBD of the copolymers

obtained from three Al-alkyl co-catalysts as TIBA, TEA and TIBA/TEA/1:1 had been systematically investigated by TREF+SSA method. In this method, the higher temperature fraction in TREF corresponded to the higher molecular weight segment, the comonomer content of the fractions of the lowest and highest temperature (corresponding to the lowest and highest MW segment) seemed to be the key factor greatly influenced SCBD and the microstructure of the copolymers, and the SSA was an indirect way to describe the relative comonomer content with lower cost and less time consumption compared with ¹³C-NMR and SC, which had been systematically investigated in our previous work [26, 34] as mentioned before. Therefore it has been an effective method to characterize the SCBD of the copolymers, where the copolymer obtained from TIBA has shown the best SCBD among the three. This SCBD was more beneficial for the high grade HDPE pipe materials as mentioned above in determining the slow crack growth rate.

CONCLUSION

In this work, three different Al-alkyl co-catalysts such as TIBA, TEA and TIBA/TEA/1:1 were used with SiO₂-supported silyl chromate S-2 catalyst for ethylene/1-hexene copolymerization in order to tune the SCBD of the copolymers. By investigating the copolymerization behavior and the microstructures of copolymer such as MW, the 1-hexene incorporation, especially SCBD through HT-GPC, DSC and TREF+SSA, etc. methods, the influences of co-catalysts were systematically investigated. Through the comparison of the activity and MWD of TIBA, TIBA/TEA/1:1 and TEA three co-catalysts, the copolymerization with TIBA showed the highest activity and produced PE with the highest MW, while copolymerization with TEA showed the lowest activity and produced PE with the lowest MW. The copolymer obtained from TIBA/TEA/1:1 showed a bimodal MWD. Then, the TREF+SSA methods were used to investigate the SCBD for the three copolymers with a small amount of 1-hexene incorporation. Through the analyses we found that the SCBD of copolymer obtained from TIBA co-catalyst was the best one among the three copolymers. Its copolymer showed similar relative SCB content in the highest MW segment as those obtained from TEA

and TIBA/TEA/1:1 co-catalysts, and in lowest MW segment, it had the least relative SCB among the three copolymers. Thus it was found that changing the co-catalyst was an effective method to tune the SCBD of the HDPE products. The results demonstrated in this work lay a foundation for further improvement of high grade HDPE as pipe materials made from Cr-based catalysts based on the proper choice of Al-alkyl co-catalyst.

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