

Unique polymerization kinetics obtained from simultaneous interaction of Phillips Cr(VI)O_x/SiO₂ catalyst with Al-alkyl cocatalyst and ethylene monomer

Wei Xia, Boping Liu*, Yuwei Fang, Kouichi Hasebe, Minoru Terano

School of Materials Science, Japan Advanced Institute of Science and Technology, 1-1 Asahidai, Nomi, Ishikawa 923-1292, Japan

Received 17 February 2006; received in revised form 24 April 2006; accepted 1 May 2006

Available online 12 June 2006

Abstract

Introduction of metal-alkyl cocatalyst in different stages from catalyst preparation to polymerization using Phillips catalyst significantly affects the active site formation, polymerization kinetics and polymer microstructure. However, the effect of the introduction of metal-alkyl cocatalyst in different stages has not been investigated systematically. In this work, ethylene homopolymerization was carried out using Phillips catalyst calcined at 600 °C (PC600). Different Al-alkyl cocatalysts (triethylaluminum (TEA) and diethylaluminum ethoxide (DEAE)) were introduced during polymerization stage with simultaneous interaction of catalyst with Al-alkyl cocatalyst and monomer. The polymerization kinetic curves using PC600/TEA catalyst systems seemed to be a hybrid type comprised of two types of basic polymerization kinetics: one is a fast formation and fast decay type and the other is a slow formation and slow decay type, which indicate the existence of two types of polymerization active sites. However, the polymerization kinetic curves using PC600/DEAE catalyst systems seemed to be a typical single type polymerization kinetics indicating only one type of polymerization sites that can be ascribed to Cr(II) species coordinated with Al-alkoxy formed by two ways. Plausible mechanisms of the formation and transformation of active sites were proposed to rationalize the unique polymerization kinetics and microstructures of polymers in terms of short chain branches (SCBs), molecular weight (MW) and bimodal molecular weight distribution (MWD). The metathesis mechanism proposed in our previous report got further experimental support in this study.

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Keywords: Phillips catalyst; Al-alkyl cocatalyst; Ethylene polymerization; Polymerization kinetics; Short chain branches; Bimodal molecular weight distribution

1. Introduction

Phillips CrO_x/SiO₂ catalyst is well known as one of the most important industrial ethylene polymerization catalysts. About one-third of the world high-density polyethylene (HDPE) is currently manufactured using this catalyst. Compared with Ziegler-Natta and metallocene catalysts, Phillips catalyst shows quite unique polymerization behavior and its products have many unique chain microstructures such as long chain branching, unsaturated chain end and ultra-broad molecular weight distribution, which contribute to excellent properties for both processing and final applications [1,2]. Despite continuous and extensive research for more than half century from early 1950s, there is

still very limited understanding of why Phillips catalyst has such unique behaviors [3–28]. In general, the states of active sites and polymerization mechanism still remain unclear and controversial [4–7].

Phillips Cr(VI)O_x/SiO₂ catalyst can be made by impregnating of aqueous solution of Cr compounds (mostly chromium(III) acetate or chromium(VI) trioxide) onto amorphous silica gel support followed by calcination in dry air at temperature usually around 600–800 °C for several hours. It must be further activated to Cr(II)O_x/SiO₂ that is the real active precursor for ethylene polymerization. The activation process in terms of reduction of Cr(VI) into Cr(II) could be performed either during catalyst preparation or within polymerization reactor by various activation agents. Generally there are three kinds of activation agents: ethylene monomer, CO and metal-alkyl cocatalysts, which are used for the activation process [5].

* Corresponding author. Tel.: +81 761 51 1622; fax: +81 761 51 1625.
E-mail address: boping@jaist.ac.jp (B. Liu).

The activation process using ethylene monomer is most frequently used in the industrial plants. In this case, ethylene monomer reduces the Cr(VI) into Cr(II) in the polymerization reactor to initiate the ethylene polymerization. Usually, there exists an induction period when temperature is lower than 150 °C. Our recent studies have elucidated some important mechanistic points concerning the induction period and subsequent typical accelerating-type polymerization behavior [22]. The induction period was found to be corresponding to not only the reduction of surface chromate Cr(VI) species into Cr(II) species but also ethylene metathesis through formation of chromium carbene species. The accelerating-type polymerization period is considered to be resulted from a gradual transformation of metathesis active sites into polymerization active sites due to the gradual desorption of formaldehyde molecules, the byproduct from the reduction of Cr(VI) into Cr(II) by ethylene monomer.

The activation of Phillips catalysts by CO has been studied rather extensively within the past decades by various spectroscopic methods [5,10–12,15,17]. Several types of Cr(II) species with different local coordination environment had been proposed. More recently, modern surface analytical techniques like FTIR, EXAFS, Roman and XANES with time and space resolution are still being actively applied for the study of CO-prereduced Phillips catalyst [15–18]. In addition, some researchers investigated the polymerization mechanism and the formation of active sites using CO-prereduced Phillips catalyst in the presence of metal-alkyl cocatalysts. Bade and Blom pre-contacted lithium-alkyl with CO-prereduced catalyst for some time before polymerization. Two kinds of active sites, oligomerization sites and polymerization sites, were proposed corresponding to the formation of linear low-density polyethylene (LLDPE) production due to the in situ incorporation of α -olefin oligomers [29,30]. Our recent studies [23] on CO-prereduced Phillips catalyst by XPS and TPD-MS revealed that CO and CO₂ derived from the reaction between chromate Cr(VI) species and CO were still partially coordinated with the divalent Cr(II) species after a normal CO-prereduction procedure. According to XPS results, it was further found that almost one-third of chromate Cr(VI) species cannot be reduced into Cr(II) site and still existed in hexavalent oxidation state. Based on these results about the CO-prereduced Phillips CrO_x/SiO₂, TEA cocatalyst was introduced to ethylene polymerization using the CO-prereduced Phillips catalyst in order to assist the desorption of the CO or CO₂ coordinated with Cr(II) sites as well as the reduction of residual chromate Cr(VI) species. A hybrid type polymerization kinetics was found during ethylene homo- and copolymerization with 1-hexene using a CO-prereduced Phillips CrO_x/SiO₂ catalyst in the presence of TEA cocatalyst [23,31], which indicated the existence of two types of polymerization active sites including one type of sites formed through the CO or CO₂ desorption from Cr(II) sites by Al-alkyl cocatalyst with fast activation, high activity and fast decay and the other type of sites formed by the reduction of residual chromate Cr(VI) species by Al-alkyl cocatalyst with slow activation, relatively low activity and slow decay. Moreover, the Cr(II) sites coordinated with CO or CO₂ were proposed as ethylene metathesis sites, which can

be transformed into polymerization sites through desorption of the CO or CO₂ by TEA. Formation of methyl, *n*-butyl and other SCBs with both even and odd number of carbon atoms during ethylene homopolymerization can be rationalized well through in situ incorporation of various short olefins formed from ethylene metathesis reaction.

The activation of Phillips catalysts by metal-alkyl cocatalysts had not been fully investigated because it was scarcely used in the industrial field up to now. However, more recently, some industrial interests have appeared on the development of new Phillips catalyst system using metal-alkyl cocatalyst. Therefore, better and deeper understanding on the activation process by metal-alkyl cocatalyst is indispensable for further development in this direction. In the case of using metal-alkyl cocatalyst for the activation of Phillips catalyst, its introduction in which stage had been reported to be crucial to affect the polymerization behavior as well as polymer properties according to Blom and co-workers [29,30]. Typically there are three stages for introduction of metal-alkyl cocatalyst: catalyst preparation stage, catalyst aging or pretreatment stage in polymerization reactor just before introduction of monomer and polymerization stage with simultaneous interaction of catalyst with metal-alkyl cocatalyst and monomer. Therefore, the stage in which metal-alkyl cocatalyst is introduced should be highlighted because the introduction of metal-alkyl in different stages might significantly affect the active site formation, polymerization kinetics and microstructures of polymers produced. Spitz et al. introduced small amount of TEA during catalyst aging or pretreatment stage in polymerization reactor just before introduction of monomer using a Phillips catalyst [32]. The significant effect of even small amount of TEA, on the activity, kinetics and 1-hexene incorporation for ethylene-1-hexene copolymerization in liquid 1-hexene was reported [32]. McDaniel and Johnson introduced triethylborane (TEB) during catalyst aging or pretreatment stage in polymerization reactor just before introduction of monomer using Phillips catalysts [33,34]. The effect of TEB on the polymerization kinetics and chain transfer of Phillips catalyst using different supports (AlPO₄, SiO₂ and Al₂O₃) was reported [33,34]. Tait and co-workers studied on the effects of Tri-isobutylaluminium (TIBA) on kinetics and polymer morphology using Phillips CrO_x/SiO₂ catalyst [35]. TIBA was introduced during catalyst aging or pretreatment stage in polymerization reactor just before introduction of monomer [35]. Woo and co-workers also investigated the effect of TIBA on polymerization kinetics and active sites of a Phillips CrO_x/SiO₂ catalyst [36]. Instead of introducing TIBA during catalyst aging or pretreatment stage, they introduced TIBA during polymerization stage with simultaneous interaction of catalyst with metal-alkyl cocatalyst and monomer. Polymerization was started by breaking the glass ampoule containing the Phillips catalyst within the polymerization reactor [36]. In our recent work [27], TEA cocatalyst was introduced into the catalyst preparation stage to pre-modify Phillips CrO_x/SiO₂ catalyst. The ethylene polymerization kinetics and active sites of Phillips catalyst were investigated [27]. As demonstrated in these previous reports mentioned above [27,32–36], the introduction of metal-alkyl cocatalyst in different stages from catalyst prepara-

tion to polymerization indeed significantly affects active site formation, polymerization kinetics and microstructure of the polymers produced. However, the effect of the introduction of metal-alkyl cocatalyst in different stages from catalyst preparation to polymerization using Phillips catalyst has not been investigated systematically.

In this work, the polymerization kinetics and microstructures of polymers obtained from Phillips catalyst in the presence of Al-alkyl cocatalysts were studied further proceeded with our previous work [27]. Instead of introducing Al-alkyl cocatalyst during catalyst preparation stage, Al-alkyl cocatalyst was introduced during polymerization stage with simultaneous interaction of catalyst with Al-alkyl cocatalyst and monomer. Polymerization was started by breaking the glass ampoule containing PC600 catalyst within the polymerization reactor. Effects of different Al-alkyl cocatalysts and Al/Cr molar ratio for the kinetic curves and microstructures of polymers obtained were investigated. It was found that the PC600/TEA catalyst system showed completely different polymerization kinetics compared with that of the PC600 catalyst pre-modified by TEA during catalyst preparation stage as reported in our previous work [27]. Furthermore, this could be significantly changed in the case of using PC600/DEAE catalyst system. Plausible mechanism of the formation of active sites will be proposed on the Phillips catalyst in the presence of different Al-alkyl cocatalysts introduced during polymerization stage with simultaneous interaction of catalyst with cocatalyst and ethylene monomer.

2. Experimental

2.1. Raw materials

All gas media used in the preparation procedure including nitrogen of G-2 grade (total impurity <2 ppm, in which $O_2 < 0.3$ ppm, $CO < 0.3$ ppm, $CO_2 < 0.3$ ppm, $CH_4 < 0.1$ ppm, $NO_x < 0.1$ ppm, $SO_2 < 0.1$ ppm, dew point of $H_2O < -80^\circ C$), and pure air of G-1 grade (total impurity <1 ppm, $CO < 0.1$ ppm, $CO_2 < 0.1$ ppm, $THC < 0.1$ ppm, $NO_x < 0.01$ ppm, $SO_2 < 0.01$ ppm, dew point of $H_2O < -80^\circ C$) were purchased from Uno Sanso Co. Ethylene monomer (research grade, $C_2H_4 > 99.9\%$, air <0.03%, methane <0.01%, ethane <0.05%, propane <0.01%, analyzed by Gas Chromatography method) was donated by Mitsubishi Chemical Co. Molecular sieves 13X and 4A, used for further purification of gas media as moisture scavenger, were purchased from Wako Pure Chemical Industries, Ltd. Q-5 reactant catalyst (13 wt% of copper(II) oxide on alumina) was purchased from Aldrich as oxygen scavenger for gas media. The catalyst precursor used for catalyst preparation was Crosfield ES370X with 1.0 wt% Cr loading and 280–350 m^2/g surface area, which was donated by Asahi Kasei Co. TEA and DEAE, donated by Tosoh Fine Chem. Co., were used without further purification. Heptane, which was purchased from Wako Pure Chemical Industries, Ltd., was purified by passing through a column of molecular sieves 13X and subsequently purged by pure nitrogen bubbling flow for more than 2 h before use. TEA and DEAE were used as heptane solution.

2.2. Preparation of catalyst

Details about catalyst preparation of the Phillips catalyst could be found in our previous report [23,31]. About 15 g of catalyst precursor was added into a spouted fluidized-bed reactor using a temperature-programmed heating controller and subsequently calcined at $600^\circ C$ for 6 h under 200 ml/min flow of dry air. Dry air was further purified by passing through a 13X molecular sieve column before entering the catalyst preparation system. Then, the catalyst was cooled down to room temperature in nitrogen (200 ml/min). Nitrogen was further purified by passing through a Q-5 catalyst column and a 13X molecular sieve column before entering the catalyst preparation system. Finally, the PC600 catalyst was distributed and sealed into several glass tubes for storage under nitrogen atmosphere. Thereafter, the PC600 catalyst was further distributed and sealed in many smaller glass ampoule bottles and the amount of catalyst in each ampoule bottle was regulated for about 100 mg, which was weighed precisely before polymerization.

2.3. Ethylene polymerization

The same semi-batch slurry polymerization system was utilized as in our previous work [23,31]. One ampoule bottle including ca. 100 mg of PC600 catalyst was set in the top part of a glass polymerization reactor (volume ca. 100 ml) with water-jacket and a magnetic stirrer inside. The reactor system was heated and vacuumed for 2 h before introduction of heptane. Heptane solvent was purified by 13X molecular sieve and 24 h bubbling under high purity nitrogen. Cocatalyst (TEA or DEAE) was subsequently injected into reactor under nitrogen atmosphere. The solution was then saturated with 0.13 MPa of ethylene, which was purified by passing through a 4A molecular sieve column, a Q-5 catalyst column and a 13X molecular sieve column. Polymerization started after breaking the ampoule bottle with catalyst by screwing of a steel bar. Thus, cocatalyst (TEA or DEAE) and monomer simultaneously interact with catalyst during polymerization stage instead of introducing Al-alkyl cocatalyst during catalyst preparation stage. Polymerization was carried out at $60^\circ C$ for 90 min. An on-line mass flowmeter was used to record the real-time ethylene consumption profile. The polymerization was terminated by the addition of 20 ml ethanol/HCl solution. The obtained polymer was washed with ethanol and dried under vacuum at $60^\circ C$ for 6 h.

2.4. Characterization of polymers

A Varian Gemini-300 spectrometer at 75.46 MHz was used to characterize the obtained polymer by ^{13}C NMR measurement. The polymer samples were added into sample tube (a diameter of 10 mm) with the mixture of 1,2,4-trichlorobenzene, 1,1,2,2-tetrachloroethane- d_2 and hexamethyldisiloxane (40/10/1, v/v/v) as the solvent (sample concentration: ca. 18 mg/ml). Each polymer sample was measured with 6 s pulse repetition at $140^\circ C$ for 40 h. The chemical shifts were referenced internally to the backbone carbon of polymer which was taken as 30.00 ppm. The amount of branches was normal-

ized as the number of branching carbon per 1000 CH₂ in the main chain. MW and MWD of polymers were obtained on GPC (Waters Alliance GPCV2000CV) with a polystyrene gel column (Shodex UT-806 M) at 140 °C using 1,2,4-trichlorobenzene as solvent.

3. Results and discussion

Introduction of metal-alkyl cocatalyst in different stages from catalyst preparation to polymerization might significantly affect active site formation, polymerization kinetics and microstructures of the polymers obtained. However, the effect of the introduction of metal-alkyl cocatalyst in different stages from catalyst preparation to polymerization using Phillips catalyst has not been investigated systematically. Proceeded with our previous work [27], the Al-alkyl cocatalyst was introduced during polymerization stage with simultaneous interaction of catalyst with Al-alkyl cocatalyst and monomer in this work, instead of introducing Al-alkyl cocatalyst during catalyst preparation stage. Polymerization was started by breaking the glass ampoule containing PC600 catalyst within the polymerization reactor. The effects of different Al-alkyl cocatalysts and Al/Cr molar ratio for the polymerization kinetics and microstructures of polymers obtained were investigated.

PC600/TEA catalyst systems (runs 1, 2 and 3) showed a hybrid type (as shown in Fig. 1) polymerization kinetics comprised of two types of basic polymerization kinetics: one is a fast formation and fast decay type and the other is a slow formation and slow decay type, completely different compared with that of the PC600 catalyst pre-modified by TEA during catalyst preparation stage as reported in our previous work [27]. It is reasonable to ascribe the origins of the two basic types of polymerization kinetics to two different types of active sites (named as site-A and site-B). The precursors of site-A and site-B were shown in Scheme 1. TEA and ethylene monomer were simultaneously interact with PC600 catalyst. Some chromate Cr(VI) species were reduced to Cr(II) species by ethylene monomer, subsequently Cr(II) species were coordinated with formaldehyde which is the byproduct of reaction between ethy-

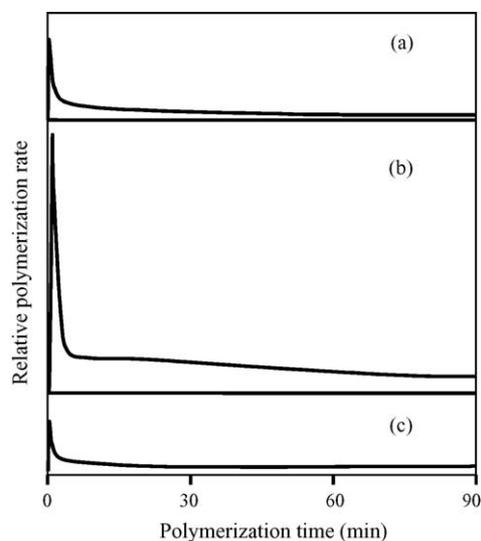
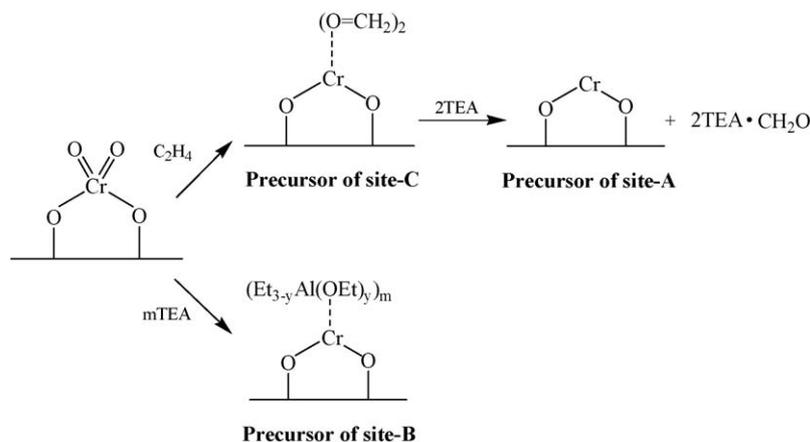
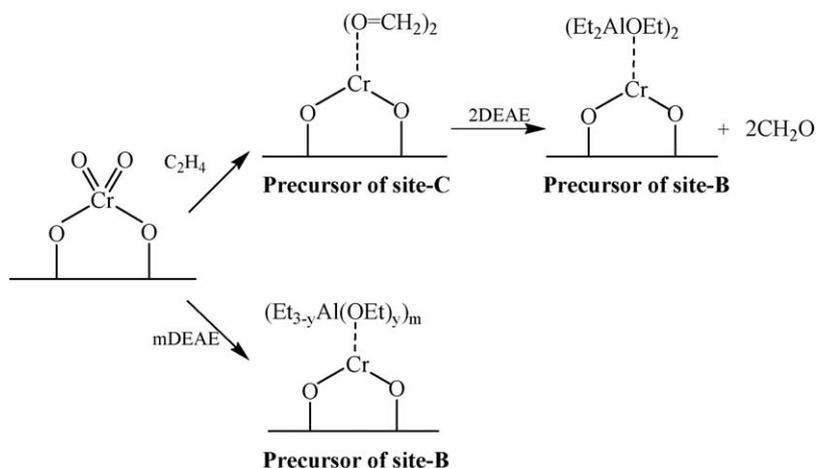


Fig. 1. Kinetic curves of ethylene homopolymerization using PC600/TEA catalyst systems with Al/Cr molar ratio: (a) 7.5 (run 1); (b) 15.0 (run 2); (c) 22.5 (run 3). Polymerization conditions: catalyst amount, 100 mg; polymerization temperature, 60 °C; polymerization time, 1.5 h; ethylene pressure, 0.13 MPa; solvent heptane, 20 ml; cocatalyst TEA in heptane, 1 M.

lene and chromate, then the instant activation and fast decay active site-A (as shown in Scheme 1) were formed through desorption of formaldehyde from metathesis site (named as site-C, the precursor of site-C was shown in Scheme 1) by TEA. Site-A was very exposed and can be easily coordinated with ethylene monomer and over-reduced by TEA cocatalyst as well. So such active site had higher activity but faster decay. On the other hand, some chromate Cr(VI) species were reduced by TEA and then coordinated with Al-alkoxy resulting in site-B (as shown in Scheme 1) with slow activation and slow decay. Cr(II) sites strongly coordinating with Al-alkoxy, formed by oxidation of TEA with chromate(VI) species, were protected from further over-reduction by TEA [23,31,33] and influenced by electron donating of Al-alkoxy. So site-B had low activity and high stability compared with site-A. Comparing with our recent work [27], the polymerization kinetics of PC600 catalyst pre-modified by TEA during catalyst preparation stage was found to be the typi-



Scheme 1. Plausible mechanism of the formation of two kinds of active site precursors on PC600 catalyst with simultaneous interaction with TEA and monomer: $y=1$ or 2 and $m=1$ or 2 .



Scheme 2. Plausible mechanism of the formation of one kind of active site precursors on PC600 catalyst with simultaneous interaction with DEAE and monomer: $y = 1$ or 2 and $m = 1$ or 2 .

cal kinetics form, in which the polymerization rate was built-up quickly from zero to a maximum followed by gradual decrease to stationary rate. That can be explained that when TEA was introduced during catalyst preparation stage. Some chromate Cr(VI) species were reduced to Cr(II) species. Al-alkoxy byproduct from the reduction reaction was supposed to be coordinated with the Cr(II) species. Although there were residual chromate Cr(VI) species, it may be reduced to Cr(II) species by ethylene monomer during polymerization stage and then coordinated with formaldehyde. The desorption of formaldehyde from the Cr(II) species is difficult under the polymerization condition ($60\text{ }^{\circ}\text{C}$ and 0.13 MPa). That is to say site-C cannot be transformed to site-A through desorption of formaldehyde (as shown in Scheme 1) due to the non-existence of free Al-alkyl compounds in the solvent. So no instant activation and fast decay active site formed. The polymerization kinetics for all the TEA pre-modified Phillips catalysts were found to be the typical single type kinetics form [27].

PC600/DEAE catalyst systems (runs 4, 5 and 6) showed a typical single type polymerization kinetics (as shown in Fig. 2) com-

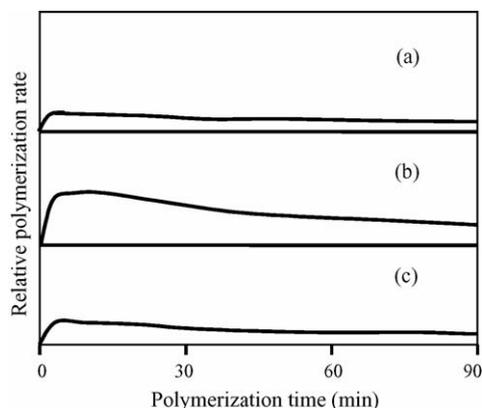


Fig. 2. Kinetic curves of ethylene homopolymerization using PC600/DEAE catalyst systems with Al/Cr molar ratio: (a) 7.5 (run 4); (b) 15.0 (run 5); (c) 22.5 (run 6). Polymerization conditions: catalyst amount, 100 mg; polymerization temperature, $60\text{ }^{\circ}\text{C}$; polymerization time, 1.5 h; ethylene pressure, 0.13 MPa; solvent heptane, 20 ml; cocatalyst DEAE in heptane, 1 M.

pletely different with PC600/TEA catalyst systems (as shown in Fig. 1). This type of polymerization kinetics could be ascribed to one type of active sites (named as site-B) formed by two ways. The precursors of site-B are shown in Scheme 2. Similarly, with PC600/TEA catalyst systems, some chromate Cr(VI) species were reduced to Cr(II) species by ethylene monomer and coordinated with formaldehyde, then formaldehyde-coordinated Cr(II) sites were transformed to DEAE-coordinated Cr(II) sites by displacement. On the other hand, some chromate Cr(VI) species were reduced by DEAE, and then the Al-alkoxy coordinated with Cr(II) site. Site-B had relative low activity and high stability.

The activities of PC600/TEA and PC600/DEAE catalyst systems in ethylene homopolymerization were shown in Table 1. For both PC600/TEA and PC600/DEAE catalyst systems, the activity firstly increased with increase of Al/Cr molar ratio, and then reached a maximum value followed by a decreasing of activity with further increase of Al/Cr molar ratio.

All the polymers obtained from PC600/TEA and PC600/DEAE catalyst systems were characterized by ^{13}C NMR method. As an example, the ^{13}C NMR spectra of polymers obtained from PC600/TEA catalyst systems (runs 1, 2 and 3) were shown in Fig. 3. The peaks found at 33.23, 39.86, 37.78 and 38.21 ppm were assigned to the branching carbons of methyl, ethyl, propyl and *n*-butyl, respectively. These were consistent with the results of Randall's [37] (methyl, 33.21 ppm; propyl, 37.78 ppm; butyl, 38.10 ppm) and Axelson et al.'s works [38] (ethyl, 39.86 ppm; butyl, 38.27 ppm).

The microstructure of polymer was described by the number of carbon on short chain branches (SCBs) per 1000 backbone carbon in the main polymer chain as shown in Table 1. It was obviously found that the relative amount of SCBs (including methyl, ethyl, propyl and *n*-butyl) decreased with increase of Al/Cr molar ratio for PC600/TEA and PC600/DEAE catalyst systems. Comparing runs 4, 5 and 6 with runs 1, 2 and 3, the relative amount of SCBs of polymers obtained from PC600/DEAE is more than that of polymers obtained from PC600/TEA.

According to the literatures [5,22,28], there are two types of mechanism about the formation of methyl branches. McDaniel

Table 1
Activities of PC600 catalyst in ethylene homopolymerization and microstructures of polymers obtained

Run	Cocatalyst	Al/Cr molar ratio	Activity (kg/(mol Cr h))	Methyl branches ^a	Ethyl branches ^a	Propyl branches ^a	<i>n</i> -Butyl branches ^a	M_w^b ($\times 10^5$)	M_w/M_n^b	Polymer from site-A (wt%) ^c
1	TEA	7.5	6.1	3.93	1.39	0.56	0.44	5.25	35.4	15.9
2	TEA	15.0	23.6	2.38	1.18	0.49	0.36	6.55	53.1	13.5
3	TEA	22.5	6.4	2.28	1.01	0.35	0.30	3.49	26.7	9.5
4	DEAE	7.5	5.8	4.10	2.17	1.77	1.46	6.38	19.7	–
5	DEAE	15.0	9.3	3.10	1.64	1.36	1.02	8.55	33.0	–
6	DEAE	22.5	4.1	3.00	1.17	0.98	0.77	7.31	27.8	–

Polymerization conditions: catalyst amount, 100 mg; polymerization temperature, 60 °C; polymerization time, 1.5 h; ethylene pressure, 0.13 MPa; solvent heptane, 20 ml; cocatalyst TEA and DEAE in heptane, 1 M.

^a Number of methyl, ethyl, propyl or *n*-butyl branches per 1000 backbone carbon determined by ¹³C NMR method.

^b Characterized by GPC method.

^c Weight percentage of polymer obtained from active site-A was determined by integral area of kinetic curve of site-A and site-B after deconvolution.

considered that methyl branches formed by isomerization on active site and the possibility of such isomerization reaction would be promoted if the growing polymer chain had more time around the active site [5]. On the other hand, in our previous work [22,28], it was found that some short α -olefins, especially propylene, could be formed through an ethylene metathesis reaction on Cr(II) sites coordinated with formaldehyde, the byproduct of the redox reaction between chromate Cr(VI) species and ethylene. The conversion of ethylene metathesis into ethylene polymerization can be expected by desorption of the coordinated formaldehyde. That is to say, site-C (as shown in Schemes 1 and 2) contributed to the formation of some short α -olefins, especially propylene. The propylene formed in situ can insert into polymer chain to form methyl branches.

Formation of butyl branches in ethylene homopolymerization had been ascribed to the in situ insertion of 1-hexene byproducts in the polymerization process. 1-Hexene is the predominant byproduct from ethylene during the early stage of polymerization. But the formation mechanism of 1-hexene is still controversial [39–43]. Traditionally, there are two types of mechanism about the formation of butyl branching: one considered that the

1-hexene was generated through monomer oligomerization [39]; the other thought that 1-hexene was originated from intramolecular β -H transfer of the chromacycloheptane intermediate, as speculated in literature [43].

Considering conventional opinions, methyl branches could form through isomerization. Butyl branches could form by 1-hexene, byproducts of oligomerization or intramolecular β -H transfer, in situ insertion into polymer chain. But these mechanisms cannot explain the formation of other SCBs like ethyl, propyl, etc. (as shown in Table 1). Furthermore, the in situ ethylene metathesis reaction can interpret well the formation of all SCBs and the relative amount of SCBs (including methyl, ethyl, propyl and *n*-butyl).

The relative amount of SCBs of polymers obtained from PC600/TEA and PC600/DEAE catalyst systems decreased with increase of Al/Cr molar ratio. That could be explained by the following reasons. Firstly, there existed a competition between ethylene monomer and TEA or DEAE to reduce the chromate Cr(VI) species into Cr(II) sites for polymerization. When Al/Cr molar ratio increased, the amount of chromate Cr(VI) species reduced by TEA or DEAE cocatalyst increased, the amount of chromate Cr(VI) species reduced by ethylene monomer decreased, then the amount of short α -olefins, especially propylene, formed on site-C decreased (as shown in Schemes 1 and 2). Secondly, the presence of more TEA or DEAE cocatalyst could accelerate the conversion of metathesis active site-C to polymerization active site-B (as shown in Schemes 1 and 2). In addition, for PC600/TEA catalyst systems, the kinetic curves of runs 1, 2 and 3 were deconvoluted into two types of kinetic curves using same way with our previous work [31]. The weight percentage of polymer obtained from site-A was calculated by integral area of kinetic curves (as shown in Table 1). The relative content of polymer formed by site-A decreased (from 15.9 to 9.5 wt%) with increase of Al/Cr molar ratio. The relative content of polymer obtained from site-A decreased, the relative amount of site-C (as shown in Scheme 1) decreased. Therefore, the amount of α -olefins formed by metathesis reaction on site-C decreased.

The relative amount of SCBs of polymers obtained from PC600/DEAE catalyst systems was more than that of polymers obtained from PC600/TEA catalyst systems. That could

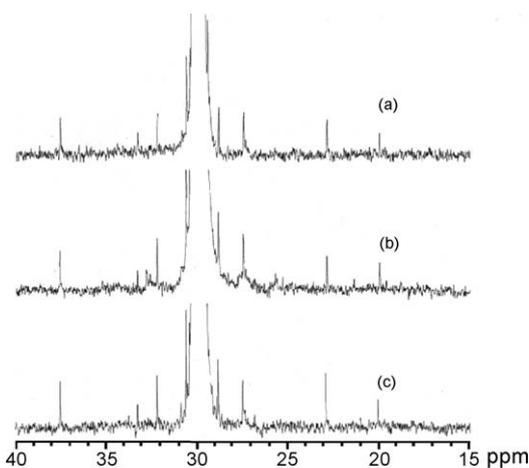


Fig. 3. ¹³C NMR spectra of polymers obtained from PC600/TEA catalyst systems: (a) run 1; (b) run 2; (c) run 3. The peaks found at 33.23, 39.86, 37.78 and 38.21 ppm were assigned to the branching carbons of methyl, ethyl, propyl and *n*-butyl, respectively.

be explained by following reasons. Firstly, reduction ability of DEAE was weaker than TEA. Under the same conditions of competition with ethylene monomer, more amount of chromate Cr(VI) species reduced by ethylene and coordinated with formaldehyde, more site-C (as shown in Scheme 2) formed. Secondly, DEAE need longer time for the conversion of metathesis active sites into polymerization active sites. More α -olefin will be formed from metathesis active sites, thus more comonomers inserted to polymer chain. Thirdly, different Al-alkoxy, the byproduct of the reaction between TEA or DEAE and chromate, subsequently coordinated with chromium active site, will also affect the incorporation rate of α -olefin comonomers. For runs 1–6, the relative amount of SCBs decreased in the following order: methyl > ethyl > propyl > *n*-butyl. The formation and relative amount of SCBs were consistent with our previous work [22], in which propylene was the firstly formed hydrocarbon species, butene was the second hydrocarbon species formed after propylene, the subsequent were 1-pentene and 1-hexene. So the relative amount of comonomer decreased in the following order: propylene > butylene > 1-pentene > 1-hexene. These α -olefin in situ insert to polymer chain, the relative amount of SCBs decreased in the following order: methyl > ethyl > propyl > *n*-butyl. Thus, the ethylene metathesis reaction on Cr(II) sites coordinating with formaldehyde got further experimental support from this study.

The GPC curves of polymers obtained from PC600/TEA and PC600/DEAE catalyst systems were shown in Fig. 4. Table 1 showed the MW, MWD and microstructures of polymers obtained. It was obviously found both of the PC600/TEA and PC600/DEAE catalyst systems produced polymers with bimodal MWD. The MW and MWD increase with increase of Al/Cr molar ratio and then reach a maximum value followed by a decreasing of MW and MWD with further increase of Al/Cr molar ratio. For PC600/TEA and PC600/DEAE cat-

alyst polymerization systems, MW and MWD of polymers obtained are determined by two chain transfer effects. One is chain transfer from active sites to Al-alkyl. MW of polymers decreases with increase of Al/Cr molar ratio. The other is the β -H elimination (or β -H transfer) to monomer. For PC600/TEA and PC600/DEAE catalyst systems, the relative amount of SCBs including methyl, ethyl, propyl and *n*-butyl branches decreased with increase of Al/Cr molar ratio as shown in Table 1. The proton in the tertiary β -carbon can be easily transferred or β -eliminated leading to chain transfer to monomer. So the MW of polymers increases with decrease of the comonomer insertion. Combining the effects of chain transfer from active sites to Al-alkyl and β -H elimination (or β -H transfer) to monomer, the MW increase with increase of Al/Cr molar ratio and then reach a maximum value followed by a decreasing with further increase of Al/Cr molar ratio. It could be found from Fig. 4 that the low-MW fractions of runs 1 and 3 were more than those of run 2 for PC600/TEA catalyst system. Similarly, for PC600/DEAE catalyst system, the low-MW fractions of runs 4 and 6 were more than those of run 5. That could be explained that when the Al/Cr molar ratio was 7.5 (runs 1 and 4), more comonomers formed from metathesis reaction. More low-MW fractions formed because of β -H elimination to monomer. When the Al/Cr molar ratio was 22.5 (runs 3 and 6), more low-MW fractions formed because of the chain transfer from active sites to Al-alkyl. So, when the Al/Cr molar ratio was 15, the MW and MWD are higher than those when the Al/Cr molar ratio was 7.5 and 22.5. In addition, because the chain transfer ability of PC600/TEA catalyst systems stronger than that of PC600/DEAE catalyst systems, the low-MW fractions of polymers obtained from PC600/TEA catalyst systems were more than high-MW fractions. Furthermore, the low-MW fractions of polymers obtained from PC600/DEAE catalyst were less than high-MW fractions.

4. Conclusions

In this work, the ethylene polymerization kinetics and microstructures of polyethylenes obtained from calcined Phillips CrO_x/SiO₂ catalyst (PC600) in the presence of Al-alkyl cocatalysts (TEA and DEAE) were investigated. The Al-alkyl cocatalyst was introduced during polymerization stage with simultaneous interaction of catalyst with Al-alkyl cocatalyst and ethylene monomer. PC600/TEA catalyst systems showed a hybrid type polymerization kinetics comprised of two types of basic polymerization kinetics: one is a fast formation and fast decay type and the other is a slow formation and slow decay type, which is completely different compared with that of the PC600 catalyst pre-modified by TEA during catalyst preparation stage. The two types of polymerization kinetics indicated the existence of two types of polymerization active sites, which are derived from chromate Cr(VI) species competitively activated by ethylene monomer and TEA cocatalyst, respectively. On the other hand, the PC600/DEAE catalyst system showed typical single type polymerization kinetics significantly different with that of using PC600/TEA catalyst system. This type

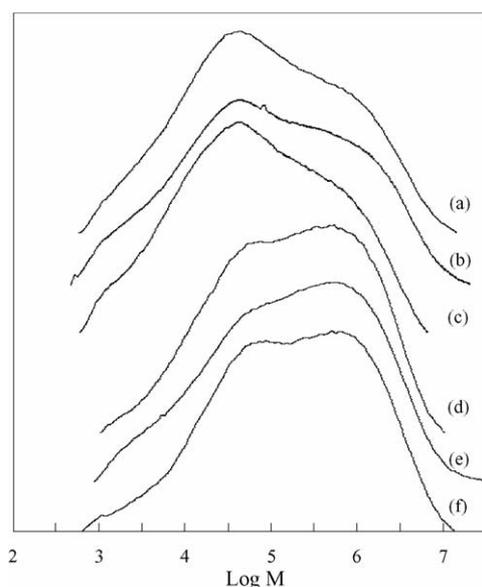


Fig. 4. GPC curves of polymers obtained from PC600/TEA and PC600/DEAE catalyst systems. PC600/TEA: (a) run 1; (b) run 2; (c) run 3; PC600/DEAE: (d) run 4; (e) run 5; (f) run 6.

of polymerization kinetics can be ascribed to only one type of active sites originated from chromate Cr(VI) species competitively activated by ethylene monomer and DEAE cocatalyst. The formation of SCBs of ethylene homopolymers obtained from PC600/TEA and PC600/DEAE catalyst systems can be rationalized well through in situ formation of various short α -olefins through ethylene metathesis reaction. In addition, both of the PC600/TEA and PC600/DEAE catalyst systems produced polyethylenes with bimodal MWD. The results of MW and MWD could be interpreted very well by the competitive chain transfers to Al-alkyl cocatalyst and β -H elimination to monomer.

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