Copolymerization of Ethylene and Cyclopentene with the Phillips CrO$_x$/SiO$_2$ Catalyst in the Presence of an Aluminum Alkyl Cocatalyst

Wei Xia,[1,2] **Kiwamu Tonosaki,**[1] **Toshiaki Taniike,**[1] **Minoru Terano,**[1] **Tadahiro Fujitani,**[2] **Boping Liu**[3]

[1]*School of Materials Science, Japan Advanced Institute of Science and Technology, 1-1 Asahidai, Nomi, Ishikawa 923-1292, Japan*
[2]*Research Institute for Innovation in Sustainable Chemistry, National Institute of Advanced Industrial Science and Technology, Tsukuba West 16-1 Onogawa, Tsukuba, Ibaraki 305-8569, Japan*
[3]*State Key Laboratory of Chemical Engineering, East China University of Science and Technology, 130 Mei Long Road, Shanghai, People's Republic of China 200237*

ABSTRACT: The Phillips CrO$_x$/SiO$_2$ catalyst is an important industrial catalyst for ethylene polymerization. However, understanding of the state of active sites and chain propagation mechanisms concerning the Phillips catalyst is still waiting for conclusive evidence. In this work, the Phillips CrO$_x$/SiO$_2$ catalyst, having been calcined, was used for investigating the copolymerization of ethylene and cyclopentene in the presence of triethylaluminum as a cocatalyst for the first time. The microstructures of the polymers were investigated with ^{13}C-NMR and gel permeation chromatography methods. Because of the absence of internal double bond (C=C) in the copolymer main chain, the ring-opening metathesis polymerization of cyclopentene was excluded during the copolymerization stage of ethylene and cyclopentene. Also, the 1,2-insertion and 1,3-insertion of cyclopentene into the polyethylene main chain were confirmed. This evidence strongly implies that Cr=C species may not be the active sites for chain propagation; instead, the Cr—C active site model under the Cossee–Arlman chain propagation mechanism may be responsible for the chain propagation during the normal polymerization period. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 111: 1869–1877, 2009

Key words: active sites; chain propagation mechanism; copolymerization; cyclopentene; Phillips catalyst

INTRODUCTION

The Phillips CrO$_x$/SiO$_2$ catalyst for ethylene polymerization was discovered by Hogan and Banks at Phillips Petroleum Co. in 1958. The catalyst can be easily prepared by the impregnation of an aqueous solution of Cr compounds [mostly Cr(III) acetate, Cr(III) nitrate, and Cr(VI) trioxide] into a porous, amorphous silica gel support followed by calcination in dry air at 600–800°C for several hours. The Phillips CrO$_x$/SiO$_2$ catalyst is known to be highly active for ethylene polymerization with or without a preliminary activation step using organometallic cocatalysts or other reducing agents. Furthermore, its high-density polyethylene products have many unique microstructures,[1] such as long-chain branches (ca. one long-chain branch per 10,000 ethylene units), an ultrabroad molecular weight distribution (the typical polydispersity is between 10 and 30), and unsaturated chain ends. Because of the easy preparation process, unique polymerization performance,[2–22] and

polymer properties, the Phillips catalyst is still attracting intense interest in industrial and academic research. In industry, the Phillips CrO$_x$/SiO$_2$ catalyst is still responsible for more than one-third of the worldwide commercial high-density polyethylene production. In academia, despite continuous and extensive research since its discovery, two main questions still remain unresolved. The first is the structure of the real active sites, and the second is the polymerization mechanism, especially the initiation step (the formation of the first growing polymer chain).[3,4] In recent years, Groppo et al.[5,6] investigated the coordination environment of the surface Cr species and the nature of the active sites on the Phillips catalyst by many modern spectroscopic techniques, such as ultraviolet–visible diffuse reflectance spectroscopy, Fourier transform infrared (FTIR) spectroscopy, Raman spectroscopy, resonant or pre-resonant Raman spectroscopy, X-ray absorption spectroscopy, and X-ray photoelectron spectroscopy. Gaspar and Dieguez[7] investigated the effects of Cr precursor on ethylene polymerization and CO reduction and adsorption on the Phillips catalyst by means of chemisorption and spectroscopic techniques. Van Kimmenade et al.[8] studied ethylene

Correspondence to: W. Xia (wei-xia@aist.go.jp).

polymerization at the molecular level with a flat model Phillips catalyst using a silicon wafer [Si(100)] as a support. Espelid and Børve[9] and Schmid and Ziegler[10] studied the active sites and polymerization mechanism with different theoretical analytical approaches. Hanmura et al.[11] and MacAdams et al.[12] investigated the polymerization mechanisms with homogeneous model systems. Our group has systematically studied the various activation procedures of the Phillips catalyst for ethylene polymerization by experimentation (including thermal activation, ethylene monomer activation, aluminum alkyl activation, and CO activation)[13–19] and some theoretical calculations.[20,21]

On the basis of the academic and industrial importance of the Phillips catalyst, the study of the active sites and initiation mechanism of the Phillips catalyst is a longstanding subject of controversy. Within the past 5 decades, various active site models and initiation mechanisms have been proposed,[3,4,23–34] and they are summarized in our previous report.[14] The generally accepted mechanism is the Cossee–Arlman chain propagation mechanism,[35] with either Cr—C or Cr—H as active sites similar to conventional Ziegler–Natta and metallocene catalysts.[23] The vinyl chain end of the polymer is supposed to be derived from chain transfer through β-hydride elimination. However, the origin of the initial chain and the first hydride scrambling have not been explained clearly.[4] Ivin et al.[36] first proposed a carbene chain propagation mechanism for olefin polymerization using a titanium chloride system. Ghiotti et al.[26] also found chromium–carbene spectra and proposed a modified Ivin–Rooney–Green chain propagation via an alkylidene structure. However, the modified Ivin–Rooney–Green chain propagation via chromium–alkylidene species[26–28,30,33,34] as active sites could not be confirmed conclusively because the existence or absence of a chromium–alkylidene species (also called chromium–carbene)[33,37] and IR band assignments of the C—H bond vibration in a plausible chromium–alkylidene species[26,38] remain controversial. In addition, because of the absence of vinyl or methyl groups in the IR spectra, a metallacycle model for initiation and propagation was proposed, with a metallacyclobutane or polymethylene chain bridged over two nearby Cr ions as active sites.[27,30–32,34] More recently, Groppo et al.[6] reported that they had captured the intermediate of the first stage of polymerization by FTIR, and they proposed that the initial mechanism follows a metallacycle route.

All these active site models and initiation mechanisms were mostly proposed on the basis of $Cr(II)O_x/SiO_2$ catalysts (CO-prereduced catalysts) with either pure speculation or controversial evidence.[23–34] The investigation based on $Cr(II)O_x/SiO_2$ catalysts was somewhat limited by the short lifetime of the initial species and the low detectability of traditional IR instruments. Our research group proposed some important mechanistic points by probing the induction period before ethylene polymerization based on industrial Phillips catalyst (a non-prereduced Phillips catalyst) in a more controllable manner (room temperature and atmospheric pressure) for the first time.[13,14] Surprisingly, the first and second hydrocarbon species were found to be propylene and butene, respectively, during the induction period by temperature-program desorption equipped with quadrupole mass spectroscopy. An ethylene metathesis initiation mechanism was proposed for the Phillips catalyst during the induction period. Cr(II) species coordinated with formaldehyde, which is formed by the redox reaction between hexavalent chromate species and ethylene, acts as the metathesis active precursor. Thus, the induction period corresponds to not only the reduction of surface chromate Cr(VI) species to Cr(II) species but also the initiation of bonding between Cr and C through an ethylene metathesis mechanism. Furthermore, we successfully obtained the first evidence of chromium–carbene (Cr=C) species during the induction period using X-ray photoelectron spectroscopy. It was assumed that the desorption of formaldehyde from the Cr(II) site would transform the metathesis site into a polymerization site; this transformation corresponds to a switch from the induction period to the normal polymerization. The subsequent gradual increase in the activity of the Phillips catalyst during the normal polymerization stage is presumably due to a gradual desorption of residual formaldehyde from the surface Cr(II) species. However, during the normal polymerization stage, views concerning the real active sites (Cr—C or Cr=C) and chain propagation mechanism are still in conflict. Hogan[23] proposed a Cr—C active site model under a Cossee-type chain propagation mechanism, which is still favored by many researchers. Ivin et al.[36] first proposed a carbene chain propagation mechanism for olefin polymerization. After that, Ghiotti et al.[26] also found chromium–carbene spectra and proposed propagation via an alkylidene structure. McDaniel and Cantor[39] ruled out the carbene mechanisms by investigation of hydrogen scrambling during polymerization using an isotopically labeled monomer. Kantcheva et al.[33] proposed that the polymer chain grows by the insertion of ethylene molecules into the Cr=C bond, which is accompanied by the formation of a metallocyclic compound and followed by Cr=C bond restoration and additional insertion. Very recently, Schmid and Ziegler[10] studied the reaction by means of density function theory calculations and proposed that a cationic system formed by protonation of the alkylidene shows a lower barrier than neutral alkylidene or bisalkyl

complexes for chain propagation. As demonstrated by the literature results discussed here, the investigation of the active sites and chain propagation mechanisms during the normal polymerization stage is very crucial to understanding the Phillips catalyst, but conclusive evidence is still lacking. To shed light on these problems, carrying out the copolymerization of ethylene and cycloolefin was considered to determine whether ring-opening metathesis polymerization occurs during the polymerization stage. From the microstructure of the obtained polymer, the existence or absence of internal double bond (C=C) could be confirmed in the polymer chain. We could speculate on the active sites and polymerization mechanism. According to the literature,[40–43] the copolymerization of ethylene and cyclopentene using the Phillips catalyst had never been carried out before. Therefore, in addition to providing mechanistic information, our investigation could also make a contribution to developing new materials with new properties.

In this work, a Phillips catalyst, calcined at 600°C (PC600), was adopted for the first time to catalyze the copolymerization of ethylene and cyclopentene in the presence of triethylaluminum (TEA) as a cocatalyst. The microstructures of the polymers were investigated with ^{13}C-NMR and gel permeation chromatography (GPC) methods. Because internal double bond (C=C) was not found in the copolymer main chain, ring-opening metathesis polymerization was ruled out during the polymerization stage of ethylene and cyclopentene. This evidence strongly implies that Cr=C is not the active site for chain propagation. The chain propagation during the normal polymerization period should be due to Cr—C active sites under the Cossee–Arlman chain propagation mechanism.

EXPERIMENTAL

Materials

Nitrogen (G-2 grade; total impurities < 2 ppm: O_2 < 0.3 ppm, CO < 0.3 ppm, CO_2 < 0.3 ppm, CH_4 < 0.1 ppm, NO_x < 0.1 ppm, and SO_2 < 0.1 ppm; dew point of H_2O < −80°C) and pure air (G-1 grade; total impurities < 1 ppm: CO < 0.1 ppm, CO_2 < 0.1 ppm, THC < 0.1 ppm, NO_x < 0.01 ppm, and SO_2 < 0.01 ppm; dew point of H_2O < −80°C) were purchased from Uno Sanso Co. (Fukui, Japan). Ethylene monomer (research grade; C_2H_4 > 99.9%, air < 0.03%, methane < 0.01%, ethane < 0.05%, and propane < 0.01%, as analyzed by gas chromatography) was donated by Mitsubishi Chemical Co. (Tokyo, Japan). Molecular sieves (13X and 4A), used as moisture scavengers to purify gas media, were purchased from Wako Pure Chemical Industries (Osaka, Japan). The Q-5 reactant catalyst [13 wt % copper(II) oxide on alu-

mina] was purchased from Aldrich (Missouri, USA) as an 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. (Tokyo, Japan) TEA, donated by Tosoh Fine Chemical Co. (Tokyo, Japan), was used without further purification. Heptane was also purchased from Wako Pure Chemical Industries. TEA was used in a heptane solution.

Preparation of the catalyst

Details of the preparation of the Phillips catalyst can be found in our previous report.[15–19] A catalyst precursor (ca. 15 g) was calcined at 600°C for 6 h under dry air (flow rate = 200 mL/min) in a spouted fluidized-bed reactor equipped with a temperature-programmed heating controller. The dry air was further purified by passage through a 13X molecular sieve column before it entered the catalyst preparation system. Then, the catalyst was cooled to room temperature under nitrogen (flow rate = 200 mL/min). Nitrogen was further purified by passage through a Q-5 catalyst column and a 13X molecular sieve column before it entered the catalyst preparation system. Finally, the PC600 catalyst was placed in several glass tubes, which were sealed for storage under a nitrogen atmosphere. Before the polymerization reactions, precisely weighed portions (ca. 100 mg) of the PC600 catalyst were placed in smaller glass ampules, which were then sealed.

Copolymerization of ethylene and cyclopentene

For the copolymerization reactions, we used the semibatch slurry polymerization system described in previous publications.[15–19] One ampule bottle containing the PC600 catalyst (ca. 100 mg) was fixed on the top part of a glass polymerization reactor (volume ≈ 100 mL) equipped with a water jacket and a magnetic stirrer inside. The reactor system was heated *in vacuo* for 2 h, and then heptane that had been purified with 13X molecular sieves and bubbled with high-purity nitrogen for 24 h was added. The cocatalyst (TEA) was subsequently injected into the reactor under nitrogen. The solution was then saturated with 0.15 MPa of ethylene that had been purified by passage through a 4A molecular sieve column, a Q-5 catalyst column, and a 13X molecular sieve column. After the introduction of cyclopentene as a comonomer (purified with Na metal), polymerization was started by the breaking of the ampule containing the catalyst; and the reaction was allowed to proceed at 40°C for 90 min. An online mass flow meter was used to record the real-time ethylene consumption profile. The
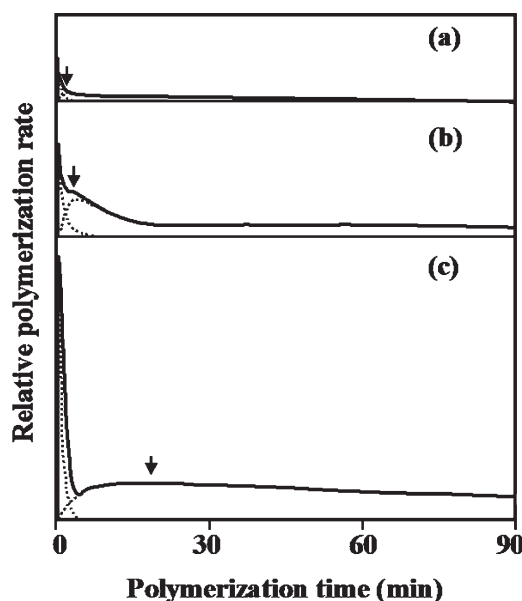
Figure 1 Kinetic curves of ethylene and cyclopentene copolymerization using PC600/TEA catalyst systems with (a) 0 vol % cyclopentene (run 1), (b) 5 vol % cyclopentene (run 2), and (c) 20 vol % cyclopentene (run 3). The polymerization conditions were as follows: catalyst amount, 100 mg; polymerization temperature, 40°C; polymerization time, 1.5 h; ethylene pressure, 0.15 MPa; solvent, heptane (20 mL); and cocatalyst, TEA in heptane (1M).

polymerization was terminated by the addition of an ethanolic solution of HCl (20 mL). The polymers were washed with ethanol and dried *in vacuo* at 60°C for 6 h.
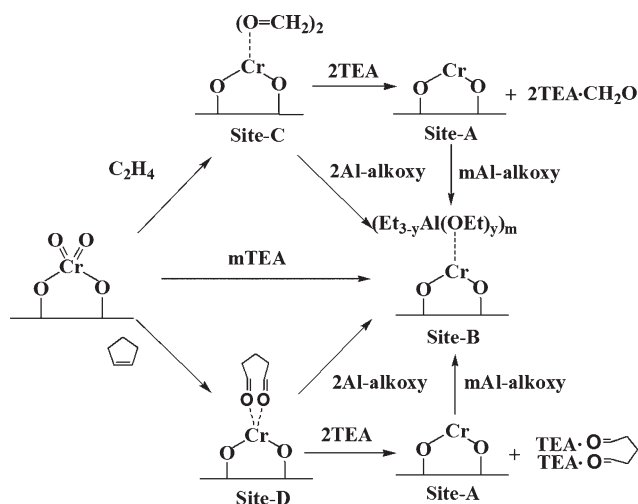
Characterization of the polymers

A Varian Gemini-300 NMR spectrometer (California, USA) operated at 75.46 MHz was used to obtain the ^{13}C-NMR spectra of the obtained polymer. The polymer samples were placed in a sample tube (diameter = 10 mm) with a mixture of 1,2,4-trichlorobenzene, 1,1,2,2-tetrachloroethylane-d_2, and hexamethyldisiloxane (volume ratio = 40/10/1) as the solvent (sample concentration ≈ 18 mg/mL). Polymer samples were measured with a 6-s pulse repetition at 140°C for 40 h. The chemical shifts were referenced internally to
the backbone carbon of the polymer at 30.00 ppm. The number of branches was determined as the number of branching carbons per 1000 —CH$_2$— groups in the main chain. The molecular weight and molecular weight distribution of the polymers were measured at 140°C by means of GPC (Alliance GPCV2000CV, Waters (Tokyo, Japan)) with a polystyrene gel column (UT-806M, Shodex (Tokyo, Japan)) with 1,2,4-trichlorobenzene as the solvent. The IR spectra were obtained with a Jasco FT/IR-460 Plus spectrometer (Tokyo, Japan) with a 2-cm^{-1} re-

solution and 24 accumulation cycles with KBr disks (sample/KBr = 1 : 100 w/w).

RESULTS AND DISCUSSION

In this work, we carried out the copolymerization of ethylene and cyclopentene with the PC600 catalyst in the presence of TEA as a cocatalyst for the first time. The effect of cyclopentene as a comonomer on the polymerization was studied. The polymerization kinetic curves seemed to be a hybrid type composed 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 (as shown in Fig. 1). It is reasonable to ascribe the origins of the two basic types of polymerization kinetics to two different types of active sites (named site A and site B, as shown in Scheme 1). During the polymerization, TEA, ethylene, and the cyclopentene comonomer simultaneously interacted with the PC600 catalyst. The instant activation and fast decay sites composed of site A (in Scheme 1) were formed through the desorption of formaldehyde and glutaraldehyde from Cr(II) sites (site C and site D, respectively, in Scheme 1) by TEA. As mentioned in our previous reports,[16,17] site A was relatively exposed and could be easily coordinated with ethylene monomer or over-reduced by the TEA cocatalyst. These active sites had higher activity, but they decayed faster. The slow activation and slow decay sites composed of site B (in Scheme 1) were formed through three routes. First, the chromate Cr(VI) species (as shown in Scheme 1) could be reduced to Cr(II) species by TEA and then coordinated with

Scheme 1 Plausible mechanism for the formation of two kinds of active sites on the PC600 catalyst for the copolymerization of ethylene and cyclopentene ($y = 1$ or 2; $m = 1$ or 2).

TABLE I
Activities of the PC600 Catalyst in Ethylene and Cyclopentene Homopolymerization or Copolymerization and Microstructures of the Obtained Polymers

Run	CPE (vol %)	Activity (kg/mol of Cr h)	Methyl branches[a]	Ethyl branches[a]	Propyl branches[a]	n-Butyl branches[a]	CPE 1,2-insertion ratio[a]	CPE 1,3-insertion ratio[a]	M_w ($\times 10^5$)[b]	M_w/M_n[b]	Polymer from site A (wt %)[c]
1	0	1.9	0.91	0.55	0.30	0.29	—	—	3.6	43.6	12.9
2	5	10.8	0.45	0.31	0.23	0.22	0.50	0.44	8.1	54.2	10.9
3	20	28.4	0.40	0.29	0.23	0.19	0.54	0.45	9.5	52.1	9.1
4	100	Trace	—	—	—	—	—	—	—	—	—

The polymerization conditions were as follows: catalyst amount, 100 mg; polymerization temperature, 40°C; polymerization time, 1.5 h; ethylene pressure, 0.15 MPa; solvent, heptane (20 mL); cocatalyst, TEA in heptane ($1M$); and Al/Cr molar ratio, 22.5. CPE = cyclopentene; M_n = number-average molecular weight; M_w = weight-average molecular weight.
[a] The number of methyl, ethyl, propyl, or n-butyl branches or cyclopentane units per 1000 backbone carbons was determined by ^{13}C-NMR.
[b] Characterized by GPC.
[c] The weight percentage of the polymer obtained from active site A was determined from integral areas of the kinetic curves of sites A and B after deconvolution.

aluminum alkoxy compounds formed by the oxidation of TEA with chromate Cr(VI) species. Second, some site A could be transformed to site B by coordination with aluminum alkoxy. Third, some of the formaldehyde-coordinated or glutaraldehyde-coordinated Cr(II) sites (site C or site D) could be transformed to aluminum alkoxyl coordinated Cr(II) sites (site B) by displacement. Cr(II) sites strongly coordinating with aluminum alkoxy were protected from further over-reduction by TEA and influenced by electron donation from aluminum alkoxy. Therefore, site B had low activity and high stability in comparison with site A. As shown in Figure 1, the polymerization activity of site A and site B clearly increased as the cyclopentene concentration was increased from 0 to 20 vol %. Furthermore, with an increase in the cyclopentene concentration from 0 to 20 vol %, the time to reach maximum activity from site B changed from 1.6 to 18.8 min, as labeled by arrows in Figure 1. It could be expected that more chromate Cr(VI) species would be activated by cyclopentene with an increase in the cyclopentene concentration from 0 to 20 vol %. The amounts of site D and site A increased, because more of site D and site A could be transformed to site B, the amount of site B also increased with the cyclopentene concentration increasing. Therefore, the time required to reach maximum activity from site B was delayed. Thus, the polymerization activity was increased because of the increase in the amounts of site A and site B. The introduction of the cyclopentene comonomer resulted in the delay of the appearance of maximum activity from site B.

The results of homopolymerization and copolymerization are shown in Table I. As the cyclopentene comonomer concentration was increased from 0 to 20 vol %, the polymerization activity increased from 1.9 to 28.4 kg/mol of Cr h. There are two

possible explanations for this result. First, the presence of the cyclopentene comonomer could have increased the activation of chromate Cr(VI) species to Cr(II) species with respect to ethylene homopolymerization under the same conditions. Second, the copolymerization effect of the cyclopentene comonomer increased the activity. The activity of
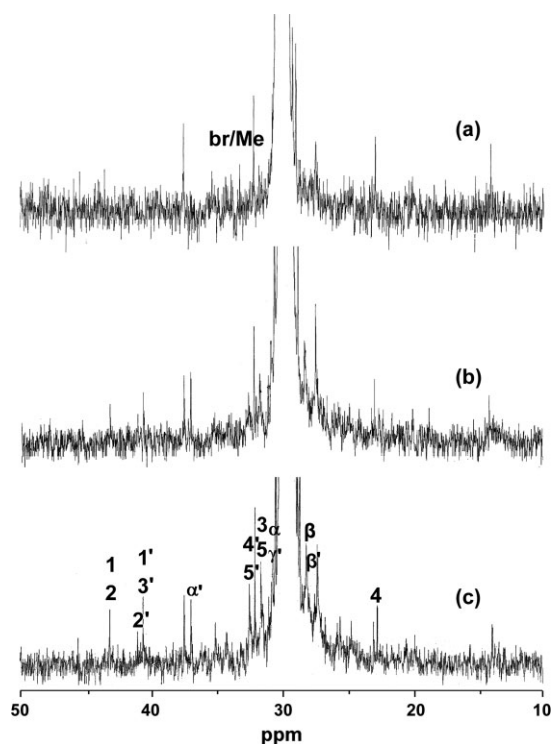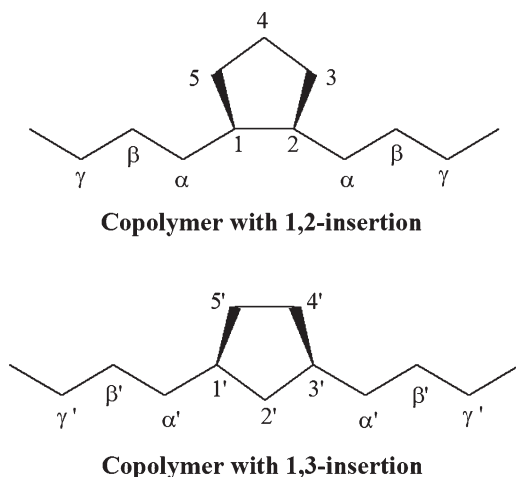

Figure 2 ^{13}C-NMR spectra of ethylene and cyclopentene homopolymers and copolymers obtained from PC600/TEA catalyst systems: (a) run 1, (b) run 2, and (c) run 3. The peaks at 33.25, 39.88, 37.77, and 38.21 ppm were assigned to the branching carbons of methyl, ethyl, propyl, and n-butyl, respectively.

cyclopentene homopolymerization was very low in the absence of ethylene under the same polymerization conditions; only trace amounts of the polymer were obtained.

Polymers obtained from homopolymerization and copolymerization were investigated with ^{13}C-NMR. Figure 2 presents the ^{13}C-NMR spectra of the polymers. The cyclopentene content and the structure of the inserted cyclopentene units in the copolymer were determined from the ^{13}C-NMR spectra. Scheme 2 illustrates the structures of the polymers corresponding to the ^{13}C-NMR spectra. As labeled in Figure 2, the signals at 43.23 (1, 2), 31.73 (3, 5), and 22.87 (4) ppm were assigned to isolated *cis*-1,2-cyclopentane units in the ethylene sequence. The signals at 41.11 (2′), 40.68 (1′, 3′), and 32.65 (4′, 5′) ppm were assigned to the isolated *cis*-1,3-cyclopentane units on the basis of literature references[40–43] (as labeled in Fig. 2). Cyclopentene insertion ratios, defined as the number of cyclopentane units per 1000 backbone carbons in the main chain, are shown in Table I. The cyclopentane content in the copolymer was low. The cyclopentene insertion ratio did not obviously increase with the cyclopentene concentration increasing from 5 to 20 vol % in the feed. This result can be rationalized in terms of the proposed mechanism shown in Scheme 1. Because of the steric hindrance caused by the aluminum alkoxy groups, the cyclopentene comonomer could more easily insert to site A than to site B. Although the amounts of site A and site B increased with the cyclopentene concentration increasing, the relative amounts of polymers formed from site A decreased (from 10.9 to 9.1 wt %) with the cyclopentene concentration increasing from 5 to 20 vol %. Therefore, the cyclopentene insertion ratio did not obviously increase with the increase in the cyclopentene concentration from 5 to 20 vol %.

Both 1,2-substituted cyclopentane and 1,3-substituted cyclopentane were found in the main polymer

Scheme 2 Structures of ethylene and cyclopentene copolymers corresponding to the ^{13}C-NMR spectra.
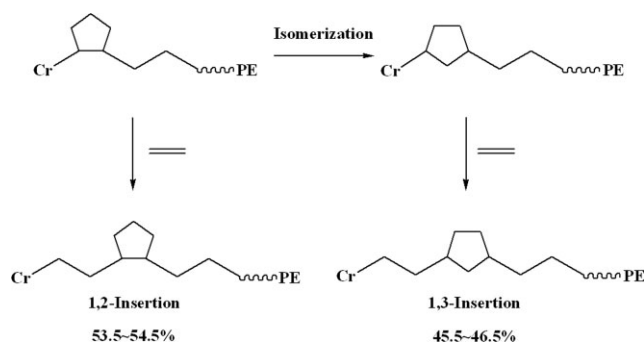
Scheme 3 Mechanisms of 1,2-insertion and 1,3-insertion of cyclopentene into the polyethylene main chain during ethylene and cyclopentene copolymerization.

chain. The formation of a 1,3-substituted cyclopentane structure can be explained in terms of isomerization of the 1,2-substituted cyclopentane terminal by a β-H elimination–reinsertion process before ethylene insertion, as shown in Scheme 3. According to the literature,[43] the higher the concentration is of cyclopentene during the polymerization, the larger the fraction is of cyclopentene bound to the catalyst for isomerization. The relative content of 1,3-substituted cyclopentane units should increase with the cyclopentene concentration increasing in the feed. However, in this study, the increase in the 1,3-substituted cyclopentane units was not observed.

The ^{13}C-NMR peaks at 33.25, 39.88, 37.77, and 38.21 ppm were assigned to the branching carbons of methyl, ethyl, propyl, and *n*-butyl, respectively, according to our previous work[16,17] and the results of Randall[44] and Axelson et al.[45] The relative amounts of short-chain branches (SCBs) were also described by the number of carbons on SCBs per 1000 backbone carbons in the main polymer chain, as shown in Table I. The relative amounts of SCBs (including methyl, ethyl, propyl, and *n*-butyl) decreased sharply with an increase in the concentration of the cyclopentene comonomer from 0 to 5 vol %, However, the relative amounts of SCBs did not decrease substantially with a further increase in the cyclopentene comonomer concentration from 5 to 20 vol %.

According to conventional opinions, methyl branches could form through isomerization on active sites.[4] Butyl branches could form through *in situ* insertion into the polymer chain of 1-hexene, which is a byproduct of oligomerization[35] or intramolecular β-H transfer.[46] However, the formation of other SCBs such as ethyl and propyl (as shown in Table I) could not be explained by these mechanisms. In our previous work,[15–17] the *in situ* ethylene metathesis reaction can interpret well the formation of all SCBs and the relative amounts of SCBs (including methyl, ethyl, propyl, and *n*-butyl). In this work, the relative

amounts of SCBs in the polymers decreased sharply with an increase in the cyclopentene concentration from 0 to 5 vol %. This can be explained as follows. First, there was a competition between the ethylene monomer and the cyclopentene comonomer to reduce the chromate Cr(VI) species to Cr(II) sites for polymerization. When the concentration of cyclopentene was increased, the amount of chromate Cr(VI) species activated by cyclopentene increased, and furthermore, the amount of chromate Cr(VI) species reduced by the ethylene monomer decreased (i.e., the relative amount of site D increased, and the relative amount of site C decreased). Although site D species are also metathesis active sites like site C species, glutaraldehyde can be more easily desorbed from the Cr(II) sites than formaldehyde can. The amount of short α-olefins, especially propylene, formed on site C and site D decreased (as shown in Scheme 1) when the cyclopentene concentration was increased from 0 to 5 vol %. Second, the kinetic curves of runs 1, 2, and 3 were deconvoluted into two types of kinetic curves with the same method used in our previous work.[16,17] The weight percentage of the polymer obtained from site A was calculated from the integral area of the kinetic curves (as shown in Table I). The relative content of the polymer formed from site A decreased (from 12.9 to 10.9 wt %) when the cyclopentene concentration was increased to 5 vol %. The relative amount of the polymer obtained from site A decreased, and the relative amounts of site C and site D (as shown in Scheme 1) decreased. Therefore, the amount of α-olefins formed by a metathesis reaction on site C and site D decreased. The relative amount of SCBs in the polymers did not obviously decrease with a further increase in the cyclopentene comonomer concentration from 5 to 20 vol %. In the case of the cyclopentene concentration increasing from 5% to 20 vol %, more chromate Cr(VI) species were activated by cyclopentene, and so the amount of site D increased. The amount of chromate Cr(VI) species reduced by the ethylene monomer relatively decreased, and so the amount of site C decreased. The amount of α-olefins formed by a metathesis reaction on site C decreased. Although a greater amount of site D formed, glutaraldehyde was more easily desorbed from the Cr(II) sites than formaldehyde was, so the relative amounts of SCBs did not obviously decrease with an increase in the concentration of the cyclopentene comonomer from 5 to 20 vol %.

The GPC curves of the polymers are shown in Figure 3. Table I shows the molecular weights and molecular weight distributions of the polymers. The molecular weights of the polymers increased with the cyclopentene concentration increasing from 0 to 20 vol %. Generally, the molecular weights and molecular weight distributions of polymers are deter-
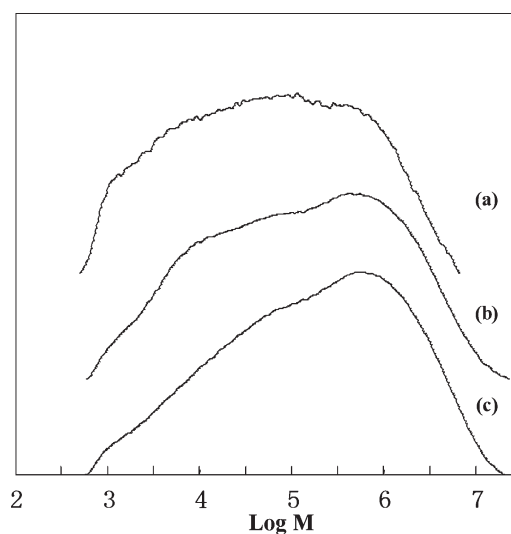

Figure 3 GPC curves of ethylene and cyclopentene homopolymers and copolymers obtained from (a) run 1, (b) run 2, and (c) run 3.

mined by two chain-transfer effects. One is chain transfer from active sites to aluminum alkyl. The molecular weight of the polymer decreases with an increase in the Al/Cr molar ratio. The other is β-H elimination (or β-H transfer) to the monomer. The proton in the tertiary β-carbon can be easily transferred or β-eliminated, and this leads to chain transfer to the monomer. In this work, the relative amounts of SCBs, including methyl, ethyl, propyl, and n-butyl branches, decreased with the introduction of cyclopentene, as shown in Table I. Therefore, the molecular weights of the polymers should have increased with a decrease in the comonomer insertion. However, the cyclopentane units also had the tertiary β-carbon in the main chain. The molecular weights of the polymers should have decreased with the increase in the number of cyclopentane units. However, from our molecular weight results, the molecular weights of the polymers increased with a decrease in the relative amount of SCBs. This indicates that β-H elimination (or β-H transfer) from the tertiary β-carbon of the cyclopentane units was not the dominant effect. As shown in Figure 3, the introduction of the cyclopentene comonomer increased the high-molecular-weight fractions and decreased the low-molecular-weight fractions. This result may have been due to the fact that the relative amount of SCBs decreased with the introduction of cyclopentene. The proton in the tertiary β-carbon that could be transferred or β-eliminated, leading to chain transfer to the monomer, decreased.

All the polymers obtained from homopolymerization and copolymerization were characterized with an FTIR spectrometer. The IR spectra are shown in Figure 4(a–d). When the concentrations of the
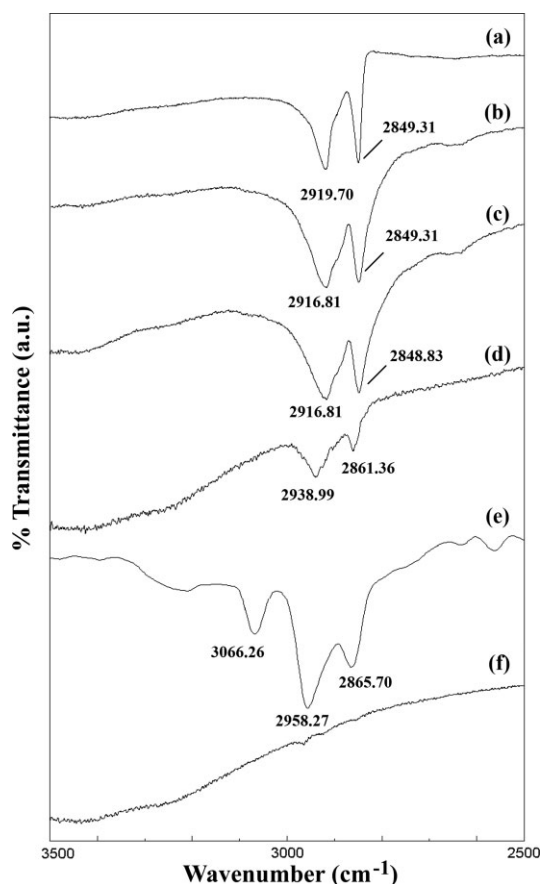
Figure 4 IR spectra of ethylene and cyclopentene homopolymers and copolymers obtained from (a) run 1, (b) run 2, (c) run 3, and (d) run 4 (×2) and of two model samples prepared (e) by dropping cyclopentene on silica gel and KBr disk (SiO_2/KBr = 1 : 100 w/w) for IR and (f) by mixing cyclopentene and silica gel for 1.5 h, drying the sample *in vacuo* at 60°C for 6 h, and then making the sample KBr disk (sample/KBr = 1 : 100 w/w) for IR.

cyclopentene comonomer were 0, 5, and 20 vol %, the usual characteristic peaks of polyethylene were found around 2917 and 2849 cm^{-1} for $—CH_2—$ groups in the main chain [as shown in Fig. 4(a–c)]. For the trace amount of the product obtained from the homopolymerization of cyclopentene, two peaks at 2938.99 and 2861.36 cm^{-1} [as shown in Fig. 4(d)] were found; these peaks appeared at wave numbers higher than those typical characteristic peaks of polyethylene. To determine whether these two peaks were from polymers or from some residual cyclopentene, we prepared two samples for comparison: the first was prepared by a little cyclopentene being dropped on a silica gel disk for IR, and the second was prepared by the mixing of cyclopentene and silica gel for 1.5 h and drying of the mixture *in vacuo* at 60°C for 6 h. As in Figure 4(e), the peaks at 3066.26, 2958.27, and 2865.70 cm^{-1} were assigned to $\nu(CH)$, $\nu_{as}(CH_2)$, and $\nu_s(CH_2)$ of cyclopentene, respectively. There was no peak between 3100 and

2000 cm^{-1} for the second sample (mixing cyclopentene and silica gel for 1.5 h and drying *in vacuo* at 60°C for 6 h), as shown in Figure 4(f). This evidence implies that there was no residual cyclopentene in the polymer obtained under the conditions used to prepare the second sample. If even a little cyclopentene remained in the polymer, three peaks at 3066.26, 2958.27, and 2865.70 cm^{-1} should have been observed. Therefore, the two peaks found in the cyclopentene homopolymer were confirmed to be from the polymer or oligomer, despite the low polymerization activity. The cyclopentene homopolymer was not characterized by NMR because the trace amount of the product that was obtained was not sufficient for further microstructure analysis.

Because the internal double bond (C=C) was not found in the copolymer main chain, the ring-opening metathesis polymerization was ruled out during the copolymerization stage of ethylene and cyclopentene. This evidence strongly implies that Cr=C species are not active sites for polymerization chain propagation. The Cossee–Arlman chain propagation mechanism, with either Cr—C or Cr—H as active sites, shows further evidence for polymerization chain propagation. Another important implication from the new evidence obtained in this work is that the Cr=C species might be transformed into Cr—C species during the polymerization stage, and this is supported by the report of Schmid and Ziegler.[10]

CONCLUSIONS

Calcined Phillips CrO_x/SiO_2 catalyst (PC600) was adopted for the first time to catalyze the copolymerization of ethylene and cyclopentene with TEA as a cocatalyst. The absence of an internal double bond (C=C) in the copolymer ruled out ring-opening metathesis polymerization during the copolymerization stage of ethylene and cyclopentene. The 1,2-insertion and 1,3-insertion of cyclopentene into the polyethylene main chain were confirmed. This evidence strongly implies that Cr=C may not be active sites for polymerization chain propagation. Cr—C active sites under the Cossee–Arlman chain propagation mechanism should be responsible for the chain propagation during the polymerization stage. The Cr=C species (metathesis sites) during the induction period mentioned in our previous work might be transformed into Cr—C species as polymerization active sites during the polymerization stage. The transformation mechanism needs further investigation in the future.

References

1. Pullukat, T. J.; Hoff, R. E. Catal Rev Sci Eng 1999, 41, 389.
2. Clark, A. Catal Rev 1970, 3, 145.

3. Yermakov, Y.; Zakhrov, V. Adv Catal 1975, 24, 173.
4. McDaniel, M. Adv Catal 1985, 33, 47.
5. Groppo, E.; Lamberti, C.; Bordiga, S.; Spoto, G.; Zecchina, A. Chem Rev 2005, 105, 115.
6. Groppo, E.; Lamberti, C.; Bordiga, S.; Spoto, G.; Zecchina, A. J Catal 2006, 240, 172.
7. Gaspar, A. B.; Dieguez, L. C. J Mol Catal A 2004, 219, 357.
8. van Kimmenade, E. M. E.; Kuiper, A. E. T.; Tamminga, Y.; Thune, P. C.; Niemantsverdriet, J. W. J Catal 2004, 223, 134.
9. Espelid, Ø.; Børve, K. J. J Catal 2002, 206, 331.
10. Schmid, R.; Ziegler, T. Can J Chem 2000, 78, 265.
11. Hanmura, T.; Ichihashi, M.; Monoi, T.; Matsuura, K.; Kondow, T. J Phys Chem A 2005, 109, 6465.
12. MacAdams, L. A.; Buffone, G. P.; Incarvito, C. D.; Rheingold, A. L.; Theopold, K. H. J Am Chem Soc 2005, 127, 1082.
13. Liu, B.; Nakatani, H.; Terano, M. J Mol Catal A 2002, 184, 387.
14. Liu, B.; Nakatani, H.; Terano, M. J Mol Catal A 2003, 201, 189.
15. Liu, B.; Fang, Y.; Nakatani, H.; Terano, M. Macromol Symp 2004, 213, 37.
16. Fang, Y.; Liu, B.; Hasebe, K.; Terano, M. J Polym Sci Part A: Polym Chem 2005, 43, 4632.
17. Xia, W.; Liu, B.; Fang, Y.; Hasebe, K.; Terano, M. J Mol Catal A 2006, 256, 301.
18. Fang, Y.; Xia, W.; He, M.; Liu, B.; Hasebe, K.; Terano, M. J Mol Catal A 2006, 247, 240.
19. Xia, W.; Liu, B.; Fang, Y.; Zhou, D.; Terano, M. Stud Surf Sci Catal 2006, 161, 225.
20. Liu, B.; Fang, Y.; Xia, W.; Terano, M. Kinet Catal 2006, 47, 234.
21. Liu, B.; Xia, W.; Terano, M. Stud Surf Sci Catal 2006, 161, 129.
22. Scott, S. L.; Ajjou, J. A. N. Chem Eng Sci 2001, 56, 4155.
23. Hogan, J. P. J Polym Sci Part A-1: Polym Chem 1970, 8, 2637.
24. Groeneveld, C.; Wittgen, P. P. M. M.; Swinnen, H. P. M.; Wernsen, A.; Schuit, G. C. A. J Catal 1983, 83, 346.
25. Jozwiak, W. K.; Dalla Lana, I. G.; Fiedorow, R. J Catal 1990, 121, 183.
26. Ghiotti, G.; Garrone, E.; Coluccia, S.; Morierra, C.; Zecchina, A. J Chem Soc Chem Commun 1979, 1032.
27. Ghiotti, G.; Garrone, E.; Zecchina, A. J Mol Catal 1988, 46, 61.
28. Krauss, H. L.; Hums, E. Z Naturforsch B 1979, 34, 1628.
29. Emrich, R.; Heinemann, O.; Jolly, P. W.; Kruger, C.; Verhovnik, G. P. J. Organometallics 1997, 16, 1511.
30. Ruddick, V. J.; Badyal, J. P. S. J Phys Chem B 1998, 102, 2991.
31. Rebenstorf, B.; Larsson, R. J Mol Catal 1981, 11, 247.
32. Rebenstorf, B. Z Anorg Allg Chem 1984, 513, 103.
33. Kantcheva, M.; Dalla Lana, I. G.; Szymura, J. A. J Catal 1995, 154, 329.
34. Zielinski, P.; Dalla Lana, I. G. J Catal 1992, 137, 368.
35. Cossee, P. J Catal 1964, 3, 80.
36. Ivin, K. J.; Rooney, J. J.; Stewart, C. D.; Green, M. L. H.; Mahtab, R. J Chem Soc Chem Commun 1978, 604.
37. Nishimura, M.; Thomas, J. M. Catal Lett 1993, 19, 33.
38. Al-Mashta, F.; Davanzo, C. U.; Sheppard, N. J Chem Soc Chem Commun 1983, 1258.
39. McDaniel, M. P.; Cantor, D. J Polym Sci Polym Chem Ed 1983, 21, 1217.
40. Kaminsky, W.; Spiehl, R. Makromol Chem 1989, 190, 515.
41. Jerschow, A.; Ernst, E.; Hermann, W.; Müller, N. Macromolecules 1995, 28, 7095.
42. Galimberti, M.; Albizzati, E.; Abis, L.; Bacchilega, G. Makromol Chem 1991, 192, 2591.
43. Naga, N.; Imanishi, Y. Macromol Chem Phys 2002, 203, 159.
44. Randall, J. C. J Appl Polym Sci 1978, 11, 585.
45. Axelson, D. E.; Levy, G. C.; Mandelkern, L. Macromolecules 1979, 12, 41.
46. McDermott, J. X.; White, J. F.; Whitesides, G. M. J Am Chem Soc 1973, 95, 4451.