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CRYSTAF Analysis of Polyethylene Synthesized with Phillips Catalyst

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Summary: Crystallization analysis fractionation (CRYSTAF) was used for the first time to investigate the solution crystallization behavior of ethylene homopolymers and copolymers made with Phillips CrO_x/SiO_2 catalyst. Interestingly, the crystallization peak temperatures (T_p) of copolymers of ethylene and cyclopentene increased with increasing cyclopentene molar fraction in the copolymer. Comparing two factors (short chain branches (SCBs) and cyclopentene incorporation), decreasing SCB frequency is proposed as the dominant factor to explain the increase of crystallization peak temperatures with increasing cyclopentene incorporation. In addition, SCB frequency and molecular weight might be the two significant factors determining the crystallization temperature of polyethylene made with Phillips CrO_x/SiO_2 catalyst with different cocatalysts (triethylaluminum and diethylaluminum ethoxide).

Keywords: comonomer; crystallization analysis fraction (CRYSTAF); Phillips catalyst; polyethylene (PE); short chain branches

Introduction

Phillips CrO_x/SiO_2 catalysts have occupied an especially important place among the commercial polyolefin catalysts. They are still responsible for about one-third of the world's production of high-density polyethylene (HDPE). Compared to Ziegler-Natta and metallocene catalysts, Phillips catalysts show many advantages, such as easy preparation procedure, unique polymerization performance and excellent polymer properties.[1,2] However, the nature of their active sites and polymerization mechanism still remains not well understood, in spite of continuous and extensive research for more than half a century since their discovery by Hogan and Banks in the early 1950s. There is still very limited understanding of why Phillips catalysts have such unique behavior.[3–12]

Phillips $Cr(VI)O_x/SiO_2$ catalysts can be made by impregnating aqueous solutions of Cr compounds (mostly chromium(III) acetate or chromium(VI) trioxide) onto amorphous silica gel supports, followed by calcination in dry air at temperatures usually around 600–800 °C for several hours. The catalyst must be further activated to $Cr(II)O_x/SiO_2$, which is the real active precursor for ethylene polymerization. Our group has previously systematically studied the various activation procedures and mechanism of Phillips catalyst for ethylene polymerization (including thermal activation, ethylene activation, Al-alkyl activation and CO activation).[13–23]

In the case of using metal-alkyl cocatalyst for the activation of Phillips catalyst, its

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introduction in which stage had been reported to be crucial to affect the polymerization behavior as well as polymer properties.[20,21] Typically, there are three stages for the introduction of metal-alkyl cocatalysts: catalyst preparation stage, catalyst aging or pretreatment stage (in polymerization reactor just before introduction of monomer) and polymerization stage (simultaneous interaction of catalyst with metal-alkyl cocatalyst and monomer). In our recent work, we studied the effect of different Al-alkyl cocatalysts, such as triethylaluminum (TEA) and diethylaluminum ethoxide (DEAE), introduced during the polymerization stage with simultaneous interaction of the catalyst with the Al-alkyl cocatalyst and monomer. The polymerizations were started by breaking a glass ampoule containing the Phillips CrO_x/SiO_2 catalyst calcined at 600 °C (PC600) within the polymerization reactor. Effects of different Al-alkyl cocatalysts and Al/Cr molar ratio (7.5, 15 and 22.5) on the polymerization kinetic curves and polymer microstructures were investigated.[21] It was found that the PC600/TEA system showed completely different polymerization kinetics from that of the PC600 catalyst pre-modified by TEA during the catalyst preparation stage.[20,21] Furthermore, the polymerization kinetics significantly changed in the case of using PC600/DEAE catalyst system.

More recently, in order to investigate the state of active sites and chain propagation mechanisms concerning Phillips catalyst, calcined Phillips CrO_x/SiO_2 catalyst (PC600) was adopted for the first time to catalyze copolymerization of ethylene and cyclopentene with TEA cocatalysts. The absence of internal double bond (C=C) in the copolymer ruled out the ring-opening metathesis polymerization during the copolymerization stage of ethylene and cyclopentene. Also, the 1,2- and 1,3-insertions 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 Cossee-Arlman chain propagation mechanism should be responsible for the chain propagation during the polymerization stage. Based on the above results, plausible mechanisms for the formation and transformation of active sites were proposed to explain the unique polymerization kinetics and polymer microstructure in terms of comonomer insertion ratio, short chain branches (SCBs), molecular weight (MW) and molecular weight distribution (MWD).

Crystallization analysis fractionation (CRYSTAF) is one of the most important techniques for polyolefin characterization. It can be used to measure chemical composition distribution (CCD) based on the continuous crystallization of polymer chains from a dilute solution. The knowledge of a polymer's CCD is essential in investigations of structure-property relationships, polymerization kinetics and mechanisms, and polymer reaction engineering. CRYSTAF is most commonly used to analyze linear low-density polyethylene (LLDPE) [24–30] and there is practically no systematic investigation for HDPE made with Phillips catalysts.

The microstructures of polyolefins made with Phillips catalyst under the conditions described above have been previously investigated with ^{13}C NMR and GPC. In order to further understand polymerization mechanism details and structure-property relationships, a series of polyethylene and ethylene/cyclopentene copolymers made with Phillips catalyst was characterized by CRYSTAF in this work. This is the first example of a systematic CRYSTAF analysis of these polymers published in the literature.

Experimental Part

Catalyst Preparation

Details about raw materials and Phillips catalyst preparation procedure can be found in our previous publications.[21,22] About 15 g of catalyst precursor was added into a spouted fluidized-bed reactor with a temperature-programmed heating controller and subsequently calcined at 600 °C for 6 hours under 200 ml/min flow of dry air. Before entering the catalyst preparation system, dry air was purified by flowing through a 13X molecular sieve column. Then, the catalyst was cooled to room temperature under nitrogen flow (200 ml/min), which was 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 measured to about 100 mg, which was weighed precisely before polymerization.

Copolymerization of Ethylene and Cyclopentene

Copolymerizations were done in a semi-batch slurry polymerization reactor system, previously described in the literature.[22] One ampoule bottle with approximately 100 mg of PC600 catalyst was fixed on the top part of the 100 ml glass polymerization reactor, provided with a water-jacket and a magnetic stirrer. Heptane was purified by contacting with 13X molecular sieves and 24-hour bubbling under high purity nitrogen. The reactor system was heated and vacuumed for 2 h. After the introduction of heptane, cocatalyst (TEA) was subsequently injected into the reactor under nitrogen atmosphere. The solution was then saturated with 0.15 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. After the introduction of cyclopentene (purified with Na metal), the polymerization was started after breaking the ampoule bottle with the catalyst screwing of a steel bar and carried out at 40 °C for 90 minutes. 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 of ethanol/HCl solution. The polymer obtained was washed with ethanol and dried under vacuum at 60 °C for 6 hours.

Ethylene Homopolymerization

The same semi-batch slurry polymerization reactor system described above was used. After introduction of heptane, cocatalyst (TEA or DEAE) was subsequently injected into the 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 containing the catalyst. The polymerization was carried out at 60 °C for 90 minutes.

CRYSTAF Analysis

CRYSTAF analysis was performed with a CRYSTAF model 200 manufactured by PolymerChar S.A., having five 60 ml, stirred stainless steel crystallization vessels. Prior to the fractionation, the polymer sample was dissolved in 1,2,4-trichlorobenzene (TCB) (0.07 w/w %) at 160 °C for 90 minutes to ensure complete dissolution of the polymer sample inside the crystallization vessel. Then, the polymer solution was kept at 120 °C for 60 minutes for thermal stabilization. A stirring rate of approximately 200 rpm was used during both the dissolution and stabilization periods, but this rate was reduced to approximately 100 rpm for the subsequent crystallization steps to minimize shear-induced chain scission. During the crystallization step, the temperature of the solution was decreased at a continuous cooling rate of 0.1 °C/min. The concentration of the polymer in the solution as a function of the crystallization temperature was monitored through an on-line infrared detector and recorded by the data acquisition software. The plot of the amount of the polymer crystallized as a function of the crystallization temperature is called the derivative

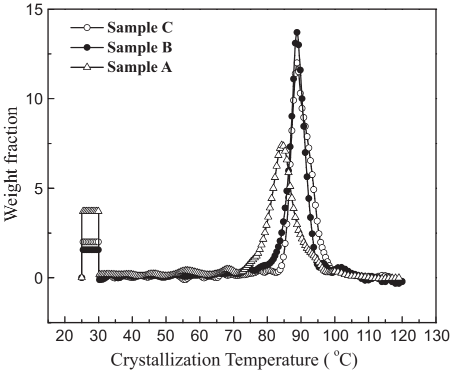

Figure 1.
CRYSTAF profiles of polyethylene and ethylene/cyclopentene copolymers made with different cyclopentene concentrations. Polymerization conditions: catalyst amount, 100 mg; polymerization temperature, 40 °C; polymerization time, 1.5 h; ethylene pressure, 0.15 MPa; solvent, heptane (20 ml); cocatalyst, TEA in heptane (1M); Al/Cr molar ratio, 22.5.

CRYSTAF profile, or simply the CRYSTAF profile.[30]

Results and Discussion

Copolymers of Ethylene and Cyclopentene

In order to shed light on the polymer chain propagation mechanism, the PC600 catalyst was adopted for the first time to catalyze the copolymerization of ethylene and cyclopentene in the presence of TEA.[22] A series of ethylene homopolymers and ethylene and cyclopentene copolymers was synthesized. ^{13}C NMR and GPC were used for the investigation of polymer microstructure. In this work, the homopolymers and copolymers were characterized by CRYSTAF for the first time.

CRYSTAF profiles for one homopolymer and two copolymer samples are shown in Figure 1. Table 1 shows CRYSTAF characterization results for these samples. The crystallization peak temperatures (T_p) are 84.5 °C, 88.7 °C, and 88.8 °C for polymers made with cyclopentene reactor volume fractions of 0, 5 and 20 vol %, respectively.

In general, comonomer fraction is the dominant factor determining the crystallization temperature (the CRYSTAF peak temperatures and profile shapes) of ethylene and α-olefin copolymers. Chains with lower comonomer fractions will precipitate at higher temperatures, whereas chains with higher comonomer fractions will precipitate at lower temperatures.[29] In our work, low contents of cyclopentane units (including 1,2- and 1,3-insertions) were found in the copolymer chains (approximately one cyclopentane unit per 1000 backbone carbon atoms in the main chain). The content of cyclopentane units were 0.94 and 0.99 per 1000 backbone carbon atoms in the main chain when the cyclopentene concentrations were 5 and 20 vol %.[22] That is to say, the cyclopentene insertion ratio did not increase with increasing cyclopentene concentration in the reactor from 5 to 20 vol %. If we were to predict T_p merely from the fraction of cyclopentene in the copolymer, the crystallization peak temperature should decrease with increasing cyclopentene fraction.

Table 1.
CRYSTAF characterization results and microstructures of homo- and co- polymer samples made with Phillips catalyst[a].

Sample	Cyclopentene Concentration (vol%)	T_p (°C)	Cyclopentene insertion ratio[b]	SCBs[b]
A	0	84.5	–	2.05
B	5	88.7	0.94	1.21
C	20	88.8	0.99	1.11

[a] Polymerization conditions: 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); Al/Cr molar ratio, 22.5.

[b] Number of cyclopentane or short chain brances (including methyl, ethyl, propyl, n-butyl branches) per 1000 backbone carbon determined by ^{13}C-NMR.

However, we observed exactly the opposite behavior: T_p increased when the cyclopentene concentration was varied from 0 to 5 vol % and T_p did not change appreciably when the cyclopentene concentration increased from 5 to 20 vol %.

Our recent results have shown that some short α-olefins, especially propylene, could be formed through an ethylene metathesis reaction on a chromium (II) site coordinated with formaldehyde. The short α-olefins formed in situ can insert into the polymer chain to form SCBs (methyl, ethyl, propyl and n-butyl).[15,16,21] For the series of ethylene and cyclopentene copolymers studied in this investigation, the relative amount of SCBs decreased sharply, from 2.05 to 1.21 SCB per 1000 carbon atoms, when the fraction of cyclopentene added to the reactor increased from 0 to 5 vol %.[22] On the other hand, the relative amount of SCBs did not change significantly with further increase of cyclopentene concentration from 5 to 20 vol %.[22] Therefore, it seems clear that the increase in T_p from 84.5 °C to 88.7 °C upon adding 5 vol % of cyclopentene in the reactor is due to the decrease in SCB frequency. The T_p remains almost unchanged with further increase of cyclopentene concentration from 5 to 20 vol % because the SCB frequency is hardly affected by this formulation (from 1.21 to 1.11 SCB per 1000 carbon atoms).

In conclusion, short chain branches are the dominant factor determining T_p of the ethylene and cyclopentene copolymers synthesized under these conditions.

Ethyelene Homopolymers Made with PC600/TEA and PC600/DEAE

Ethylene homopolymerization was carried out with PC600 and two different Al-alkyl cocatalysts, TEA and DEAE. The cocatalysts were introduced at the very beginning of the polymerization to interact simultaneously with the catalyst and monomer.[21] All the homopolymers made with PC600/TEA and PC600/DEAE were characterized by CRYSTAF. The CRYSTAF characterization results are given in Table 2.

Table 2.

CRYSTAF characterization results and microstructures of homopolymer samples made with Phillips catalyst with Al-alkyl cocatalyst (TEA or DEAE)[a].

Sample	Cocatalyst	Al/Cr molar ratio	T_p (°C)	SCBs[b]
D	TEA	7.5	87.6	6.32
E	TEA	15.0	88.2	4.41
F	TEA	22.5	89.1	3.94
G	DEAE	7.5	89.6	9.50
H	DEAE	15.0	89.9	7.12
I	DEAE	22.5	89.6	5.92

[a] 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 or DEAE in heptane (1M).

[b] Number of short chain brances (including methyl, ethyl, propyl or n-butyl branches) per 1000 backbone carbon determined by ^{13}C-NMR.

Figure 2 shows the CRYSTAF profiles for three polyethylenes made with PC600/TEA at different Al/Cr molar ratios. The crystallization peak temperatures are $T_p = 87.6$ °C, 88.2 °C, and 89.1 °C for Al/Cr molar ratios of 7.5, 15 and 22.5, respectively. According to our previous microstructure result,[21] for polyethylene made with PC600/TEA, the relative amount of short chain branches were 6.32, 4.41 and 3.94 per 1000 backbone carbon, respectively.[21] The number of SCBs decreased

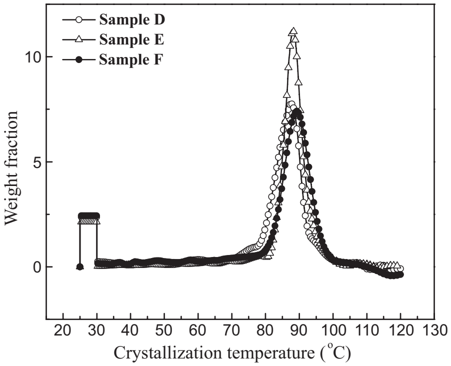

Figure 2.

CRYSTAF profiles of ethylene homopolymers made with PC600/TEA at different Al/Cr molar ratios. 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 (1M).

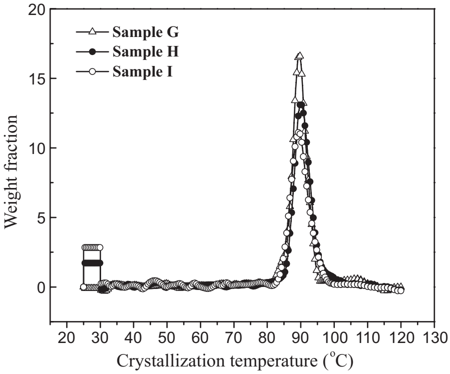

Figure 3.
CRYSTAF profiles of ethylene homopolymers made with PC600/DEAE at different Al/Cr molar ratios. Polymerization conditions: catalyst amount, 100 mg; polymerization temperature, 60 °C; polymerization time, 1.5 h; ethylene pressure, 0.13 MPa; solvent, heptane (20 ml); cocatalyst, DEAE in heptane (1M).

with the increase of the Al/Cr molar ratio, leading to a consequent increase in T_p.

Figure 3 shows the CRYSTAF profiles of the homopolymers made with PC600/DEAE at different Al/Cr molar ratios (7.5, 15 and 22.5). The crystallization peak temperatures are $T_p = 89.6\,°C$, $89.9\,°C$, and $89.6\,°C$ for Al/Cr molar ratio of 7.5, 15 and 22.5, respectively. The SCB frequency were 9.50, 7.12 and 5.92 per 1000 backbone carbon, respectively when the Al/Cr molar ratio is 7.5, 15 and 22.5.[21] Similarly to polyethylene made with PC600/TEA, the SCB frequency decreased with the increase of Al/Cr molar ratio. It would reasonable to expect that T_p should increase with the decrease in SCB frequency. But from our CRYSATF results, the crystallization temperatures are almost the same (the error associated with each measurement is about $\pm 0.2\,°C$).

Even though the dominant factor determining T_p of ethylene homopolymers is the SCB frequency, molecular weight can also play a secondary role. Chains with low molecular weights have a high frequency of terminal methyl groups (chain ends) per 1000 carbon atoms than higher molecular weight chains. Chain ends have a similar effect on crystallization temperature as SCBs resulting from comonomer incorporation, and terminal methyl groups are to be taken into account for M_n values less than about 5000.[29] From the GPC spectra of these samples,[21] sample I has a larger fraction of low-MW chains than samples G and H. This low-MW fraction increases the frequency of terminal methyl groups that is responsible for the lower than expected T_p of this polymer.

As shown in Table 2, at the same Al/Cr molar ratio, the CRYSTAF peak temperatures of polyethylenes made with TEA are lower than of those produced with DEAE, although their SCB frequency is also lower. This counterintuitive observation likely derives from the fact that polyethylenes made with TEA have lower M_w, broader MWD (larger M_w/M_n) and, consequently, higher frequency of terminal methyl groups, than polymers made with DEAE.[21]

Conclusions

CRYSTAF was used for the first time to systematically investigate the crystallization peak temperature of polyethylene and ethylene/cyclopentene copolymers made with the Phillips CrO_x/SiO_2 catalyst (PC600). Most remarkably, the crystallization peak temperatures of these polymers increased with increase of cyclopentene reactor concentration from 0 to 20 vol %. We have proposed that the decreasing short chain branch frequency was the dominant factor to explain the increase of crystallization peak temperatures. For ethylene homopolymers made with PC600/TEA or PC600/DEAE, the crystallization peak temperatures did not change significantly as a function of Al/Cr ratio and cocatalyst type. We have also found small but significant molecular weight effect on the crystallization peak temperature of these polymers.

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