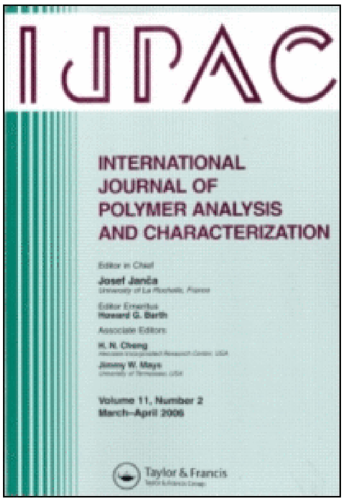

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# Simple Ways to Characterize Non-isothermal Crystallization of Homogeneous Poly(ethylene-1-co-octene) Copolymer

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# Simple Ways to Characterize Non-isothermal Crystallization of Homogeneous Poly(ethylene-1-co-octene) Copolymer

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**Abstract:** Non-isothermal crystallization of homogeneous poly(ethylene-co-1-octene) copolymers with different octene contents was studied using power-compensating differential scanning calorimetry as functions of cooling rate and comonomer content. With increasing cooling rate, the crystallization temperature decreases for all polymers. A single crystallization peak was observed for polyethylene, while multiple crystallization peaks were observed for copolymers. The non-isothermal crystallization rate of these copolymers was estimated by continuous cooling transformation (CCT) curves, crystallization rate coefficient (CRC), and crystallization rate parameter (CRP). With increasing comonomer content, the CRC value decreases and CCT curves shift to longer time under the same degree of supercooling, indicating the crystallization rate decreases. However, the CRP value can't successfully estimate the crystallization rate of these copolymers.

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**Keywords:** Homogeneous poly(ethylene-co-1-octene); Non-isothermal crystallization

## INTRODUCTION

Non-isothermal crystallization study has received increasing interest due to its similarity to real industrial processing conditions, such as fiber spinning, film blowing, and injection molding. Also, from a scientific point of view, the study of crystallization under non-isothermal conditions may expand general understanding of crystallization behavior of polymers, since isothermal methods are often restricted to narrow temperature ranges.

Many models have been developed to describe non-isothermal crystallization kinetics and most of them are based on Avrami equation,[1] which was developed for isothermal crystallization conditions. Ziabicki[2] suggested that the non-isothermal crystallization process can be regarded as a sequence of isothermal steps. The proposed equation was a series expansion of the Avrami equation. Ozawa[3] proposed a model for the process of nucleation and subsequent growth under constant cooling rate by modifying the Avrami equation. Nakamura et al.[4,5] derived a model based on the presumption that the kinetics of primary nucleation and of crystal growth rate are similar so that the ratio of growth rate to nucleation rate is constant (isokinetic conditions). Patel and Spruiell[6] later suggested a differential form of the Nakamura model. Dietz[7] also proposed a kinetic equation for non-isothermal crystallization with consideration of secondary crystallization. More recently, Ziabicki[8–10] presented a new model where transient thermal and athermal effects were included.

All of the above models have been widely used and claimed to successfully describe the non-isothermal crystallization process for certain polymers, although each of them has its own drawbacks and restrictions.[11] Moreover, all these models are complicated and inconvenient to determine the non-isothermal crystallization rate of polymers in practical processes. The results from these models are also not always easy to explain. From an industry point of view, we need a more simplified and reliable method to estimate the non-isothermal crystallization rate. Based on this, several attempts have been made. Spruiell and White[12] constructed continuous cooling transformation (CCT) curves, which were plotted from the crystallization onset temperatures and the corresponding elapsed times. The CCT curves of materials with faster crystallization rate will be shifted to the shorter elapsed time. Khanna[13] introduced crystallization rate coefficient (CRC), which allowed a direct comparison of the crystallization rates of various polymers on a single scale. The crystallization rate coefficient can be measured from the slope of the cooling rate versus crystallization peak temperature plot, and this parameter represents a change in cooling rate required to bring an approximately 1°C change in the supercooling of the polymer melt. Zhang et al.[14] suggested using the crystallization rate parameters (CRP), which can be obtained from the slope of the plot of the reciprocal of crystallization half-time ($1/t_{1/2}$) against the cooling rate. Both CRC and CRP values will become higher for polymers with faster crystallization rate.

In recent years, with the emergence of the so-called metallocene catalyst, it is possible to synthesize ethylene-α-olefin copolymer with narrow molecular weight distribution and homogeneous comonomer distribution, compared to linear low density polyethylene from the Ziegler catalyst. The primary comonomers are 1-octene, 1-hexene, and 1-butene. Several studies on these new materials have been done since then.[15–18] The Dow Chemical Company commercialized a series of ethylene octene copolymers using their Insite® Technology homogeneous catalyst. With these copolymers, it would seem possible to study crystallization behavior systematically as a function of comonomer or branch content and probably avoide heterogeneous molecular weight and sequence length distribution of copolymers produced from Ziegler catalyst.

In this article, we will first describe the characterization of these copolymers and then study their non-isothermal crystallization behavior.

# EXPERIMENTAL SECTION

## Materials

The materials used are listed in Table I. These are ethylene-octene copolymers with different octene levels prepared by Dow's Insite® Technology homogeneous catalyst. A linear polyethylene was also studied

**Table I.** Characteristics of polymers used in this study

| | Polymer designation | | | | |
|---|---|---|---|---|---|
| Parameter | EO958 | EO916 | EO902 | EO885 | EO870 |
| Density (g/cm$^3$) | 0.958 | 0.916 | 0.902 | 0.885 | 0.870 |
| Content of comonomer (wt.%) | 0 | 15 | 20 | 30 | 38 |
| Content of comonomer (mol.%) | 0 | 4.2 | 5.9 | 9.7 | 13.3 |
| $M_w$ | 141500 | 110100 | 94500 | 106000 | 75900 |
| $M_n$ | 18600 | 29200 | 36300 | 41200 | 35700 |
| $M_w/M_n$ | 7.6 | 3.8 | 2.5 | 2.5 | 2.1 |
| $T_m^\circ$ (°C) | 145 | 123 | 102 | 88 | 67 |

for comparison. The samples are identified with initials EO (ethylene/octene) followed by a number corresponding to the density of the copolymer.

## Material Characterization

### Comonomer Contents

The comonomer contents (weight percent) of copolymers were determined by Fourier transform-infrared (FTIR) spectroscopy with the integral of the absorbance between 1381 and 1373 $cm^{-1}$, which is proportional to the number of -$CH_3$- groups. Accordingly, the 1-octene content of the investigated samples was 15, 20, 30, and 38 wt%, and the corresponding density was approximately 0.916, 0.902, 0.885, and 0.870 $g^*cm^{-3}$, respectively.

### Molecular Weight and Molecular Weight Distribution

The molecular weight and the molecular weight distribution were determined by gel permeation chromatography (GPC). The solvent used was 1,2,4 trichlorobenzene. Calibration of the GPC column set was performed with 21 narrow molecular weight distribution polystyrene standards. The narrow standards mixtures were run first and in order of decreasing highest molecular weight component to minimize degradation. The polystyrene standard peak molecular weights are converted to polyethylene molecular weights using the following equation:[19]

$$M_{\text{polyethylene}} = A \times (M_{\text{polyethylene}})^B$$

where $M$ is the molecular weight, $A$ has a value of 0.431, and B is equal to 1.0.

The molecular weight and molecular distribution of polyethylene and its copolymers are given in Table I. We can see that Dow Insite octene copolymers have narrower molecular distribution than Ziegler polyethylene. All these polymers have roughly same weight-average molecular weight.

### Comonomer Distribution

The comonomer distributions were determined using crystallization analysis fractionation (CRYSTAF) for EO916 and EO902. We could not analyze EO885 and EO870 due to their fairly low crystallinity. The cumulative soluble concentration was measured as the polymer crystallizes while the temperature was decreased. The derivative of the cumulative profile reflects the short chain branching distribution of the

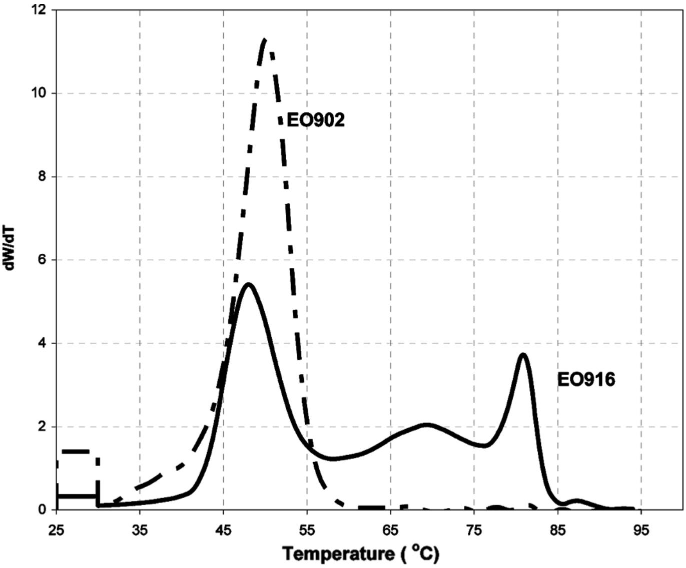


Figure 1. CRYSTAF of EO916 and EO902.

polymer. More peaks indicate a more heterogeneous comonomer distribution. The result shows that EO916 has more heterogeneous comonomer distribution than EO902 (Figure 1).

### Thermal Stability

Thermo-gravimetric analysis (TGA) was investigated using a TA Instruments TGA 2050 at the heating rate of 20°C/min over the temperature range from room temperature to 700°C under $N_2$ atmosphere. The TGA scans are shown in Figure 2. It is evident from the figure that these samples are neat polymers without any fillers or additives, since the weight loss (%) of them goes to zero after burning up. We can also see that although all materials are degraded at approximately 480°C, the copolymers synthesized by Dow Insite technology have a little higher degradation temperature than polyethylene, which was synthesized by the Ziegler catalyst system. Also, for copolymers, with increasing comonomer contents, the degradation temperature decreases.

## Non-isothermal Crystallization Study

Non-isothermal crystallization study was carried out with a Perkin-Elmer DSC-7 system using $N_2$ as purging gas. The instrument was calibrated with indium for temperature and heat change. The sample of approximately

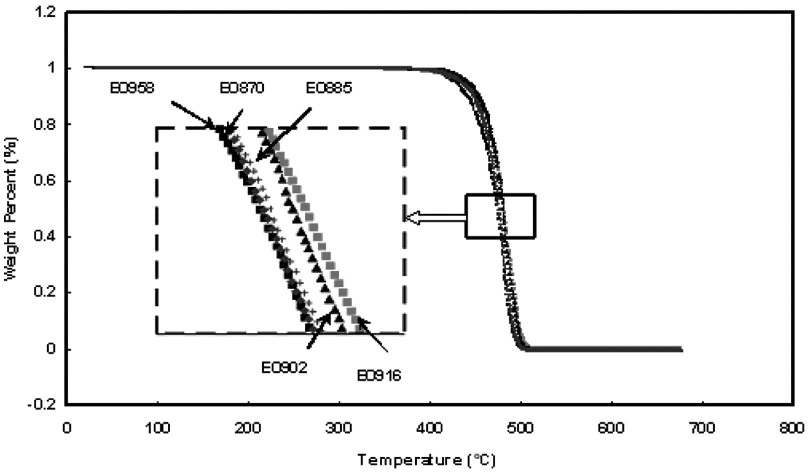


Figure 2. TGA curves of polyethylene and its copolymers.

10 mg was first heated to a temperature 50°C above its melting temperature under 10°C/min, held at that temperature for five minutes, and then cooled down at different cooling rates up to 80°C/min. It is reported that when the cooling rate is higher than 80°C/min, results are not reliable because of the large deviation between sample and programmed temperature and thermal gradients across the sample thickness.[13] The relative degree of crystallinity $X_r$, which developed on cooling to temperature $T$, was obtained as:

$$X_r = \frac{\int_{T_0}^{T} \left(\frac{dH_c}{dt}\right) dT}{\int_{T_0}^{T_\infty} \left(\frac{dH_c}{dt}\right) dT}$$

where $T_0$ and $T_\infty$ represent the initial and final crystallization temperature, respectively, and $H_c$ is the crystallization enthalpy.

## RESULTS AND DISCUSSION

### Non-isothermal Crystallization Behavior

#### Effect of Cooling Rate

Figure 3(a)–(e) shows crystallization curves during cooling after melting of polyethylene and its octene copolymers at different cooling rates. The maximum peak temperature was defined as the crystallization temperature ($T_c$). The crossover between the baseline and the right side of the peak was defined as the crystallization onset temperature ($T_o$). The time used to reach half of the peak area was defined as the half-time

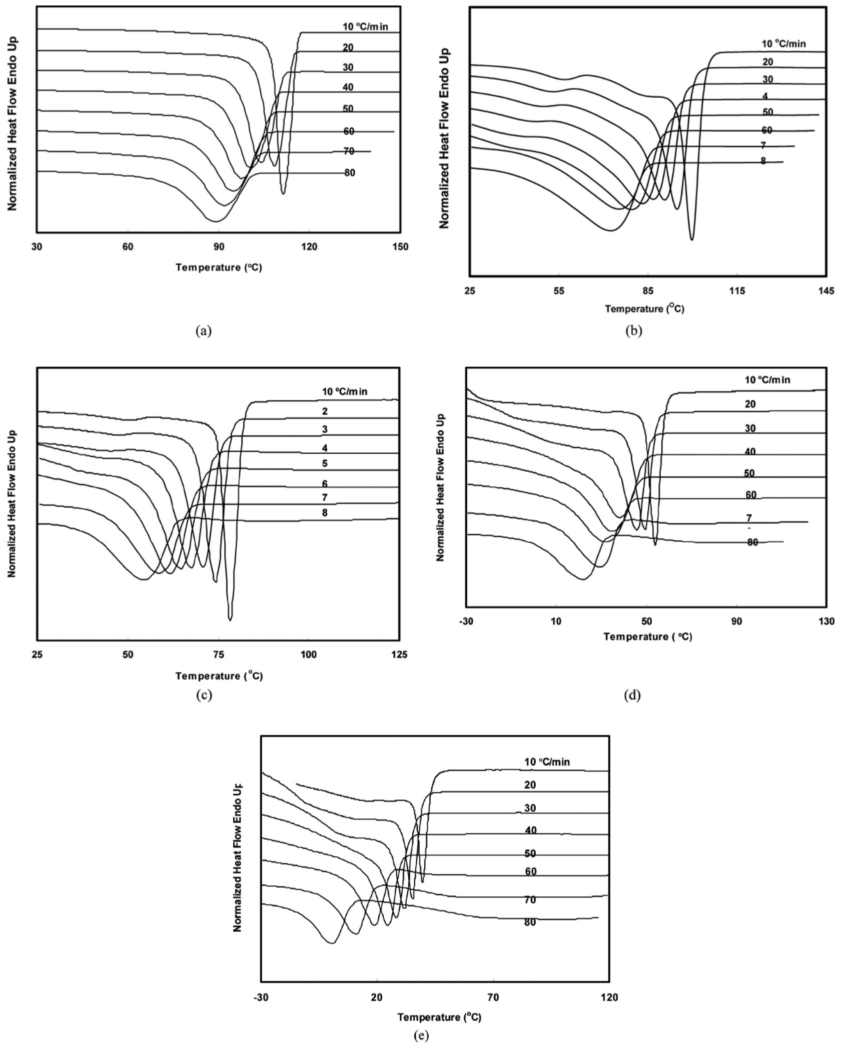


**Figure 3.** Non-isothermal crystallization curves of (a) EO958, (b) EO916, (c) EO905, (d) EO885, and (e) EO870, measured during cooling from the melt at different cooling rates.

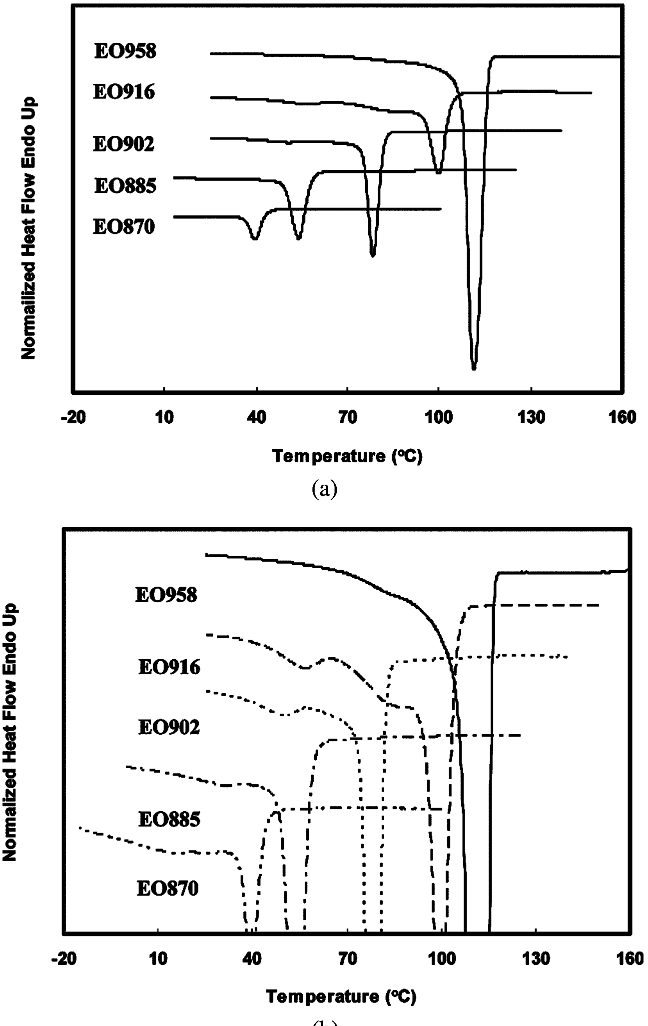
($t_{1/2}$). During the non-isothermal crystallization process, two main factors should be considered regarding cooling rate and crystallization peak. One is the effect of the cooling rate on nucleation rate: the higher the cooling rate, the higher the supercooling under which crystallization takes place, and the faster the nucleation rate. Then a sharper exothermic peak will be exhibited. The other is the mechanical width factor from the cooling rate: the higher the cooling rate, the wider the crystallization exothermic peak. These two competing factors will determine the final shape of the crystallization peak. Figure 3 demonstrates that the mechanical width factor has the dominant effect on the shape of the crystallization peak.

The curves also reveal a remarkable decrease of $T_c$ and $T_o$ with increasing cooling rate for all polymers. This behavior might be ascribed to cooling rate affects on nucleation and the crystal growth process. As the cooling rate increases, the motion of the polymer chain cannot follow the cooling temperature and thus polymer crystallization begins at lower temperatures. It thus suggests to us that supercooling ($\Delta T = T_m - T_c$) may be a measure of a polymer's crystallizability, i.e., the smaller the $\Delta T$, the higher the overall crystallization rate. However, due to delayed nucleation, there are some exceptions to this approach as indicated by Khanna.[13]

## Effect of Comonomer Content

The crystallization behaviors of polyethylene and its copolymer under cooling rate of 10°C/min are shown in Figure 4(a) and (b). We can observe some differences in crystallization behavior between EO958 and the copolymers. First, with increasing comonomer content, the crystallization temperature decreases under 10°C/min. The reason might be due to less mobility of the polymer chain with introducing more conomomonomer along its backbone.

Second, a sharp crystallization peak was observed under all cooling conditions for EO958. A weak shoulder was also observed for crystallization under 10°C/min (Figure 4(b)). For copolymers, EO916–EO870, we can observe two or three crystallization exotherms at slow cooling rate (10°–30°C/min). The first are large, sharp exotherms at high temperature, and the other are small, broad exotherms at low temperature. As the cooling rate increases, the multiple crystallization behavior disappears and only one crystallization peak was observed. According to Wilfong and Knight,[20] the sharp peak is due to the crystallization of polymer chains with high molecular weight and low branching content, while the broad peaks are caused by polymer chains with low molecular weight and high branching content. So, although these copolymers were polymerized using homogeneous catalyst (single-site catalyst), which means the branching distribution should be quite random without localization of branching along the main chain, the experimental results shows there still exists the second lower temperature crystallization process, which means the nonuniform distribution of branching. The results of CRYSTAF support this conclusion. EO916 has more heterogeneous comonomer distribution than EO902. And we observed three crystallization peaks for EO916 and two crystallization peaks for EO902.



(a)

(b)

Figure 4. Crystallization curves of polyethylene and its copolymers under cooling rate of 10°C/min.

Third, with increasing comonomer content, the crystallization process takes place over a wider temperature range at cooling rates up to 30°C/min. The crystallization still goes on even at the lowest temperature (−30°C) for EO870. This may be due to hindrance coming from the comonomer. With more comonomer, it will become more difficult for the polymer chain to fold and form a crystal.

## Non-isothermal Crystallization Rate

As pointed out earlier, due to delayed nucleation, the supercooling $\Delta T$ ($T_m - T_c$) is not a good way to determine a polymer's crystallizability. Khanna[13] thus introduced a new parameter for characterizing the crystallization rate, i.e., a "crystallization rate coefficient" (CRC), defined as $|\Delta\beta\ \Delta T_c|$. The cooling rate is thus plotted against corresponding $T_c$ of polyethylene and its copolymers in Figure 5. Good linearity was found for all polymers, except EO870. The slope of each curve was calculated and is given in Table II. Apparently, with more octene, the CRC value decreases, which suggests to us that the crystallization rate decreases, since generally, the copolymers with more comonomer will have slower crystallization rate. The CRC value thus accurately predicts the crystallization rate of these copolymers.

Zhang et al.[14] argued that materials having the same $T_c$ under the same cooling rate might have different half-height widths. The crystallization rate of these materials would be apparently different, although they have the same CRC value. They thus proposed the crystallization rate parameter (CRP), which is calculated from the slope of the curve after plotting the reciprocal of half crystallization time against cooling rate, as shown in Figure 6. The half crystallization time is defined as:

$$t_{1/2} = \frac{(T_o - T_{1/2})}{\beta}$$

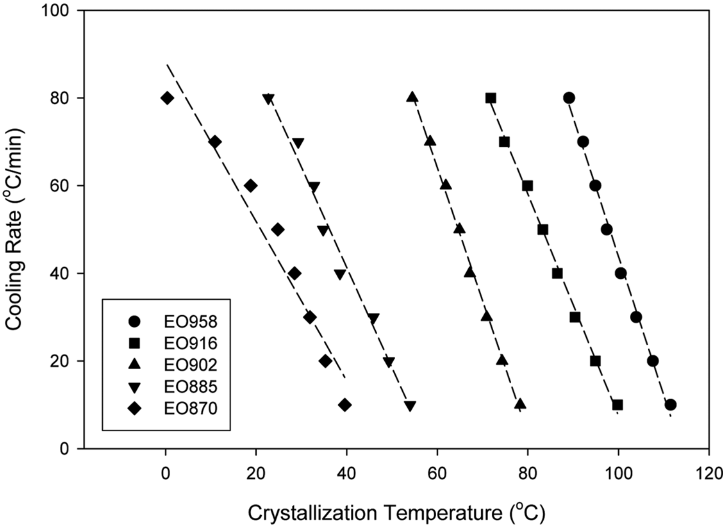


**Figure 5.** Cooling rate as a function of the crystallization temperature for different copolymers.

**Table II.** CRC and CRP values of polyethylene and its copolymers

| | Samples | | | | |
|---|---|---|---|---|---|
| | EO958 | EO916 | EO902 | EO885 | EO870 |
| CRC ($\text{min}^{-1}$) | 3.165 | 2.527 | 3.040 | 2.286 | 1.816 |
| CRP | 0.0496 | 0.0521 | 0.1242 | 0.0661 | 0.153 |

where $T_{1/2}$ is the temperature under which the crystallinity reaches half completion. Due to slow crystallization rate of copolymers, it is impossible to reach the final crystallinity for copolymers, as seen from Figure 3. We thus assume the copolymers complete their crystallization at $-30°\text{C}$. The CRP values of polyethylene and its copolymers are given in Table II. Surprisingly, the CRP values show an almost contrary trend to the CRC values. This may be due to multi-crystallization behavior and broader crystallization range observed for copolymers. The crystallization half-time calculated from the crystallization curve might thus be not as accurate as the crystallization temperature measured.

The continuous cooling transformation (CCT) curves are constructed from onset crystallization temperatures ($T_o$) and corresponding elapsed time. Spruiell and White[12] calculated the corresponding elapsed

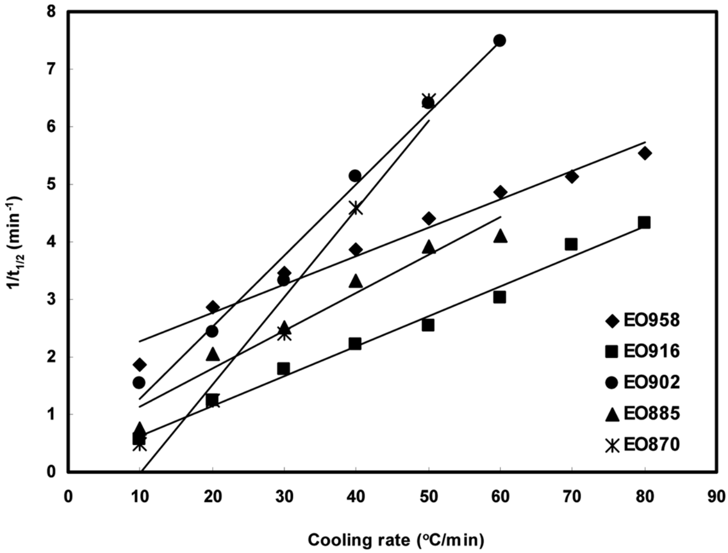


**Figure 6.** Reciprocal half crystallization time as a function of cooling rate for different copolymers.

time from a melt temperature (150°C for polyethylene in their study) to the onset of crystallization temperature divided by the cooling rate. However, for copolymers with more comonomer, the melting temperature is lower. It would thus be better to calculate the elapsed time as the time interval between equilibrium melt temperature ($T_m^\circ$) and crystallization temperature for copolymers. The equilibrium melt temperatures of copolymers are taken from the work of Kim et al.[18] and are given in Table I.

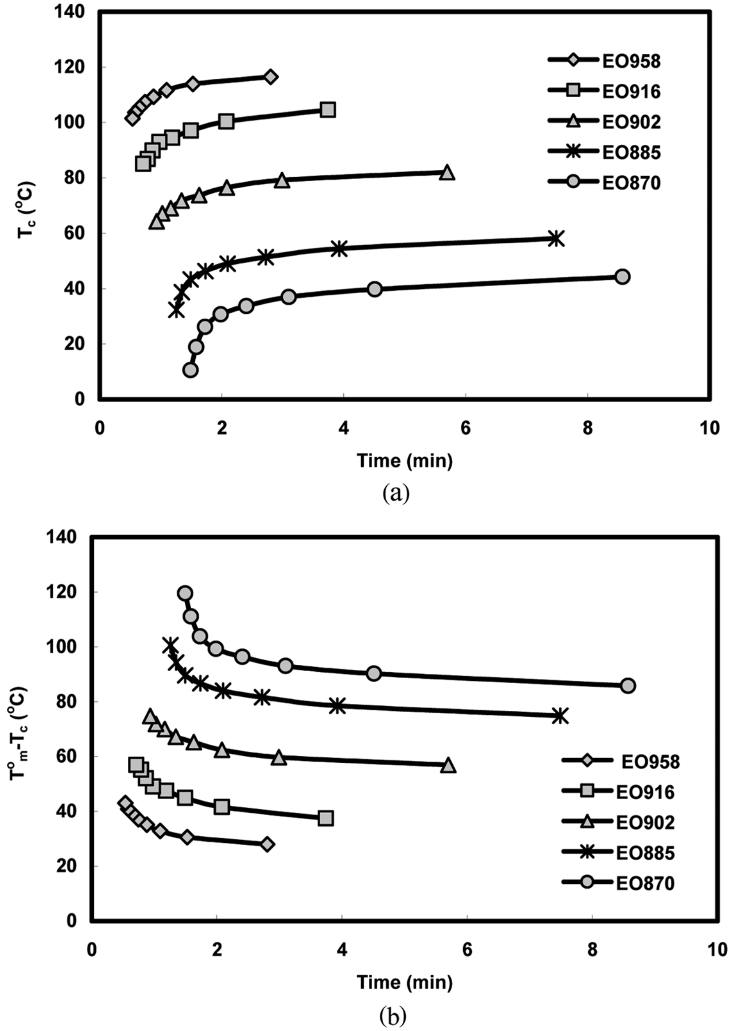


**Figure 7.** CCT curves of different copolymers: (a) onset crystallization temperature as a function of time; (b) degree of supercooling as a function of time.

The results are shown in Figure 7a. In order to compare the non-isothermal crystallization rate, the degree of super cooling ($T_m^\circ - T_c$) is plotted against the elapsed time, as shown in Figure 7b. As we can see, for copolymers with less comonomer content, the CCT curve shifts to shorter time, which indicates faster non-isothermal crystallization rate.

We would like to make some comments on these three methods. CRC is the easiest one to calculate, since we can get all information needed from the DSC curve directly. The CCT curve is easier. However, we need equilibrium melt temperature for calculating the elapsed time. For some polymers, especially the newly invented or seldom used, we may lack this information. The CCT curves will be more powerful if used to describe phase diagram, such as crystal structure transformation during polymer melt solidification under certain stress level and thermal condition, which usually happened during polymer processing, like fiber spinning, film blowing and injection molding. White et al.[21–23] used the CCT curve to describe phase transformation during processing polypropylene. CRP is the most cumbersome one. The problem comes from calculating the half crystallization time. In order to accurately calculate the crystallinity development with time, we first need to build up a straight baseline. Second, the completeness of crystallization should be at the same level as where it starts. Otherwise, we may introduce error from the instrument. Third, we should cover the whole crystallization process, which may be not easy for polymers with slow crystallization rate and crystallize in extremely low temperatures.

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