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Comparison of Crystallization and Melting Characteristics of Quiescent and Melt-Spun Poly(ethylene-co-octene) Copolymers

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Abstract: An experimental study of crystallization and melting of polyethylene and its octene copolymers under quiescent conditions and their melt-spun fibers is presented. This includes copolymers produced by both Dow's Insite[®] Technology homogeneous catalyst and by a Ziegler heterogeneous catalyst. It is found that with increasing comonomer content, both isothermal and non-isothermal crystallization rate decrease. The melting peaks become broader and the melting temperatures decrease for polymers with more comonomer. Multiple melting peaks are observed for copolymers. Except the unchanged peak with the highest melting temperature, the other peaks move to higher temperature after being annealed under higher temperature. Attempts were made to correlate crystallization kinetics and melting behavior under quiescent conditions with melting temperatures and crystallinities determined for their melt-spun fibers. The results show that besides cooling effects, the melt temperatures and the crystallinities of the melt spun fibers are also affected by the degree of molecular orientation, which is mainly decided by the spin-line stress. These two competitive factors determine the final melt temperatures and crystallinities of the melt-spun fibers.

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INTRODUCTION

There have been extensive studies on the melting and crystallization behavior of ethylene/ α -olefin random copolymers with a variety of different α -olefins.^[1-10] These studies include the use of fractions of ethylene copolymers with narrow molecular weight distribution. Many of the earlier articles on this subject necessarily demonstrated the importance of comonomer distribution, or sequence length distribution, along the copolymer chains.

Dow Chemical Company's Insite[®] Technology catalysts apparently yield homogeneous ethylene/ α -olefin copolymers with narrow molecular weight distributions and homogeneous comonomer distributions. In contrast, the older conventional heterogeneous catalysts, i.e., Ziegler catalysts, yield linear low-density polyethylenes (LLDPEs), which have broader molecular weight distributions and more heterogeneous comonomer distributions.

Using Dow Chemical's Insite[®] Technology copolymers, it would seem possible to study melting and crystallization behavior systematically as a function of comonomer or branch content and avoid the heterogeneous molecular weight and sequence length distribution of copolymers produced from a Ziegler catalyst. There have been several studies on these copolymers in recent years, including investigations of melt spinning and cold drawing filaments in our own laboratories.^[9,10]

This article reports on a study of isothermal and non-isothermal crystallization kinetics and melting behavior of these Dow Insite[®] Technology poly(ethylene-co-octene) copolymers with different comonomer contents and its comparison with Ziegler homopolymer polyethylene and linear low-density poly(ethylene-co-octene) copolymer. We will also compare the crystallization and melting behavior of these polymers under quiescent conditions with those of melt-spun filaments. This study is unique in that we have tried to correlate the melting and crystallization behavior under quiescent conditions with those of melt-spun fibers.

EXPERIMENTAL SECTION

Materials

Four commercially available ethylene-octene copolymers with different octene levels prepared by Dow's Insite[®] Technology catalysts were chosen for this study. A Ziegler homopolymer polyethylene and a Ziegler

linear low-density polyethylene (LLDPE) containing an octene comonomer were also studied for comparison. The samples are identified with the initials EO (ethylene/octene) followed by a number corresponding to the density of the copolymer, and z and h refer to Ziegler catalyst and homogeneous catalyst system respectively.

Melt Spinning

The polyethylene and its copolymer were extruded through a 1.6 mm diameter capillary with a length/diameter ratio of 19.3. They were melt spun through air and taken up on a rotation roll. Tensions in the filaments were measured on a Rothschild tension meter.

Differential Scanning Calorimetry (DSC)

The differential scanning calorimetry (DSC) experiment was performed using a Perkin Elmer DSC-7. Nitrogen gas was purged in the DSC chamber throughout experiments. About 10 mg samples were prepared. The melting temperatures were measured at the heating rate of 10°C/min. The crystallinities of the materials were estimated from the heat of fusion data by assuming that ΔH_m° (100% crystallinity) is 290 J/g.^[11]

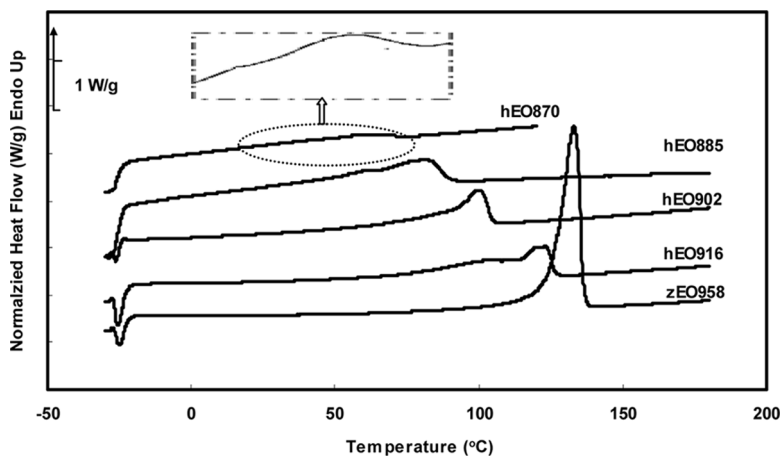
The isothermal crystallization kinetics was studied at various crystallization temperatures. The melts were rapidly quenched to a specified crystallization temperature and then were maintained at that temperature until the crystallization completed. We determined the crystallization half-time ($t_{1/2}$), i.e., the time required for crystallization to reach 50% of final crystallinity, at each crystallization temperature. The non-isothermal crystallization kinetics was studied by cooling the melts at 180°C to room temperature at various cooling rates (10°C/min ~ 80°C/min). Continuous cooling transformation (CCT) curves^[12–15] were constructed from the crystallization onset temperatures and the corresponding elapsed times.

RESULTS AND DISCUSSION

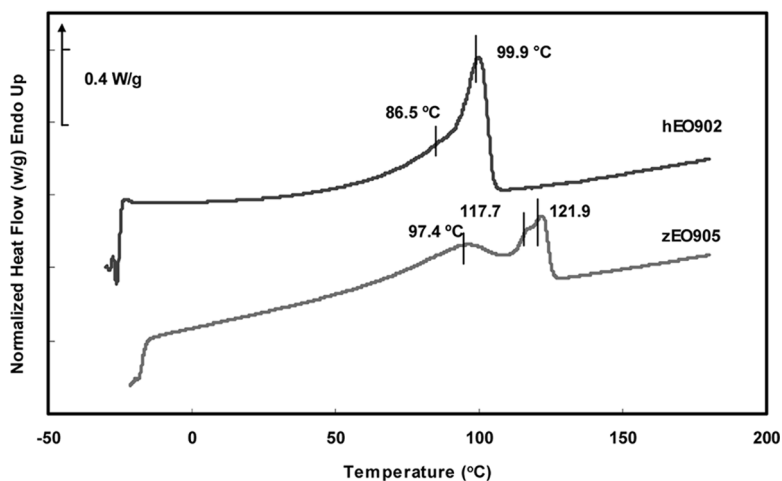
Melting and Crystallization Behavior under Quiescent Conditions

Melting Temperatures and Crystallinities of Polyethylene and Its Copolymer

DSC curves of polyethylene and its copolymers are given in Figure 1(a) and (b). The degree of crystallinity and melting point are summarized



(a)



(b)

Figure 1. DSC thermograms of raw materials measured at a heating rate of $10^{\circ}\text{C}/\text{min}$: (a) comparison between zEO958, hEO916, hEO902, hEO885, and hEO870; (b) comparison between zEO905 and hEO902.

in Table I. It can be seen that zEO958 shows a sharp melting peak. However, for the copolymers, a broad melting peak is observed. The melting temperature, which was measured from the highest melting peak, decreases with increasing octene content. The crystallinity also decreases with increasing octene content. The broad peak may be due to the distribution of lamellar thicknesses and/or crystal perfection. It becomes

Table I. List of materials used in this study

	Polymer designation					
	zEO958	hEO916	zEO905	hEO902	hEO885	hEO870
Density (g/cm ³)	0.958	0.916	0.905	0.902	0.885	0.870
Type of comonomer	None	Octene	Octene	Octene	Octene	Octene
Content of comonomer (wt.%)	0	15	19	20	30	38
Content of comonomer (mol.%)	0	4.2	5.6	5.9	9.7	13.3
M _w	141500	110100	130500	94500	106000	75900
M _n	18600	29200	29200	36300	41200	35700
M _w /M _n	7.6	3.8	4.5	2.5	2.5	2.1
Melting point (°C)	133.0	122.9	121.9	99.9	80.0	61.2
DSC crystallinity	70.5	36.1	31.2	28.3	23.2	16.5
Crystallization temperature (°C)	111.5	99.8	97.8	78.3	54.0	39.6
MI (g/10 min)	0.95	1.0	0.8	1.0	1.0	5.00
Catalyst	Ziegler	Insite [®]	Ziegler	Insite [®]	Insite [®]	Insite [®]
Grade	Alathon M6210	Elite 5400	Attane 4203	Affinity PL1880	Engage 8003	Engage 8200
Manufacturer	Equistar	Dow Chemical	Dow Chemical	Dow Chemical	DuPont	Dow

broader as comonomer content increases. In more detail, increasing comonomer content decreases the sequence length between comonomer points and probably results in thinner lamellae if the comonomer (i.e., defects) is excluded from the crystalline phase. Thus, that may be also a reason why melting temperatures and crystallinities decrease with comonomer contents.

We specifically compare the melting behavior of Dow Insite[®] technology sample hEO902 and Dow LLDPE zEO905. The hEO902 sample shows a strong melting peak plus a weak shoulder, while zEO905 shows three distinct melting peaks. The highest melting temperature of hEO902 is 99.9°C, while that of zEO905 is 121.9°C. The melting temperature and the crystallinity of zEO905 are higher and larger than those of hEO902, even though they have roughly the same comonomer content (Table I). We suspect this may be due to the heterogeneous distribution of comonomer along the molecular chain and/or among the various molecular chains. As we can see from the CRYSTAF data, the hEO902, which is synthesized using Dow Insite[®] technology catalyst, probably has more homogeneous comonomer distribution than zEO905, which is synthesized using the Ziegler catalyst. The crystallizable sequence length of hEO902 is perhaps relatively shorter than that of zEO905. It may thus crystallize into thinner lamellae, which will melt at a lower temperature.

Crystallization Kinetics

Isothermal Crystallization Kinetics. In order to compare the isothermal crystallization rate of polyethylene and its copolymers, we plot $1/t_{1/2}$ versus the degree of supercooling $(T_m^\circ - T_c)$,^[16] where T_m° is the theoretical equilibrium melting temperature, as shown in Figure 2(a). The T_m° values for polyethylene and its copolymers are taken from Kim et al.'s work.^[8] The isothermal crystallization rate thus orders as follows:

$$\text{zEO958} > \text{hEO916} > \text{zEO905} > \text{hEO902} > \text{hEO885} > \text{hEO870}$$

This ordering corresponds well with the amount of comonomer content, which suggests to us that the isothermal crystallization rate decreases with more octene. Since these materials have different molecular weight, it is of interest to further investigate the effect of molecular weight on isothermal crystallization rate. Thus, in Figure 2(b) we compare the isothermal crystallization rate of polyethylene with those having different molecular weights, which are from the work of Lambert and Phillips.^[4] Clearly, with increasing molecular weight, the isothermal crystallization rate decreases. In our work, zEO958 has a little larger weight-average molecular weight than zEO905, hEO916 has a little larger weight-average molecular weight than hEO885, and hEO902 has a little larger weight-average molecular weight than hEO870. However, since

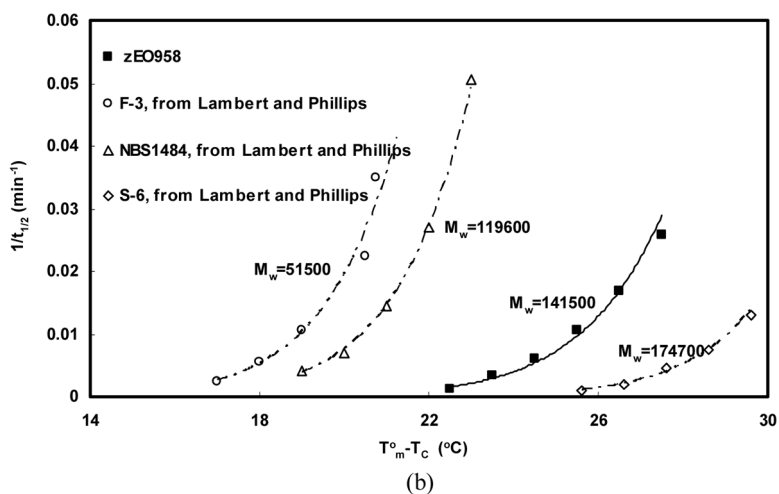
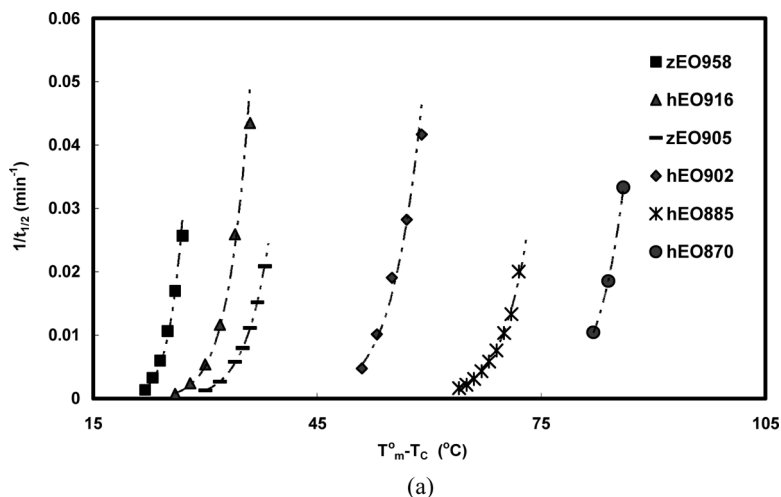


Figure 2. Isothermal crystallization rate expressed as reciprocal crystallization half-time ($1/t_{1/2}$) as a function of supercooling ($T_m^o - T_c$): (a) for poly(ethylene-co-octene) with different octene content; (b) for polyethylene with different molecular weights.

the latter samples all have more octene, they have a slower isothermal crystallization rate than the former.

Non-Isothermal Crystallization Kinetics. CCT curves were constructed from the crystallization onset temperatures (T_o) and the corresponding elapsed time. The elapsed time is calculated as the time interval between the equilibrium melt temperature (T_m^o) and the crystallization onset

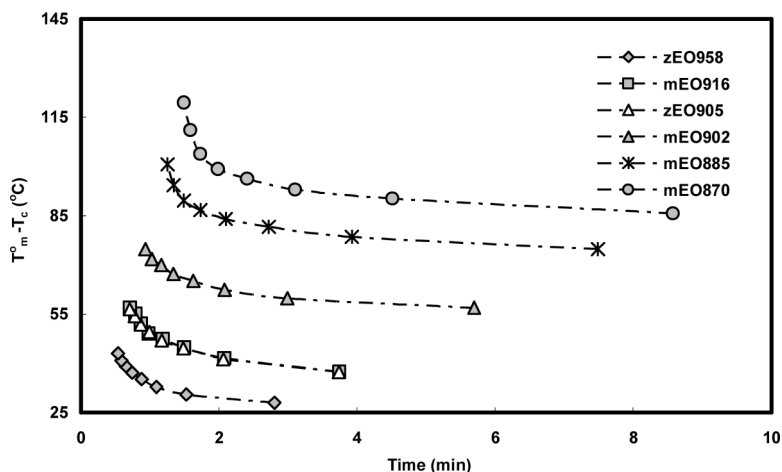


Figure 3. Supercooling ($T_m^0 - T_c$) vs. elapsed time of CCT curves for the quiescent melts of polyethylene and its copolymers.

temperature (T_0). The results are shown in Figure 3. The non-isothermal crystallization rate of the six polymers orders as follows:

$$zEO958 > hEO916 > zEO905 > hEO902 > hEO870 > hEO885$$

The ordering is similar to that of isothermal crystallization rate, which indicates to us that non-isothermal crystallization rate is also mainly determined by the comonomer content.

Melting Behavior of Materials with Certain Thermal History

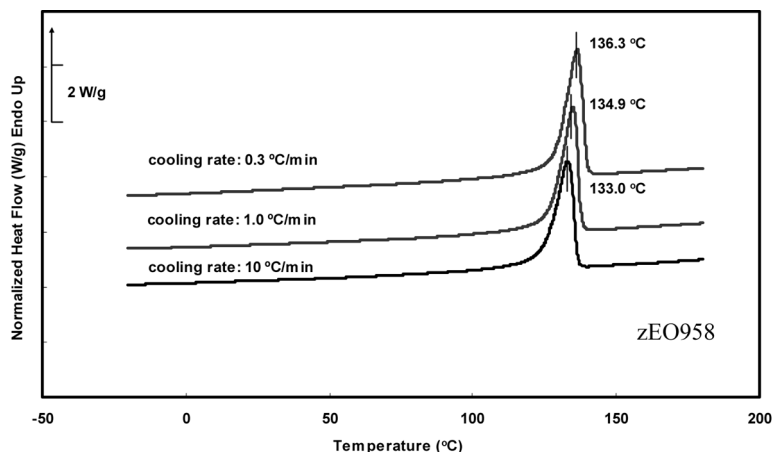
Cooling Rate Effect on Melting Behavior. The DSC heating curves of materials after being cooled under different cooling rates (0.3°C/min, 1°C/min, 10°C/min) are shown in Figure 4(a)–(f).

For zEO958, only one melting peak was observed after being cooled under different cooling rates. For samples cooled under slower cooling rate, the melting peak increases from 133.0°C, to 134.9°C, to 136.3°C (Figure 4(a)).

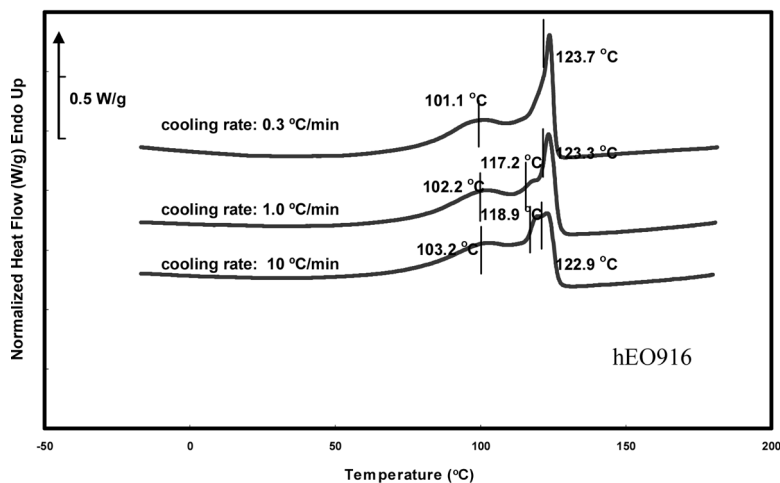
For hEO916, a broad peak at 103.2°C and two relative sharp peaks at 122.9° and 118.9°C were observed after samples cooled under 10°C/min. For samples cooled under slower cooling rate, the broad peak moves to a little lower temperature, the amount remains almost unchanged, while the sharp peak at 122.9°C moves to a little higher temperature and the peak at 118.9°C moves to a lower temperature, 117.2°C, and then disappears (Figure 4(b)).

For zEO905, after being cooled under $10^{\circ}\text{C}/\text{min}$, there was a broad peak at 97.3°C , and two relatively sharp peaks at 118.8° and 122.3°C . For material being cooled under slower cooling rates, the broad melting peak moves to a higher temperature, while the relatively sharp peak becomes a little higher in temperature (Figure 4(c)).

For hEO902, two melting peaks were observed after being cooled under different cooling rates. The peak at 99.9°C shows a little increase

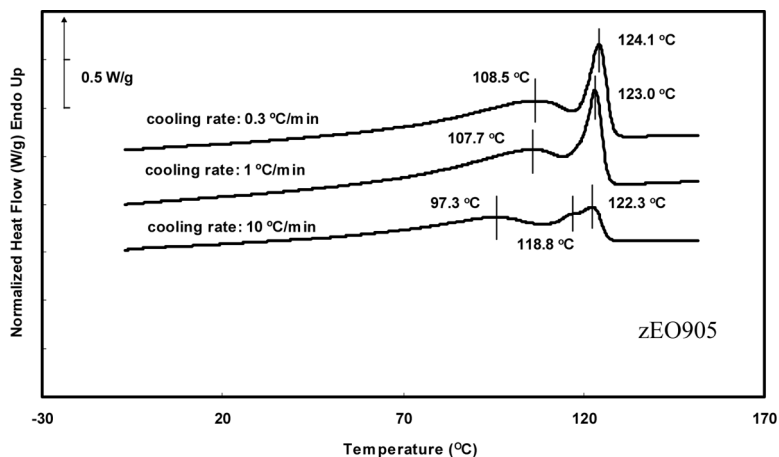


(a)

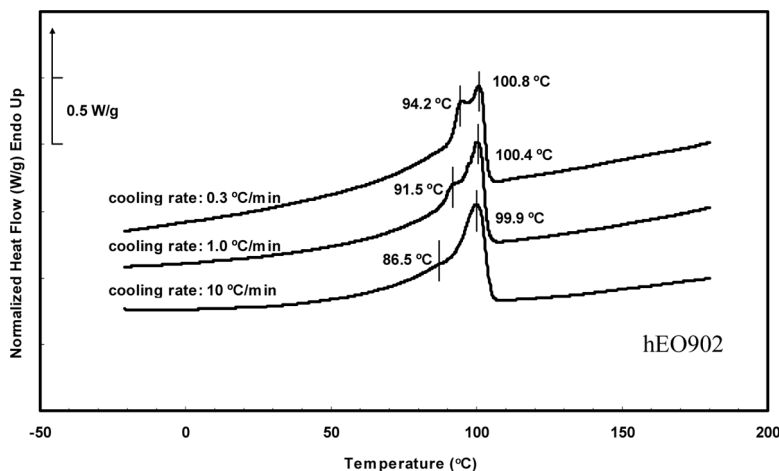


(b)

Figure 4. DSC heating curves (scanning rate: $10^{\circ}\text{C}/\text{min}$) of the polymers crystallized from the melts at various cooling rates: (a) zEO958; (b) hEO916; (c) zEO905; (d) hEO902; (e) hEO885; (f) hEO870.



(c)

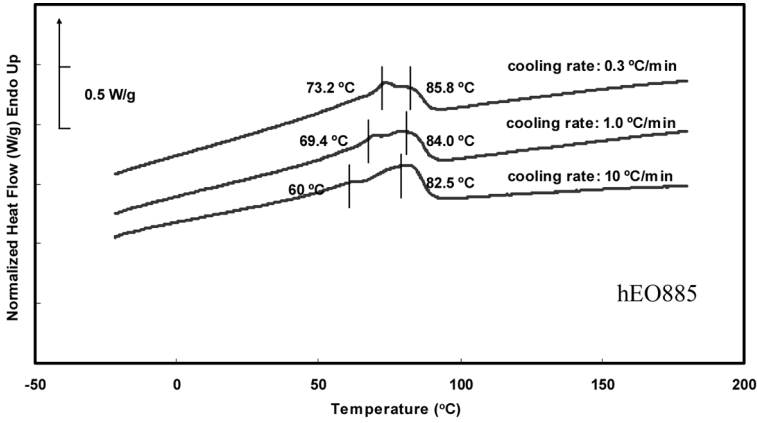


(d)

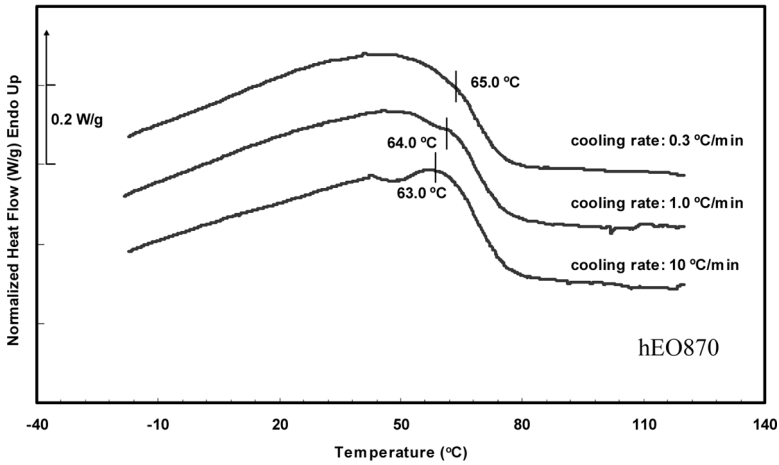
Figure 4. Continued.

with the decrease of cooling rate. The other peak, which is a shoulder at 86.5 °C at 10 °C/min case, shows an increase both in the temperature and in its amount (Figure 4(d)).

For hEO885, two melting peaks were observed for materials cooled under different cooling rates. One is broad and the other is relatively sharp. With decreasing cooling rate, the broad peak moves slightly to higher temperature. The other peak evolves from a small bump to a relative sharp peak for materials undergoing slower cooling (Figure 4(e)).



(e)



(f)

Figure 4. Continued.

For hEO870, two broad peaks were observed after materials being cooled under 10°C/min. For material cooled under a slower cooling rate, the melting peak at 63.0°C moves to a higher temperature and disappears (Figure 4(f)).

Annealing Effects on Melting Behavior. A series of melting curves of polyethylene and its copolymers that have been annealed at specific temperature (T_a) for one hour is shown in Figure 5(a)–(f). All copolymers show similar melting behavior. Generally, the curves exhibit one broad melting peak below T_a and two or three peaks above T_a . However, there

is little annealing effect on the polyethylene homopolymer. We mark the peak below (T_a) as T_1 , while the others as T_2 , T_3 , and T_4 . T_a is also shown in Figure 5(a)–(f).

We first briefly describe the melting behavior of hEO870 after being annealed at temperatures between 37° and 55°C (Figure 5(f)). Each curve consists of three endothermic peaks: a broad endothermic peak (T_1) below T_a , a relative sharp melting peak (T_2) just above T_a , and a second

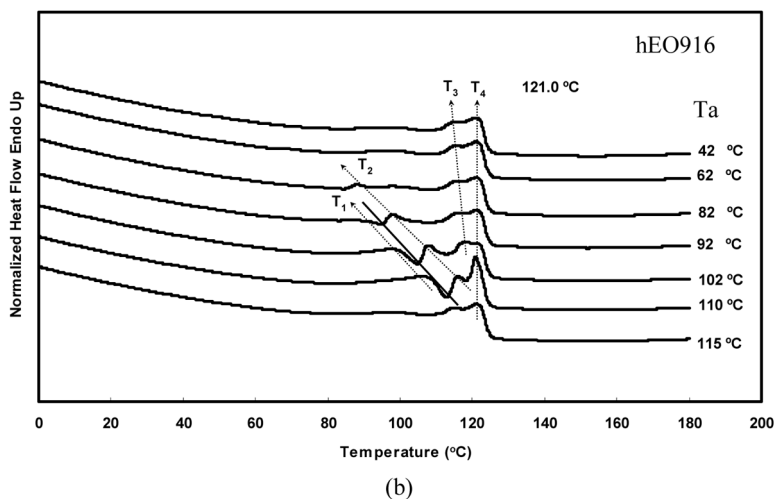
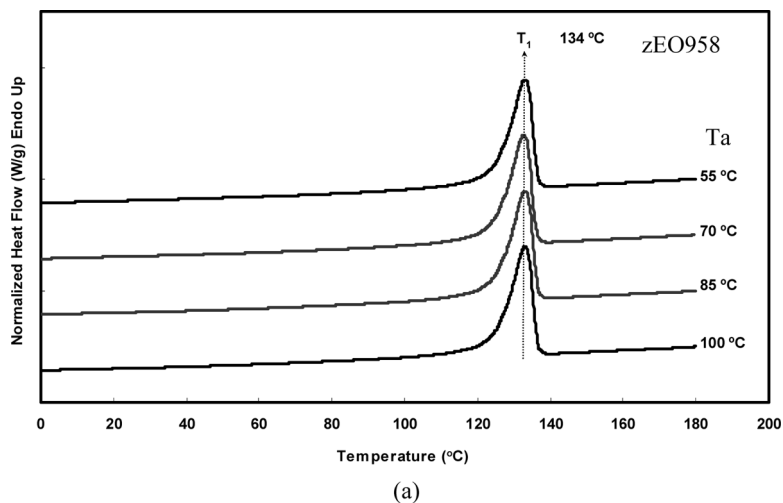
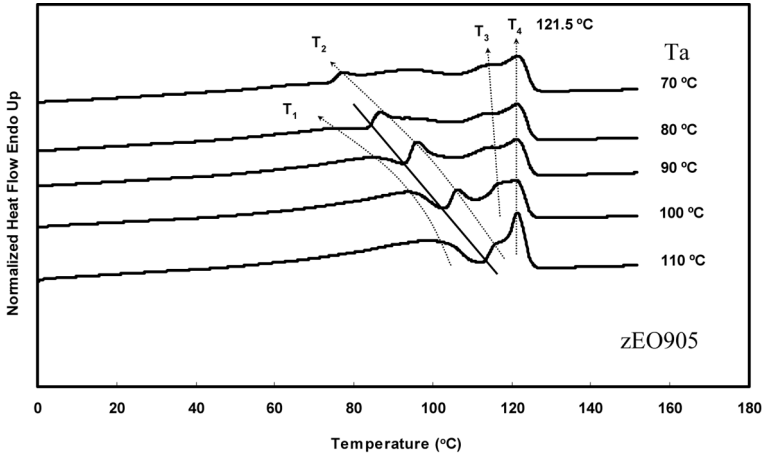
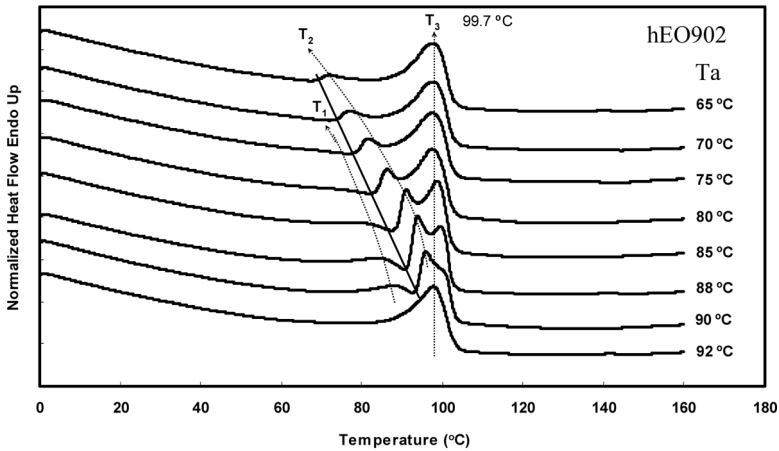


Figure 5. DSC heating curves (scanning rate: $10^\circ\text{C}/\text{min}$) of annealed copolymers: (a) zEO958; (b) hEO916; (c) zEO905; (d) hEO902; (e) hEO885; (f) hEO870. The annealing temperature (T_a) is indicated.



(c)

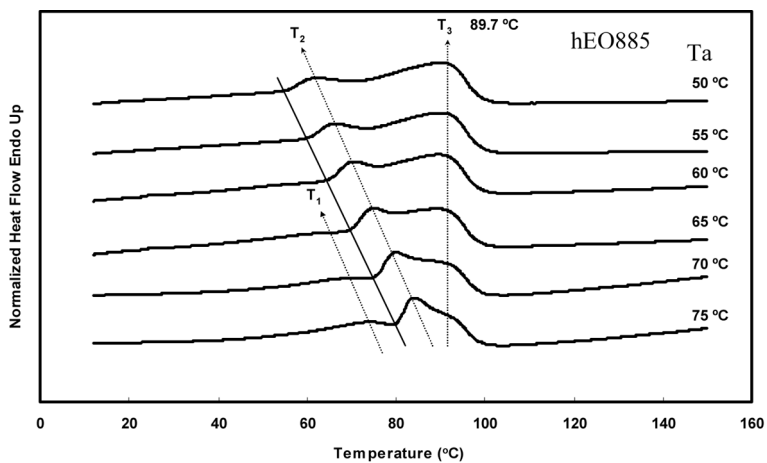


(d)

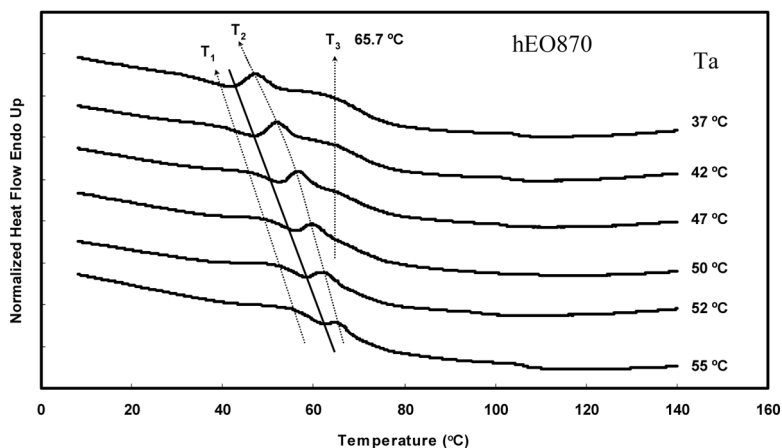
Figure 5. Continued.

broad melting peak (T_3) at approximately 65°C . The temperature of this peak remains almost constant as the annealing temperature increases until the peak merges with the sharper, lower-temperature melting peak (T_2). With decreasing annealing temperature, T_1 and T_2 move to lower temperatures, while T_3 remains constant.

We now consider the other copolymers. The hEO885 sample shows very similar melting behavior to hEO870, except the T_3 is larger and broader than that of hEO870 (Figure 5(e)). The hEO902 sample also



(e)



(f)

Figure 5. Continued.

shows very similar melting behavior to that of hEO870, except the T_3 is larger and sharper than hEO870 (Figure 5(d)).

The hEO916 and zEO905 samples show slightly different melting behavior from hEO870 (Figure 5(b) and (c)). In addition to T_2 , two more melting peaks (T_3 and T_4) above the annealing temperature (T_a) are observed. T_4 remains constant, while T_3 shows a slight decrease with annealing temperature.

The zEO958 sample shows only one melting peak after being annealed at different temperatures.

The melting behavior of these copolymers suggests to us that these melting peaks come from the different crystal populations, which are formed from chains with different crystallizable lengths. After being annealed for a certain time, thinner crystals will be melted, while thicker crystals will be annealed to even larger crystals. We also observe a melting peak that remains constant and represents the highest melting point after materials being annealed under different temperatures. This peak may come from the most stable crystal population, which is formed by the longest crystallizable length. The above observation further suggests to us that there might be heterogeneity along the chain. The heterogeneity may come from the comonomer distribution. We compare the melting behavior of these three copolymers: hEO902 has three melting peaks, while zEO905 and hEO916 have four melting peaks. So, copolymers with more heterogeneity seem to have more melting peaks.

Crystallinities and Melting Temperatures of Melt-Spun Fibers

The crystallinities and melting temperatures of melt spun fibers were measured by DSC and show a little increase with spin-line stress.

Correlation of Crystallization Behavior with Crystallinities of Melt-Spun Fibers

As we have found from this study, crystallization is influenced by the comonomer content, molecular weight, and cooling rate under quiescent conditions. Now, if we turn to the melt-spinning case, we should also pay attention to the molecular orientation, which correlates with the spin-line stress.^[10,12-15] It is well known that increasing the spin-line stress will significantly increase crystallization rate and thus shift CCT curves toward shorter times.^[12] We may express this by the following equation:

$$\text{Crystallization Rate} = G [dT/dt, \sigma, \text{Comonomer Content}, \text{Molecular Weight}] \quad (1)$$

where dT/dt is the cooling rate and σ is spin-line stress. For a specific polymer during melt spinning, the crystallization is mainly determined by the cooling rate and the spin-line stress.

Nakamura et al.,^[17] based on a quasi-static approximation of non-isothermal orientation induced crystallization, proposed the following equation:

$$\frac{X_c(t)}{X_\infty} = 1 - \exp\left(-\left\{\int_0^t K[T(\tau), f_a(\tau)] d\tau\right\}^n\right) \quad (2)$$

where X_∞ is the degree of ultimate crystallinity, K the crystallization rate function, f_a the amorphous (melt) orientation, and n the Avrami index.

Equation (2) makes it quite clear that crystallization in the spin line is controlled by a competition between crystallization kinetics, which are largely controlled by the level of molecular orientation, and the cooling rate, which is controlled by the mass flow rate, spinning speed, and cooling medium. The balance of this competition determines final crystallinities of the melt-spun fibers. Whenever the effect of increased molecular orientation overwhelms the effect of increased cooling rate, an increase of spinning speed will result in an increase in the crystallinities. But when the effect of cooling rate is more significant than the influence of molecular orientation, the crystallinities will decrease with an increase of spinning speed. However, quantitative estimation of crystallization behavior is difficult to achieve at the present moment because of the lack of detailed information on the mechanism of molecular orientation during crystallization, the crystallization kinetics under molecular orientation, and the effects of molecular orientation and crystallization on viscoelastic properties of polymer fluids. From the results of our experiments, the crystallinities of the melt-spun fibers slightly increase with the increase of drawdown ratio, which suggests to us that the molecular orientation plays a little more important role than cooling rate.

Correlation of Melting Behavior with Melting Temperatures of Melt-Spun Fibers

As we have discussed in the previous section, the melting temperature of polyethylene and its copolymer under quiescent conditions is influenced by the comonomer content (Figure 1) and the thermal treatment materials received (Figures 4 and 5). In the melt-spinning case, since polymer melt flows under spin-line stress, polymer chains will orient along the flow direction. Increasing spin-line stress increases polymer chain orientation. In the following section, we will first discuss how polymer melt orientation affects the melting temperature of as-spun fibers. Then we will discuss the effect of comonomer content on the melting temperatures of melt-spun polyethylene and its copolymers. Finally, we will propose a general equation.

Effect of Polymer Chain Orientation on Melting Temperatures of As-Spun Fibers

Following the work of Alfrey and Mark,^[18] we may discuss the effect of polymer chain orientation on the melting temperature of as-spun fibers, which is shown below.

For unoriented polymer melt (*u*: unoriented; *c*: crystal; *m*: melt):

$$G_{uc} = G_{um} \tag{3a}$$

$$H_{uc} - T_{um}S_{uc} = H_{um} - T_{um}S_{um} \tag{3b}$$

$$\frac{1}{T_{um}} = \frac{S_{um} - S_{uc}}{H_{um} - H_{uc}} = \frac{\Delta S_u}{\Delta H_u} \tag{3c}$$

For oriented polymer melt (*o*: oriented; *c*: crystal; *m*: melt):

$$G_{oc} = G_{om} \tag{4a}$$

$$H_{oc} - T_{om}S_{oc} = H_{om} - T_{om}S_{om} \tag{4b}$$

$$\frac{1}{T_{om}} = \frac{S_{om} - S_{oc}}{H_{om} - H_{oc}} = \frac{\Delta S_o}{\Delta H_o} \tag{4c}$$

We may assume

- (1) $\Delta H_u \approx \Delta H_o = \Delta H$
- (2) $S = k \ln \Omega$, where k is the Boltzmann constant and Ω is the distribution functions of polymer chains in the oriented and unoriented melts.

So,

$$\frac{1}{T_{om}} - \frac{1}{T_{um}} = \frac{R}{\Delta H} \ln \frac{\Omega_{om}}{\Omega_{um}} \tag{5}$$

As the amorphous phase is oriented, the number of configurations is reduced. This might be roughly taken as:

$$f_m \cong 1 - \left(\frac{\Omega_{om}}{\Omega_{um}} \right)^n \tag{6}$$

Then

$$\frac{1}{T_{om}} - \frac{1}{T_{um}} = \frac{R}{\Delta H} \ln(1 - f_m)^{1/n} = \frac{R}{n\Delta H} \ln(1 - f_m) \tag{7}$$

The chain orientation in melts is small and given by the rheo-optical law.^[19] We might roughly estimate it through suggesting a linear relationship between it and the crystalline orientation factor (f_c):

$$f_m = \alpha f_c \tag{8}$$

where α is of the order 0.1.

So,

$$\frac{1}{T_{om}} - \frac{1}{T_{um}} = \frac{R}{n\Delta H} \ln(1 - \alpha f_c) \quad (9)$$

Thus, the melting temperature of as-spun fibers should increase with the increase of crystalline orientation factor.

Effect of Comonomer Content on Melting Temperatures of As-Spun Fibers

Flory^[20,21] derived his equilibrium melting point depression equation of a nonpolar copolymer assuming the exclusion of all defects including chain ends and noncrystallizable *B* comonomer from the crystalline lattice. The equilibrium melting temperature of the copolymer $T_m^o(X_B)$ is expressed by the relationship of the equilibrium melting point of the homopolymer T_m^o , the enthalpy of fusion (ΔH_u) per crystallizable repeating *A* unit, and the mole fraction of the non noncrystallizable *B* comonomer:

$$\frac{1}{T_m^o(X_B)} = \frac{1}{T_m^o} + \left(\frac{R}{\Delta H}\right) X_B \quad (10)$$

Combining Equations (9) and (10), we may further obtain a generalized equation on melting temperatures of as-spun polyethylene and its copolymers:

$$\frac{1}{T_m(X_B)} = \frac{1}{T_m^o} + \left(\frac{R}{\Delta H}\right) X_B + \left(\frac{R}{n\Delta H}\right) \ln(1 - \alpha f_c) \quad (11)$$

It is not possible to include nonequilibrium effects such as cooling rate in these arguments without doing greater violence to statistical thermodynamics than we have already done.

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