Chapter 5 Study of Crystallization and Melting Processes in Ethylene – Styrene Copolymers by Conventional DSC and Temperature Modulated Calorimetry: High Styrene Content Copolymers.

#### 5.1 Introduction

In the preceding chapter,<sup>1</sup> we have correlated the generation of excess heat capacity during quasi-isothermal crystallization with the primary crystallization and lamellar thickening process for linear polyethylene and low styrene content ethylene copolymers. It was speculated<sup>1</sup> that reversible crystallization and melting during temperature modulation is associated with the reversible segmental exchange between the amorphous and crystalline phases on the fold surface. For linear polyethylene and a number of other flexible homopolymers, primary crystallization consists of the formation of chain-folded lamellar crystals and the dominant mechanism for secondary crystallization is lamellar thickening.

However, when bulky comonomers are introduced in the chain backbone of linear polyethylene, they act as defects in the polymer chain and are rejected from the crystalline region during the crystallization process.<sup>2-8</sup> The resulting crystallites exhibit lower thickness and reduced lateral dimensions. An evolution of the morphology from regular chain-folding lamellae to fringed-micellar like or bundle-like crystals with increasing comonomer content has been reported for a series of ethylene random copolymers.<sup>9-12</sup> For high comonomer content copolymers, the tight adjacent re-entry chain-folding is absent and non-crystallizable co-units accumulate on the basal surfaces. As a result the lamellar thickening process is strongly suppressed. In this case, the mechanism for reversible crystallization and melting during temperature modulation must be reconsidered.

In contrast with linear polyethylene which exhibits a single endotherm melting behavior, the multiple endotherm melting behavior is characteristic of ethylene copolymers with high enough comonomer content.<sup>13-20</sup> This multiple melting behavior is also found in some linear homopolymers such as it-PP,<sup>21-23</sup> it-PS, <sup>24</sup>, <sup>25</sup> s-PS, <sup>26</sup> polyurethane, <sup>27</sup> PLLA, <sup>28</sup> PEEK,<sup>29-37</sup> PET,<sup>38-41</sup> and BAPC. <sup>42</sup>, <sup>43</sup> To understand the mechanism of reversible crystallization and melting for high comonomer content

copolymers, the origin of the multiple melting behavior must be clarified. On the other hand, a better understanding of reversible crystallization and melting phenomena can also shed some light on the issue of multiple melting behavior. Discussions on the origin of multiple melting behavior are abundant in the literature. Several mechanisms have been proposed including: (1) melting-recrystallization-remelting (MRR),<sup>24,30,32,36,38,39,44</sup> (2) multiple populations of crystallites<sup>29, 31, 33, 35, 36, 45-48</sup> and (3) different stability at different locations of single lamella<sup>49, 50</sup> or in different sectors of a single crystal.<sup>51-53</sup>

Evidence for the MRR phenomenon is found in some cases, 1) by observation of a recrystallization exotherm between the low and high melting endotherms in a DSC heating trace<sup>28</sup> or 2) by observation of an exothermic contribution in the non-reversing heat flow in TM-DSC<sup>36, 39, 41</sup> or 3) through variable heating rate studies.<sup>30,32,38,39,41</sup>

Heating rate studies for an ethylene random copolymer with 12.3 mol% octene show no significant MRR effect after low temperature crystallization.<sup>14</sup> In this specific case, the multiple melting endotherms are assigned to the melting of different crystal populations with different thermal stability. The absence of MRR effects is attributed to an inhibition of the reorganization of low melting crystallites into thicker, more stable crystallites due to presence of hexyl side groups.<sup>14</sup> However, systematic studies of the dependence of MRR effects on the crystallization temperature and comonomer content are still missing. For instance, one should anticipate that these effects will be important for ethylene copolymers with low comonomer content or at high crystallization temperature. This issue will be discussed in this report.

Multiple melting behavior has also been associated with the melting of different sections of a single lamella. Using hot stage atomic force microscopy (AFM), Zhou et al.<sup>51</sup> found that the {100} and {010} sectors of syndiotactic polypropylene single crystals exhibit different thicknesses, thus different melting temperatures. A similar phenomenon was also observed in hexagonal single crystals of PLLA<sup>52</sup> and truncated polyethylene single crystals.<sup>53</sup> Differences in thermal stability of different sectors were tentatively assigned to variation in chain folding. Similarly, the assignment of different melting temperatures to different locations of a given melt-crystallized lamella was proposed for it-PS<sup>49</sup> and BAPC<sup>50</sup> on the basis of TEM and hot stage AFM observations, respectively.

In some cases, recrystallization might occur after melting of the least stable crystals.<sup>50,51,53</sup> Hence, both effects might contribute to the multiple melting behavior.

Many researchers have used the multiple crystallite population model to explain the multiple melting behavior.<sup>14,15,29,31,33,35,36,43,45,46,54</sup> In this model, it is speculated that small secondary (or subsidiary) crystals develop between large primary (or dominant) crystallites. Since secondary crystals have significantly reduced thickness and lateral dimensions compared to primary crystals, they melt at lower temperature and contribute to the low endotherm in a DSC heating trace. However, there are still some arguments about the structure and location of these secondary crystals. Researchers have speculated that secondary crystals might be in the form of lamellar stacks<sup>39,46</sup> or thin single lamellae<sup>33,47</sup> or fringed-micellar type crystallites located in-between existing primary thick lamellae.<sup>14,35,43</sup>

In random ethylene copolymers, the distribution of crystallizable sequence lengths is well approximated by the binomial distribution. Different sequence lengths impart different ranges of crystallization temperature. Therefore a wide melting range is expected in random copolymer. To explain the multiple melting behavior, Crist et al.<sup>15</sup> proposed a bimodal kinetic model for random copolymers consisting of crystallizable and noncrystallizable units. Two types of crystal thickness were established as  $l^*$  and  $l_f$ . The former corresponds to the minimum sequence length above which the sequence is undercooled and can crystallize.  $l^*$  can be calculated with Gibbs-Thomson equation:

$$l^* = \left(\frac{2\sigma_e}{\Delta H_f}\right) \left(\frac{T_m}{T_m - T_x}\right) \tag{5.1}$$

where  $T_{\rm m}$  and  $T_{\rm x}$  are the copolymer equilibrium melting temperature and the crystallization temperature, respectively,  $\sigma_{\rm e}$  is the basal surface free energy of crystallites and  $\Delta H_{\rm f}$  is the heat of fusion.  $l_{\rm f}$  is the thickness of lamellae corresponding to the final melting temperature at which the crystal is in equilibrium with melt. This quantity can also be calculated with the Gibbs-Thomson equation:

$$l_f = (\frac{2\sigma_e}{\Delta H_f})(\frac{T_m}{T_m - T_f})$$
(5.2)

Here,  $T_{\rm f}$  is the final melting temperature. Crist et al.<sup>15</sup> pointed out that only sequences of length larger than  $2l_{\rm f}$  have chance to fold. Sequences of length between  $l^*$  and  $2l_{\rm f}$  can only

crystallize in the extended form, i.e., forming a fringed-micellar type crystal. Two types of crystallization behavior are therefore established based on the magnitude of the sequence length. Long sequences can form chain-folded lamellar crystals with high stability and shorter sequences can only form fringed-micellar crystallites, thus explaining the existence of two crystal populations and two melting endotherms in random copolymers.

In the present study, we first focus on the mechanism multiple melting behavior. Specifically, we will try to answer the following questions: (1) How significant is the MRR effect in the case of random copolymers and if so, what are the comonomer content and temperature dependences? (2) Is the multiple melting behavior associated with different crystal populations? If so, what are the differences in morphology and crystallization kinetics? We will attempt to elucidate these issues through studies of 1) the overall crystallization kinetics, 2) the partial melting behavior and 3) superheating.

Second, we intend to correlate the mechanism of reversible crystallization and melting during temperature modulation to that of primary and secondary crystallization. Considering the evolution of morphology from regular chain-folded lamellae to fringed-micellar crystals with increasing comonomer content<sup>9-12</sup> and associated change of crystallization kinetics, ethylene random copolymers provide an ideal model polymer system to study the mechanism of primary and secondary crystallization. The generation of excess heat capacity in the quasi-isothermal experiment using temperature modulated calorimetry should also be morphology dependent. Therefore it is expected that the correlation between the results from temperature modulated calorimetry and DSC would shed some light on the mechanism of primary and secondary crystallization, and also on the origin of reversible crystallization and melting processes.

#### **5.2 Experimental Section**

**Materials:** A series of statistical ethylene copolymers with composition ranging from 0.35 to 11.7 mol% styrene were used as received from the Dow Chemical Company. Their molecular characteristics are shown in Table 5.1. These materials (trade name INDEX<sup>®</sup>) were synthesized using the Insite<sup>®</sup> technology and are called "pseudorandom ethylene/1-styrene interpolymers" (ESI) due to the absence of successive head-to-tail

styrene insertions. They can also be appropriately described as random copolymers of ethylene units and ethylene/styrene dyads.

Sample	Wt% Styrene	M <sub>w</sub> (g/mol)	PDI $(M_{\rm w}/M_{\rm n})$	Mol% Styrene
ESI-0.35	1.3	168000	2.0	0.35
ESI-1.9	6.8	160200	2.3	1.9
ESI-3.4	11.6	175100	2.2	3.4
ESI-5.5	17.7	164600	3.5	5.5
ESI-8.9	26.5	182300	2.3	8.9
ESI-11.7	33	208900	2.2	11.7

 Table 5.1: Molecular characteristics of ethylene-styrene copolymers

**DSC and Temperature Modulated Calorimetry:** The technique and procedure of DSC and temperature modulated calorimetry have been described in the preceding chapter and will not be repeated here.

#### 5.3 Results

## 5.3.1 DSC Studies of the Melting Behavior Subsequent to Isothermal Crystallization

We showed in the preceding paper that linear polyethylene and low styrene content copolymers, when crystallized under isothermal conditions, lead to a morphology that is characterized by single melting endotherm. Multiple melting behavior can however be observed in the case of ESI-1.9 where both peaks shift to higher temperature at longer crystallization time. For copolymers with larger styrene content (e.g. ESI-8.9 and ESI-11.7) multiple melting behavior is observed over wide range of crystallization temperatures (see Figure 5.1.a – 5.1.c). For these materials, the low endotherm shifts to higher temperature with time. However, in contrast with ESI-1.9, the high endotherm peak position and the high temperature shoulder (in samples crystallized at low temperatures) do not show any evidence of shifting.



**Figure 5.1** Evolution of the melting trace with crystallization time for ESI-8.9 at (a)  $T_x =$  73 °C and (b)  $T_x = 60$  °C and for ESI-11.7 at (c)  $T_x = 53$  °C (range of crystallization times as indicated).

b

c

Since the melting temperature is often found to increase linearly with the natural logarithm of crystallization time, we define the melting temperature shift rate  $B(T_x)$  by:

$$B(T_x) = \left(\frac{\partial T_m'}{\partial \ln(t)}\right)_{t_x}$$
(5.3)

The quantity  $B(T_x)$  characterizing the low endotherm after crystallization at different temperatures is plotted in Figure 5.2 for a number of ethylene copolymers. The systematic decrease in  $B(T_x)$  with increasing crystallization temperature observed for the low endotherm is in marked contrast with the systematic increase in  $B(T_x)$  with increasing crystallization temperature which was characteristic of the single endotherm for linear polyethylene and low styrene content ethylene copolymers.



**Figure 5.2** Melting temperature shift rate  $B(T_x)$  as a function of crystallization temperature for various ESI materials (ESI-3.4, ESI-5.5, ESI-8.9 and ESI-11.7).

#### **5.3.2 Overall Isothermal Crystallization Kinetics**

In the present study, evolution of the heat of fusion ( $\Delta H_f$ ) with crystallization time was obtained from the DSC melting traces recorded subsequent to isothermal crystallization for different times (see Figure 5.3.a-d for ESI-1.9, ESI-3.4, ESI-8.9 and ESI-11.7, respectively). The sigmoidal shape, characteristic of linear polyethylene and low styrene content copolymers,<sup>1</sup> can still be clearly seen only in the case of ESI-1.9, but becomes difficult to discern in high styrene content samples. In addition, the induction time shows a much weaker dependence on crystallization temperature for the high styrene content copolymers than for the low styrene content copolymers.

The Avrami analysis was then carried out for each isothermal crystallization temperature. The Avrami exponents (n), estimated as shown in Figure 5.4, exhibit a systematic decrease with increasing crystallization temperature.

We also obtained the degree of crystallinity  $(X_c^*)$  associated with the end of the linear regime in the Avrami plot, as a function of the crystallization temperature (see Figure 5.5).  $X_c^*$  is a measure of the degree of crystallinity at the end of the primary crystallization stage. For the low styrene content samples such as ESI-1.9 and ESI-3.4,  $X_c^*$  changes significantly with crystallization temperature while for high styrene content samples like ESI-8.9 and ESI-11.7, the change is very limited, keeping at degree of crystallinity ranging from 0.5% to 1%.

#### **5.3.3 Heating Rate Studies**

Here, we are interested in the multiple melting behavior subsequent to isothermal crystallization at high temperature. It is therefore imperative to know whether the multiple endotherms are caused by the MRR effect or by multiple populations of crystallites or both, and to understand the influence of both the comonomer content and the crystallization temperature on this behavior. Comparing the DSC melting trace generated at different heating rates is an effective approach to investigate the melting-recrystallization-remelting (MRR) effect in the multiple melting behavior. If the rate of recrystallization of the amorphous material formed by melting the lowest stability crystals is comparable with the heating rate, then, one should expect to obtain a larger and more clearly defined high melting endotherm when using a lower heating rate.



а

b



**Figure 5.3** Heat of fusion as a function of crystallization time at various temperatures for (a) ESI-1.9, (b) ESI-3.4, (c) ESI-8.9 and (d) ESI-11.7. (crystallization temperature as indicated)

d



**Figure 5.4** Avrami exponent (*n*) as a function of crystallization temperature for various ESI materials (ESI-1.9, ESI-3.4, ESI-5.5, ESI-8.9 and ESI-11.7).



**Figure 5.5** Critical degree of crystallinity  $(X_c^*)$  as a function of crystallization temperature for various ESI materials (ESI-1.9, ESI-3.4, ESI-5.5, ESI-8.9 and ESI-11.7).

The results of heating rate studies for ESI-1.9 and ESI-3.4 are shown in Figure 5.6.a and 5.6.b, respectively. Note that each melting trace has been calibrated using a sandwich standard sample to account for thermal lag effects. It is noted that for ESI-1.9, the high melting peak is more distinct at low heating rate (2.5 to 10 K/min). Additionally, a third melting peak can be recognized at heating rate 2.5 and 5 K/min. With increasing the heating rate, the high melting side becomes a shoulder. It is also observed that the peak melting temperature for the low endotherm shifts to high temperature with increasing heating rate while that of high endotherm remains almost constant.

For ESI-3.4, the variation in the shape of the melting trace with heating rate is not as obvious as for ESI-1.9. As shown in Figure 5.6.b, at all five heating rates investigated, three melting peaks can be clearly identified. It is noticeable that the third melting peak increases with decreasing heating rate. This suggests that the MRR effect might be associated with the second and third melting peaks. Similar to ESI-1.9, the melting temperature for the low endotherm increases with heating rate. However, the second highest endotherm slightly shifts to lower temperature with increasing heating rate.

From the information provided above, there is no doubt that the MRR effect exists at high crystallization temperature in low styrene content samples, and at least partially contributes to the observation of multiple melting peaks. With increasing comonomer content, the MRR effect diminishes considerably at all but the highest crystallization temperatures. To determine whether multiple populations of crystallites exist in the ESI-1.9 and ESI-3.4 will be studied further through the partial melting experiments discussed in the following section.

The increase in the melting temperature with increasing heating rate after thermal lag corrections is defined as the superheating. The study of superheating behavior is helpful to further understand the melting mechanism and the nature of polymer crystals. Here, we investigate the superheating behavior of ESI-3.4 crystals over a wide range of crystallization temperatures. The selection of ESI-3.4 is based on the speculation that the multiple melting behavior in this copolymer results from multiple crystal populations, which we will justify later. In addition, the MRR effect seems absent over a wide temperature range. Therefore the melting trace for ESI-3.4 should provide a good representation of the true crystal population formed at a given temperature and should not

be obscured by effects of reorganization during melting. The extent of superheating thus obtained can reflect the real properties of the crystallites associated with the corresponding endotherms.

To characterize the superheating, the melting temperatures obtained at different heating rate (HR) are plotted against the square root of heating rate as shown in Figure 5.6.c. The slope is defined as  $C(T_x)$ . Justifications for choosing the square root of the heating rate will be offered later. We note however that these plots exhibit good linearity when  $T_x < 100$  °C and that the slope  $C(T_x)$  decreases with increasing crystallization temperature as shown in Figure 5.6.d. However, a significant non-linearity is observed in the plot  $T_m$  vs. HR<sup>1/2</sup> when  $T_x \ge 100$  °C. The existence of different superheating behaviors in different temperature ranges is giving us some hints on the change in mechanism of melting with temperature and most importantly, on changes in the nature of crystals associated with the low endotherm. This will be further discussed in the context of our study of the multiple melting behavior.

### **5.3.4 Partial Melting Experiments**

We now discuss the results of partial melting experiments designed to further elucidate whether multiple crystal populations are produced as a result of isothermal crystallization. The present study focuses on ESI-1.9 and ESI-3.4 for which prominent multiple melting behavior can be observed. In these partial melting experiments (Figure 5.7.a), a sample is initially held at temperature  $T_{x1}$  for a period of time ( $t_{x1}$ ) to develop some crystals that can show multiple melting behavior. The sample is then partially melted by raising the temperature to  $T_{x2}$  and annealed at that temperature for a period of time  $t_{x2}$ . One expects that a fraction of the high melting crystals will survive and possibly be reorganized by this annealing treatment. We then study the role played by these high melting crystals on the formation of the lower melting crystals by quenching the sample to the initial isothermal crystallization temperature  $T_{x1}$ , holding for some time ( $t_{x3}$ ) and finally heating the sample to a high enough temperature to obtain the complete melting trace.



a

b



**Figure 5.6**: DSC melting trace after isothermal crystallization generated at different heating rate (in the range from 2.5 to 30 K/min as indicated) for (a) ESI-1.9 at  $T_x = 112$  °C,  $t_x = 20$  min, (b) ESI-3.4 at  $T_x = 108$  °C,  $t_x = 120$  min. (c) Melting temperature as a function of square root of heating rate for ESI-3.4 (Data was arbitrarily shifted along the temperature axis for the sake of clarity.) (d) The value of  $C(T_x)$  as a function of crystallization temperature.

d

In Figure 5.7.b (ESI-3.4),  $T_{x1}$  and  $T_{x3}$  are set to 108 °C and  $T_{x2}$  is varied. As a comparison, the melting trace for a sample isothermally crystallized at 108 °C after quenching from melt is added (smoothed curve, defined as A). It is noted, that for  $T_{x2}$  in the range 119 - 121 °C, no endotherm is observed on Figure 5.7.b around 115 to 118 °C where the second melting peak is observed in trace A. However, a higher endotherm is observed above 119 °C in both melting curves. When  $T_{x2}$  exceeds 123 °C, the second endotherm is recovered while the third endotherm weakens. Similar observations are made in the case of ESI-1.9. Therefore we conclude that the second and third endotherms are highly correlated and cannot be associated with independent features of the morphology.

To investigate the role played by the crystals remaining after partial melting in the subsequent isothermal crystallization at lower temperature, partial melting experiments were also carried out for ESI-1.9 (see Figure 5.9.c). In this case, the holding time  $t_{x2}$  at  $T_{x2}$  is varied from 1 to 150 min. An increase in  $t_{x2}$  is expected to lead to the development of higher crystallinity during annealing at  $T_{x2}$ . In the subsequent step, the sample is quenched to 112 °C where isothermal crystallization is carried out for a fixed time. The resulting melting behavior shown on Figure 5.7.c indicates that the highest endotherm increases with  $t_{x2}$  due to annealing. The lowest endotherm, however, is not affected at all. In addition, the second endotherm decreases with increasing  $t_{x2}$ . The evolution of the second and third endotherms with  $t_{x2}$  further confirms that these endotherms are highly correlated.

We also studied the influence of the initial degree of crystallinity developed at  $T_{x1}$  on subsequent isothermal crystallization at  $T_{x3}$ . Here,  $t_{x1}$  is varied and  $t_{x2}$  and  $t_{x3}$  remain constant. As shown on Figure 5.7.d, both the highest and the lowest endotherms increase significantly with increasing  $t_{x1}$  but cease to grow after  $t_{x1} = 50$  min. Figure 5.7.e shows the evolution with  $t_{x1}$  of the heat of fusion associated with each endotherm. Note that the low endotherm is defined for this calculation as the section of the melting trace below  $T_{x2}$  (i.e. below 119°C). Both heats of fusion show the same trend. Two very important observations deserve special attention. First, the melting temperature associated with the low endotherm remains constant when  $t_{x1}$  increases, indicating that this melting temperature depends only on time but not on the actual crystallinity. Second, as shown on

Figure 5.7.d, the low and middle endotherms exhibit different trends. These two observations must be related to (1) the kinetics of formation of the lowest melting crystals and the associated mechanism controlling the evolution of their melting temperature and (2) their ability or lack thereof to reorganize into higher melting crystals. These issues will be discussed in detail later.

# 5.3.5 Generation of Excess Heat Capacity under Quasi-Isothermal Conditions

The differences in melting behavior observed for low and high styrene content copolymers imply different mechanisms of secondary crystallization and different types of crystals. One would like to see whether different secondary crystallization mechanisms can be reflected in the evolution of the excess heat capacity generated under quasiisothermal conditions. It was noted<sup>1</sup> that the low and high endotherms increase simultaneously in magnitude during the early stage of isothermal crystallization at high temperature. Therefore, evolution of the excess heat capacity at high crystallization temperature is likely to receive contributions from both crystal populations. In contrast to the situation at high temperature, evolution of the excess heat capacity at low temperature should reflect evolution of the low endotherm, only, since only the low endotherm is observed to change with time under these conditions (see Figure 5.1.b).

The evolution of the excess heat capacity at various temperatures is given in Figure 5.8.a and 5.8.b for ESI-3.4 and ESI-8.9, respectively. In the case of ESI-3.4, the ratio  $C_p^{\text{excess}}(t_x) / \Delta H(t_x)$ , remains almost constant during the initial stage at  $T_x = 104 \text{ °C}$  and 106 °C (see Figure 5.9.a), suggesting that the excess heat capacity is proportional to the crystallinity, at least initially. Interestingly, this ratio starts to decrease at the time when the high endotherm ceases to grow (25 min at  $T_x = 104 \text{ °C}$  and 80 min at  $T_x = 106 \text{ °C}$ ). The inserts in Figure 5.9.b and 5.9.c represent the evolution of the height of the high endotherm with time and allow unambiguous identification of this crossover. The correlation between the evolution of the  $C_p^{\text{excess}}(t_x) / \Delta H(t_x)$  ratio and the evolution of melting traces indicates that low and high melting crystals play significantly different roles in the evolution of the excess heat capacity.

а

Temperature













**Figure 5.7:** (a) Temperature program for partial melting experiments; (b) The effect of  $T_{x2}$  on the melting behavior ( $T_{x2}$  as indicated) in the case of ESI-3.4. Here,  $T_{x1} = 108$  °C,  $t_{x1} = t_{x3} = 55$  min; (c) Effect of  $t_{x2}$  on the melting behavior for ESI-1.9 ( $t_{x2}$  as indicated). Here,  $T_{x1} = 112$  °C,  $T_{x2} = 120$  °C,  $t_{x1} = 20$  min,  $t_{x3} = 4$  min; (d) Effect of  $t_{x1}$  on the melting behavior for ESI-1.9 ( $t_{x1}$  as indicated), here,  $T_{x2} = 119$  °C,  $t_{x2} = 2$  min,  $t_{x3} = 20$  min. (e) Evolution of the heat of fusion with  $t_{x1}$  for low and high endotherms from (d).

For the case of ESI-8.9, the situation is somewhat different. Figure 5.10.a shows the evolution of the excess heat capacity during quasi-isothermal crystallization at 70 °C and 73 °C. The excess heat capacity increases initially and subsequently remains almost

e

constant. The crossover time is again approximately equal to the time when the high melting shoulder ceases growing as shown in Figure 5.10.b and 5.10.c. In addition, it is noted that the low endotherm still increases significantly after the crossover time while the excess heat capacity reaches a plateau. This behavior differs from that exhibited by ESI-3.4 where the excess heat capacity keeps increasing even after the high endotherm remains constant. This observation suggests that the low melting crystallites play different roles in the evolution of the excess latent heat in the above two cases.

Above we provided results from quasi-isothermal studies at high crystallization temperature. At lower crystallization temperature, the usual decay behavior is observed.<sup>1</sup> In the present study of ESI-3.4 and ESI-8.9, the KWW analysis is also carried out to analyze the relaxation in excess heat capacity. The excess heat capacity decay curve is fit with the Kohlrausch-Williams-Watts (KWW) equation:<sup>55</sup>

$$C_{\rm p}^{\rm exc}(t) = C_{\rm p}^{\rm exc}(\infty) + [C_{\rm p}^{\rm exc}(0) - C_{\rm p}^{\rm exc}(\infty)] \exp[-(t/\tau)^{\beta}]$$
(5.4)

where  $C_p^{\text{exc}}(0)$  and  $C_p^{\text{exc}}(\infty)$  are the upper and lower bounds of the excess heat capacity at time zero and infinity, respectively,  $\tau$  is a characteristic relaxation time, and  $\beta$  is an exponent characterizing the heterogeneity of the relaxation process ( $\beta = 1$  implies a single relaxation time process, while  $\beta < 1$  suggests a distribution of relaxation times). To estimate the characteristic relaxation time. τ, а plot of  $\ln\{-\ln[(C_p^{exc}(t) - C_p^{exc}(\infty))/(C_p^{exc}(0) - C_p^{exc}(\infty))]\}$  vs.  $\ln t$  was prepared. The values for  $C_{p}^{exc}(\infty)$  are obtained by minimization of the variance associated with the linear regression. Apparent activation energy for the underlying relaxation process is obtained by plotting  $\ln \tau$  vs. 1/T. Figure 5.11 gives Arrhenius plots for these samples. The apparent activation energy (E<sub>a</sub>) calculated for ESI-3.4 is much lower than for LPE-119K, ESI-0.35 and ESI-1.9. In contrast, a much larger activation energy is obtained for ESI-8.9.

#### 5.3.6 Quasi-Isothermal Melting Experiments

To investigate the reversing heat capacities as function of temperature, quasiisothermal melting experiments were carried out for a series of ESI samples (ESI-0.35, ESI-1.9, ESI-3.4, ESI-5.5, ESI-8.9 and, ESI-11.7) as shown in Figure 5.12.a-f. In these plots, the solid curves represent the apparent heat capacity measured using a conventional DSC with a heating rate of 10 K/min. The sample was prepared by cooling from 160  $^{\circ}$ C to room temperature at the rate –10 K/min. The open circles stand for the reversing heat capacity obtained in quasi-isothermal melting experiments by temperature modulated calorimetry. The baseline heat capacities in these plots were calculated using eq 3 in ref 1.

It can be observed in Figure 5.12.a - f that the reversing heat capacities on the low temperature side is closer to the apparent heat capacities compared with those on the high temperature side. Obviously, the area under the reversing heat capacity curve for lower styrene content copolymers is less than that for higher styrene content copolymers. To characterize the extent of reversible crystallization and melting, we define the overall degree of reversibility, which is the ratio of the area between reversing heat capacity and the baseline. It is noted that the overall degree of reversibility increases with comonomer content as shown in Figure 5.13.

To further characterize the reversible crystallization and melting behavior, we define a new quantity — the degree of reversibility (DR) as follows:

$$DR = (C_{\rm p}^{\rm rev} - C_{\rm p}^{\rm BL}) / (C_{\rm p}^{\rm app} - C_{\rm p}^{\rm BL})$$
(5.5)

where  $C_p^{\text{rev}}$  is the reversing heat capacity,  $C_p^{\text{app}}$  is the apparent heat capacity obtained from the DSC heating trace and  $C_p^{\text{BL}}$  is the baseline  $C_p$ . The degree of reversibility should reflect the local reversibility of crystals at the corresponding temperature. It is noted that a degree of reversibility has also been defined by Androsch and Wunderlich as the reversible crystallinity change per Kelvin, <sup>56, 57</sup> which is obtained by  $(C_p^{\text{rev}}-C_p^{\text{BL}})/(X_c\Delta H_f(\infty))$ . Here,  $\Delta H_f(\infty)$  is the heat of fusion for the perfect crystal and  $X_c$  is the degree of crystallinity. The degree of reversibility defined in this way cannot reflect the true reversibility of crystals with different stability (i.e. with different melting temperatures).

Figure 5.14 gives the degree of reversibility as a function of temperature for these materials. Two temperature regions can be observed, a low temperature region with high degree of reversibility and a high temperature region with dramatically decreased degree of reversibility. Additionally, the crossover temperature between these regions increases with decreasing comonomer content. This plot will provide another point of view to

understand the mechanism of reversible crystallization/melting and secondary crystallization as a function of temperature and comonomer content.



**Figure 5.8:** Evolution of the excess heat capacity with time under quasi-isothermal conditions for (a) ESI-3.4 and (b) ESI-8.9 (for the indicated crystallization temperatures).



Figure 5.9: Evolution of  $C_p^{\text{excess}} / \Delta H$  with time during quasi-isothermal experiments for (a) ESI-3.4 (for the indicated temperature). The crossover times are indicated; Evolution of the melting trace with crystallization time for ESI-3.4 at (b)  $T_x = 104$  °C and (c)  $T_x = 106$  °C.

а

b

с



**Figure 5.10** (a) Evolution of  $C_p^{\text{excess}}$  with time during quasi-isothermal experiments for ESI-8.9 (for the indicated temperature). The onset times for the leveling off are 4 min and 25 min for  $T_x = 70$  °C and  $T_x = 73$  °C, respectively; Evolution of the melting trace with crystallization time for ESI-8.9 at (b)  $T_x = 70$  °C and (c)  $T_x = 73$  °C.

b

с



**Figure 5.11** Arrhenius plots for  $\tau$  obtained with the KWW analysis. (samples as indicated)

#### 5.4 Discussion

Correlations between the mechanism of isothermal crystallization (primary and secondary) and the magnitude of reversible crystallization/melting have been clearly shown in a previous study<sup>1</sup> and are again emphasized with the above experimental results. In the preceding paper<sup>1</sup> which focused on linear polyethylene (PE-119K) and low styrene content ethylene copolymer (ESI-0.35), we analyzed the secondary crystallization process in these materials in terms of lamellar thickening. We confirmed that the generation of excess latent heat results from the reversible exchange of segments at the fold surface induced by chain-sliding in the crystalline phase. In the case of high styrene content copolymers, the observation of multiple melting suggests the existence of crystal populations characterized by different thermal stability. Therefore, before further discussing the mechanism of reversible crystallization and melting, it is imperative to first address the kinetics of formation of multiple crystal populations. One needs to understand how these crystals form, how they differ morphologically and how these differences are affected by crystallization temperature and styrene content? On this basis, a better understanding of the mechanism of reversible crystallization and melting may be achieved.



b

а



c





**Figure 5.12** Comparison of DSC melting traces (solid curves) and the reversing heat capacity (empty circle) obtained from quasi-isothermal melting experiments for (a) ESI-0.35, (b) ESI-1.9, (c) ESI-3.4, (d) ESI-5.5, (e) ESI-8.9 and (f) ESI-11.7. The baseline heat capacities as a function of temperature are also showed.

d

e

f



Figure 5.13: Overall degree of reversibility as a function of styrene content.



Figure 5.14 Degree of reversibility as a function of temperature for various copolymers.

#### 5.4.1 Crystallization Kinetics Revealed by Conventional DSC

In a previous paper from this laboratory, Alizadeh et al.<sup>14</sup> discussed the low temperature secondary crystallization behavior of a series of ethylene/1-octene random copolymers. Secondary crystallization below a crossover temperature  $T^*$  was

characterized by an Avrami exponent of  $\frac{1}{2}$  suggesting a one-dimensional diffusioncontrolled crystallization mechanism. The Avrami exponent was shown to increase with crystallization temperature above  $T^*$ . These authors suggested that, in contrast to the chain-folded lamellar structures formed in the homopolymer or at high crystallization temperature, secondary crystallites developed below  $T^*$  were of the fringed-micellar type.<sup>14</sup> In the present study, we investigate the crystallization and melting behavior at high temperature ( $T > T^*$ ) where the entire crystallization process (primary and secondary) can be observed.

As shown in Figures 4.1.e, 4.1.g and Figures 5.1.a, 5.1.c, the low and high melting endotherms develop simultaneously during the early stage of crystallization at high temperature. One needs to determine whether the origin of this multiple melting behavior is the same as that characterized by Alizadeh et al.<sup>14</sup> at low temperatures. Specifically, is the low melting peak still associated with the melting of fringed-micellar crystals formed under constraint environment?

First, we find that the melting temperature shift rate,  $B(T_x)$ , characteristic of the low endotherm decreases with temperature for crystallization at high temperature but is qualitatively compatible with the  $B(T_x)$  curve obtained at lower temperatures by Xu.<sup>17</sup> Marand et al.<sup>14, 35, 43</sup> suggested that the increase in the low endotherm melting temperature with crystallization time may result from a reduction in the conformational entropy of the amorphous phase constrained between primary and secondary crystals. A decrease of  $B(T_x)$  with crystallization temperature would indicate a gradual release of the conformational constraints with increasing temperature. The evolution of  $B(T_x)$  as a function of temperature in the present study is consistent with this mechanism. We also note that the high endotherm always appears before the low endotherm, as is clearly shown by the melting trace for ESI-3.4 crystallized at  $T_x = 106$  °C (see Figure 5.15). This can also be seen in Figure 5.9.c for ESI-3.4 crystallized at  $T_x = 106$  °C. Two mechanisms can explain this observation. Crist et al.<sup>15</sup> associated this with different undercoolings for the crystallizable sequences associated with the low and high endotherms. Longer crystallizable sequences exhibit a higher equilibrium melting temperature. Hence, they are characterized by a larger undercooling and their crystallization will be favored kinetically. This observation can also be explained by the mechanism proposed by Marand et al.,<sup>14, 35, 43</sup> i.e., the formation of high melting primary crystals is a prerequisite for the development of low melting secondary crystals.

To further understand the kinetics of crystallization at high temperature, an Avrami analysis was carried out. First, one needs to keep in mind that two or more crystallization mechanisms might be active simultaneously. Still, a linear region can be found in the Avrami plot for short crystallization times. However, the formation of both low and high melting crystallites contributes to the Avrami exponent thus obtained. This type of Avrami exponent should be called "apparent Avrami exponent" and great caution



Figure 5.15: Evolution of the experimental melting trace with crystallization time for ESI-3.4 at  $T_x = 109$  °C. (crystallization time as indicated)

must be taken when trying to understand its physical meaning. As shown in Figure 5.4, the apparent Avrami exponent decreases with increasing crystallization temperature. This may result from two factors; 1) a change in the geometry of the growing crystal (decrease in dimensionality) and 2) a change in the nucleation pattern. According to Flory's theory, at any given temperature, there is a minimum sequence length below which crystallization is no longer possible on thermodynamic grounds. Hence, the fraction of crystallizable sequences and the resulting degree of crystallinity decrease when the crystallization temperature is raised. Therefore a more open semicrystalline

superstructure should be generated at higher temperatures. This is fully consistent with the observed decrease in the Avrami exponent. Another factor responsible for the decrease of Avrami exponent is the change in nucleation rate with time. For homopolymers, the nucleation rate is usually approximately constant in the free melt. However, for random copolymers, the systematic decrease in the concentration of long crystallizable sequences during the initial stages of crystallization eventually leads to a parallel decrease in the nucleation rate. As a consequence, most nuclei will form at the very beginning of crystallization, suggesting that the nucleation process in random copolymers is best described as athermal. Cheng et al.<sup>58</sup> have already shown that athermal nucleation would result in the decrease of the apparent Avrami exponent. The athermal character of the nucleation process is also reflected in the evolution of crystallinity with time as shown in Figure 5.3.a - 5.3.d. For ESI-1.9, the sigmoidal shape of the crystallinity evolution and the large sensitivity of the induction time to a change in crystallization temperature are characteristic of a thermally-controlled nucleation process. In higher styrene content samples, the sigmoidal character of the crystallinity curves is lost and the induction time is almost constant in an even wider crystallization temperature range. This is a typical athermal nucleation processes. Since most nuclei form at a very early stage of the solidification, a network is expected to develop in which the crystallites act as physical cross-links. As a consequence, the amorphous fraction around these crosslinks is constrained which further affects the kinetics of subsequent crystallization. One can imagine that long-range chain transport will be absent or significantly reduced in such a situation. Experimental evidence supporting this assertion can be found from small-angle neutron scattering (SANS) experiments, which showed the lack of chain mobility in the crystallization of hydrogenated polybutadiene (HPB), a model system for random ethylene-butene copolymers.<sup>59</sup> This behavior is different from that of PE homopolymer in which long range transport can be observed.<sup>60</sup> Horst and Winter<sup>61</sup> even measured the crystallinity at the gel point during the process of crystallization for an ethylene/1-butene random copolymer having 11 mol% comonomer content. The gel point indicates a transition from liquid to solid where long-range transport cannot be achieved. They found that the degree of crystallinity at the gel point was around 1 % over a range of crystallization temperatures. This value is very close to the critical degree of crystallinity ( $X_c^*$ ) obtained for ESI-5.5, ESI-8.9 and ESI-11.7 in present study (0.5 % to 1.5 % as shown in Figure 5.5). This observation leads us to speculate that the end of the linear region in the Avrami plot results from the formation of a global semicrystalline network, which corresponds to the transition from liquid to solid.

Next, we would like to determine whether the microstructure of the low melting crystallites is best described in terms of chain-folding lamellae or fringed-micellar crystals. This question is important because it is related to the mechanism of reversible crystallization and melting during quasi-isothermal treatment and to the deformation behavior of these materials. In the bimodal kinetic model proposed by Crist et al.,<sup>15</sup> the low melting crystals are believed to be of fringed-micelle type and the high melting crystals are chain-folding lamellae. According to this model, these two populations develop independently and the low melting crystals are not formed in a constrained environment. At this point, it is still hard to answer the question mentioned above, i.e., whether the low melting crystallites formed at high temperature are of the fringed-micelle type or chain folding lamellae and whether the low melting crystals are formed in a constrained environment. To further our understanding of this issue, we will need to wait until the following section where the results from heating rate studies and partial melting experiments are presented. Here, we speculate that both the effect of the constraints and of the low undercooling for short sequences contribute to the kinetics of low melting crystals formation at high temperature. It is reasonable to expect low melting crystals formed at high temperature to be intermediate structures between fringed-micelles and chain-folded lamellae. For kinetic reasons, some long sequences may be trapped as cilia attached to high melting crystals and have the potential for forming chain-folded structure at a later stage of crystallization.

In summary, on the basis of results from isothermal crystallization kinetic studies, it is speculated that the low melting crystals formed at high temperature contain a significantly smaller fraction of chain-folded sequences compared to the high melting crystals. The chain-folded lamellar structure might still be the dominant morphology when the low melting crystals are formed at high temperature, especially for low comonomer content copolymers. With decreasing temperature, the shorter sequences are expected to crystallize, leading to more constrained amorphous regions between crystals. In this latter case, the low melting crystals are expected to be fringed-micelle like.

## 5.4.2 Origin of the Multiple Melting Behavior Revealed by Heating Rate Studies and Partial Melting Experiments

As mentioned in the Introduction, there is no universal model for the multiple melting behavior. The mechanism of multiple melting peaks may be decided by several factors such as crystallization temperature, thermal history, morphology, different crystal forms, molecular defects, etc... For random ethylene copolymers, a comprehensive understanding of the multiple melting behavior must consider the effect of comonomer content and crystallization temperature. In the following, we attempt to clarify the origin of the multiple melting behavior at high temperature using the results from heating rate studies and partial melting experiments.

As shown in Figure 5.6.a and 5.6.b, a distinct Melting-Recrystallization-Remelting (MRR) effect can be observed for ESI-1.9, which might partially contribute to the observed multiple endothermic behavior. However, in ESI-3.4, the MRR effect is not associated with the first two endotherms but with the second and third endotherms. The fact that short ethylene sequences making-up the low melting crystals do not exhibit any recrystallization above the low endotherm is attributed to the presence of neighboring styrene co-units, which prevent the participation of short sequences into thicker crystals. In addition, it is noted that high styrene content copolymers crystallize at much lower temperature than low styrene content materials. Hence, the ability of high styrene content copolymers to reorganize during heating is further reduced as a result of the lower segmental mobility at lower temperature.

To further clarify whether low and high melting crystals have a different origin, partial melting experiments were carried out as shown in Figure 5.7 - 5.10. In Figures 5.7 and 5.8, the second endotherm disappears after partial melting, suggesting that the crystallizable sequences associated with the second endotherm can reorganize to participate in higher melting crystals, which is consistent with the above results from heating rate studies. The partial melting experiments shown in Figure 5.9.a and 5.9.b support this conclusion further. As shown in Figure 5.9.b, annealing at  $T_{x2}$  increases the

fraction of highest melting crystals and simultaneously decreases the crystalline fraction associated with the second melting peak. However, annealing does not change the amount of lowest melting crystals. The highest melting crystals which survive partial melting are likely to act as nucleating agents for the subsequent isothermal crystallization at lower temperature ( $T_{x1}$ ). Annealing at  $T_{x2}$  is likely to change only the size of these nuclei but not their number. Examination of Figure 5.9.b clearly indicates that the second and third endotherms share the same origin. In addition, the ethylene sequences associated with the second and third endotherms do not participate in crystals melting at the lowest endotherm. These observations provide strong support to the idea that the sequences responsible for the first two endotherms are of different length thus of different reorganization ability. However, this does not exclude the possibility that the lowest melting crystals could at least partially be reorganized into higher melting crystals, which is what we infer from heating rate studies.

In the partial melting experiments shown in Figure 5.10, the initial isothermal crystallization time,  $t_{x1}$ , is changed so that different initial crystallinities are generated before partial melting. If reorganization during heating was significant, we would expect the amount of highest melting crystals formed by reorganization of the lower melting ones to be determined by  $t_{x1}$ . This would be reflected in a steady increase in the peak area of the highest endotherm with increasing  $t_{x1}$ . However, the endotherm area associated with the highest melting crystals reaches a plateau as shown in Figures 5.7.d and 5.7.e. This limitation is possibly due to the limited concentration of long ethylene sequences. Interestingly, the peak melting temperature for the lowest endotherm remains constant when  $t_{x1}$  is changed (Figure 5.7.d). Note that the crystallization time  $t_{x3}$  during the isothermal process at  $T_{x1}$  subsequent to partial melting is kept constant for the different runs. This implies that the melting temperature associated with the lowest endotherm is only time dependent but not crystallinity dependent. Recall the mechanism proposed by Marand et al.,<sup>14, 35, 43</sup> the increase in melting temperature for the low endotherm with crystallization time is caused by the decrease of conformational entropy in the amorphous fraction induced by an increase of crystallinity. In the present case, the increase in crystallinity does not enhance the melting temperature of low melting crystallites, suggesting that the low melting crystallites might not develop in a constrained

environment or that the constraints are not sufficient (low crystallinity). It is therefore to speculate that the increase in the melting temperature associated with the low endotherm for isothermal crystallization at high temperature ( $T_x > 112$  °C) of ESI-1.9 is due to an increase in perfection or size of these low melting crystals. In the case of linear PE homopolymer,<sup>1</sup> a similar increase in the melting temperature of primary crystals with crystallization time was shown to be consistent with an increase in crystal size.

At lower temperature, primary crystals develop very quickly at the initial stage of the isothermal crystallization process. Hence, the subsequent formation of low melting crystals must take place between the existing primary lamellae. Constraints exerted on amorphous chains by primary crystals will be enhanced with a further increase in crystallinity, leading to an increase in the low endotherm melting temperature. Therefore the development of secondary crystals occurs in very different environments at low and high crystallization temperatures. The situation in random ethylene copolymers is somewhat different from that characteristic of homopolymers such as PEEK, PET or BAPC which have also been studied in our laboratory.<sup>35, 42, 43</sup> In these polymer systems, a crossover temperature is found below which multiple melting behavior is observed which was believed to result from the formation of secondary crystals between primary crystals. Above this crossover temperature, a single melting peak is observed which shifts to higher temperatures with time, a behavior associated with lamellar thickening. In contrast with PEEK, PET, BAPC and other homopolymers, multiple melting behavior is observed over the whole temperature range for random ethylene copolymers. However, the intrinsic mechanisms are still believed to be the same as for homopolymers. A crossover temperature can also be found for ethylene copolymers. In the low temperature region, the formation of secondary crystals is at the origin of the low endotherm and an increase in amorphous constraints explains the temporal evolution of this endotherm. For crystallization at high temperatures, the shift of the low endotherm melting temperature is associated with thickening and reorganization effects that are similar to these observed in homopolymers. Reorganization effects can be particularly important for the lowest styrene content copolymers.

## 5.4.3 Superheating Behavior of Low Melting Crystals as a Function of Temperature

When polymer crystals melt, the melting temperature may exceed the equilibrium or zero entropy production melting temperature  $(T_m^{0})$ . This phenomenon is called superheating. Two types of mechanisms for the superheating of polymer crystal have been proposed.<sup>62</sup> The first one is believed to relate to the size of crystals. Since the melting cannot start inside the crystalline region due to the constraint exerted by the surrounding segments, the melting of crystals has to be initiated on the crystal surface. Therefore one should expect that large crystals would lead to a slow kinetics of melting. crystals,<sup>63-71</sup> been found in chain Such superheating has extended polvtetrafluoroethylene <sup>72</sup> and trigonal selenium. <sup>73</sup> Another possible origin for superheating comes from the constraints in the amorphous phase, which tends to reduce the entropy of fusion upon melting therefore increases the melting temperature.<sup>62, 70, 74</sup> Tie chains and entangled loops in the crystal/liquid interphase are responsible for this mechanism. This mechanism is supported by experiments on polyethylene extended chain crystals where acid etching which can break tie chains between crystals, is able to significantly reduce the extent of their superheating.<sup>69</sup> It was also found <sup>75</sup> that superheating increases for melt-crystallized polyethylene when the molar mass is increased. This observation is thought to relate to the larger concentration of entanglements exerting some constraints on the crystallites. Such a mechanism was also invoked to explain the superheating of secondary crystals which are associated with the low endotherm.<sup>42</sup> Since secondary crystals are expected to grow in the constrained environment induced by high melting primary crystals, their melting behavior must be affected by the level of constraints.

The degree of superheating can be characterized using the heating rate dependence of melting temperature after calibration of instrumental thermal lag effects.<sup>76,77</sup> It was pointed out<sup>62, 76</sup> that a calibrated melting temperature should vary linearly with the square root of the heating rate,  $\beta^{1/2}$ , if the melting rate is proportional to the degree of superheating ( $T_m^0 - T_m$ ), implying that melting does not require nucleation. Recently, Toda et al.<sup>76</sup> systematically investigated the superheating behavior of several polymer systems using conventional DSC and TMDSC. A linear relationship between  $T_m$ 

and  $\beta^{1/2}$  was found for low-density polyethylene and linear polyethylene.<sup>76</sup> On the other hand, non-linear behavior was observed in other polymers such as isotactic polypropylene, poly(ethylene terephthalate) and poly( $\varepsilon$ -caprolactone),<sup>76</sup> surprisingly suggesting the existence of a nucleation-controlled mechanism of melting with these polymers. Toda et al.<sup>76</sup> proposed that the nucleation-controlled melting process results from the heterogeity of stability for the fold surface. However, further experiments are still needed to clarify this issue and explain the different behaviors of polyethylene and poly( $\varepsilon$ -caprolactone).

Here, to study the superheating behavior of low melting crystals we selected ESI-3.4 in view of its distinct multiple melting behavior and weak MRR effect at high crystallization temperatures. Figure 5.6.c shows the low endotherm temperature after thermal lag calibration as function of the square root of heating rate. While a linear behavior is observed in the low temperature region (<100 °C), a non-linear behavior is observed at high temperatures ( $\geq 100$  °C). It is also noted that the slope,  $C(T_x)$ , of the plot  $T_{\rm m}$  vs  $\beta^{1/2}$ , which stands for the degree of superheating, decreases with increasing temperature when  $T_x < 100$  °C as shown in Figure 5.6.d. These observations suggest that low melting crystallites formed in different temperature ranges exhibit different melting kinetics. The low temperature behavior implies a non-nucleation-controlled melting kinetics. Note that  $B(T_x)$  for the low endotherm exhibits the same trend as  $C(T_x)$  as shown by Figure 5.2. It has been suggested that  $B(T_x)$  characterizes the degree of constraint in the amorphous phase.<sup>14, 35, 43</sup> Thus, we speculate that superheating at low temperature may result from the constraints accumulated in the amorphous fraction. When crystallization takes place at higher temperature, the constraints exerted in the amorphous fraction are lower as a result of a lower crystallinity. Hence, in these conditions, a low degree of superheating is expected. The increase in the degree of superheating with decreasing crystallization temperature can also be understood in terms of the morphology of secondary crystallites. One expects secondary crystals to become more fringed-micelle like with decreasing crystallization temperature. An increasing fringe-micelle character can be described by a lower frequency of chain-folding and a stronger coupling between the secondary crystal and the amorphous fraction. Hence, the evolution of the superheating behavior with temperature in the low temperature region is consistent with that of the morphology of secondary crystallites.

If Toda's conclusions are correct, non-linearity in the  $T_{\rm m}$  vs  $\beta^{1/2}$  plot suggests the existence of a nucleation barrier for the melting process at high temperatures ( $\geq 100$  °C). Due to the non-linear behavior, it is hard to characterize the degree of superheating using  $C(T_{\rm x})$ . We speculate that the superheating of low melting crystals formed at high temperature is not due to the effect of topological constraints, especially in the initial stage when the crystallinity is very small. We have shown that in the partial melting experiments, the evolution of low melting temperature is not a critical factor to determine the low melting temperature at high crystallization temperature. As discussed above, the low melting crystals formed at high temperature may still contain partially chain-folded structure although the folding may not be as regular as in the case of high melting crystals.

With this morphological picture in mind, we suggest that the non-nucleation controlled melting kinetics results from the large concentration of styrene defects and possibly trapped entanglements on the surface of secondary crystals. Therefore a high concentration of melt "nuclei" is already present on the crystal surfaces. Furthermore, it is well known that the enrichment of non-crystallizable co-units on the basal planes of secondary crystals exerts steric stresses on the crystalline region, leading to an expansion of the crystal lattice structure thus an easier melting. This effect becomes even more important when the crystal thickness is small (i.e. at low crystallization temperature). The combination of the above factors is likely to be responsible for reducing considerably the activation energy associated with the melt nucleation barrier for fringed-micelle crystals.

In summary, the differences in the superheating behavior of low melting crystals formed at low and high temperatures are consistent with the differences in their crystallization kinetics and morphology. Constraints in the amorphous fraction are suggested to be at the origin or both the superheating ( $C(T_x)$ ) and the temporal evolution of the melting temperature ( $B(T_x)$ ) for low melting secondary crystals formed at low crystallization temperature (<100 °C). On the other hand, the melting of secondary crystals formed at high temperature (>100 °C) was shown to be less influenced by topological constraints and is suggested to be a nucleation-controlled process.

## 5.4.4 Mechanism for the Generation of Excess Heat Capacity Revealed by Quasi-Isothermal Experiments

As shown in the Results section (Figures 5.11 – 5.13), the evolution of the excess heat capacity and of the  $C_p^{\text{excess}}(t_x) / \Delta H(t_x)$  ratio shows a different behavior for ESI-3.4 and ESI-8.9 at high crystallization temperature. In ESI-3.4, the excess heat capacity steadily increases at all times and a crossover in the evolution of the  $C_p^{\text{excess}}(t_x) / \Delta H(t_x)$ ratio is observed when the high melting endotherm no longer changes. The change in the  $C_p^{\text{excess}}(t_x) / \Delta H(t_x)$  ratio is very limited before the crossover time. After the crossover time, a dramatic decrease is observed. In ESI-8.9, the excess heat capacity increases during the initial stage of crystallization and remains constant after the crossover time, which in this case is defined as the time when the high melting shoulder no longer increases. Both crossover times are associated with the end of the primary crystallization stage (formation of the high melting crystals). However, one crossover time is also observed in the evolution of  $C_p^{\text{excess}}(t_x) / \Delta H(t_x)$  (ESI-3.4) while the other is observed in the evolution of excess heat capacity (ESI-8.9). This difference in behavior may give us some hint for understanding the role of low and high melting crystallizes for the generation of excess heat capacity and thus for the mechanism responsible.

As concluded in the previous work<sup>1</sup>, the generation of excess heat capacity in linear polyethylene (PE-119K) and low styrene content ethylene copolymer (ESI-0.35) is related to the reversible exchange of segments at the melt-crystal fold interface. This segmental exchange is associated with the balance between an elastic force (rubber elasticity) in the amorphous phase and the crystallization force. As indicated in the above discussion, the high melting crystals of ESI-1.9 and ESI-3.4 formed at high temperature are chain-folding lamellae. Therefore one can easily speculate that the fold surface model discussed in the previous chapter for LPE-119K and ESI-0.35 is still applicable here for of ESI-1.9 and ESI-3.4 samples crystallized at high temperatures. In the case of ESI-3.4, the crossover in the evolution of  $C_p^{\text{excess}}(t_x) / \Delta H(t_x)$  is suggestive of a different

reversibility for the low and high melting crystals. As the low melting crystals are more fringed-micelle like, they have a lesser chain-folded character. Hence, they provide fewer sites on the fold surface for reversible segment exchanges. Consequently, the formation of low melting crystals contributes less to the excess heat capacity than the formation of high melting crystals. We speculate that the difference between ESI-3.4 and ESI-8.9 results from the fact that low melting crystals in ESI-3.4 have a larger fraction of chain-folded stems which contribute to reversible crystallization and melting on the fold surface. In contrast, chain-folded structures are almost absent in low melting crystals of ESI-8.9. Hence, they contribute very little to the excess heat capacity.

Figure 5.16 shows some possible molecular mechanisms for the reversible segment exchange on the fold surface. Among them, Figure 5.16.a should apply for the cases of a linear homopolymer and a very low comonomer content copolymer, where regular chain-folded lamellae are expected. Figure 5.16.b was given by Hu et al.<sup>78</sup> while Figure 5.16.c is more applicable to the case of an ethylene based copolymer. One should note that in the cases of PE-119K and ESI-0.35, the excess heat capacity generated at high crystallization temperature after long time is still much larger than zero although some decay can be observed. This indicates that some source of reversible crystallization and melting can never be completely eliminated through long-range cooperative motion in the crystalline region. Mechanisms "b" and "c" give an explanation for this situation. For copolymers with high comonomer content, mechanism "a" would be totally absent since adjacent reentry folding is non-existent in this case. On the other hand, mechanisms such as "b" and "c" could continuously contribute to the excess heat capacity. Therefore it is speculated that in both cases of ESI-3.4 and ESI-8.9, the excess heat capacity generated at high temperature is mostly contributed by mechanisms "b" and "c" but not mechanism "a" which tends to eliminate some of the available sites for reversible segmental exchange on the fold surface thus leading to a decay of excess heat capacity.



**Figure 5.16** Examples (a, b, and c) of possible reversible segmental exchange on the fold surface. See the text for a description.

In the following, we turn our attention to the applicability of the lateral surface model at high crystallization temperature. In the preceding chapter,<sup>1</sup> we showed that the lateral surface model is not applicable to linear PE and low comonomer content copolymers. In the case of higher comonomer content materials, the formation of small secondary crystals is associated with the generation of a very large specific lateral surface area. Hence, secondary crystallization leads to the generation of a large number of sites where chain segments could be reversibly deposited and removed during temperature modulation. Hence, secondary crystal formation should be accompanied by the generation of a significant amount of excess heat capacity under quasi-isothermal conditions. However, as is shown in Figures 5.8.a-b for ESI-3.4 and ESI-8.9 at high crystallization temperature, the excess heat capacity does not increase significantly and may even appear to reach a plateau value while the low melting endotherm keeps increasing dramatically. One may argue that the formation of small crystals generates constraints in the amorphous phase thus limits the attachment/detachment of segments on the lateral surface. As a consequence, the excess heat capacity adopts a value which results from a compromise between the increase in lateral surface area and the enhancement of constraints. At this point, we cannot deny that the development of constraints in the amorphous fraction affects the evolution of the excess heat capacity. Both a decrease in the rate of formation of high melting crystals and an increase in constraints in the amorphous fraction contribute to the slower increase in excess heat capacity after the crossover time, especially in the case of ESI-3.4. However, consideration of the region of constant excess heat capacity subsequent to the crossover time (Figure 5.10.a), suggests that high melting crystals formed at high temperature rather than low melting ones play the major role in the evolution of the excess heat capacity.

Here, we propose that reversible crystallization and melting on the lateral surface of lamellar crystals as initially described by Wunderlich et al.<sup>79</sup> will preferentially take place at low temperatures where the entropy barrier to deposition will be lower. As the temperature decreases, sliding diffusion of chain segments within crystalline regions becomes extremely difficult. Hence, this mechanism is not viable for reversible melting and crystallization. At low temperature, the reversible attachment and detachment process

is more likely to take place on the lateral surface of high stability crystals with large thickness. There are at least two reasons for this statement. First, the absence of chainfolded structures in fringed-micellar crystals makes their basal face sterically crowded. Crowding induces stresses in the crystal which inhibit further deposition of segments on their lateral surfaces after they reach a certain dimension. The bulky comonomer units (styrene) accumulated on the basal crystal face induce further steric repulsions. Second, at low temperature, the excess heat capacity always decreases with time. If one were to assume that the reversible crystallization and melting processes occur on the lateral surface of fringed-micellar crystals, one could not explain why the excess heat capacity does not increase during secondary crystallization (Figures 5.8 and 5.10.a). Here, we speculate that the decrease in excess heat capacity results from the consumption of crystallizable sequence that can undertake the reversible attachment and detachment on the lateral surface of high melting crystallites. The constraints developed in the amorphous fraction as a result of the formation of secondary crystals will decrease the mobility of segments, thus, restrict the reversible process. However, we do not consider this to be the major reason. On the contrary, the constraints should decrease the conformational entropy of segments in the amorphous region thus facilitate their deposition on the lateral surface of crystals. In other words, the presence of constraints may decrease the free energy barrier for deposition. As a consequence, crystals form and melt over a narrower temperature range. Evidence can be obtained from the study by Androsch et al.,<sup>80</sup> which shows that chain deformation is capable of increasing the reversibility. It is a natural result if one considers that the deformation leads to some orientation of segments in the amorphous phase thus to a decrease in the conformational entropy of the amorphous fraction.

The above discussion suggests that the mechanism responsible for both the generation of excess heat capacity and secondary crystallization exhibits significant temperature dependence. Evidence can also be found from the quasi-isothermal melting experiments shown in Figures 5.12 to 5.14 in which a systematic evolution of the degree of reversibility with temperature and comonomer content can be observed.

Alizadeh et al.<sup>14</sup> and Xu<sup>17</sup> have estimated the Avrami exponent for the low endotherm for a series ethylene/1-octene and ethylene/styrene copolymers, respectively.

A crossover temperature was observed in plots of the Avrami exponent as a function of crystallization temperature, indicating a change in secondary crystallization mechanism. Below the crossover temperature, an Avrami exponent of 0.5 was obtained, which was explained in terms of a diffusion-controlled one-dimensional growth mechanism for the formation of fringed-micellar crystals.<sup>14</sup> Above the crossover temperature, the Avrami exponent increased with temperature, suggesting the formation of chain-folded lamellar crystals.<sup>14</sup> It is noted that the crossover temperatures shown in Figure 5.14 for the temperature dependence of the degree of reversibility are very close to those reported for the Avrami exponent. This observation suggests that the change in mechanism for the secondary crystallization corresponds to the change in mechanism for reversible crystallization and melting. Therefore, the nature of the secondary crystallization process and the ability of segments to undergo reversible crystallization and melting are correlated.

On Figure 5.11, we show the temperature and comonomer content dependences of the relaxation time (KWW analysis) associated with the decay in excess heat capacity. The apparent activation energy deduced from the Arrhenius plot for ESI-3.4 is only 36 kJ/mol. This value is much smaller than these reported for linear polyethylene and low styrene content samples, suggesting a different mechanism for the decay in excess heat capacity. In addition, a much larger  $E_a$  value is obtained for ESI-8.9 as shown in Figure 5.11. At this point, it is difficult to give a plausible interpretation for these apparent activation energies. As mentioned in the preceding chapter, the KWW analysis can only be reliably used when the relaxation process takes place by a single mechanism. Therefore, application of the KWW analysis in the present study only has phenomenological meaning, especially if multiple mechanisms are simultaneously responsible for the excess heat capacity decay. The activation energy obtained in the preceding chapter for linear polyethylene and for a low styrene content copolymer was very close to these obtained by other techniques for the characterization of slidingdiffusion in the crystalline phase.<sup>1</sup> Therefore, application of the KWW analysis to the study for high styrene content copolymers might provide some information on the mechanism for their reversible crystallization and melting. Figure 5.11 shows that the characteristic relaxation time for ESI-3.4 is smaller than these measured in the same

temperature range for linear polyethylene and low styrene content copolymers and is not very sensitive to the temperature, as reflected in the low activation energy. Since only low melting crystals can develop in the temperature range where the excess heat capacity decay can be studied for high comonomer content copolymers, the excess heat capacity decay must be related to the formation of these small secondary crystals. Decreasing the temperature lowers the critical crystallizable sequence length thus increases the number of ethylene sequences that can crystallize. However, decreasing temperature also leads to a decrease in chain mobility in the amorphous region. We speculate that both factors compete with each other leading to a relatively weak dependence of the characteristic time ( $\tau$ ) on the crystallization temperature in the case of ESI-3.4. For the case of ESI-8.9, we noted that the apparent activation energy increases with decreasing temperature (slope on the Arrhenius plot is changing), implying a much stronger temperature dependence of  $\tau$  at low temperatures. This may be due to the dramatic decrease in chain mobility as crystallization is carried out close to the glass transition temperature  $T_g$ .

#### 5.5 Conclusions

The crystallization and melting behavior of a series of random ethylene/styrene copolymers were studied using a combination of classical and temperature modulated differential scanning calorimetry. The multiple melting behavior at high temperature is investigated through studies of the overall crystallization kinetics, heating rate effects and partial melting. Low melting crystals can be classified into two categories according to their melting behavior, superheating and reorganization characteristics. Low styrene content copolymers still exhibit some chain folded lamellar structure. The shift of the low melting temperature with time in this case is tentatively explained in terms of reorganization effects. Decreasing the crystallization temperature or increasing the styrene content leads to low melting crystals more akin to fringed-micelles. These crystals exhibit a lower tendency to reorganize during heating. The shift of their melting temperature with time is attributed to a decrease in the conformational entropy of the amorphous fraction as result of constraints imposed by primary and secondary crystals.

To further understand the mechanism of formation of low melting crystals, quasiisothermal crystallization experiments were carried out using temperature modulation. The evolution of the excess heat capacity was correlated with that of the melting behavior. On the basis of these results, it is speculated that the generation of excess heat capacity at high temperature results from reversible segmental exchange on the fold surface. On the other hand, the temporal evolution of the excess heat capacity at low temperature for high styrene content copolymers is attributed to the reversible segment attachment and detachment on the lateral surface of primary crystals. The existence of different mechanism for the generation of excess heat capacity in different temperature ranges is consistent with the observation of two temperature regimes for the degree of reversibility inferred from quasi-isothermal melting experiments.

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