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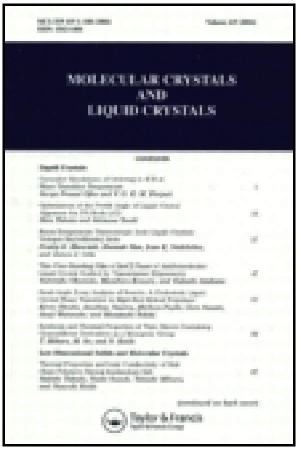

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Melting Behavior of Poly(Tetramethylene Succinate) as Studied by Time-Resolved Small Angle X-Ray Scattering

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Melting Behavior of Poly(Tetramethylene Succinate) as Studied by Time-Resolved Small Angle X-Ray Scattering

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To elucidate the morphological origin of the multiple melting endothermic peaks found in DSC scans of poly(tetramethylene succinate), a time-resolved small angle X-ray scattering study utilizing a synchrotron radiation source was conducted. The results suggested that low-temperature endothermic peak can be attributed to the melting of secondary lamellae inserted between the primary lamella stacks, while the middle and high-temperature endothermic peaks were to the melting of primary lamellae. The middle one, however, was associated only with the original ones but the high endothermic peak was with both the original ones and lamellae reorganized through the recrystallization process. A new small angle peak was observed in addition to the original peak during the late stage of melting process. The origin of the new peak was interpreted as a transient phenomenon resulted from the partial melting of primary lamellae prior to the complete melting.

Keywords: poly(tetramethylene succinate); multiple melting endotherms; real-time small angle X-ray scattering

INRODUCTION

Multiple melting endotherms during differential scanning calorimeter (DSC) heating scans have been observed in several semi-crystalline polymers.[1~10] In poly(ethylene terephthalate) (PET) or poly(aryl ether ether ketone) (PEEK), for example, two melting endothermic peaks are observed; a low-temperature endothermic peak a few degrees above the prior crystallization temperature and a high-temperature endothermic peak. Extensive studies have been conducted to elucidate the origin of the multiple melting endotherms. Among several models

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proposed, dual or more lamellar thickness model[7,8,11] (including lamellar insertion model) and melting-recrystallizaion[5,6,9,12] are the two main models applied to account for the multiple melting endotherms. However, evidences to support the different models are somewhat contradictory and the origin of this phenomenon still remains to be the subject of debate.

In the course of studying the melting behaviors of poly(tetramethylene succinate) (PTMS) in our laboratory, we also observed the multiple melting endotherms during the DSC heating scan of some particular samples. To investigate the origin of the multiple endotherms, we conducted the time-resolved small angle X-ray scattering studies on PTMS samples under the conditions identical to those for DSC measurements. In this report we present new observations in real-time SAXS intensities of PTMS upon melting, which support both the lamellar insertion and the melt-recrystallization process.

EXPERIMENTS

Commercially available PTMS (from Saehan Corporation) was used for the experiments. The DSC was a Perkin Elmer DSC 7 and the scanning rate was 5 °C/min.

Time-resolved SAXS experiments utilizing the synchrotron radiation source were carried out at the Pohang Accelerator Laboratory (PAL). For the accurate temperature control a temperature jumping device, consisting of dual thermal blocks and a pneumatic piston, was utilized. The sample was initially kept at 150 °C for 5 min in the first thermal block, then was quickly moved to the second block at the crystallization temperature by using a pneumatic piston. SAXS intensities were collected simultaneously while the specimen crystallizes isothermally at the crystallization temperatures. After the crystallization was completed, PTMS was cooled down to the room temperature. The fully crystallized specimen was then reheated above the melting temperature at a rate of 5 °C/min. SAXS intensities were also collected during melting process. All experimental conditions including the crystallization temperature and the heating

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rate were identical to those used in the DSC measurements. Each SAXS profile was collected for 5 sec using a one-dimensional position sensitive diode array.

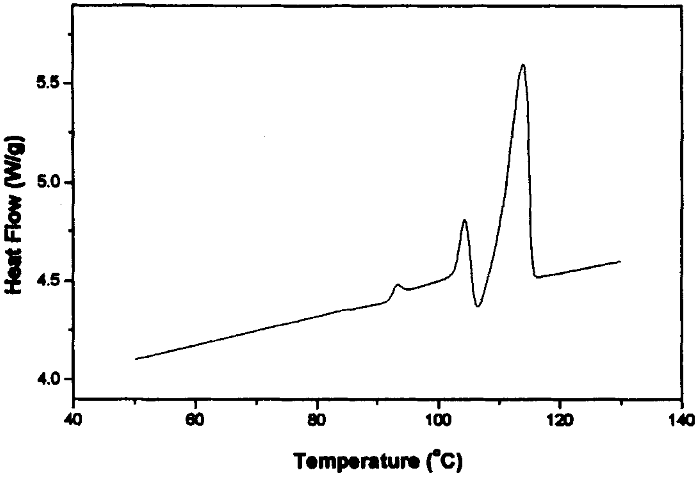

FIGURE 1. DSC heating thermogram of PTMS crystallized at 90 °C. Scan rate was 5 °C/min.

RESULTS AND DISCUSSION

A DSC heating thermogram of PTMS sample, isothermally crystallized at 90 °C, is shown in Figure 1. Three distinct melting endotherms, one small shoulder peak near 93 °C and two relatively strong melting peaks at 104 and 113 °C, can be noted. In our previous extensive study on thermal behaviors of PTMS[13], it was shown that the low endotherm is associated with the melting of secondary lamellar units of relatively thin lamellar thickness. Two strong middle and high endotherms, on the other hand, can be attributed to the melting of primary lamellar units of larger thickness. The question still remains whether the secondary lamellae are the inserted ones or the ones forming separate stacks, and whether the two middle and high endotherms are associated with the dual lamellar thickness or the melting-recrystallization process.

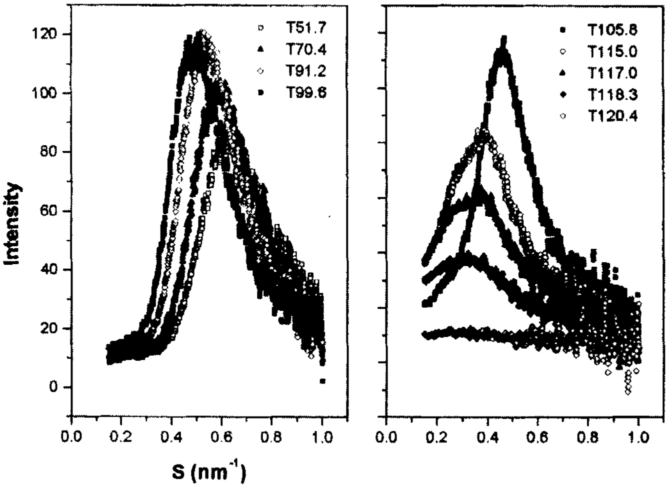

FIGURE 2. Lorentz-corrected small angle X-ray scattered intensities at different temperatures measured upon heating PTMS which was crystallized at 90 °C.

Selected Lorentz-corrected plots of SAXS profiles measured during the heating of the isothermally crystallized specimen at 90 °C are shown in Figure 2. Upon heating marked changes in SAXS intensities and peak position are noted. In Figure 3, the long-period changes and invariant (Q) derived from the raw scattering curves in Figure 2 are also plotted. The feature found in long-period change is clearly demonstrating a multi-stage melting process. When the temperature reaches the crystallization temperature (90 °C) (this temperature coincides with the onset temperature of first melting endotherm), a break in the increment of long-period is noted. Upon heating the sample further above 90 °C, a higher increasing rate in the long-period can be seen, indicating a melting of

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different structural units. Again when the temperature reaches near the onset point (100 °C) of middle endotherm, we also note another break in long-period increment. A remarkable observation in this temperature range, however, is that a new small angle peak at S ~ 0.25 nm^{-1} evolves. The two scattering peaks coexist and disappear at the same time as the crystals melt on further increase of temperature.

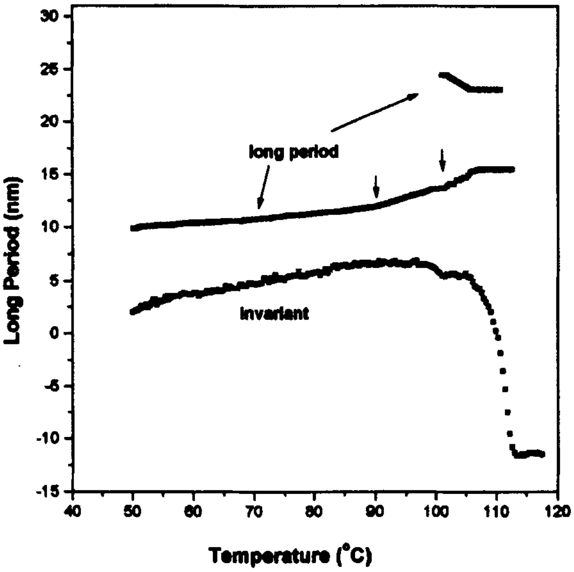

FIGURE 3. Long-period and invariant (Q) changes derived from the small angle X-ray scattered intensities.

Based on the long-period changes observed in this particular PTMS crystallized at 90 °C, we may be able to divide the melting process into three sub-stages. First, below the crystallization temperature (90 °C), we note monotonic increase of the SAXS peak intensity (Q) and the long-period. This effect is, in fact, thermally reversible on heating and cooling as long as the

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temperature is kept below the crystallization temperature. Similar reversible thermal behaviors in SAXS intensities of melt crystallized semi-crystalline polymers and single crystal mats have been reported previously.[14,15] According to Shultz[16], the small angle intensity from ideally stacked lamellae can be approximated as

$$I(S) \approx \left(\frac{N}{\pi}\right)^2 \left(\frac{d}{p}\right)^2 (\Delta\rho)^2 \sin^2\left(\pi p \frac{l}{d}\right) \qquad (1)$$

Here, N represents the number of lamella units in the stack, p the peak order, d the long-spacing, l the lamellar thickness, and $\Delta\rho$ is the density difference between crystalline and amorphous layer. The equation suggests that the SAXS intensity enhancement upon heating can be attributed to the increase of crystalline-amorphous density difference ($\Delta\rho$) or decrease in $\frac{l}{d}$. The effect of $\Delta\rho$, however, found to be minimal. The increment in SAXS intensity was, then, interpreted as being mainly due to the entropy driven thickening of intervening amorphous layer at the expense of lamellar thickness.[14] However, in our observation, the increment in long-period is nearly 20% within this temperature range, which strongly suggests the melting of intervening lamellae in addition to the lamellar thinning. The intervening lamellar units are probably formed while lowering temperature after the isothermal crystallization. When the temperature is raised above the crystallization temperature (90 °C), the long-period increase accelerates and the Q reaches a plateau. Recalling the DSC results shown in Figure 1, the melting at this stage is associated with the low endotherm and therefore the melting of secondary lamellae formed during the isothermal crystallization. Again the amount of increase in the long-period also suggests the melting of lamellar inserted between the primary lamellae stacks. The most unusual observation, however, is that a new peak at S ~ 0.25 nm^{-1} evolves during the next melting stage, where the middle endotherm is located. The new peak appearance at the onset temperature of middle endotherm indicates that the peak is associated with the melting of the primary lamellae. The results also

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imply that two distinct lamellar stacks of different long-period coexist until the crystals are completely melted. To account for the origin of the new peak observed in the small angle X-ray scattering, it is possible to apply and compare two models previously mentioned. The dual lamellar thickness model, particularly the lamellar insertion model[11] and the melting-recrystallization model.[5,6,12] For the lamellar insertion model, where thin lamellar units are inserted within the stacks of thicker lamellae, the long-period of 15 nm (S = 0.4 nm^{-1}) should correspond to the average long-spacing of the two alternating units. Melting of lamellae inserted within the thick lamellae would have left the stacks of thick or more stable lamellae, causing the long-period to increase and appearance of the new peak at S = 0.25 nm^{-1} (d = 25 nm). The above discussion based on the lamellar insertion model, however, may not be sufficient to explain our observation. The two small angle peaks still remain in the temperature range of the high endotherm, indicating both lamellar stacks having two different long-periods are equally responsible to the high endothermic melting peak. There is also a clear evidence of substantial recrystallization at this melting stage, as indicated by the shoulder in the curve of invariant (Q) (Figure 3). In the present case we may be able to adopt both the lamellar insertion and the melting-recrystallization model to account for the two middle and high melting endotherms observed in DSC scan as well as the appearance of new peak in small angle X-ray scattered intensities. The new scattering peak appeared during the melting process then can be said to originate from the melting of lamellar inserted, resulting in a new long-period. This state, however, is only a transient stage during the melting process of primary lamellae. At the same time, substantial amount of recrystallization takes place, as evidenced by the invariant plot in Figure 3. This recrystallization process, however, is not to form a completely new lamellar stack, rather involves in reorganizing the existing lamellae to become more perfect, stable, and thicker lamellae. The high endotherm is associated with both the melting of these reorganized and the original primary lamellae.

In summary, using a time-resolved SAXS, we were able to elucidate the morphological origin of the three melting endothermic peaks found in PTMS crystallized at 90 °C. The low endothermic peak was interpreted as a melting of secondary lamellae that are inserted between the primary lamellae stacks. The middle endothermic peak was associated with the melting of primary lamellae. But the high endothermic peak was originated from both the melting of original lamellae and reorganized lamellae formed by the recrystallization process. A new small angle peak was appeared during the late stage of melting process. The new peak appearance, however, was not associated with the recrystallization process but with a transient melting state where some of the primary lamellae are melting prior to the complete melting of whole lamellae units. Crystallization mechanisms and detailed melting processes of PTMS with various crystallization conditions are under further investigation.

Acknowledgments
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