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Multiple Melting Endotherms of Syndiotactic Polystyrene in β Crystalline Form

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Abstract: A series of syndiotactic polystyrene (SPS) samples in β crystalline form were prepared by cooling from the melt at various cooling rates. The effects of cooling rate from the melt, and DSC heating rate on the multiple melting behaviors of β crystals were investigated by differential scanning calorimetry (DSC) and modulated differential scanning calorimetry (MDSC), from which the nature of the multiple melting behavior was ascribed to the occurring of a recrystallization process.

Keywords: Multiple melting behavior, syndiotactic polystyrene, recrystallization.

Multiple melting behaviors have been studied extensively. Syndiotactic polystyrene (SPS), in β crystalline form exhibited such phenomena. It was suggested that a recrystallization process occurred since it has been clarified that no other modifications were observed during the DSC heating scan[1]. In this study, a series of SPS samples in β form were prepared by cooling from the melt at various cooling rates[1] and the factors that influence the multiple melting behavior of SPS in β form were examined. We also used modulated DSC (MDSC) measurement to give a direct proof of this recrystallization process.

According to the method used in Ref. 1, the SPS powder samples (M_w=3.65×10^5) were cooled from the melt (310°C) at various cooling rates, thus the β form crystals were obtained. A TA 2910 Modulated DSC differential scanning calorimeter was used for both DSC and MDSC analysis. The heating rate (if not otherwise specified) is 10°C/min.

Figure 1 shows the cooling curves of samples from the melt. It was found that the crystalline temperature decreases on increasing cooling rate, thus a less perfect crystal is formed[2-3]. Therefore, during the following DSC heating process (see **Figure 2**), the low melting temperature (T_{m1}) corresponding to the already formed crystal declines on increasing its cooling rate when prepared; moreover, the high peak temperature (T_{m2}) almost remains constant. Combined with the fact that only a single exothermic peak was observed during the melt-crystallization process, we suggest that during the DSC heating scan, a melt, recrystallization and remelt process occurred. Therefore, the lower the T_{m1}, the lower the onset of recrystallization, then the faster the recrystallization rate; moreover, the recrystallization period is longer, hence the intensity of high endotherm (I_h) increases. Similar result was also observed in **Figure 3**. On decreasing the DSC heating rate, the T_{m1} decreases, thus the recrystallization rate increases, while the recrystallization time

increases too, hence the I_h relative to the intensity of low endotherm (I_L) increases.

Figure 1. DSC cooling scans of samples from the melt at the indicated cooling rates

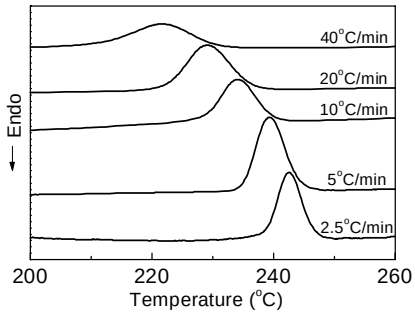
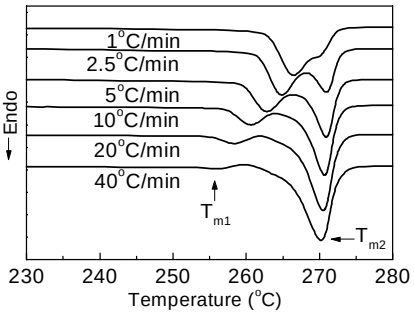


Figure 2. DSC heating scans of samples cooled from the melt at the indicated rates



A direct proof of the presence of recrystallization process during the DSC heating scan was provided by using MDSC measurement, which can effectively separate the total heat flow into a well defined non-reversing and reversing heat flow, respectively[4-5]. The non-reversing heat flow clearly shows that a recrystallization process does occur during the heating scan (see **Figure 4**), whereas the reversing curve shows the endotherms corresponded to the melting and remelting. With the discussion above, we conclude that the initial β crystals (imperfect crystals that formed during the melt-crystallization process) are melted during the DSC heating scan, with formation of more perfect crystals through recrystallization which are remelted at higher temperatures.

Figure 3. DSC heating scans of samples cooled from the melt at 5°C/min when the samples are heated at various heating rates

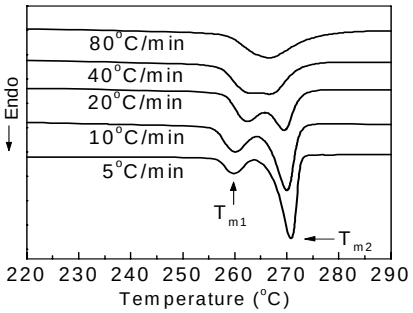
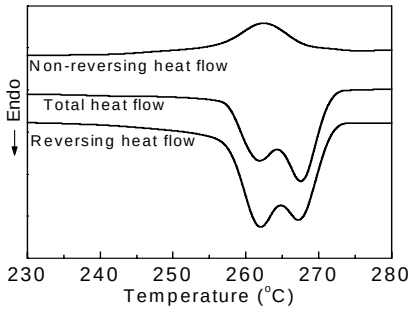


Figure 4. MDSC scans of sample that cooled at 1°C/min from the melt.



MDSC heating rate: 2.5°C/min
Oscillation amplitude: 0.4°C
Oscillation period: 60s

References

1. G. Guerra, V. M. Vitagliano, C. De Rosa, V. Petraccone, P. Corradini, *Macromolecules*, **1990**, *23*, 1539.
2. J. T. Yeh, J. Runt, *J. Polym. Sci., Polym. Phys. Ed.*, **1989**, *27*, 1543.
3. M. E. Nichols, R. E. Robertson, *J. Polym. Sci., Polym. Phys. Ed.*, **1992**, *30*, 755.
4. M. Reading, *Trends Polym. Sci.*, **1993**, *1*, 248.
5. I. Okazaki, B. Wunderlich, *J. Polym. Sci., Polym. Phys.*, **1996,** *34*, 2941.

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