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Crystal Form Transition during Heating of Solvent-induced Crystalline Syndiotactic Polystyrene

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Abstract: The phase transition of two kinds of solvent-induced crystalline syndiotactic polystyrene (sPS), γ-sPS and δ_e-sPS, has been studied *via* WAXD and DSC. γ-sPS transform to α-sPS at 195-225℃ before melt during heating, whereas δ_e-sPS transform to first γ-sPS and then α-sPS at 100-200℃ and 200-215℃, respectively. The transition of δ_e-γ and γ-α occurs far below melting point of sPS indicates they are all solid-solid transition.

Keywords: Crystal form transition, γ-sPS, δ_e-sPS, α-sPS.

Syndiotactic polystyrene (sPS), as one kind of potential engineering plastics, has enjoyed intense academic and industrial interest recently[1]. There are four different crystalline forms sPS could be formed altogether[2], among them γ and δ forms belong to solvent-induced crystal and both have chains in the S(2/1) helical conformation (δ form indicate either different clathrate structure which include molecules of solvent or emptied clathrate form-δ_e), whereas α and β forms which have chains in the trans planar conformation can be obtained under different thermal condition. The investigation on crystal form transition of solvent-induced crystalline sPS (γ and δ_e forms) is important to understand polymorphic behavior of sPS[3-5].

The phase transition during heating at 10℃/min of γ-sPS and δ_e-sPS are studied using WAXD and DSC (the sample weight of DSC are 8.690 mg and 8.203 mg). δ_e-sPS was obtained by swelling of amorphous sample in chloroform and successive removal of chloroform. γ-sPS was obtained by annealing δ-sPS at 180℃.

Successive WAXD diagrams of γ-sPS and δ_e-sPS during heating process at 10℃/min are shown in **Figure 1**. There is no crystal form transition for γ-sPS while T<195℃ as shown in **Figure 1a**. However, the reduction of characteristic peak (2θ=15.8°) of γ-sPS at 195℃ shows that γ-α transition begins at this temperature. With the increase of temperature γ-α transition continues and is complete at 210℃. There is only the perfection of α form crystal during continual heating because the diffraction pattern of 215℃ is almost the same as that of 210℃. As shown in **Figure 1b**, the diffraction diagrams of δ_e-sPS change little as T<100℃. The gradual transformation from the δ_e to the γ form accomplishes in the range 100-200℃, γ-α transition follows and completes at 215℃ while heating the δ_e-form sample

continually.

Figure 1 Successive WAXD diagrams during heating of solvent-induced crystalline sPS
a γ-sPS b δ_e-sPS

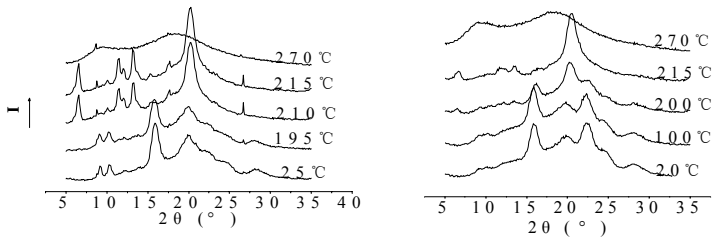
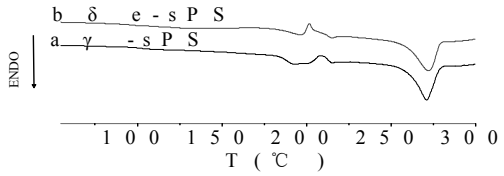


Figure 2 DSC thermograms of solvent-induced crystalline sPS at 10℃/min



DSC curves are recorded when γ and δ_e forms sPS is heated from room temperature to the molten state at the constant rate of 10℃/min, as seen in **Figure 2**. The scan of the γ form (**Figure 2a**) presents a larger endothermic peak centered at 271℃ and a smaller exothermal peak centered at 208℃. The endothermic and exothermal peak are associated with the melt down and the γ - α transition, respectively. The scan of the δ_e form (**Figure 2b**) presents besides the usual melting peak a very broad endothermic peak at 100-200℃ and a smaller exothermal peak in the range of 200-215℃, which corresponding to δ_e- γ and γ - α transition, respectively.

Acknowledgment

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References

1. N. Ishihara, *Macromol. Symp.*, **1995**, *89*, 553.
2. G. Guerra, V. M. Vitagliano, C. De Rosa, V. Petraccone, P. Corradini, *Macromolecules*, **1990**, *23*, 1539.
3. V. Vittotia, F. De Cansia, P. Iannelli, A. Immirzi, *Makromol. Chem. Rapid Commun.*, **1988**, *9*, 765.
4. C. De Rosa, G. Guerra, V.Petraccone, B. Pirozzi, *Macromolecules*, **1997**, *30*, 4147.
5. G. Guerra, C.Manfredi, P.Musto, S.Tavone, *Macromolecules*, **1998**, *31*, 1329.

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