

Relation Between Melting Behavior and Phase Transitions in Polymer Crystallization

A relation between the crystalline lamellar thickness and the melting temperature is revealed by small- and wide-angle X-ray scattering.

The equilibrium melting temperature of a crystallisable polymer, defined as the melting temperature of an infinitely thick crystal, is an important thermodynamic property for polymers, which acts as the reference temperature to define the degree of supercooling, *i.e.*, the driving force of crystallization. In general, the melting temperature is depressed with the crystallization temperature range, when an A/B random copolymer is introduced as non-crystallizable comonomer units (B) into the crystallizable homopolymer (A). There are two conditions for the distribution of the comonomer units in the crystalline structure: one is that the comonomer units are fully excluded from the crystalline structure, raising the concentration of comonomer units in the amorphous phase; the second is that the comonomer units are nondiscriminatingly incorporated into the crystalline lattice, resulting in a uniform composition in the crystalline and amorphous phases.

To clarify how the lamellar thickness affects the crystal melting in the copolymer systems, An-Chung Su (National Tsing Hua University) constructed the melting behavior for α and β crystals of syndiotactic poly(styrene-stat-3-methylstyrene) (sPS-3MS) and poly(styrene-stat-4-methylstyrene) (sPS-4MS) random copolymers with varied comonomer proportions, using simultaneous synchrotron small- and wide-angle X-ray scattering (SAXS/WAXS) heating profiles *in situ*.¹ These measurements were made at **TLS 23A1**.

Figures 1(a)–1(c) show the simultaneous SAXS/WAXS heating profiles of the cold-crystallized sPS-5%3MS specimen (for varied crystallization temperatures, T_c) at rate $2\text{ }^\circ\text{C min}^{-1}$. The lamellar peak position shifts from $q_c = 0.036$ to $0.027\text{ }\text{\AA}^{-1}$, corresponding to a long period (L_p) increased from $L_p = 17$ to 23 nm , *i.e.*, a specimen cold-crystallized at higher temperature exhibits a greater interparticle distance between nanograins. Upon heating, the lamellar peak in each profile shifts successively to smaller q positions and

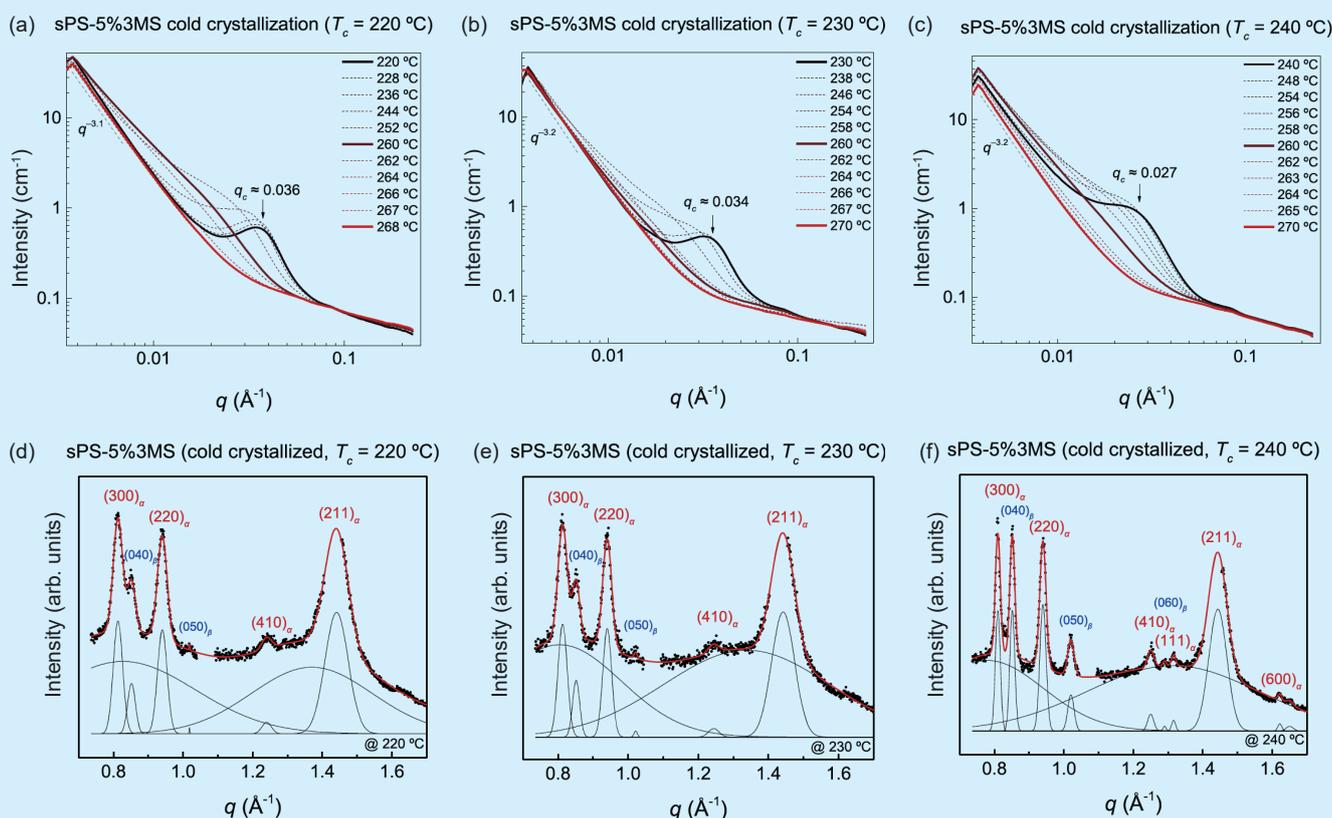


Fig. 1: (a–c) SAXS heating profiles of sPS-5%3MS cold-crystallized specimens at rate $2\text{ }^\circ\text{C min}^{-1}$. Representative deconvoluted WAXS profiles for sPS-5%3MS cold-crystallized specimens at temperatures (a) 220, (b) 230 and (c) 240 $^\circ\text{C}$. [Reproduced from Ref. 1]

becomes broader, which represents an increased L_p and a weakened nanograin spatial correlation (*i.e.*, structure factor). The SAXS profiles exhibit a power-law scattering profile $I(q) \sim q^P$ with $P = -3.2$ before reaching 270 °C, indicating that the molten state has a fractal structure with a fractal dimension ca. 3. The evolution of the normalized relative crystallinity of α and β crystals upon heating; representative deconvoluted WAXS profiles are illustrated in **Figs. 2(a)–2(c)**. As revealed by WAXS profiles, the cold-crystallized sPS-5%3MS specimens all exhibited an α -dominant structure, whereas a higher T_c results in sharper reflections, implying more perfectly ordered crystals formed at a higher T_c . Upon heating, the intensity of the reflections progressively decreases and finally exhibits amorphous halo profiles after reaching ca. 266 °C.

In this work, the SAXS and WAXS results consistently show that the polymorphic behavior of sPS-3MS and sPS-4MS depends on the crystallization condition, whereas the presence of comonomer (especially 4MS) units tends to suppress more strongly the formation of β crystals in melt

crystallization; the level of suppression enhances with increasing comonomer content. Based on the experimentally constructed melting behavior, here the corresponding T_m° of the sPS α or β crystal with varied 3MS and 4MS content was determined; the Sanchez–Eby theory² was introduced to interpret these observations from the viewpoint of thermodynamics. (Reported by Wei-Tsung Chuang)

This report features the work of An-Chung Su and his collaborators published in Macromolecules **53**, 3059 (2020).

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- SAXS, WAXS
- Materials Science, Chemistry, Condensed-matter Physics

References

1. P. H. Chen, S. J. Lin, J. C. Tsai, U. S. Jeng, A. C. Su, *Macromolecules* **53**, 3059 (2020).
2. I. C. Sanchez, R. K. Eby, *Macromolecules* **8**, 638 (1975).

