Supporting Information

Crystallization of α versus β Phases in Syndiotactic Poly(styrene-*stat*-3-methylstyrene) and Poly(styrene-*stat*-4-methylstyrene)

Po-Hsun Chen,*[,†] Yi-Kang Lan,[†] Shi-Jie Lin,[†] Jing-Cherng Tsai,[§] U-Ser Jeng,[†,‡] and An-Chung Su*[,†]

[†]Department of Chemical Engineering, National Tsing Hua University, Hsinchu 30013, Taiwan

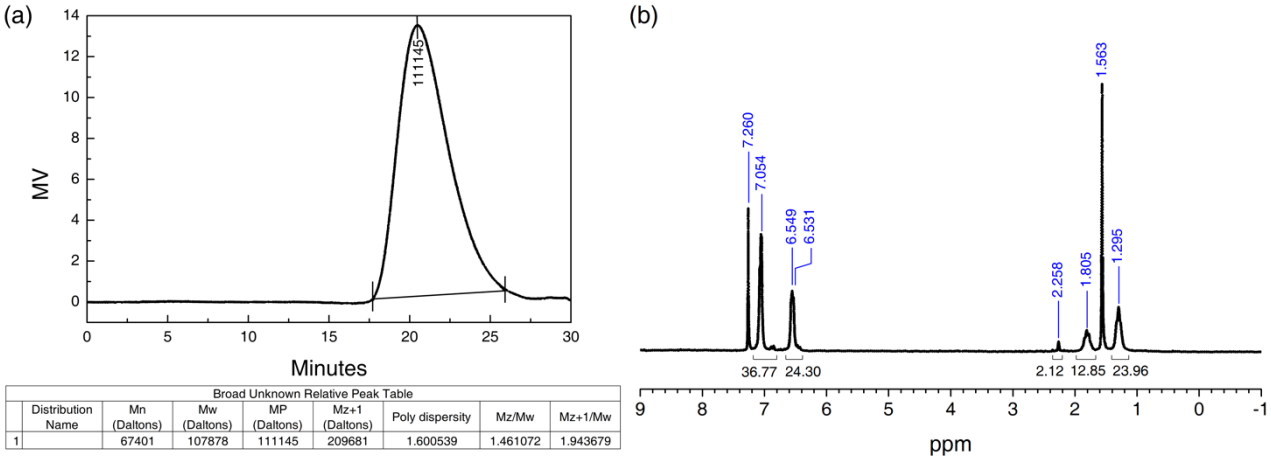
[‡]National Synchrotron Radiation Research Center, Science Park, Hsinchu, 30076, Taiwan

[§]Department of Chemical Engineering, National Chung Cheng University, Chiayi 62102, Taiwan

*E-mail: zero00023@gapp.nthu.edu.tw (Po-Hsun Chen); acsu@mx.nthu.edu.tw (An-Chung Su)

GPC and ^{1}H NMR

Illustrated in Figure S1 are the representative GPC trace and ^{1}H NMR spectrum for sPS-5%4MS specimen. The former leads to polyteyrene-equivalent values of M_w = 108 kDa and PDI = 1.6. In the NMR spectrum, the chemical shift of CH (δ1.81) represents the amount of total benzene ring and the CH_3 (δ2.26) represents the amount of hydrogen at the mehtyl group (comonomer units); thus, the comonomer contents can be calculated as 5 mol%.



Broad Unknown Relative Peak Table

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz+1 (Daltons)	Poly dispersity	Mz/Mw	Mz+1/Mw
1		67401	107878	111145	209681	1.600539	1.461072	1.943679

Figure S1. Representative (a) GPC trace and (b) ^{1}H NMR spectrum for sPS-5%4MS. The inset shows the zoom-in NMR spectrum for H resonance. [δ1.30 (CH_2), δ1.81 (CH), and δ2.26 (CH_3)]

Differential scanning calorimetry traces

Differential scanning calorimeter (DSC) measurements were carried out by using a Perkin-Elmer Diamond instrument with purging nitrogen gas (20 mL/min) at a cooling/heating rate of 10 °C/min and the instrument was calibrated with indium and zinc standard before measurement. Figure S2 shows the DSC traces of sPS-3MS and sPS-4MS series specimens cooling from amorphous molten state and subsequent reheating to 300 ºC. It can be seen that both crystallization and melting temperature shift to lower temperature range with increasing comonomer contents, showing the depression of crystallization and melting temperature (T_m and T_c); in addition, the heat of fusion (ΔH) also generally decreases, which represents the decreasing of crystallinity, except for limited cases of lower comonomer contents (i.e., sPS-5%3MS and sPS-2%4MS specimens). The increase of the ΔH implies that the tiny amount of comonomer units may improve the crystallinity.

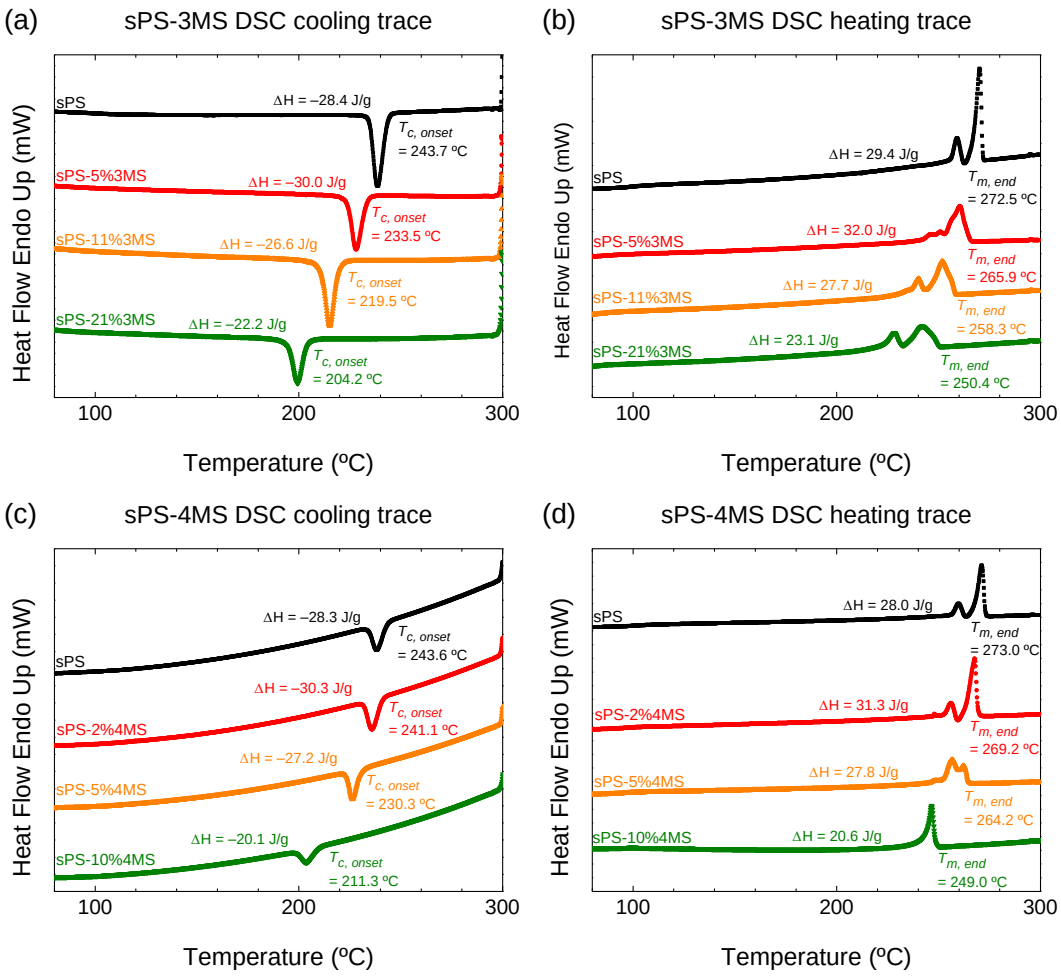


Figure S2. The DSC traces of (a)−(b) sPS-3MS series and (c)−(d) sPS-4MS series cooling from 300 to 80 ºC and subsequently reheating to 300 ºC with rate 10 ºC/min. The onset of crystallization ($T_{c, onset}$) upon cooling, the end temperature of melting ($T_{m, end}$) upon heating, and the corresponding heat of fusion (ΔH) are all indicated in the figure.

Intensities of $(020)_\beta$ vs. $(040)_\beta$ reflections

In Figures 1 and 2, the intensity of $(040)_\beta$ reflection is stronger than that of $(020)_\beta$ reflection. Here we give a tentative explanation for this peculiarity. As demonstrated in Figure S3, there are two pairs of phenyl rings (of higher electron density than the aliphatic backbones) displaying *b*/4 translation symmetry (if the low electron density backbones are neglected) whereas no such possibility exists for *b*/2 translation.

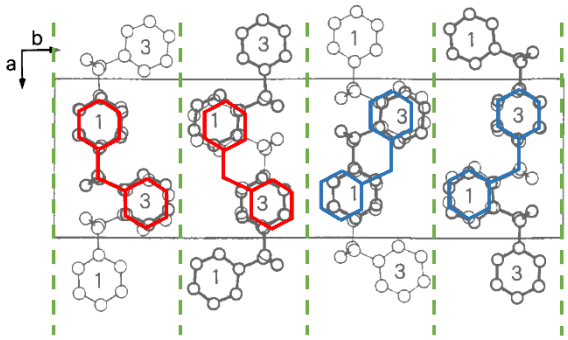


Figure S3. The unit cell structure for β′ structure as viewed along the *c*-axis.[1] Green lines indicate the position of the (040) planes and red or blue hexagons highlight two pairs of phenyl rings of *b*/4 translation symmetry if backbones of comparatively lower electron density are neglected. No such possiblity exists for *b*/2 translation. [Reprinted in part with permission from Reference 1. Copyright 1992 Elsevier.]

Crystallinity analysis

To obtain the crystallinity from the WAXS profiles in Figure 1 and 2, the PeakFit™ software was used and applied the Gauss Area to fit the whole profile. The crystallinity of α and β crystals (x_α and x_β) can be calculated based on the peak area:

$$x_\alpha = \frac{A_\alpha}{A_{total}} \quad \text{(eq. S1)}$$

$$x_\beta = \frac{A_\beta}{A_{total}} \quad \text{(eq. S2)}$$

where $A_{total} = A_\alpha + A_\beta + A_{amorphous}$ and $x_c = x_\alpha + x_\beta$; A_α, A_β, and $A_{amorphous}$ represent the total peak area of α, β reflection and amorphous halo. Figure S3 shows the representative profile after peak deconvolution, and the results of the crystallinity for WAXS profiles in Figure 1 and 2 are summarized in Table S1. Generally, decreasing the isothermal temperature (T_c) in melt-crystallization increases the crystallinity whereas, with the low comonomer content (5 and 11 mol% in 3MS series and 2 and 5 mol% in 4MS series), the crystallinity increases with higher T_c in cold-crystallization. In sPS-21%3MS and sPS-10%4MS cases, the crystallinity increases from T_c = 200 to 220 ºC but decreases from T_c = 220 to 240 ºC, which should be due to that 240 ºC is approached melting, thus, not all the polymer chain can crystallize.

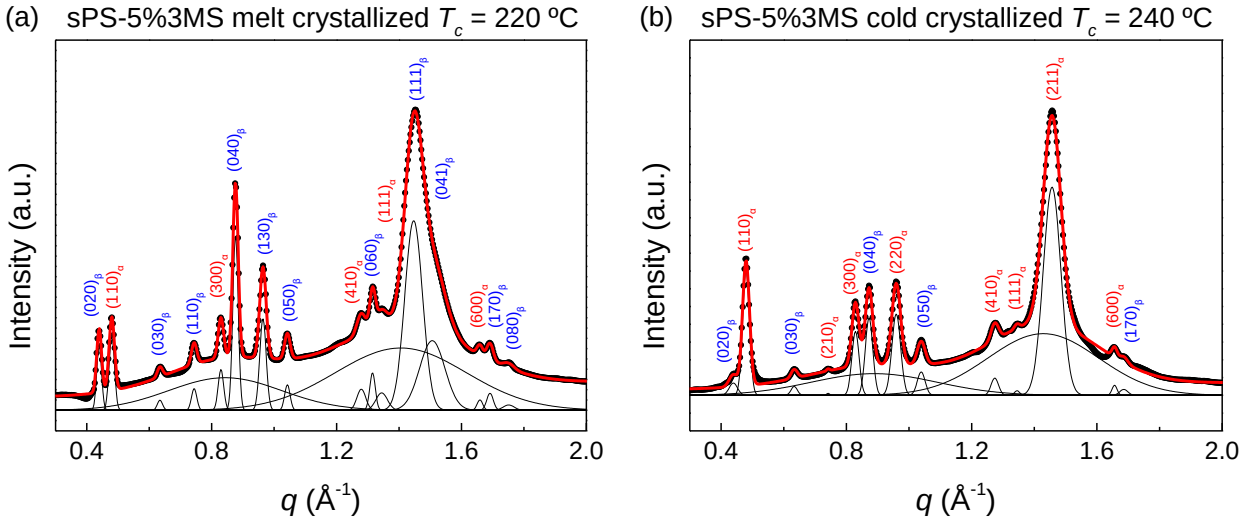


Figure S4. Deconvolution of WAXS profiles (cf. Figure 1a,d) of sPS-5%3MS specimens (a) melt-crystallized at 220 ºC, rich in β phase, and (b) cold-crystallized at 240 ºC, rich in α phase.

Table S1. The crystallinity of α (x_α), β (x_β) crystal and the total crystallinity (x_c) for sPS-3MS series obtained from WAXS profiles in Figure 1 via peak deconvolution.

Melt-Crystallization				*Cold-Crystallization*			
sPS-5%3MS	x_α	x_β	$x_c = x_\alpha + x_\beta$	sPS-5%3MS	x_α	x_β	$x_c = x_\alpha + x_\beta$
T_c = 250 ºC	0.017	0.197	0.214	T_c = 240 ºC	0.359	0.059	0.418
T_c = 245 ºC	0	0.357	0.357	T_c = 220 ºC	0.330	0.028	0.358
T_c = 240 ºC	0.010	0.336	0.346	T_c = 200 ºC	0.332	0.015	0.347
T_c = 230 ºC	0	0.310	0.310				
T_c = 220 ºC	0.052	0.373	0.425				
sPS-11%3MS	x_α	x_β	$x_c = x_\alpha + x_\beta$	sPS-11%3MS	x_α	x_β	$x_c = x_\alpha + x_\beta$
T_c = 240 ºC	0.021	0.176	0.197	T_c = 240 ºC	0.381	0.076	0.457
T_c = 235 ºC	0.013	0.191	0.204	T_c = 220 ºC	0.352	0.069	0.421
T_c = 230 ºC	0.016	0.247	0.263	T_c = 200 ºC	0.333	0.066	0.399
T_c = 220 ºC	0.047	0.286	0.333				
sPS-21%3MS	x_α	x_β	$x_c = x_\alpha + x_\beta$	sPS-21%3MS	x_α	x_β	$x_c = x_\alpha + x_\beta$
T_c = 230 ºC	0.213	0.045	0.258	T_c = 240 ºC	0.311	0.066	0.377
T_c = 220 ºC	0.221	0.046	0.267	T_c = 220 ºC	0.352	0.075	0.427
T_c = 210 ºC	0.274	0.057	0.301	T_c = 200 ºC	0.347	0.068	0.415

Table S2. The crystallinity of α (x_α), β (x_β) crystal and the total crystallinity (x_c) for sPS-4MS series obtained from WAXS profiles in Figure 2 via peak deconvolution.

Melt-Crystallization				*Cold-Crystallization*			
sPS-2%4MS	x_α	x_β	$x_c = x_\alpha + x_\beta$	sPS-2%4MS	x_α	x_β	$x_c = x_\alpha + x_\beta$
T_c = 250 ºC	0.008	0.344	0.352	T_c = 240 ºC	0.358	0.012	0.370
T_c = 240 ºC	0.014	0.343	0.357	T_c = 220 ºC	0.325	0.005	0.330
T_c = 230 ºC	0.015	0.342	0.357	T_c = 200 ºC	0.313	0	0.313
sPS-5%4MS	x_α	x_β	$x_c = x_\alpha + x_\beta$	sPS-5%4MS	x_α	x_β	$x_c = x_\alpha + x_\beta$
T_c = 250 ºC	0.144	0.001	0.145	T_c = 240 ºC	0.330	0	0.330
T_c = 240 ºC	0.261	0.008	0.269	T_c = 220 ºC	0.313	0	0.313
T_c = 230 ºC	0.296	0.009	0.305	T_c = 200 ºC	0.304	0	0.304
sPS-10%4MS	x_α	x_β	$x_c = x_\alpha + x_\beta$	sPS-10%4MS	x_α	x_β	$x_c = x_\alpha + x_\beta$
T_c = 230 ºC	0.089	0	0.089	T_c = 240 ºC	0.278	0	0.278
T_c = 220 ºC	0.247	0	0.247	T_c = 220 ºC	0.312	0	0.312
				T_c = 200 ºC	0.303	0	0.303

Geometry Optimization and Supercell Construction

In the geometry optimization process, the program will try to find the minimal total energy of the structure by adjusting the atomic coordinates and the cell parameters, which is based on reducing the magnitude of calculated forces and stresses. Therefore, after geometry optimization, the structure corresponds to a minimum in the potential energy surface.[2]

During the optimization, a forcefiled should be assigned to calculated the energy of the structure. Here, we chose COMPASS (Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies) forcefield, which has broad coverage in covalent molecules including most common organics, small inorganic molecules, and polymers.[2–5] *Accelrys® Materials Studio* also provides other forms of forcefield that also suitable for polymer structure and calculation via different forcefiled might give different *absolute value* of structure energy; however, this manuscript focuses on *the energy difference among different structure*, and the trend for the *relative difference* among the structures would not change even using different forcefield.

Illustrated in Figure S5 show the representative α structure (a) before and (b) after supercell that the unit cell was extended in *b*-direction by 2. In this manuscript, the α unit cell was supercelled in *b*-direction by 2 and in *c*-direction by 4; the β unit cell was supercelled in *a*-direction by 2, *b*-direction by 3, and *c*-direction by 3. After supercelled, both α and β supercelled structures contained 144 units of styrene.

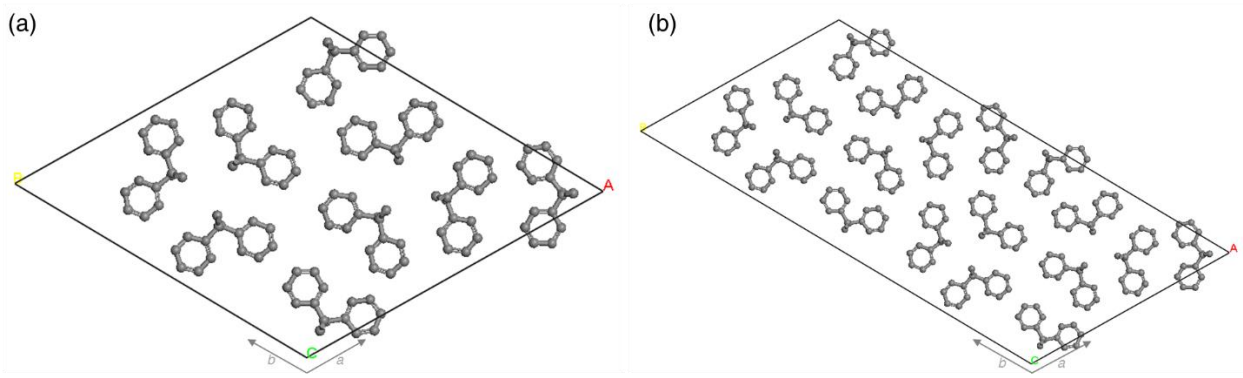


Figure S5. Representative structure of α unit cell (a) before and (b) after supercell in *b*-direction by 2. It is clear to see that the unit cell becomes larger after supercell. (the H atoms were removed for legibility concern)

Reference

(1) De Rosa, C.; Rapacciuolo, M.; Guerra, G.; Petraccone, V.; Corradini, P. On the Crystal Structure of the Orthorhombic Form of Syndiotactic Polystyrene. *Polymer* **1992**, *33*, 1423−1428.

(2) *Materials Studio*, v5.0; Accelrys: San Diego: Dassault Systèmes, 2009.

(3) Sun, H. COMPASS: An ab initio Force-field Optimized for Condensed-phase Applications Overview with Details on Alkane and Benzene Compounds. *J. Phys. Chem. B* **1998**, *102*, 7338−7364.

(4) Sun, H.; Ren, P.; Fried, J. The COMPASS Force Field: Parameterization and Validation for Phosphazenes. *Comput. Theor. Polym. Sci.* **1998**, *8*, 229−246.

(5) Rigby, D.; Sun, H.; Eichinger, B. Computer Simulations of Poly(ethylene oxide): Force Field, PVT Diagram and Cyclization Behaviour. *Polym. Int.,* **1997**, *44*, 311−330.