

Electronic Supporting Information

A Convenient Quantitative Study of Polymer Mesophase Induced by Isothermal Annealing

Yang Feng,^{a,b} Guangming Chen^{*a} and Jianjun Wang^{*a}

^a Beijing National Laboratory for Molecular Sciences (BNLMS), Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, P. R. China. E-mail: chengm@iccas.ac.cn (G. Chen), wangj220@iccas.ac.cn (J. Wang).

^b University of Chinese Academy of Sciences, Beijing 100049, P. R. China.

Experimental Details

Materials and Samples. The sPS was kindly provided by Japan Idemitsu Kosan Co. Ltd., with a commercial name of XAREC SP130. Its syndiotacticity, [rr], is larger than 97%. The amorphous films were obtained by pressing the molten sPS manually on a homemade heating stage followed by rapid quenching in cold water. Both FT-IR spectroscopic and XRD results confirmed no sign of crystalline phase. These amorphous film samples have different sizes and thicknesses, which makes the results convincing and widely applicable to common film samples.

Characterizations. FT-IR spectra were collected on a Bruker TENSOR 27 spectrometer at 2 cm⁻¹ resolution with 64 scans, and the wavenumber range was 1400–800 cm⁻¹. During the measurements, a heating cell mounted with the sPS film sample was equipped into the spectrometer, which ascertained continuous observation of *in situ* changes of characteristic bands at a fixed film position. Curve fittings were performed to quantify band positions and the corresponding band areas. The FT-IR spectra profile in the region of 870–820 cm⁻¹ was separated into several components using the software of PeakFit v4.12, where the bands were assumed to be of Gaussian function with a linear baseline. The fit standard error was 0.1–0.25%.

XRD measurements were conducted on a Rigaku D/max 2500 diffractometer, using Cu K α radiation ($\lambda = 0.15418$ nm). The scanning 2-theta angle was between 5° and 30°, and the scanning rate was 2° min⁻¹.

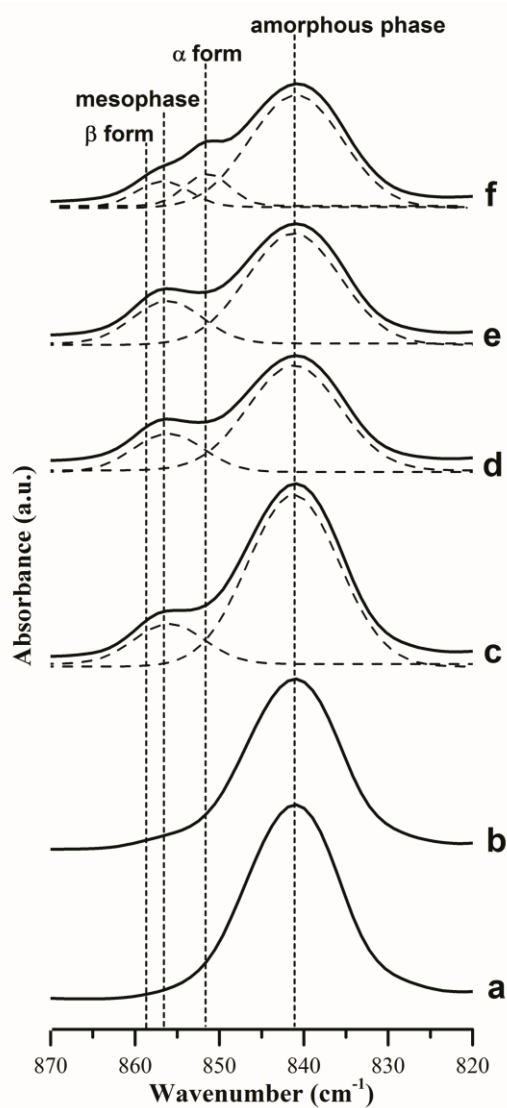


Fig. S1 FT-IR spectra in the frequency range of 870–820 cm⁻¹ for sPS films (a) before and (b–f) after being isothermally annealed at different temperatures: (b) 110 °C for 12 h, (c) 120 °C for 6 h, (d) 130 °C for 6 h, (e) 140 °C for 6 h, (f) 150 °C for 1 h.

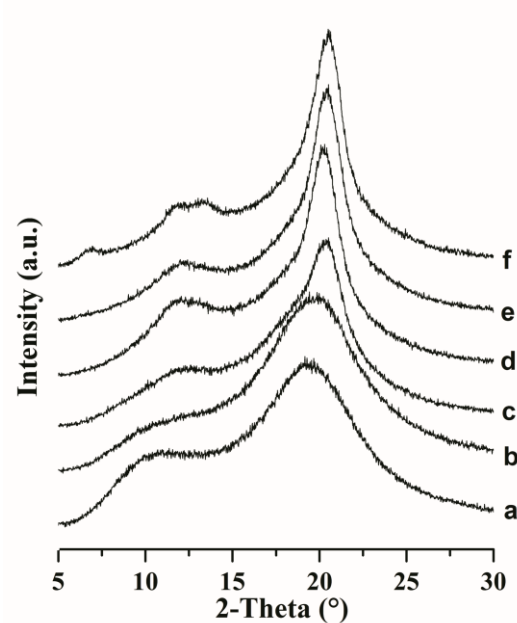


Fig. S2 XRD patterns of sPS films (a) before and (b–f) after being isothermally annealed at different temperatures: (b) 110 °C for 12 h, (c) 120 °C for 6 h, (d) 130 °C for 6 h, (e) 140 °C for 6 h, (f) 150 °C for 1 h.

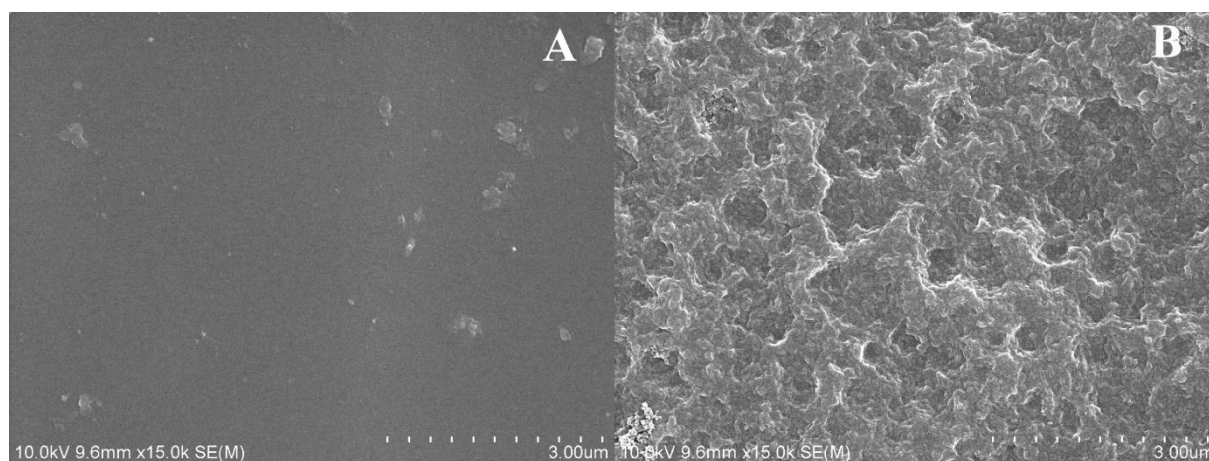


Fig. S3 SEM images of sPS films after etching treatment. (A) amorphous film; (B) film containing mesomorphic phase. Due to the existence of mesophase, film (B) showed relatively rough surface; in contrast, the surface of film (A) was relatively smooth because of the homogeneous etching effect.

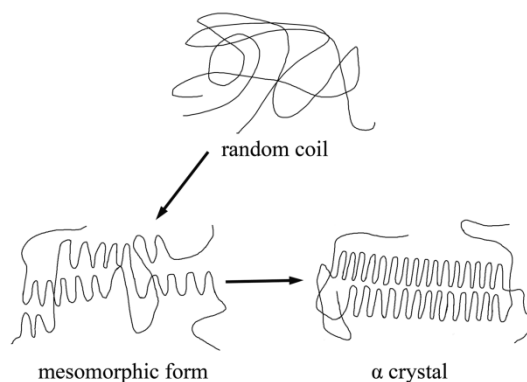


Fig. S4 Schematic illustration of sPS phase transition of amorphous → mesomorphic form → α crystalline state.^{1,2,3}

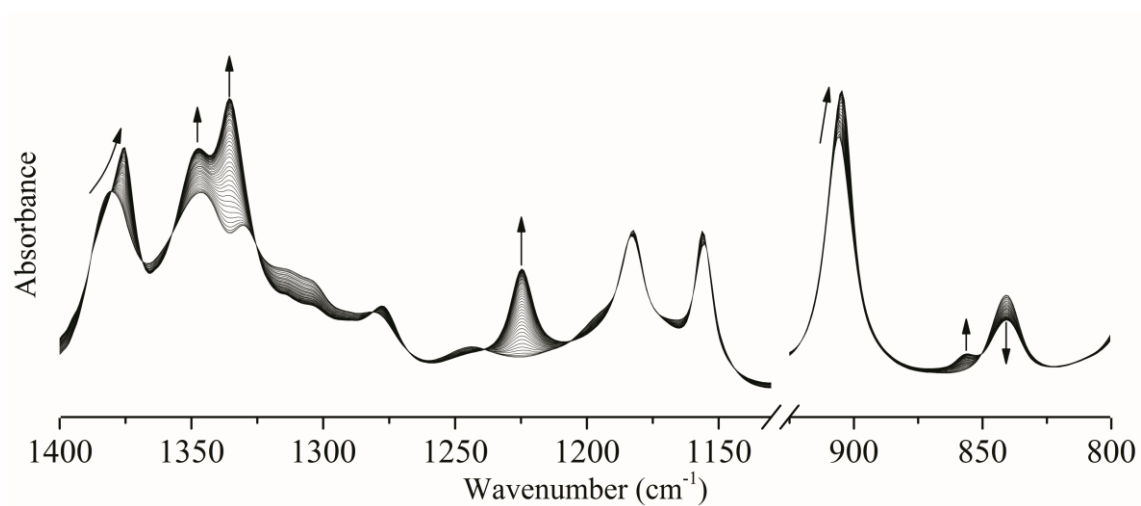


Fig. S5 *In situ* FT-IR spectra of sPS film annealed at 120 °C for 360 min (time interval: 5 min).

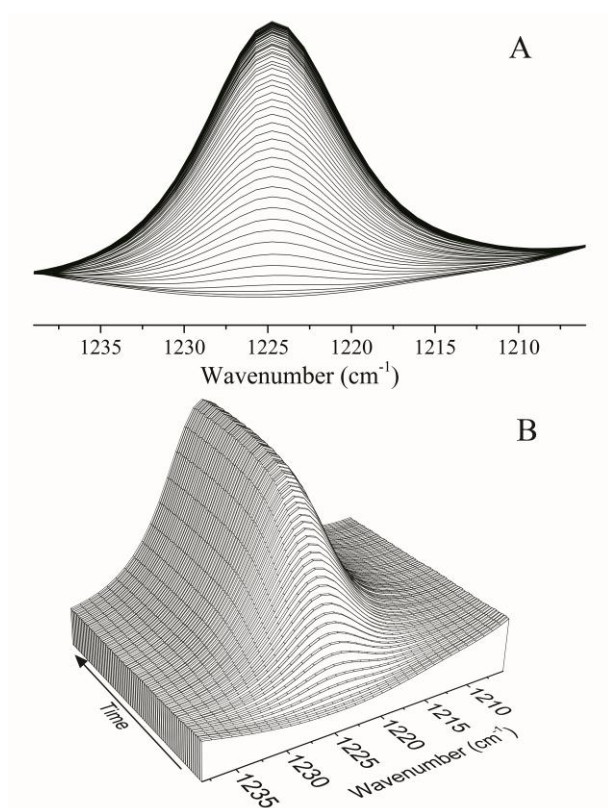


Fig. S6 *In situ* FT-IR absorption spectra for the band at 1224 cm⁻¹ (amorphous sPS film was annealed at 120 °C for 360 min). (A) original FT-IR spectra; (B) time-dependent “3D” spectra.

Table S1. Curve fitting results and the calculated absorptivity ratios (120 °C)

Time (min)	A ₈₄₁	A ₈₅₆	%(A ₈₅₆)	a _{meso}
105	2.821	0.358	11.26	0.360
120	2.729	0.397	12.69	0.366
135	2.652	0.418	13.62	0.359
150	2.588	0.440	14.53	0.359
165	2.545	0.451	15.05	0.355
180	2.517	0.465	15.59	0.358
195	2.513	0.468	15.71	0.359
210	2.506	0.483	16.14	0.369
225	2.497	0.487	16.31	0.370
240	2.487	0.487	16.37	0.367
255	2.473	0.488	16.49	0.364
270	2.460	0.486	16.50	0.359
285	2.462	0.493	16.67	0.364
300	2.466	0.500	16.85	0.371
315	2.473	0.502	16.88	0.374
330	2.456	0.506	17.09	0.372
345	2.449	0.496	16.84	0.363
360	2.439	0.494	16.84	0.359

$$A_{841}^* = 3.815; a_{\text{meso}} (\text{average}) = 0.364 \pm 0.006$$

Table S2. The calculated fraction of mesophase corresponding to Table S1 (Equation 3 was applied with a_{meso} = 0.360)

Time (min)	F _{meso}	Time (min)	F _{meso}
105	26.1	240	35.2
120	28.8	255	35.4
135	30.5	270	35.4
150	32.1	285	35.7
165	33.0	300	36.0
180	33.9	315	36.1
195	34.1	330	36.4
210	34.9	345	36.0
225	35.1	360	36.0

$$a_{\text{meso}} = 0.360$$

References

1. V. Petraccone, F. Auriemma, F. D. Poggetto, C. De Rosa, G. Guerra and P. Corradini, *Die Makromol. Chem.*, 1993, **194**, 1335-1345.
2. F. Auriemma, V. Petraccone, F. Dalpoggetto, C. De Rosa, G. Guerra, C. Manfredi and P. Corradini, *Macromolecules*, 1993, **26**, 3772-3777.
3. Y. S. Sun, E. M. Woo and M. C. Wu, *Macromolecules*, 2003, **36**, 8415-8425.