

Chapter III Characterization of Crystallization in Syndiotactic Polystyrene (s-PS) Thin Film Samples

3-1 Introduction

Pluralistic crystallizations and how they affect polymorphic behavior of syndiotactic polystyrene (s-PS) have received considerable interest, mainly in *bulk* samples.⁽¹⁻³⁾ Also having been extensively studied is the development of α - or β -form crystals in s-PS, favored either kinetically or thermodynamically during the crystallization. Upon heating at several scanning rates, the relative fraction of α - and β -form crystals varies in *bulk* samples. This phenomenon favors the formations of α -form by heating at a high scanning rate. In contrast, the β -form crystal is a preferred means packing over α -form by heating at a low scanning rate and/or by crystallizing at higher temperatures closer to its T_m .⁽⁴⁻⁶⁾ Above observations suggest that the crystal—crystal transformation indeed occurs when s-PS *bulk* sample contains the α -form as mentioned in previous literature.⁽¹⁻⁶⁾

Our earlier study investigated the crystallization mechanism of s-PS *bulk* samples using conventional absorbance FTIR spectroscopy in our previous report.⁽⁷⁾ FTIR was performed to distinguish the crystal form and crystallinity of s-PS. This work elucidates the effect of s-PS sample thickness on crystallization behavior in melt-, cold-, and heat scanning crystallizations using FTIR spectroscopy.

3-2 Experimental

The syndiotactic polystyrene (s-PS) was kindly donated by the Industrial Technology Research Institute (HsinChu Taiwan) and was used without further purification. The stereoregularity of the syndiotactic polystyrene consists of $[rr] = 99\%$ is identified by the solution ^{13}C NMR spectrum.⁽⁸⁾

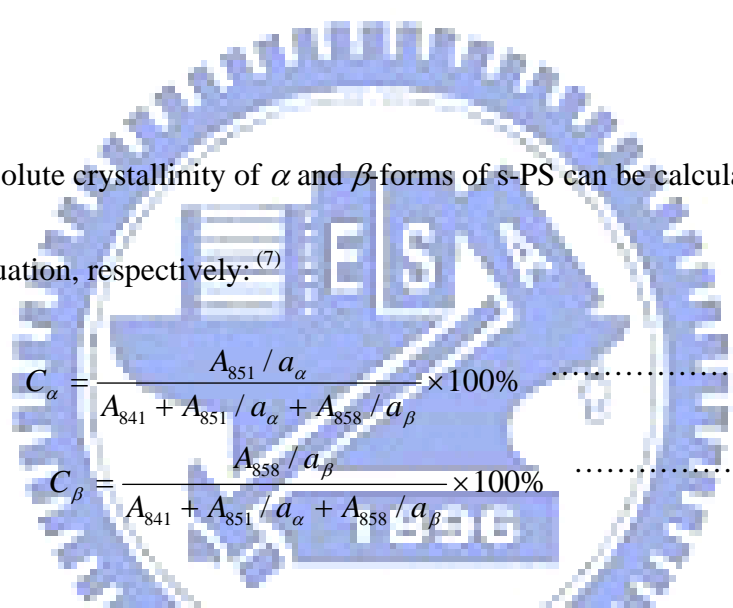
A s-PS *thin* film sample was prepared by mixing thoroughly s-PS particles (diameter less than $10\ \mu\text{m}$ obtained from precipitation) and KBr powder (s-PS/KBr = 10/90 by weight). The mixture was then compression-molded into disks under pressure of 600 psi. These small s-PS particles are dispersed uniformly and separately within KBr matrix. The s-PS *bulk* sample was prepared by the same procedure as *thin* film sample, except that the s-PS particles with diameter of around $100\ \mu\text{m}$ were obtained by mechanical grind.

Isothermal cold- and melt-crystallization of various time intervals were performed on samples in an environmental chamber with a temperature programmable controller within an accuracy of $\pm 0.1\ ^\circ\text{C}$. Next, the s-PS samples were pretreated at $320\ ^\circ\text{C}$ for 20 min to eliminate the residual crystal memory in the melt-, and then quenched by liquid nitrogen to obtain the amorphous (crystal-free) s-PS as the starting material. For cold-crystallization, the quenched s-PS sample was placed directly into the chamber at 264°C . For the melt-crystallization, the s-PS sample was heated to $320\ ^\circ\text{C}$ and quickly cooled

(-100 °C/min) to 264 °C. All samples were prepared under a continuous nitrogen flow to minimize sample oxidation or degradation.

The crystal form and crystallinity of the s-PS were characterized by infrared spectroscopy (Nicolet AVATAR 320 FTIR spectrometer, U.S.A.) with a resolution of 1.0 cm⁻¹ at 30 °C, ranging from 940~820 cm⁻¹. The frequency scale was internally calibrated using a He-Ne laser and 32 scans were single-averaged to reduce the noise.

The absolute crystallinity of α and β -forms of s-PS can be calculated from the following equation, respectively:⁽⁷⁾



$$C_{\alpha} = \frac{A_{851} / a_{\alpha}}{A_{841} + A_{851} / a_{\alpha} + A_{858} / a_{\beta}} \times 100\% \quad \text{Eq.(2-3)}$$

$$C_{\beta} = \frac{A_{858} / a_{\beta}}{A_{841} + A_{851} / a_{\alpha} + A_{858} / a_{\beta}} \times 100\% \quad \text{Eq.(2-4)}$$

where C_{α} and C_{β} represent the crystallinities of α and β -forms, respectively, A_{841} , A_{851} and A_{858} are the area fractions of amorphous, α and β -form, as obtained by the absorbance areas ranging from 865 to 820 cm⁻¹. The conversion coefficients— a_{α} and a_{β} (0.178 and 0.272 obtained from a previous investigation⁽⁷⁾) are the ratios of absorptive coefficients of A_{851} / A_{841} and A_{858} / A_{841} for α - and β -form crystal absorbances, respectively.

3-3 Results and Discussion

Table 3-1 summarizes the specific absorbance of s-PS in the IR spectrum ranging from 940 to 820 cm^{-1} .^(9,10) The specific peaks of amorphous phase appear at 905 and 841 cm^{-1} . The specific peaks of α -form are at 901 (shifted from 905 cm^{-1}) and 851 (shifted from 841 cm^{-1}) cm^{-1} , while the specific peaks of β -form are at 911 (shifted from 905 cm^{-1}) and 858 (shifted from 841 cm^{-1}) cm^{-1} .

Figure 3-1a shows the IR spectrum of *bulk* s-PS sample isothermal at 320 °C for 20 min and then cooled to 30 °C with rate of -10°C/min. The peaks corresponding to amorphous phase, α and β form crystal are apparent. Implying that s-PS crystallizes to α - and β -form crystals during cooling process. This finding corresponds to the well-known DSC trace results where two endothermic peaks corresponding to α and β -form crystals always appear simultaneously in a normal cooling rate from the melt.^(3, 11~13) Figures 3-1b and 1c show that the IR spectra of the s-PS in *bulk* and in thin films which have been heated up to 264°C from 30 °C with a scanning rate of 10 °C/min and then quenched by liquid nitrogen, respectively. Both α -form peaks (901 and 851 cm^{-1}) and β -form (911 and 858 cm^{-1}) peaks appear in FTIR spectra of *bulk* samples as shown in Figure 3-1b. The mechanism of crystal growth has been described as follows:⁽¹¹⁾ The α -form nuclei formed at lower temperatures (less than ~240 °C) induces the growth of

α -form crystal during heating scanning. In addition to the heating scan, the α -form crystal converts into the thermodynamically favored β -form crystal at higher temperatures (greater than ~ 240 °C) in s-PS *bulk* samples. Therefore, it leads to that s-PS crystallizes into α - and β -form crystals during heating up to 264 °C in the *bulk* samples.

In contrast, only α -form peaks at 901 and 851 cm^{-1} appear after heating scanning up to 264 °C in thin film s-PS samples as shown in Figure 3-1c. This finding suggests that α -form crystals transforming to β -form crystals may be physically retarded at a high temperature (above ~ 240 °C) when s-PS thin films with thickness less than 10 μm . Therefore, the s-PS thin film sample does not provide a favorable condition to overcome the energy barrier in order to induce the crystal transformation from α -form to a thermodynamically favored β -form. A critical film thickness must be met to make the α - β transformation feasible at a high temperature.

Figure 3-2 shows the FTIR spectra ranging from 940~820 cm^{-1} of the thin film s-PS sample which is melt-crystallized at 264 °C at various isothermal time durations. Notably, only two main peaks located at 905 and 841 cm^{-1} corresponding to amorphous phase appear in Figure 3-2a~3-2d where the crystallization process has not begun. The β -form characteristic peaks, 911 and

858 cm^{-1} , begin to emerge when the s-PS thin film sample is melt-crystallized at 264 $^{\circ}\text{C}$ for 20 min. Apparently, the intensity of β -form peaks gradually increases with an increasing crystallization time. Meanwhile, the relative intensity of amorphous phase peaks gradually decreases. The specific α -form peak of $\sim 901 \text{ cm}^{-1}$ seems to be observed when the s-PS thin film sample is melt-crystallized at 264 $^{\circ}\text{C}$ for more than 40 min. However, the specific α -form peak of $\sim 851 \text{ cm}^{-1}$ is not decomposed out after curve fitting. It is referred that the α -form may appear, but too weak to exhibit apparently in spectra. This feature corresponds to numerous earlier studies on s-PS crystallization mechanism which show crystallization favors the β -form crystal at a higher temperature (i.e. above 240 $^{\circ}\text{C}$) for thermodynamic reasons.⁽³⁾

Figure 3-3 shows the FTIR spectra ranging from 940~820 cm^{-1} of the s-PS thin film sample which is cold-crystallized at 264 $^{\circ}\text{C}$ for various isothermal time durations. The peaks intensity at 901 and 851 cm^{-1} reveal that the α -form crystal increases with an increasing crystallization time; meanwhile, the relative intensity of the amorphous phase at 905 and 841 cm^{-1} decreases. From this observation, we can infer that the original α -form crystal becomes more perfect with an increasing crystallization time at 264 $^{\circ}\text{C}$, which is reflected by the sharpening of 901 and 851 cm^{-1} peaks. However, this crystal does not convert into the thermodynamically

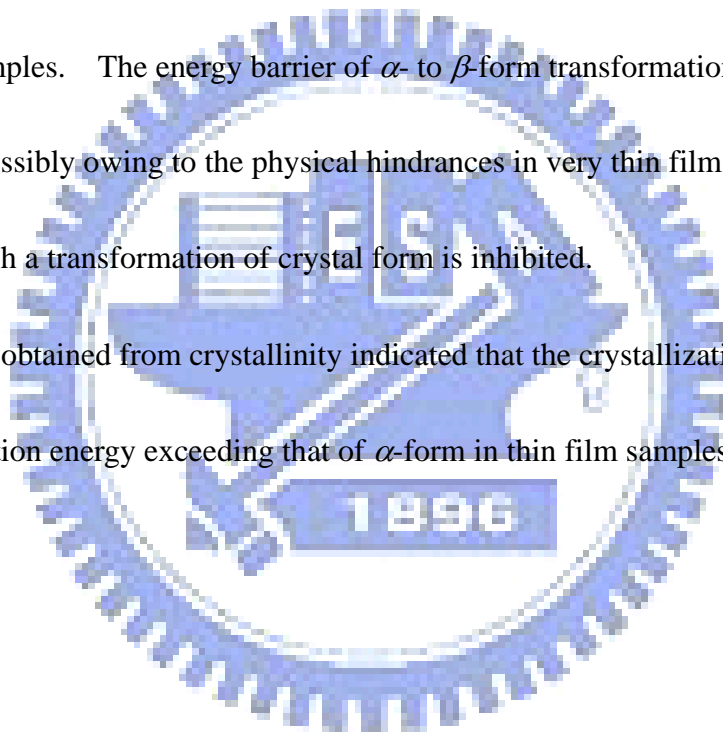
avored β -form crystal as well as the *bulk* sample does in the cold-crystallization process. In other words, the individual lamellae of α -form crystals can extend upon annealing at 264°C in s-PS thin film samples.

Comparing Figure 3-2 and Figure 3-3 reveals that the intensity of α -form peaks grows more rapidly than the corresponding β -form. Results obtained from curve fitting ranging between 865 and 820 cm⁻¹ exhibits two main Gaussian peaks that provide an adequate fit with standard deviation square less than 10⁻⁸ for systems of melt- and cold-crystallization at 264°C for 240 min, as shown in the upper-right corners of Figure 3-2 and Figure 3-3, respectively. Table 3-2 summarizes the curve-fitting results of Figure 3-2j and Figure 3-3h. The absolute crystallinity of β -form is 43.2% in the melt-crystallization; meanwhile, that of the α -form is 60.8% in cold-crystallization, calculated from equ. (3-1) and (3-2), as the s-PS is crystallized isothermally at 264°C for 240 min. Notably, the crystallization rate of the β -form appear to be slower than that of α -form in thin film samples.

3-4 Conclusions

In s-PS *bulk* samples, α -form can convert into the thermodynamically favored β -form packing when the temperature is close to the T_m . In s-PS thin film samples, α -form crystal formed at lower temperatures continue to grow along with an elevating temperature during cold-crystallization. The usually observed α - to β -form transformation at higher temperatures (above 240 °C) does not occur in thin film s-PS samples. The energy barrier of α - to β -form transformation can not overcome, possibly owing to the physical hindrances in very thin film samples, therefore, such a transformation of crystal form is inhibited.

Results obtained from crystallinity indicated that the crystallization of β -form has an activation energy exceeding that of α -form in thin film samples.



3-5 Reference:

1. Kellar, E. J. C.; Galiotis, C.; Andrews, E. H., *Macromolecules*, 1996, 29, 3515
2. Nakaoki, T.; Kobayashi, M., *J. Mol. Struct.* 1991, 242, 315
3. Sun, Y. S.; and Woo, E. M., *Macromolecules*, 2000, in press
4. Woo, E. M.; Sun, Y. S.; Lee, M. L., *Polymer Commun.* 1998, 40, 4425
5. Woo, E. M.; Wu, F. S., *Macromolecular Chemistry and Physics*, 1998, 199, 9, 2041
6. Vittoria, V.; Ruvolo, F. A., de Candia, F., *J. Macromol. Sci. Phys.*, 1992, B31, 133
7. Wu, H. D.; Wu, S. C.; Change, F. C., *Polymer*, 2001, 42, 4719
8. Wang, Y.; Herron, N., *J. Phys. Chem.* 1991, 95, 525
9. Musto, P.; Tavone, S.; Guerra, G.; De Rosa, C.; *J. Polym. Sci. B: Polym Phys*, 1997, 35, 1055
10. Wu, H. D.; Tseng, C. R.; Change, F. C., *Macromolecules*, 2000, 34, 2992
11. Arnauts, J.; Berghmans, H., *Polymer Commun.*, 1990, 31, 343
12. Guerra, G.; Vitagliano, V. M.; De Rosa, C.; Petraccone, V.; Corradini, P., *Macromolecules*, 1990, 23, 1539
13. Sun, Z.; Morgan, R. J.; Lewis, D. N., *Polymer*, 1992, 33, 3, 660

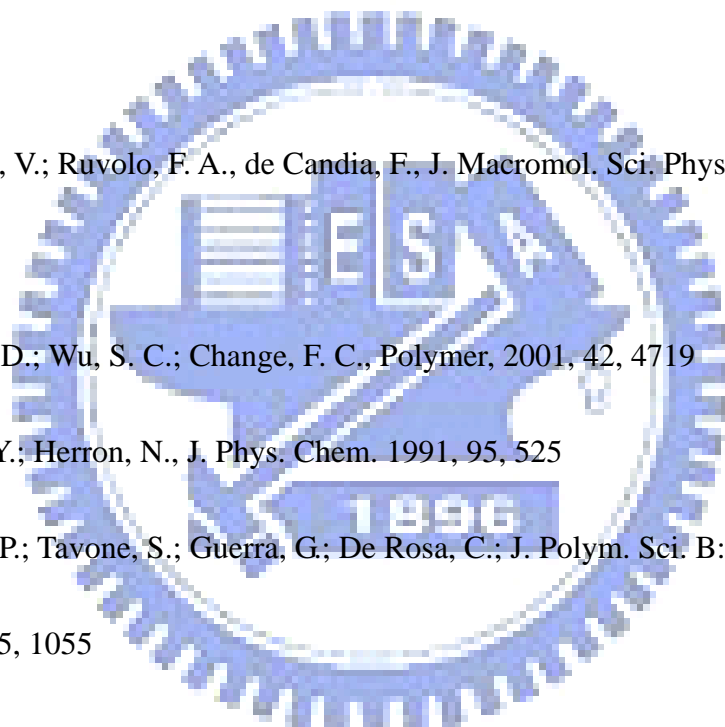


Table 3-1 the specific characterized absorbances of s-PS in IR spectra ranging from 940~820 cm^{-1} .

Morphology	Position of absorbance (cm^{-1})
Amorphous phase	905(s), 841 (m)
α -form crystal	901 (s), 851(w)
β -form crystal	911(s), 858(w)

Note: “s”, “m”, and “w” represents for the “strong”, “middle” and “weak” absorbances in IR spectrum, respectively.

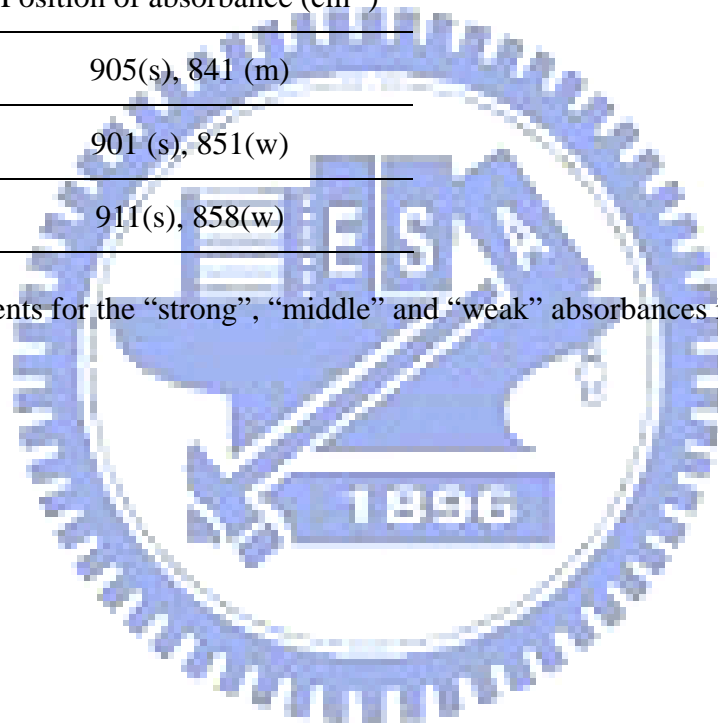


Table 3-2 The results of curve-fitting ranging between 865 and 820 cm^{-1} , absolute crystallinity of melt-crystallized and cold-crystallized s-PS at 264 $^{\circ}\text{C}$ for 240 min, results form Figure 3-2j and Figure 3-3h.

Isothermal time of 240 min	Amorphous phase			Crystal phase			Absolute crystallinity
	Area	Freq ^a , cm^{-1}	Width ^b	Area	Freq ^a , cm^{-1}	Width ^b	
Cold-Crystallization	0.410	840.81	10.836	0.113	851.49	4.370	60.8 (C_{α} , %) ^c
Melt-Crystallization	0.366	840.85	10.699	0.076	857.76	3.848	43.2 (C_{β} , %) ^d

^a Wavenumber.

^b Width at half-height, cm^{-1}

^c Absorptivity ratio of $A_{851}/A_{841} = 0.178$

^d Absorptivity ratio of $A_{858}/A_{841} = 0.272$

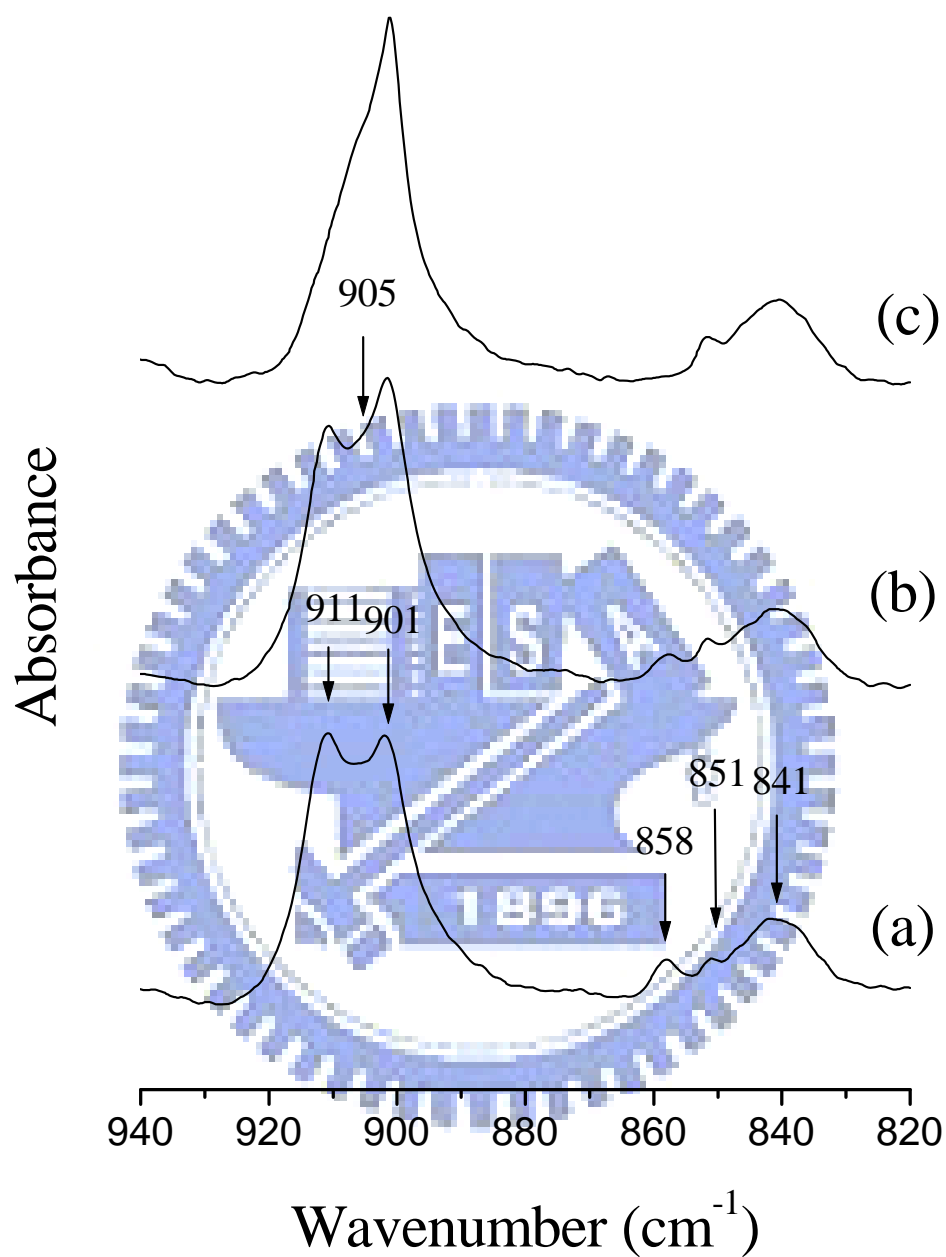


Figure 3-1 IR spectra of s-PS (a) *bulk* sample, cooling from 320 °C to 30 °C with rate of -10°C/min; (b) *bulk* sample, heated up the quenched sample to 264°C from 30 °C with scanning rate of 10 °C/min; and (c) thin film sample, heated up the quenched sample to 264 °C from 30 °C with scanning rate of 10 °C/min.

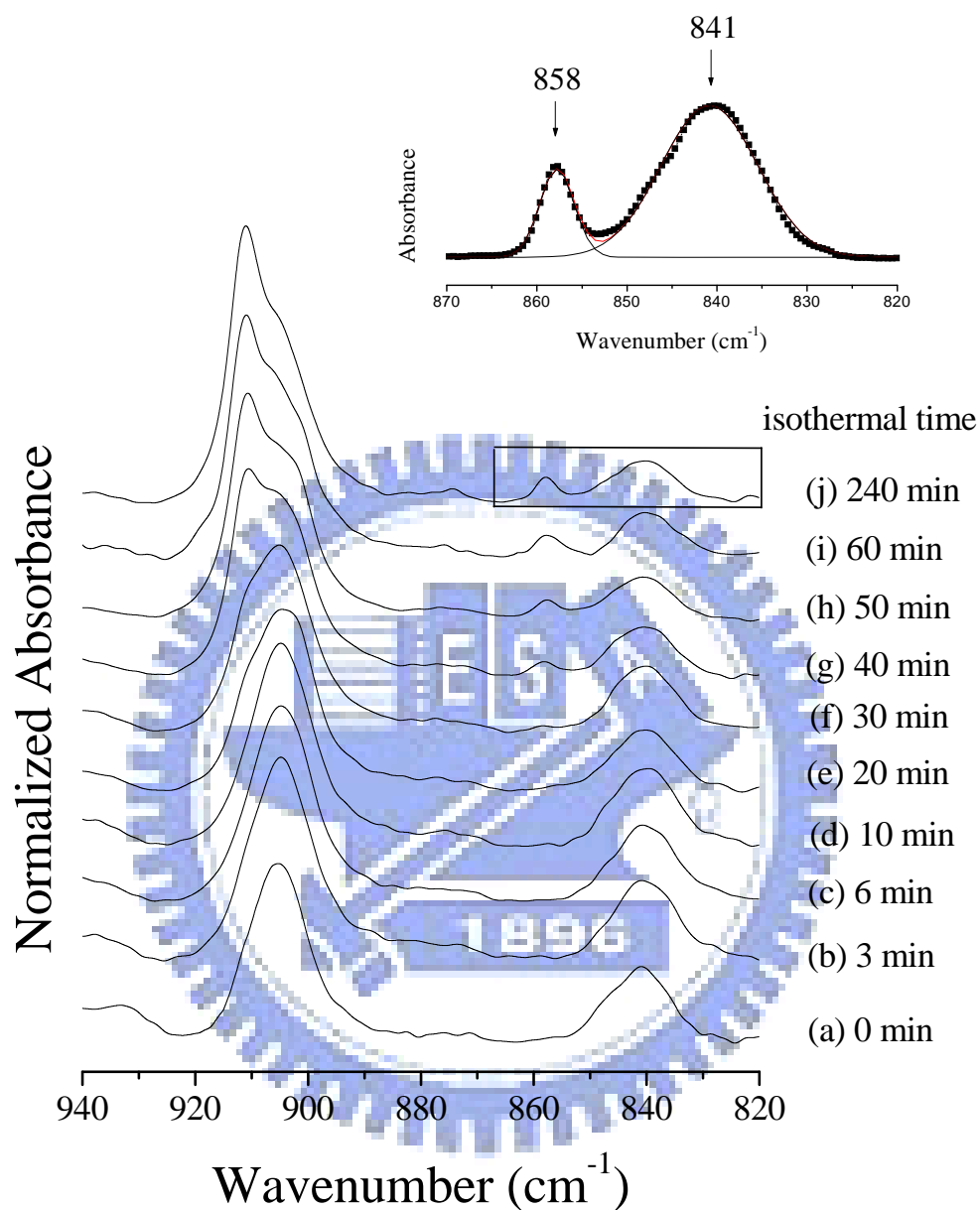


Figure 3-2 IR spectra of melt-crystallized s-PS thin film at 264 °C for (a) 0 min; (b) 3 min; (c) 6 min; (d) 10 min; (e) 20 min; (f) 30 min; (g) 40 min; (h) 50 min; (i) 60 min; (j) 240 min durations ranging from 940~820 cm^{-1} . (Upper-right corner exhibits the curve-fitting ranging between 865 and 820 cm^{-1} for Figure 3-2j.)

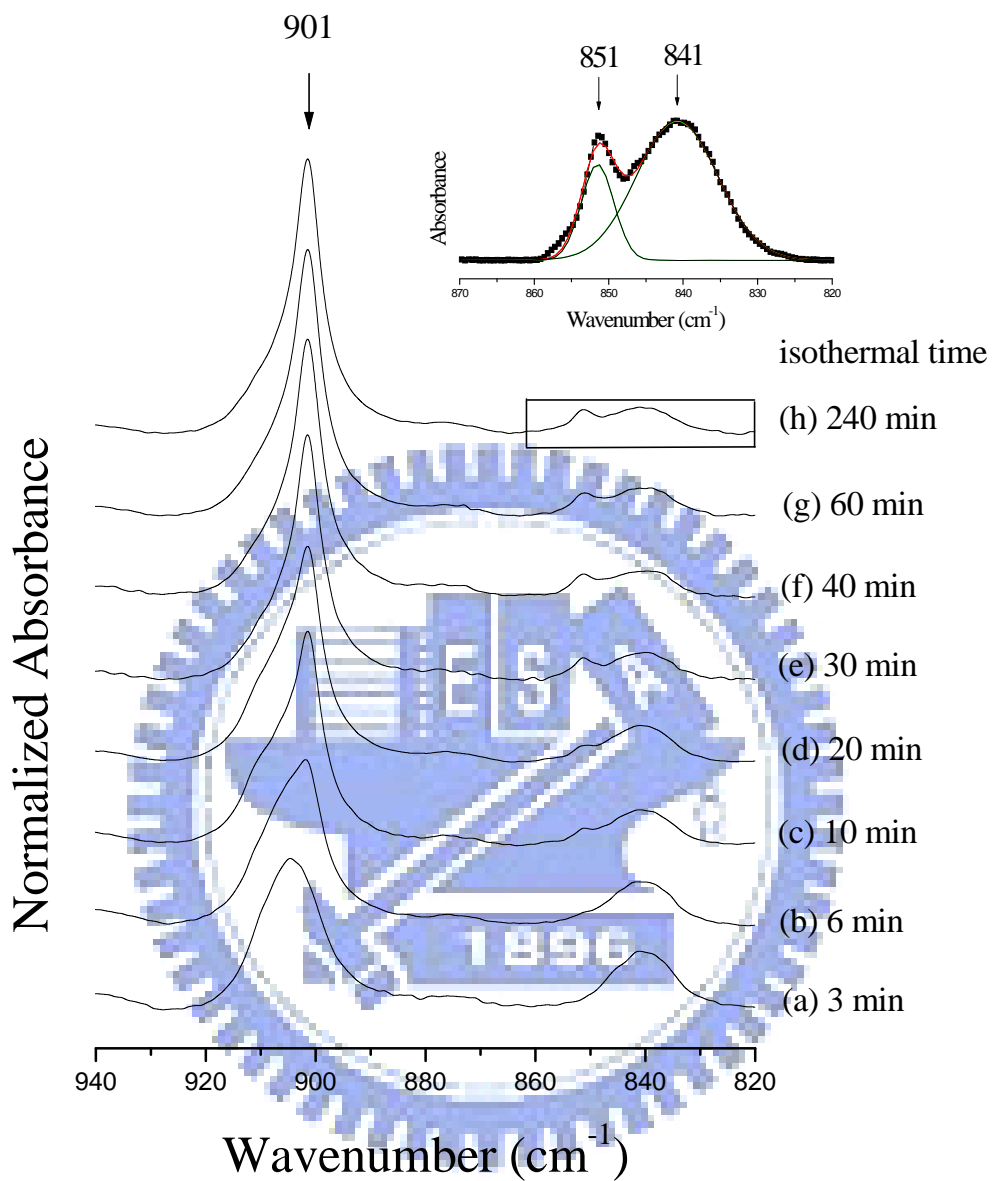


Figure 3-3 IR spectra of the cold-crystallized s-PS thin film at 264 °C for (a) 3 min; (b) 6 min; (c) 10 min; (d) 20 min; (e) 30 min; (f) 40 min; (g) 60 min; (h) 240 min durations ranging from 940~820 cm^{-1} . (Upper-right corner exhibits the curve-fitting ranging between 865 and 820 cm^{-1} for Figure 3-3h.)