

中文題目：以霍氏紅外線光譜儀探討高分子結晶行為及高分子與鋰
離子的交互作用

**TITLE: The Study on Polymer Crystallization Behavior and Polymer
Interaction with Lithium Salt Using FTIR Spectrum**

中文摘要

因應高分子的奈米應用，在分子科學中微細結構的型態學及分子間的交互作用力成了十分熱門的研究主題。但是，仍有許多高分子的物理性質，無法由一般的儀器得到相關的數據。例如絕對結晶度及計量分子間交互作用力等，這些都將會成為高分子微結構科學研究的瓶頸。

霍氏紅外線光譜在分子科學的領域有著舉足輕重的地位，如官能基的確定，型態學及交互作用等等... 因此，在本研究中，使用霍氏紅外線光譜，分別在兩個系統來研究對排聚苯乙炔的絕對結晶及高分子電解質中的交互作用。由本研究的結果中證明，使用霍氏紅外線光譜可以十分深入觀察高分子的結晶行為及高分子電解質中的交互作用的行為。

在本論文中，將實驗分成兩個部分分別討論：

- (a) 使用霍氏紅外線光譜研究對位聚苯乙炔 α 結晶相與 β 結晶相的結晶行為。“ α -crystal/amorphous, a_α ” and “ β -crystal/amorphous, a_β ”吸收率參數(absorptivity ratio) 可以在 865 to 820 cm^{-1} 區段的光譜得到量化數據。經由霍氏紅外線光譜曲線數據分析結果，可得到 α - 與 β - 結晶相的吸收曲線，及 a_α 與 a_β 吸收率分別為 0.178 ± 0.005 and 0.272 ± 0.005 。薄片樣本(thin film sample) 在 $240\text{ }^\circ\text{C}$

等溫過程熱處理中，可發現 α -結晶相的結晶速率高於相同狀況熱處理的 β -結晶相的結晶速率。由霍氏紅外線光譜研究中，可發現 α -結晶相是屬於動力學優勢(kinetically more favorable)的結晶型態，而 β -結晶相屬於熱力學優勢(thermodynamically more favorable)的結晶型態。

在小於 $10\mu\text{m}$ 厚度的 thin film 的樣品之中，在 264°C 的熱處理溫度中，分別使用冷結晶 (cold-crystallization) 及 融熔結晶 (melt-crystallization) 可以分別得到純的 α 及 β 對排聚苯乙烯結晶。而且在熱處理的過程之中，沒有發生 α 相轉移到 β 相的相變化過程。可以在 264°C 的冷結晶程序中，可以得到單一的 α 相對排聚苯乙烯結晶。因此， α 相對排聚苯乙烯結晶在 thin film 的型態之中，可以在 264°C 冷結晶程序下熱處理中繼續成長。相對的，單一的 β 相對排聚苯乙烯結晶，無論在 thin film 或是 bulk 的狀態下，都可以在融熔結晶程序中得到。

- (b) 其次，利用霍氏紅外線光譜的另外一個研究對象是固態高分子電解質與離子間的交互作用力。使用霍氏紅外線光譜及固態核磁共振研究 poly (vinyl pyrrolidone)(PVP) 與 Lithium Perchlorate (LiClO_4) 系統中的固態高分子電解質的分子間交互作用。我們發現 PVP 的氮原子能夠貢獻獨立電子對給 $\text{C}=\text{O}$ 官能基，造成 $\text{C}=\text{O}$ 有更高的鹽基度。鋰離子與 $\text{C}=\text{O}$ 間的錯合鍵可以分成兩種形式：a. 鋰離子與 $\text{C}=\text{O}$ 以一對一的方式緊密結合形成的“一階錯合鍵”； b. 鋰離子以較鬆散的方式同時與幾個 $\text{C}=\text{O}$ 形成的“二階錯合鍵”。實驗發現當 $[\text{Li} : \text{O}]$ 當量比大於 0.281 時就會形成二階錯合鍵，在此濃度下過氯酸根離子會逐漸稀釋原有的電解質系統，並同時再與鋰離子結合成過氯酸鋰使得解離度降低。

利用線型不同 C=O 密度的 Polyester 高分子電解質系統做為進一步研究。在本研究中，使用霍氏紅外線光譜探討一系列的 Polyester 高分子電解質。在 80 °C 的霍氏紅外線光譜量測下，吸收範圍在 1800 ~ 1650 cm^{-1} 的 C=O 吸收峰中，可以得到“free/Li⁺ bonded” C=O 吸收率參數。由高斯函數曲線的解析，可以得到 “free/Li⁺ bonded” C=O 吸收率參數是 0.144 ± 0.005 。Li⁺ 離子與 polyester 中的 C=O 有很強的交互作用力，當 Li⁺ 離子的當量分率為 0.28 時，有高達 95% 的 C=O 會跟 Li⁺ 有交互作用的現象。在本研究中，Polyester 電解質的分子結構的立體因素，並沒有影響其中 Li⁺ 與 C=O 之間的交互作用力。



Abstract

The morphology and specific interaction within polymer micro-structure have been a topic of intense interest in polymer science due to their fine application. However, there are many polymer physical properties cannot study from the general instrument, such as intrinsic crystallinity, molecular interaction in quantity so far. It would be a choke point for polymer science to study the molecular structure of polymer in detail.

The Fourier transfer infrared spectroscopy is a powerful tool used to identify the functional group, morphology, and interaction... etc. The FTIR has been widely described in terms of many scientists for a long time. Therefore, in this study, we will choose two systems to study the polymer intrinsic crystallization behavior of syndiotactic-polystyrene and intrinsic interaction within polymer electrolyte by using Fourier transfer infrared spectroscopy. The results in this research have demonstrated it is more in detail that the Fourier transfer infrared spectroscopy could observe the crystallization behavior and interaction with Lithium of polymer matrix.

The experiment work in this dissertation was divided into two areas:

- (1) The first, the crystallinity and crystallization behavior of syndiotactic polystyrene α - and β -crystals have been thoroughly examined using the Fourier Transform Infrared. It is shown that absorptivity ratio of respective absorbances of “ α -crystal/amorphous, a_α ” and “ β -crystal/amorphous, a_β ” can be quantitatively determined using FTIR spectra ranging from 865 to 820 cm^{-1} . Results from curve fitting show that both absorptivity ratios of a_α and a_β are 0.178 ± 0.005 and 0.272 ± 0.005 for α - and β -crystal absorbances, respectively. The crystallization rate and crystallinity of α -crystal calculated from the absorptivity ratios are higher

than that of β -crystal crystallized at 240 °C for the same isothermal duration in *thin* film sample. The formation of β -crystal is thermodynamically more favorable while of α -crystal is kinetically more favorable from FTIR spectra.

Crystallization of α and β -form crystals of syndiotactic polystyrene can be achieved from cold- and melt-crystallization at 264 °C in thin film samples (less than 10 μ m), respectively. The normal crystal transformation of α - to β -form is not found in the *cold*-crystallization in s-PS thin film samples, result in exclusively α -form crystals. This allows to the individual lamellae of α -form crystal to extend continuously with further crystallization time at 264°C in s-PS thin film samples. On the contrary, only β -form crystals are formed in *melt*-crystallization at 264 °C, in either thin film or *bulk* s-PS samples.

(2) The second, the interaction behavior of polymer electrolytes composed of poly (vinyl pyrrolidone) (PVP) and Lithium Perchlorate (LiClO₄) has been investigated in details by solid state NMR and Fourier transfer infrared spectroscopy. It is found that the N atom of the PVP polymer is able to donate its lone pair electrons toward the C=O group and results in higher basicity of the C=O group. The complex bond of Li⁺—C=O is comparted into two types: the tight primary complex bond of Li⁺—C=O; and the secondary complex where Li⁺ loosely complexed with several C=O groups simultaneously. The secondary complex is dominant when the [Li : O] ratio is greater than 0.281. The ClO₄⁻ anion is free in the diluted PVP/LiClO₄ electrolyte. When the LiClO₄ concentration is increased, the ClO₄⁻ anion will interacts with both N quasi-cation and/or Li⁺ cation. Solvated Li⁺ and “free” ClO₄⁻ ions are more favorable in diluted electrolyte; whereas neutral solvation—shared ion pair formation increases the incremental addition

the LiClO₄.

Take polyester electrolyte system as further study. Characterization and interaction behavior between Li⁺ ion and C=O groups of a series polyester electrolyte have been thoroughly examined using Fourier Transform Infrared (FTIR). The “free/Li⁺ bonded” C=O absorptivity coefficient of the LiClO₄/Polyester can be determined quantitatively using FTIR spectroscopy ranging from 1800 to 1650 cm⁻¹ at 80°C. Results from curve fitting show that the “free/Li⁺ bonded” C=O absorptivity coefficient is 0.144 ± 0.005. The ion shows a strong interaction with the C=O group of polymer electrolyte; and a limit value of 95% “Li⁺ bonded” C=O is approached in the polymer electrolyte system when the Li⁺ ion equivalent fraction is about 0.28. The molecular structure of polyester electrolyte does not affect significantly the efficiency of interaction between Li⁺ ion and C=O.

