

Chapter VI General Conclusions

We have described, in this dissertation, crystallization behavior of syndiotactic-polystyrene (s-PS) and interaction mechanism of Li ionic within polymer electrolyte by using FTIR spectroscopy as followings:

1. The unique crystalline pattern absorption of syndiotactic-polystyrene is located at fingerprint region ($940\sim 820\text{ cm}^{-1}$) in FTIR spectroscopy with weak absorption. Each of the two individual absorption of crystal patterns (α , β type crystal) and amorphous pattern is easy to be identified from FTIR spectroscopy. The absorptivity ratios of “ α -crystal/amorphous” and “ β -crystal/amorphous” can be obtained from FTIR spectra. From the absorptivity ratios, it is possible to calculate the crystallinity of α - and β -crystals and sorts out their crystallization behavior in quantitative manner. The absence of crystal transformation of α - to β -crystal provides a convenience way to study the crystallization behavior and crystallinity of s-PS.

The absorptivity ratio of respective absorbances of “ α -crystal/amorphous— a_α ” and “ β -crystal/amorphous— a_β ” are found to be 0.178 ± 0.005 and 0.272 ± 0.005 , respectively. The α -crystal is more kinetically favorable and the β -crystal is

more thermodynamically favorable.

Based on the above result of absorptivity ratio, it is possible to study the different crystalline behavior of syndiotactic-polystyrene between *bulk* and *thin film*

sample from FTIR spectroscopy. 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 cannot overcome, possibly owing to the physical

hindrances in very thin film samples, therefore, such a transformation of crystal

form is inhibited.

2. The interaction behavior between C=O contain polymer electrolyte (PVP) and

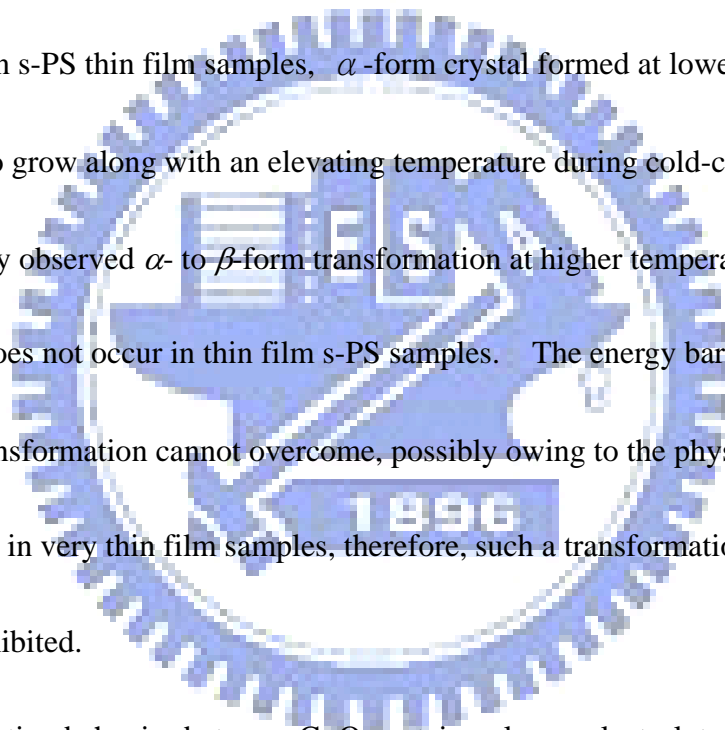
LiClO₄ salt is demonstrated from the FTIR spectroscopy. It is found that a direct

evidence to support the proposed ionic interaction behavior in solid state polymer

electrolyte from FTIR spectroscopy. The N atom within PVP is able to donate its

electron to increase the basicity of the C=O to interact with Li⁺ ion. It implies that

the solvated Li⁺ cation ion and the “free” ClO₄⁻ anion are favored in the diluted



LiClO₄ salt electrolyte; whereas the solvation—shared ion pair is formed in the concentrated LiClO₄ salt electrolyte.

FTIR spectroscopy can be used to identify and quantify the interaction between Li⁺ and C=O in different linear solid polymer electrolytes within various LiClO₄ concentrations. The band corresponding to “Li⁺ bonded” C=O group (1705 cm⁻¹) is shifted from the band of “free” C=O group (1730 cm⁻¹) in FTIR spectroscopy.

The absorptivity coefficient of respective absorbances of “free/Li⁺ bonded” C=O is found to be 0.144 ± 0.005 . From the absorptivity coefficient, it is found that the sensitivity of “Li⁺ bonded” C=O group band in FTIR spectroscopy is significantly higher than that of the “free” C=O group. Based on this result, it is possible to study the behavior mechanism of Li⁺ within polyester base polymer electrolyte from FTIR spectroscopy directly.

3. Based on the above result, we can study in detail the polymer crystallization behavior and Lithium ion interaction behavior within polymer. In this study, it has been proved a further application of FTIR.

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Publications

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