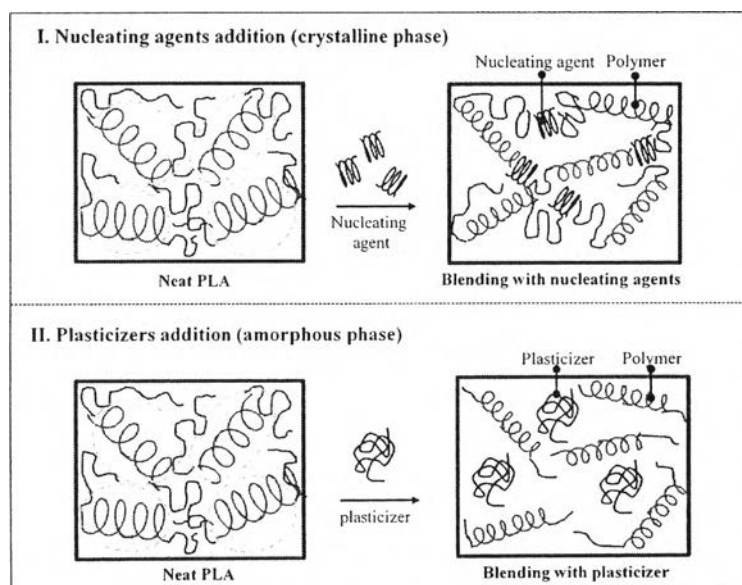


CHAPTER I

INTRODUCTION

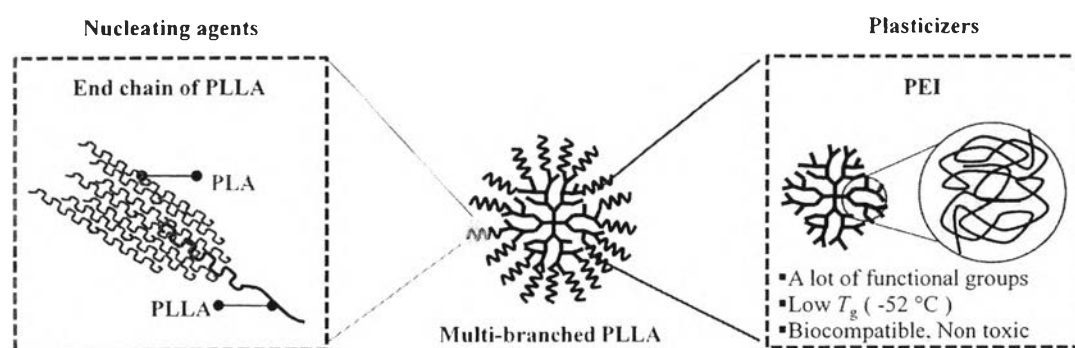
In recent years, biodegradable polymers are of interests because they are obtained from renewable resources and can be used as environmental friendly materials. The most reliable biodegradable polymer is poly(*L*-lactic acid) (PLLA) (Pillin *et al.*, 2006) since it is the only biodegradable polymer obtained from a complete industrial scale production using renewable resources. As PLLA is an aliphatic polyester, PLA products can be made in various forms, such as films, sheets, plates, fibers, etc., through different processing techniques of film blowing, sheet casting, injection moulding, tray thermoforming, spun-bond fiber spinning, etc. It should be noted that PLLA has an extremely slow crystallization rate which leads to the product brittleness, low impact resistance and time consuming production, in comparison with other commercial petrochemical-based polymers such as polyethylene (PE), polypropylene (PP) (Kim *et al.*, 2010). Theoretically, Avrami crystallization rate constants (k_a) of high-density polyethylene (HDPE) at 120 °C was 1.21 whereas k_a of PLA was only 0.01573 min⁻¹, approximately 1/70 times of HDPE (Sobkowicz *et al.*, 2008; Suryanegara *et al.*, 2010).

Scheme 1.1 Practical approaches for PLA crystallization improvement.



The crystallization rate and free volume of PLLA can be enhanced significantly by blending both nucleating agents and plasticizers with PLA. The effective nucleating agents reported in the past were starch (Cai *et al.*, 2011), talc (Li and Huneault, 2007), and calcium carbonate (CaCO_3) (Suksut and Deeprasertkul, 2011). Meanwhile, many polyols were utilized as plasticizer such as PEG (Hu *et al.*, 2003), and Glycerol (Li and Huneault, 2011). Scheme 4.1 shows a graphical abstract of methods to improved crystallization rate of PLA. As the fact that the main disadvantage of those nucleating agents and plasticizers is the phase separation from PLLA. Basically, the crystallization of short chain polymers is faster and more effective than the longer ones. In order to accelerate crystallization completely in short time, the short chain PLLA is an attractive candidate. Here, we consider the short chain PLLA as nucleating agent for not only helical crystalline structure formation in a short time but also effective induction of co-crystallization with long chain PLLA at the same time.

Scheme 1.2 Crystallization based on multi-branched PLLA.



Therefore, the present work proposes the molecular design and synthesis of multi-branched PLLA with dual function as both nucleating agent and plasticizer for PLLA. Scheme 4.2 shows how multi-branched PLLA induces helical crystalline phase and increases free volume of PLA simultaneously. It can be expected that multi-branched core molecules intrinsically create amorphous phase while their PLLA arms initiate crystalline phase in the system.