CHAPTER II
BACKGROUND AND LITERATURE REVIEW

The biodegradable polymers (poly(ε-caprolactone), poly(DL-lactide), and polycaprolactam) are the most interested in the recent. There has been much research to improve and generate new type of materials such as changing the chemistry and architecture of main chain polymers, increasing or reducing the percentage of graft polymers, etc. Most poly(ε-caprolactone) were used to graft on various polymers, e.g. aliphatic polyester-grafted starch by in situ ring-opening polymerization (ROP) of ε-caprolactone (Duboisa *et al.*, 1999), and aliphatic polyester-grafted starch-like polysaccharides by ring-opening polymerization (Cretua *et al.*, 2004). For poly(DL-lactide), a brush-like poly(DL-lactide) grafted onto chitosan backbone was investigated. The graft copolymerization was carried out with triethylaluminum as catalyst in toluene at 70 °C (Wu *et al.*, 2005). . It was found that the greater lactide content in the feeding ratio (Liu *et al.*, 2004), the more water soluble chitosan (CS) derivatives (containing polylactide unit) were synthesized by reacting DL-lactide (DLLA) to chitosan in dimethyl sulfoxide solution with triethylamine. Studying about polycaprolactam, are found that the anionic polymerization of caprolactam in the presence of polystyrene-ethyl acrylate copolymer was chosen as the preparative route. The reasons for the choice were (1) the fact that ester groups are known to be good initiators for the lactam polymerization and (2) that it has been previously established that uniform copolymers can be obtained from styrene and acrylate esters (Matzer *et al.*, 1973). Testing was used to verify the in situ formation of polyethylene-g-nylon 6 graft copolymers bridged by maleic anhydride in the melt-blending process (Li *et al.*, 1998).

Graft copolymers are important polymeric materials, which possess a number of variable molecular parameters, such as main- and side-chain polymer type, degree of polymerization of the main chain, grafting density and graft length. Using special polymerization techniques, graft copolymers with defined structures can be prepared. Three main strategies are usually used for the synthesis of graft copolymers (**Figure 2.1**): (i) "grafting through" method (or macromonomer method) is one of the simplest ways to synthesize graft copolymers. Typically a low molecular weight monomer is radically copolymerized with a methacrylate functionalized macromonomer. This method permits incorporation of various macromonomers such as polyethylene, poly(ethylene oxide), polysiloxanes, poly(lactic acid), polycaprolactone into a polystyrene or polymethacrylate backbone. Moreover, it is possible to design well-defined graft copolymers by combining the "grafting through" method and controlled radical polymerization (CRP). This combination allows control of polydispersity, functionality, copolymer composition, backbone length, branch length and branch spacing; (ii)"grafting-onto", where an ω-functional or living polymer with reactive end group is coupled with reactive groups on another polymer; (iii)"grafting-from", is found when a multifunctional polymeric precursor with predetermined initiation sites is used to initiate polymerization of a second monomer. In the “grafting-from” method, different polymerize mechanisms can be applied to the build-up of the grafts; among them, anionic, controlled/ “living” radical, coordination-insertion ring opening and cationic mechanisms have been mostly applied.

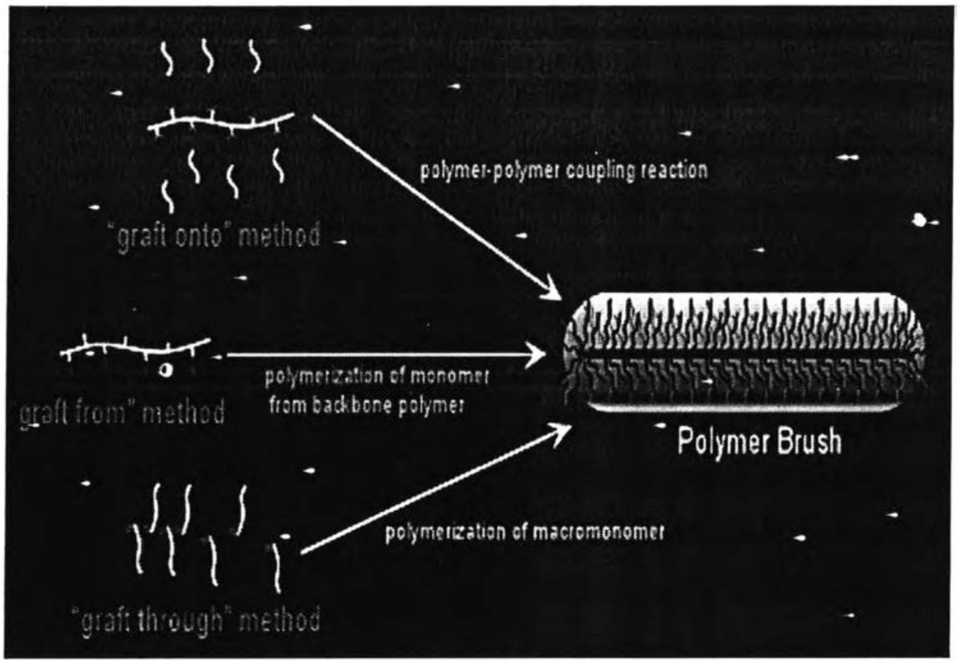

Figure 2.1 Grafting method.

Polymer grafting on PS can be carried out by several methods. Janata *et al.* (2001 and 2003) use the Friedel-Crafts acetylation of PS as the first step for functionalization acetyl group to benzene ring. In the second step, they accomplished reduction of carbonyl groups to secondary hydroxyl groups followed by grafting of polymers via ring opening polymerization. Li *et al.* (2004) described that starting Friedel-Crafts acetylation of polystyrene led to the polymer ring substituted with acetyl group. In the second step, polymer anion (polystyrene) attacked at carbon position of carbonyl group. Kee *et al.* (2002) showed grafting poly(2-vinylpyridene) on polystyrene via chloromethylation reaction. This reaction is danger because dichloromethyl causes cancer disease.

In this work, the main chain polymer was synthesized from polystyrene backbone followed by grafting with DL-lactide or ε-caprolactone or caprolactam via Friedel-Crafts acetylation of polystyrene; i.e. benzene ring substituted with acetyl groups (Janata *et al.*, 2001), and ring-acetylated polystyrene was reduced to hydroxyl substituted which was then grafted with DL-lactide or ε-caprolactone or caprolactam (Janata *et al.* 2003) via ring opening. Slomkowski *et al.* (1998 and 1999) showed that ε-caprolactone can polymerize via cationic, anionic or pseudoanionic. For polymerizations of DL-lactide, the most widely used initiator was tin(II) 2-ethylhexanoate (stannous octoate), in order to obtain high molecular weight polymer. Side reaction (intermolecular and intramolecular) could be occurred and resulted in a broadening of the molecular weight distribution.

NMR is the general technique for characterization of new synthesized polymers. NMR data can reveal structure of polymer, grafting percentage of polymer, degree polymerization, etc. The characteristic of NMR spectrum is depended on the grafting ratio, temperature and solvent (Tajouri *et al.*, 2003). Li *et al.* (2004) used ^{1}H NMR to determine acetylation level (%mol) from acetyl coupling sites randomly distributed on polystyrene substrate. The calculation of the graft copolymer constitution can be carried out by NMR using the degree of polymerization of the employed macromonomer and the ratio of the proton signal of the comonomer in the graft copolymer (Schaller *et al.*, 1999). Kohori *et al.* (1988) showed the ratios of poly(N-isopropylacrylamide) to poly(DL-lactide) blocks analyzed by the area of two peaks from NMR spectrum (poly(N-isopropylacrylamide) and DL-lactide at $\delta = 4.0$ and 5.2 ppm, respectively).

Dubis *et al.* (1999) described that HATR FT-IR was convenient and a rapid method of preliminary evaluation of surface plant material composition, especially for esters, ketones and aldehydes. Based on IR spectra (Liu *et al.*, 2004), the band that appeared in the copolymer at ~1758 cm^{-1} was assigned as the carbonyl group of the branched polylactide. The ~1188 and ~1215 cm^{-1} doublets observed in the copolymer are assigned to the symmetric C-O-C stretching modes of ester group. Chen *et al.* (2004) showed that poly(ε-caprolactone) has a characteristic peak at ~1730 cm^{-1}.

Liu *et al.* (2004) showed that a brush like poly(DL-lactide) grafted onto chitosan as the backbone was synthesized using triethylaluminium as catalyst in toluene at 70°C. It was found that a greater lactide content in the feeding ratio results in a higher grafting percentage. A copolymer has a definite melting point and the ΔH of the copolymers increases with the feed ratio of lactide to chitosan. Moreover, the grafting percentage was defined by

Grafting percentage(%) = [(graft copolymer(g) – chitosan(g))/chitosan(g)] x 100%

Glass transition temperature (T_g), melting temperature (T_m) and enthalpy of melting (ΔH_m) were characterized by DSC. Poly(ε-caprolactone) has $T_g = -68°C$, $T_m = 53\text{-}60°C$ and $\Delta H_m = 47\text{-}67$ J/g (Huang *et al.*, 2004, Chen *et al.*, 2003 and Maio *et al.*, 2004). Poly(DL-lactide) has $T_g = 57.3°C$, $T_m = 175.1°C$ and $\Delta H_m = 39.7$ J/g (Chen *et al.*, 2003). Nylon6 has $T_m = 223°C$ (Jiang *et al.*, 2005). Degradation temperature was characterized by TGA analysis. Chen *et al.* (2003) found that thermal onset degradation temperatures were determined for poly(DL-lactide) to be at 308.8°C and poly(ε-caprolactone) to be at 358°C.

Tomita, *et al.* (2004) found that poly(L-lactide) film was degraded and investigated by total organic carbon (TOC) concentration.

The most popular liquid chromatographic technique for polymer characterization is size exclusion chromatography (SEC). As known, SEC separates macromolecules according to their size in solution. Size of copolymer species depends on their molar mass, chemical structure and architecture. Capek, *et al.*

(2000) observed that retention volume of polystyrene-graft-poly(ethyleneoxide) copolymer corresponded solely to the SEC retention of second kind of chains(graft or main chain). Block and graft copolymer of styrene-maleic anhydride copolymer and polyamide66 were investigated by GPC that showed hydrodynamic volume of the latter was higher than the former (Jeon *et al.*, 2004).