

## CHAPTER I

### INTRODUCTION

In recent years, many scientists paid their great attention to create specialized copolymers of various architectures for new properties. One kind of the most attractive copolymers is graft copolymers due to that the graft copolymers exhibit good phase separation and have been used for a variety of applications, such as impact resistant plastics, thermoplastic elastomers, compatibilizers, and polymeric emulsifiers, hydrogels, drug delivery polymers, gas permeation membranes. On the other hand, graft copolymers generally have lower melt viscosities due to their branched structure, which is advantageous for processing. Since graft copolymers have many structural variables (composition, backbone length, branch length, branch spacing, etc.), they have great potential to realize new properties. To realize graft copolymers with specific properties, the structural variables of graft copolymers must be considered. By so far, many structural variables of graft copolymers, such as composition, backbone length and branch length can be easily controlled, however, branch spacing length and the grafting positions of the side chains are very difficult to control even using living polymerization method.

It was reported that the macromonomer method is one of the useful ways to prepare graft copolymers, in which the composition, backbone length, branch length, grafting sites and branch spacing length of graft copolymers can be controlled. However, the macromonomer method is still deficient in controlling the spacing length and grafting sites. The spacing distribution is determined by the reactivity ratios of the macromonomer and the low molecular weight comonomer. The reactivity ratios are influenced by many factors especially (1) the inherent reactivity of the macromonomer and the comonomer based on their chemical structure, (2) the diffusion or kinetic excluded volume associated with the large size of the macromonomer, and (3) the potential incompatibility of the macromonomer and propagating comonomer chain due to thermodynamic repulsive interactions.

Amphiphilic graft copolymers are conveniently prepared in solution or disperse media by the functional copolymerization of a hydrophobic macromonomer

and hydrophilic comonomer. These materials are of great interest because of their surface-active properties.

Polystyrene (PS) plastic is among the most dominant packaging materials in today's society and is not capable of self-decomposition. Like other packaging products, when products from PS reach the end of their useful life, most are discarded in open dumps, landfills, or as simple litter. For a polymer to be degradable, a side chain or main chain with a hydrolyzable group must be present and accessible. Plastic degradability has been introduced as a method to solve the disposal problem of plastics. Extensive studies are being carried out to develop plastics that are either photodegradable or biodegradable. This is being done either by the use of additives or by the development of new or modified structures that are degraded by various mechanisms.

Poly lactide and poly( $\epsilon$ -caprolactone) are family of biodegradable and biocompatible polymers that have been widely used in biomedical applications, such as absorbable sutures, sustained drug delivery systems, implants for orthopedic devices and absorbable fibers. Polyamides are engineering plastics with various commercial applications due to their outstanding properties.

In the "grafting-from" method, different polymerization 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.

Carbonyl functionalities are well-known for their addition reaction with nucleophilic compounds such as Grignard reagents and other reactive anions. Acylation of polystyrene was considered as a path for the introduction of coupling sites for macroanions in this study. The acylation of polystyrene is conveniently carried out with propionyl chloride in the presence of a Lewis acid (e.g.,  $\text{AlCl}_3$ ) in nitrobenzene.

We focus on the synthesis of graft copolymers by ring-opening (ROP) process using appropriate copolymers, functionalized with secondary hydroxyl groups along the polymer chain, as multifunctional initiators. Thus, the first aim of our study was to synthesize suitable macroinitiators. Chain-shortened polystyrene (PS) was used as a starting material, and functionalized by introducing the 1-

hydroxypropyl functionality into the benzene rings of PS. Then, the ROP of  $\epsilon$ -caprolactone or DL-lactide or caprolactam initiated with the hydroxyl group was followed as a “grafting-from” fashion. Lastly, copolymers were synthesized in many ratio (PS: grafting polymer) that were 1:1, 1:2 and 1:3. In this paper, the synthesis and characterization of the obtained graft copolymers were described.