

CHAPTER 4

CONCLUSIONS

The problem using the PTOL as star-core initiator for the ROP of ϵ -caprolactone (CL) to controlled polymer molecular weight is the difficulty of dissolving PTOL in CL monomer and the steric hindrance of PTOL initiating led to imperfect 4-arm star-shaped poly(ϵ -caprolactone) (PCL). In this research, the star-shaped PCL was synthesized using a novel pentaerythritol tetrakis(6'-hydroxyhexanoate) star-core macroinitiator. The route of synthesis for star-shaped PCL in this study was the core-first method where polymer chains were grown directly from a multifunctional core. The effects of differing molecular architecture on the thermal, morphological, mechanical and rheological properties and *in vitro* hydrolytic degradation studies of linear and star-shaped PCLs were investigated.

Most of the results presented in the Chapter 3 have already been discussed in detail. This final Chapter 4 of this thesis now aims to bring together the main conclusions and correlate them as far as possible. These conclusions can be summarized as follows:

4.1 Synthesis of Pentaerythritol tetrakis(6'-hydroxyhexanoate) Star-Core Macroinitiator

Novel pentaerythritol tetrakis(6'-hydroxyhexanoate) as star-core macroinitiator can be prepared using CL to cap the OH groups of PTOL in a ratio of 4:1 as shown in Figure 4.1. The synthesis of star-core macroinitiator can be achieved via a sequence

of simple reactions: methanolysis (79%), alcohol protection (92%), hydrolysis (75%), esterification and deprotection (43%) respectively, resulting in colorless oil and a moderate yield of the final product. It could be dissolved in common organic solvents and CL monomer. The chemical structure of star-core macroinitiator was confirmed by IR, NMR and ESI-MS. The IR spectrum shows the absorption peaks of C=O stretching (ester) at 1740 cm^{-1} and O-H stretching (alcohol) at 3400 cm^{-1} . The $^1\text{H-NMR}$ spectrum show $\delta = 3.91\text{ ppm}$ (multiplet), $\delta = 3.67\text{ ppm}$ (triplets), and $\delta = 2.42\text{ ppm}$ (multiplets) ppm. Electrospray ionization mass spectrometry (ESI-MS) data revealed in a signal at 625.3356 m/z ($\text{M} + \text{Na}$) $^+$ of $\text{C}_{29}\text{H}_{52}\text{O}_{12}\text{Na}$.

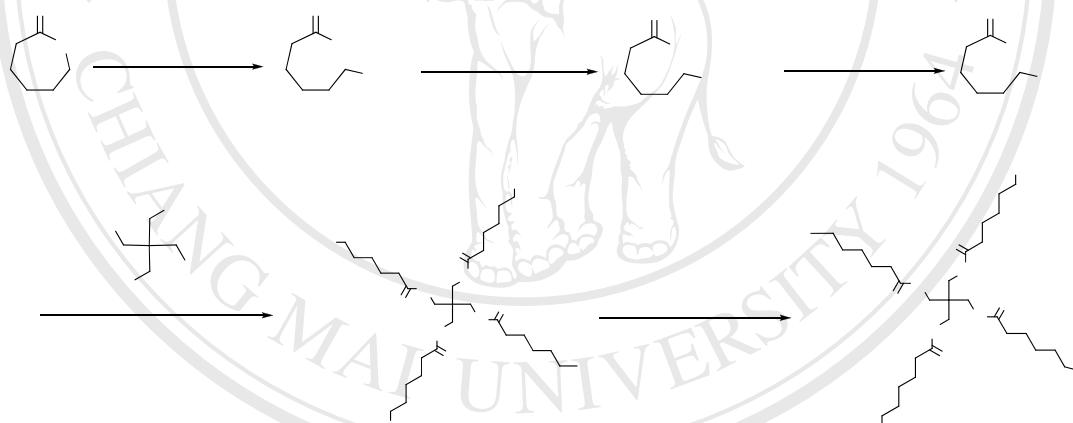


Figure 4.1 Synthesis of pentaerythritol tetrakis(6'-hydroxyhexanoate).

4.2 Synthesis of Low Molecular Weight PCLs Model Compounds with Different Molecular Architectures

Linear and star-shaped low molecular weight PCLs were synthesized using 4 mole% of hydroxyl initiators (1-hexanol, PTOL and star-core macroinitiator) through ROP of CL in the presence of 0.1 mole% stannous octoate as catalyst. Relatively

○

○

○

transmethylation

OMe

alcohol pr

OH

1

2

high amounts of initiators (4 mole%) were used in order to obtain low molecular weight ($\bar{M}_{n,cal} \approx 3,000$) polymers for confirming the structure and evaluate the influence of short-chain branched structure on the properties.

Low molecular weight PCLs with different molecular architectures were characterized by $^1\text{H-NMR}$, DSC and TG analyses. The molecular architectures of the low molecular weight PCLs obtained depended on the functionality of the alcohol used as the initiator. Mono-functional alcohols (1-hexanol) yielded linear polymer, while PTOL and star-core macroinitiator gave star-shaped polymers, as confirmed by their $^1\text{H-NMR}$ spectra. It was found that the average number of hydroxyl groups initiating polymerization, as calculated from the average degree of polymerization per arm (DP_n/arm) determined experimentally by $^1\text{H-NMR}$, were close to the actual hydroxyl functionalities. Subsequently, degree of branching of star polymers can be estimated by comparing the mean-square radii with linear polymer. The branched structures contained some arm defects as evidenced on the $g^{1/2}/g'$ values, where $g^{1/2}$ and g' denote the ratios of mean-square radius of gyration and intrinsic viscosity of branched and star-shaped polymers to those of a linear structural reference with similar absolute molecular weight. It could be seen that the $g^{1/2}/g'$ value of star-shaped PCL_macroinitiator (0.98) was very close to 1.0 for an ideal star-shaped polymer with perfect arm architecture. Deviations from this relationship for PCL_PTOL (0.88) would point to steric hindrance of PTOL initiating led to imperfect star-shaped polymer.

The DSC and TG results showed that the star-shaped PCLs had lower melting temperatures, degrees of crystallinity and decomposition temperatures than the linear PCL. The thermal properties will be affected when branching points are introduced into

the polymer. The reduction in melting point with branching (more steric architecture) is attributed to shorter chain length and the increase in the number of free chain ends, which disrupts the orderly fold pattern of the crystal. Also, the melting peaks of star-shaped PCL initiated by star-core macroinitiator could not be observed. It can ascribe to the relatively slow crystallization rate and the amorphous phase in the sample increased. The lower melting temperatures and lower degradation temperatures of the star-shaped polymers widen the “processing window”, an important advantage in the melt processing of PCL. As would be expected, the short chain branches mostly affect the thermal properties and crystallinity. This offers the possibility of being able to adjust the crystallinity by varying the shape of the polymer molecules, thus providing a useful means of controlling polymer properties and can be utilized and optimized for each application.

4.3 Effect of Molecular Architectures on the Properties of High Molecular Weight PCLs and PLLs

To study the effect of molecular architecture on the polymer properties (thermal, crystallinity, mechanical and rheological properties and *in vitro* hydrolytic degradation), the high molecular weight linear and star-shaped PCLs and PLLs were synthesized by using 1-hexanol, PTOL and star-core macroinitiator.

From the dilute-solution viscometry results, it was found that star-shaped PCLs exhibited lower intrinsic viscosities than linear PCL at same molecular weight (\bar{M}_n), supportive of the expected star-shaped structure. This is due to the fact that intrinsic viscosity reflects the chain conformation of the polymer in dilute solution.

The star-shaped PLL occupies a smaller hydrodynamic volume in solution than the linear PLL at the same molecular weight.

The melting temperatures (T_m) and degree of crystallinity of star-shaped PCLs (PCL_PTOL and PCL_macroinitiator) are slightly lower than that of linear (PCL_1-hexanol). The results seem to suggest that the crystallization rearrangement of polymer chain ends is interrupted by the highly branched architecture of these polymers. In theory, short-chain branching influences thermal behavior and mechanical properties and limit chain crystallization, while long chain branching is utilized to control the rheological properties. DSC results could be combined with TG data for defining the melt processing range of polymers and it was found that the star-shaped PCLs can be processed at lower temperature than their linear counterparts because lower T_m and lower T_d , which could be advantageous, especially in the melt processing of thermo-labile polyesters.

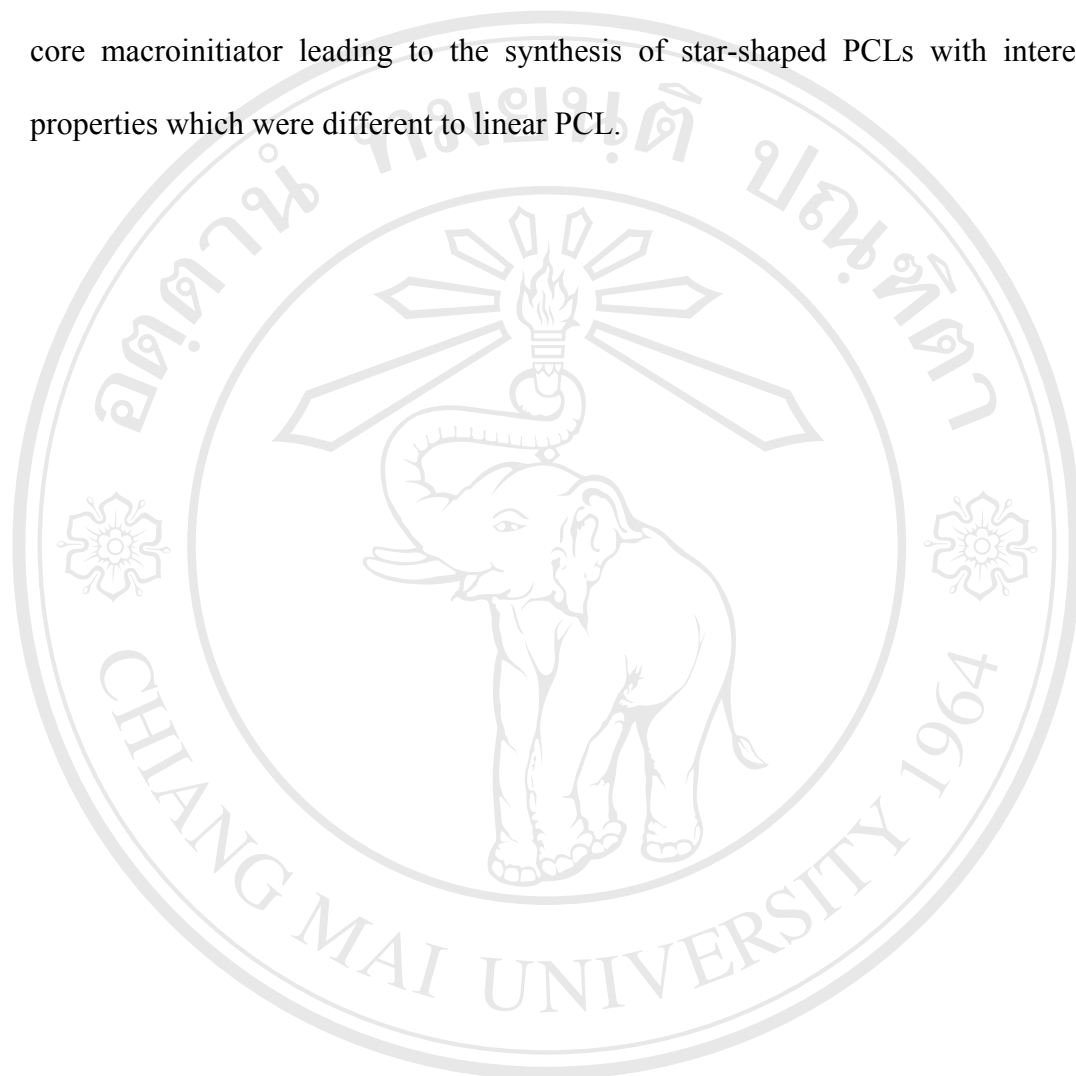
The effects of molecular architecture of PCLs on the rheological properties were also found. All of linear and star-shaped PCLs exhibit a clear zero shear viscosity (η_0) followed by a shear thinning region at high shear rate. The η_0 of linear PCL_1-hexanol is higher than star-shaped PCL_macroinitiator at low shear rate. The expected behavior for a material with long chains is evident. It is generally found that the η_0 decreases as short chain are added to a polymer backbone. The reason for these phenomena is that the overall size is decreased. The lower η_0 of star-shape PCL_macroinitiator, which can be utilized in melt processing at lower temperature.

The hydrolytic degradation of linear and star-shaped PCLs and PLLs were also investigated. At the same polymer molecular weight, linear and star-shaped PCLs and PLLs films has been subjected to *in vitro* biodegradation in a phosphate

buffer saline (PBS) solution at pH 7.40 ± 0.01 as an immersion medium at body temperature $37 \pm 1.0^\circ\text{C}$ for 21 weeks. The weight loss, pH and thermal stability changes have been characterized in order to determine the degradation pathway. From the results obtained, the PLL films were still translucent and fixable appear almost unchanged surface interior and weight during the period of study because of the long degradation time. The biodegradation rate of the star-shaped PLL_macroinitiator is faster than imperfect star-shaped PLL_PTOL and linear PLL_hexanol during 21 weeks due to higher density of chain-end of star-shaped PLLs than linear chain of comparable molecular weight. The simple hydrolysis reaction can be acid-catalyzed in the event that the new carboxylic acid end groups formed causes the pH of the medium to drop below 7. The effect of branching leads to a dramatically decreasing of pH values of star-shaped PLL_macroinitiator more than imperfect star-shaped PLL_PTOL and linear PLL. The degradation prefers occur in amorphous region more than crystalline region due to water molecules can penetrate easy in amorphous region. Because of star-shaped had more chain end short chain length due to disordered polymer chains.

Thermal analysis from DSC revealed that the % crystallinity of PLLs films increased during 21 weeks indicated to the molecules in the amorphous region of a polymer were crystallized slowly in immersion medium. In the earlier stage of *in vitro* biodegradation, the low degradation rate of these PLLs occurred with the molecules in the amorphous region were crystallized at the same time. As the time increase, the degradation rate increased, which also could be attributed to water penetrates the polymer matrix and facilitates the hydrolytic chain cleavages.

On the basis of all of these results, it was concluded that the problem of the insolubility and steric hindrance of PTOL could be overcome by using the novel star-core macroinitiator leading to the synthesis of star-shaped PCLs with interesting properties which were different to linear PCL.



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