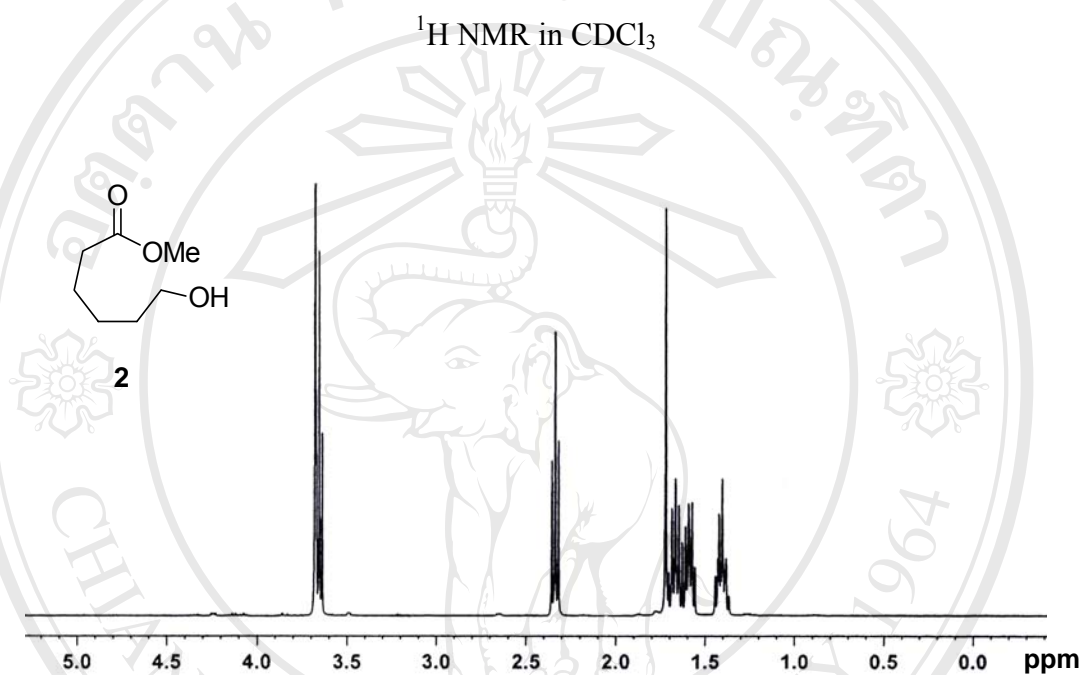


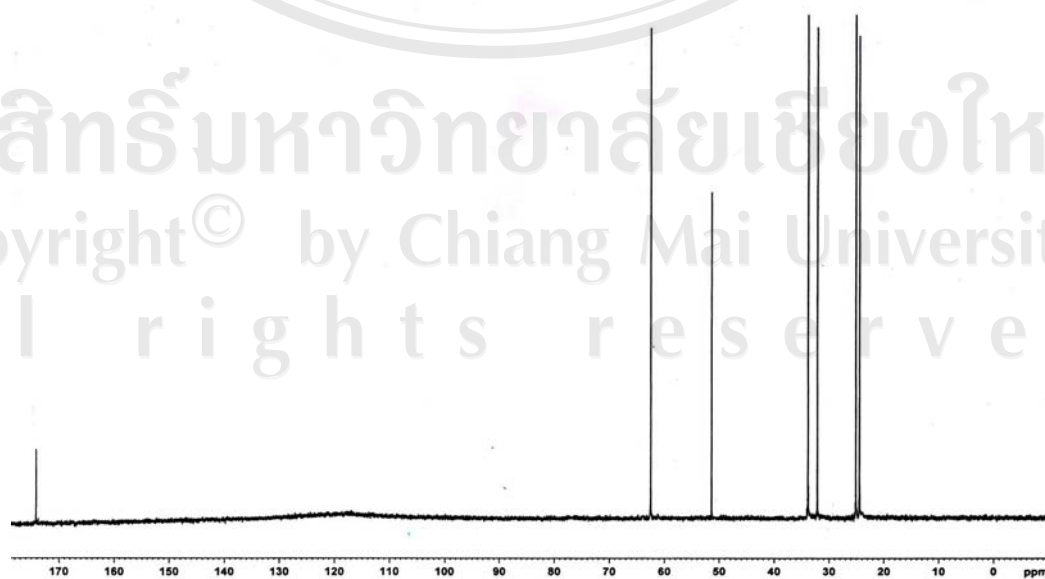
## RELEVANCE OF THE RESEARCH WORK TO THAILAND

In the Biomedical Polymers Technology Unit, Department of Chemistry, Faculty of Science, Chiang Mai University, the possibility is being studied of using novel polyesters based on L-lactide and  $\epsilon$ -caprolactone as biomedical applications such as absorbable nerve guides and drug delivery matrix that are of sufficiently high quality and lower cost in Thailand. The application using “biomedical” polymers range from the long-term, as with a pacemaker casing, to a short-term like a suture. Because of the wide spectra of applications, the rate and extent of degradability of a polymeric biomaterial must be predetermined for each assigned function. Factors influencing the degradability are, for example, chemical structure, copolymer composition, architecture, molecular weight, morphology, surface area and medium character. Branched and star-shaped biodegradable aliphatic polyesters have gained widespread attention due to their unique properties, often differing significantly from their linear counterparts. Structure-property studies have shown that variations in the macromolecular architecture can have substantial effects on the morphological, thermal, rheological and physico-mechanical properties and also on the biodegradability of biomaterials. The main propose of this thesis is to synthesize star-shaped polymer using a novel pentaerythritol tetrakis(6'-hydroxyhexanoate) star-core macroinitiator *via* the ring-opening polymerization of  $\epsilon$ -caprolactone (CL) for use in biomedical applications. The effects of differing molecular architecture on the poly( $\epsilon$ -caprolactone) (PCL) properties of linear and star-shaped PCLs are being investigated.

## APPENDIX

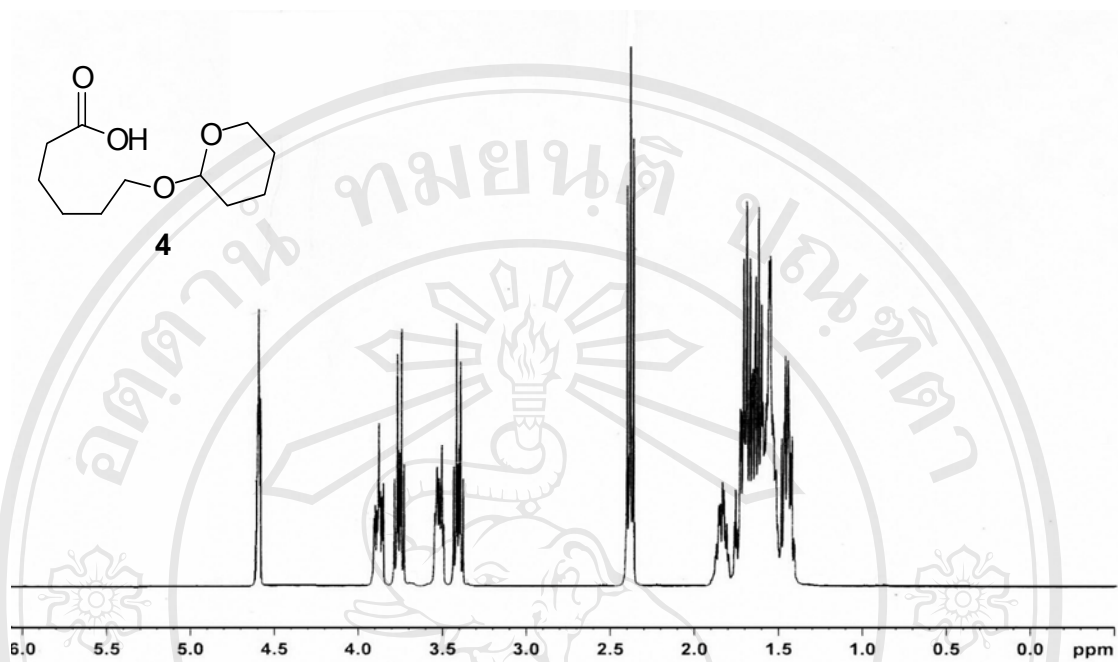
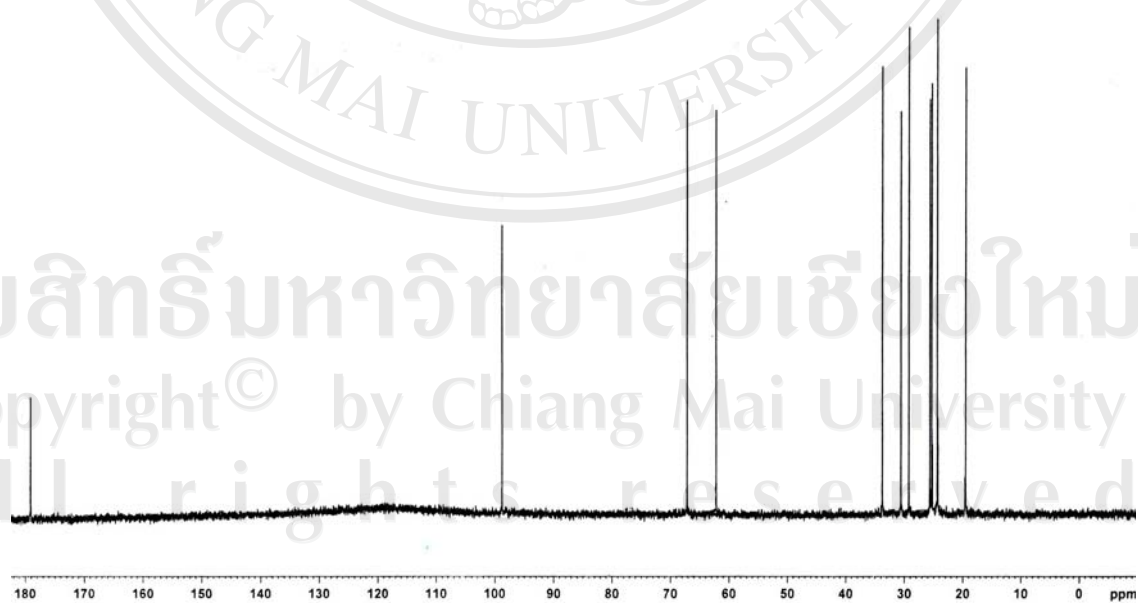
 $^1\text{H}$  and  $^{13}\text{C}$  NMR

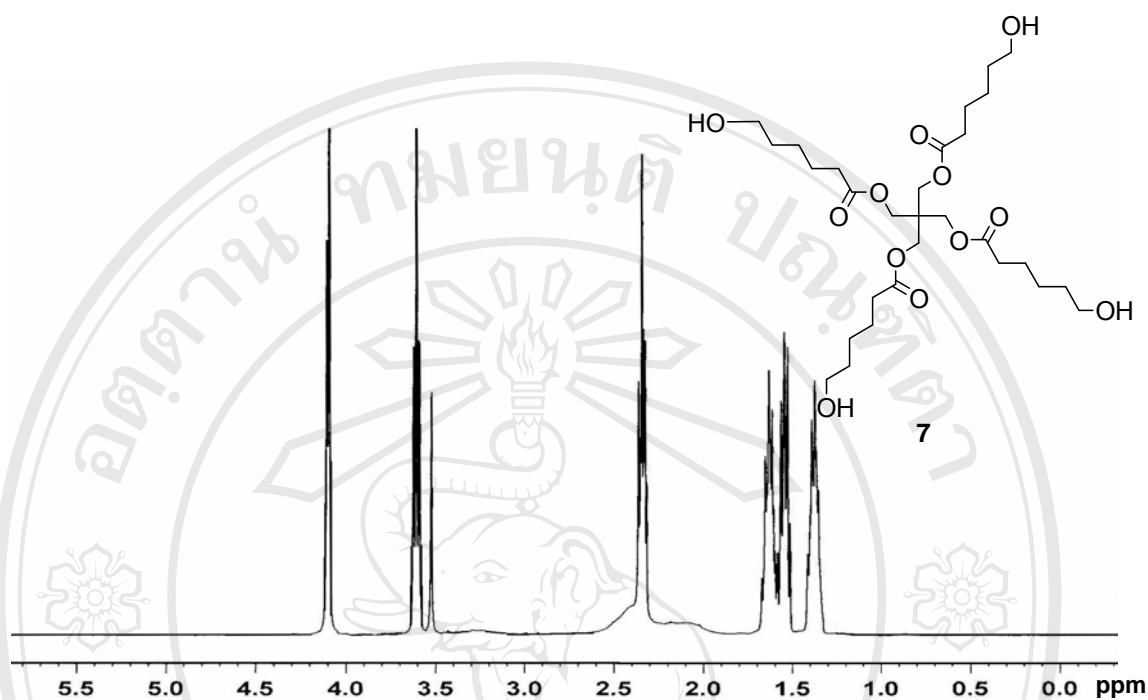
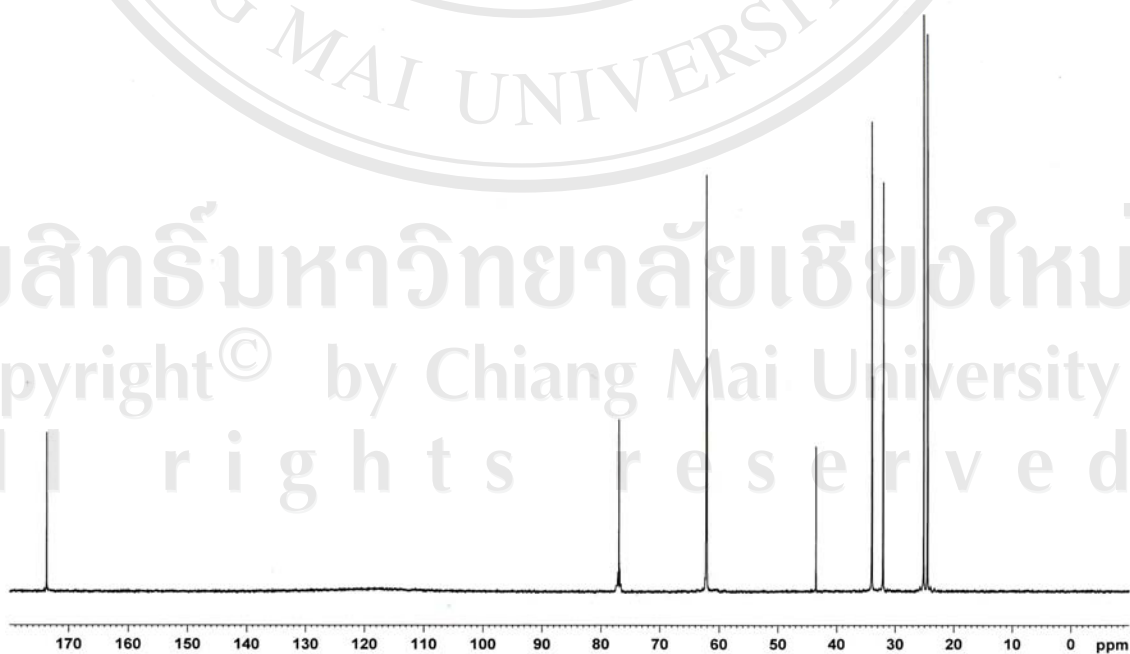
$^{13}\text{C}$  NMR in  $\text{CDCl}_3$



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$^1\text{H}$  NMR in  $\text{CDCl}_3$  $^{13}\text{C}$  NMR in  $\text{CDCl}_3$ 

$^1\text{H}$  NMR in  $\text{CDCl}_3$  $^{13}\text{C}$  NMR in  $\text{CDCl}_3$ 

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## CONFERENCE PRESENTATIONS

### 1. **POSTER PRESENTATION (Extended Abstract)**

**Kathongthung Sawitree**, Punyodom Winita, Molloy Robert and Meepowpan Puttinan, “*Synthesis and Characterisation of Novel Star-Core Macroinitiators for use in the Ring-Opening Polymerisation of  $\epsilon$ -caprolactone*”, **The 5<sup>th</sup> PERCH Annual Scientific Congress (PERCH-CIC CONGRESS V)**, Pattaya, Chonburi, Thailand (2007).

### 2. **POSTER PRESENTATION (Proceeding)**

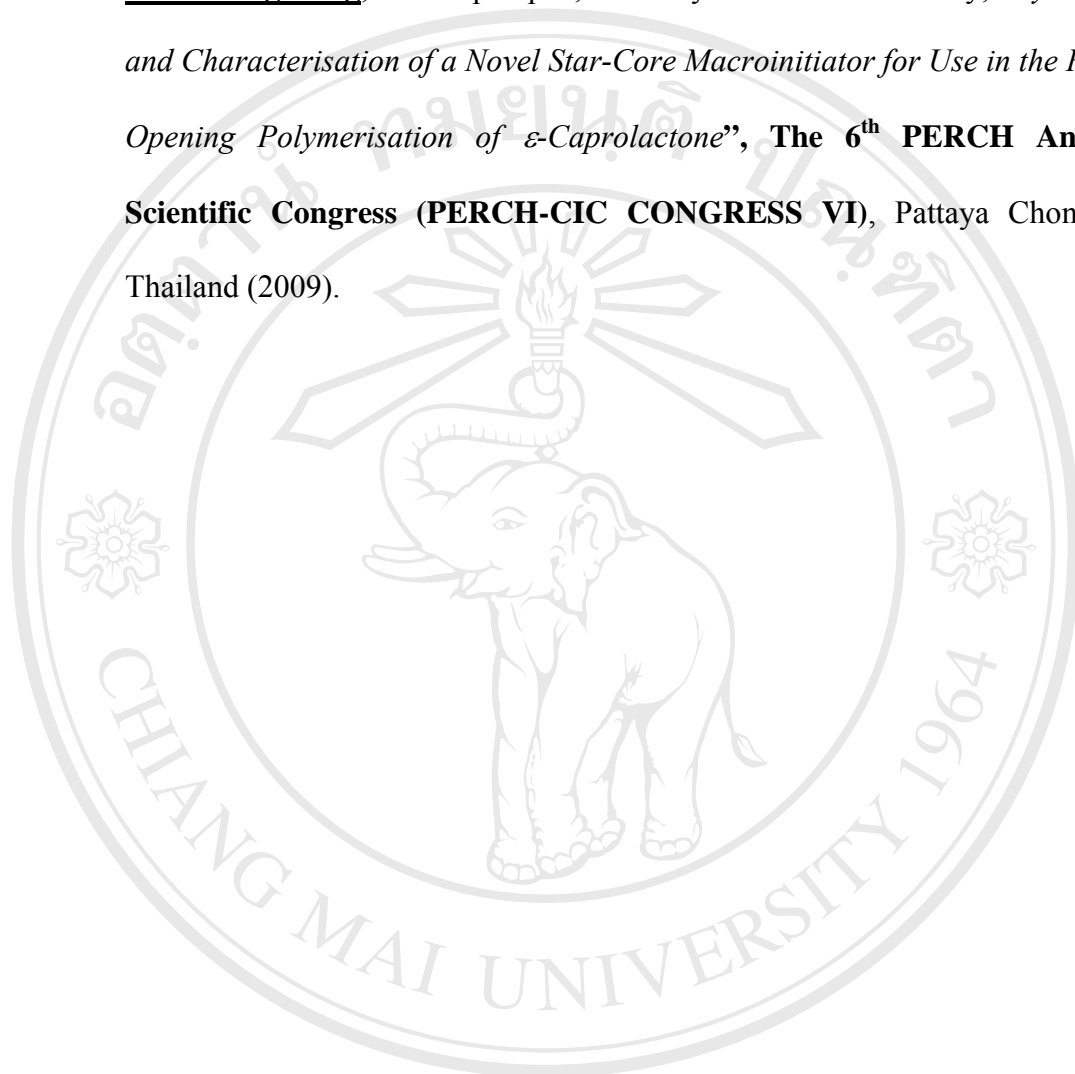
**Sawitree Kathongthung**, Puttinan Meepowpan, Winita Punyodom and Robert Molloy, “*Synthesis and Characterisation of Novel Star-Core Macroinitiators for use in the Ring-Opening Polymerisation of  $\epsilon$ -caprolactone*”, **1<sup>st</sup> Polymer Graduate Conference of Thailand**, Bangkok, Thailand (10-11 May 2007).

### 3. **POSTER PRESENTATION (Proceeding)**

**Sawitree Kathongthung**, Puttinan Meepowpan, Robert Molloy and Winita Punyodom, “*Synthesis and Characterization of Novel Star-Core Macroinitiator for Use in the Ring-Opening Polymerization of L-Lactide*”, **The 2<sup>nd</sup> International Conference on Advances in Petrochemicals and Polymers (ICAPP 2007)**, June 25<sup>th</sup>-28<sup>th</sup> 2007, Bangkok.

4. **POSTER PRESENTATION (Extended Abstract)**

**S. Kathongthung**, P. Meepowpan, W. Punyodom and R. Molloy, “*Synthesis and Characterisation of a Novel Star-Core Macroinitiator for Use in the Ring-Opening Polymerisation of  $\epsilon$ -Caprolactone*”, **The 6<sup>th</sup> PERCH Annual Scientific Congress (PERCH-CIC CONGRESS VI)**, Pattaya Chonburi, Thailand (2009).



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**Kathongthung Sawitree**, Punyodom Winita, Molloy Robert  
and Meepowpan Puttinan

*“Synthesis and Characterisation of Novel Star-Core  
Macroinitiators for use in the Ring-Opening  
Polymerisation of  $\epsilon$ -caprolactone”*

**The 5<sup>th</sup> PERCH Annual Scientific Congress  
(PERCH-CIC CONGRESS V)**

Pattaya, Chonburi, Thailand (2007)

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## Synthesis and Characterisation of Novel Star-Core Macroinitiators for use in the Ring-Opening Polymerisation of $\epsilon$ -caprolactone

**Kathongthung Sawitree,<sup>a</sup> Meepowpan Puttinan,<sup>a</sup> Punyodom Winita<sup>a</sup> and Molloy Robert<sup>a</sup>**

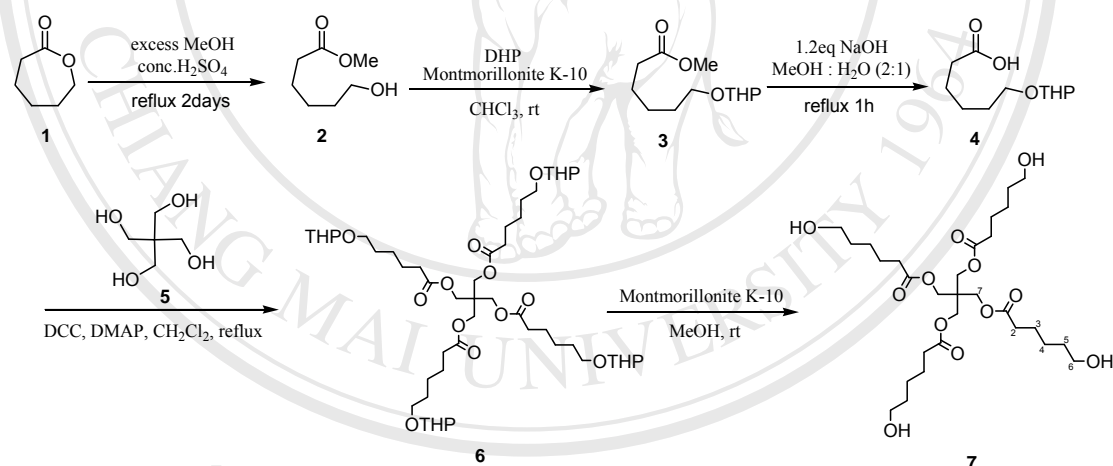
<sup>a</sup>*Department of Chemistry, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand*

### Objective

The main objective is to synthesize pentaerythritol tetrakis(6'-hydroxyhexanoate), **7**, as a star-core macroinitiator for use in the ring-opening polymerization (ROP) of  $\epsilon$ -caprolactone.

### Methods

Methyl 6-hydroxyhexanoate, **2**, was prepared by methanolysis of  $\epsilon$ -caprolactone, **1**, using sulfuric acid as a catalyst. Protection of alcohol group as compound **2** with dihydro(2H)pyran in refluxing chloroform using montmorillonite K-10 as catalyst gave methyl 6-(tetrahydro-2H-pyran-2-yloxy)hexanoate, **3**, which was hydrolyzed by methanol with sodium hydroxide to give 6-(tetrahydro-2H-pyran-2-yloxy)hexanoic acid, **4**. Pentaerythritol, **5**, with N,N'-dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP) in refluxing chloroform, and then deprotected of alcohol in methanol and montmorillonite K-10 as a catalyst.



### Results

The star-core macroinitiator, **7** was successfully synthesized via methanolysis (79%), alcohol protection (92%), hydrolysis (75%), esterification and deprotection (43%) respectively.

### Conclusion

The synthesis of the star-core macroinitiator, **7** can be achieved via a sequence of simple reaction: methanolysis, alcohol protection, hydrolysis, esterification and deprotection, resulting in a moderate yield of the final product. In further work, star-shaped poly( $\epsilon$ -caprolactone) (PCL) will be synthesized using the star-core macroinitiator **7** and its properties will be compared with linear PCL synthesized using 1-hexanol instead of PTOL.

**Keywords:** macroinitiators, pentaerythritol, pentaerythritol tetrakis(6'-hydroxyhexanoate) star-shaped poly( $\epsilon$ -caprolactone)

### Selected Reference:

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2. Guohua Jiang; Liwang; Wenxing Chen. *European Polymer Journal* **2006**, 42, 3333-3340.

**Sawitree Kathongthung**, Puttinan Meepowpan, Winita

Punyodom and Robert Molloy

*“Synthesis and Characterisation of Novel Star-Core  
Macroinitiators for use in the Ring-Opening  
Polymerisation of  $\epsilon$ -caprolactone”*

**1<sup>st</sup> Polymer Graduate Conference of Thailand**

Bangkok, Thailand (10-11 May 2007)

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## Synthesis and Characterization of Novel Star-Core Macroinitiator for Use in the Ring-Opening Polymerization of $\epsilon$ -Caprolactone

Sawitree Kathongthung, Puttinan Meepowpan, Robert Molloy and Winita Punyodom\*  
 Biomedical Polymers Technology Unit, Department of Chemistry, Faculty of Science, Chiang Mai  
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### Abstract

Novel pentaerythritol tetrakis(6'-hydroxyhexanoate) (**4**) has been synthesized from  $\epsilon$ -caprolactone (**1**) as a star-core macroinitiator for use in the ring-opening polymerization (ROP) of cyclic esters. Compound **2** was prepared by methanolysis of **1**, with protection of the alcohol group by dihydro(2H)pyran, and hydrolysis to give the ether acid in high yield. The ether acid could then be reacted with pentaerythritol (PTOL, **3**) to give the star-core macroinitiator **4** in moderate yield which, in turn, could then be used to synthesize star-shaped poly( $\epsilon$ -caprolactone) (PCL) via the ROP of  $\epsilon$ -caprolactone (CL) in bulk using stannous octoate as an initiator. The microstructure of the PCL obtained was characterized by means of  $^1\text{H-NMR}$ , gel permeation chromatography (GPC), dilute-solution viscometry and differential scanning calorimetry (DSC) and its properties compared with linear PCL synthesized using 1-hexanol. The effect of chain architecture on polymer properties is discussed.

**Keywords:** linear and star-shaped poly( $\epsilon$ -caprolactone), macroinitiator, pentaerythritol (PTOL), pentaerythritol tetrakis(6'-hydroxyhexanoate), polymer properties

### 1. Introduction

Branched and star-shaped biodegradable aliphatic polyesters have gained widespread attention due to their unique properties, often differing significantly from their linear counterparts. Structure-property studies have shown that variations in the macromolecular architecture can have substantial effects on the morphological, thermal, rheological and physico-mechanical properties and also on the biodegradability of biomedical materials such as absorbable surgical sutures, absorbable nerve guides, drug delivery systems and internal bone fixation devices [1]. Nowadays, the ROP of lactones is the method of choice for the production of biodegradable polymeric materials. Poly( $\epsilon$ -caprolactone), PCL, is one of the most frequently used compounds due to its biocompatibility, low glass transition temperature ( $T_g$ ), high flexibility at low temperatures and high permeability [2]. Recently, a series of linear and star-shaped homo and copolyesters between  $\epsilon$ -caprolactone and L-lactide with variable numbers of arms were synthesized by ROP using alcohols with different numbers of hydroxyl groups (1-hexanol, 2,2-dimethyl-1,3-propanediol (DMP), 1,1,1-tris(hydroxymethyl)propane (TMP) and

pentaerythritol (PTOL)) as initiators and the effects of branching on polymer properties studied [3-4]. By introducing star-branched structures into linear polyesters, physical property changes such as lower crystallinity, decrease melting temperature and increasing biodegradation rate were observed. The drawback is that it is difficult to achieve the required molecular architecture without any imperfections because of the difficulty of dissolving the PTOL initiator in cyclic esters monomers [5].

The main propose of this study is to synthesize star-shaped PCL using a novel pentaerythritol tetrakis(6'-hydroxyhexanoate) (**4**) star-core macroinitiator (Scheme 1). This macroinitiator is to be prepared using CL to cap the OH groups of PTOL in a ratio of 1:1. The effects of differing molecular architecture on the thermal and morphological properties of linear and star-shaped PCLs will be investigated.

### 2. Experimental

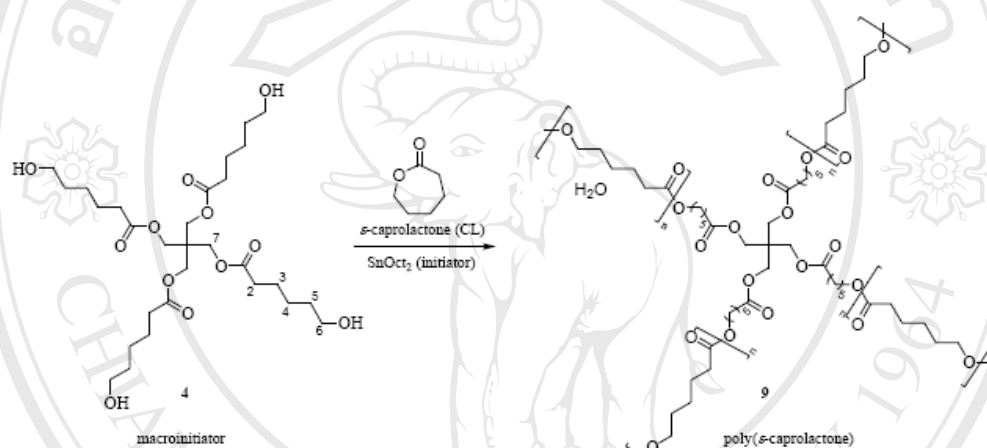
#### 2.1 Synthesis of Pentaerythritol Tetrakis(6'-hydroxyhexanoate) (**4**)

Methyl 6-hydroxyhexanoate (**5**) was prepared by methanolysis of  $\epsilon$ -caprolactone (**1**) using concentrated sulfuric acid as a catalyst.

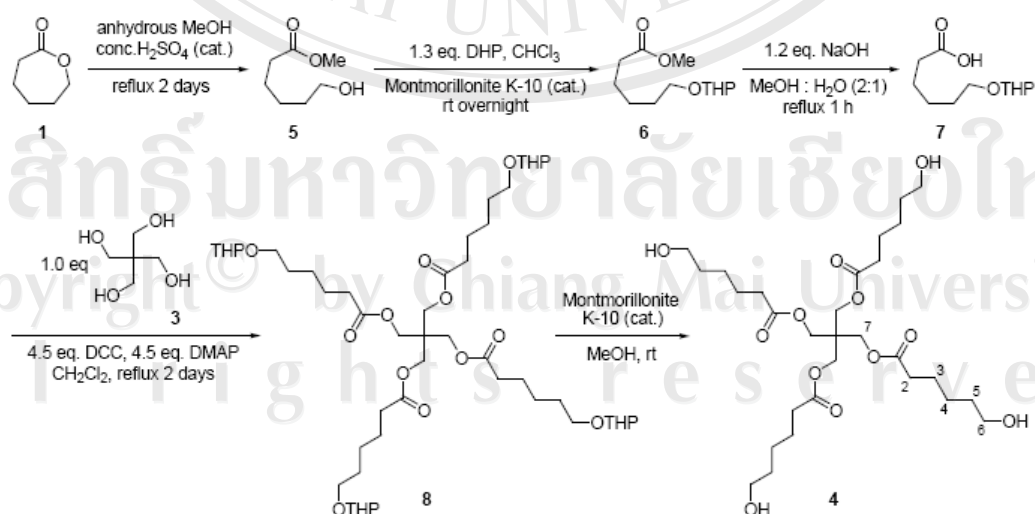
The hydroxyl group of compound **5** was protected by dihydro(2H)pyran in chloroform using montmorillonite K-10. The methyl 6-(tetrahydro-2H-pyran-2-yloxy)hexanoate product (**6**) was hydrolyzed by sodium hydroxide to give 6-(tetrahydro-2H-pyran-2-yloxy)hexanoic acid (**7**) and then reacted with pentaerythritol (PTOL, **3**) in the presence of *N,N'*-dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP) to yield compound **8**. Finally, the THP group of **8** was removed by stirring with montmorillonite K-10 in methanol to yield the star-core macroinitiator (**4**) as shown in Scheme 2.

## 2.2 Synthesis and Characterization of Linear and Star-Shaped PCLs

Linear and star-shaped PCL were synthesized by ROP of CL in bulk at 120°C for 48 hours using SnOct<sub>2</sub> and either 1-hexanol (1-OH) and pentaerythritol tetrakis(6'-hydroxyhexanoate) (4-OH) as the initiating system. The number-average molecular weight ( $\bar{M}_n$ ) was controlled by the monomer to initiator ratio (100:0.05 mol %). The crude product was dissolved in chloroform and then precipitated in cold methanol. The polymers were dried under vacuum at 50°C to constant weight and characterized by <sup>1</sup>H-NMR, DSC, GPC and dilute-solution viscometry



**Scheme 1** Polymerization of  $\epsilon$ -caprolactone using a star-core macroinitiator (**4**).



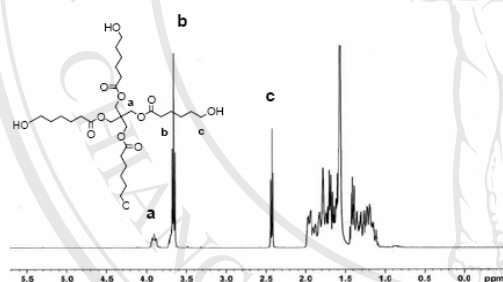
**Scheme 2** Synthesis of pentaerythritol tetrakis(6'-hydroxyhexanoate) (**4**).



### 3. Results and Discussion

#### 3.1 Synthesis and Characterization of Star-core Macroinitiator (4)

Pentaerythritol tetrakis(6'-hydroxyhexanoate) was successfully synthesized via methanolysis (79%), alcohol protection (92%), hydrolysis (75%), esterification and deprotection (43%) respectively. The star-core macroinitiator was characterized by IR, ESI-MS and <sup>1</sup>H-NMR spectroscopy. The IR spectrum shows that the absorption peaks of C=O stretching (ester) at 1740 cm<sup>-1</sup> and O-H stretching (alcohol) at 3400 cm<sup>-1</sup>. The <sup>1</sup>H-NMR spectrum data shows 8 protons at a-position appearing as multiplets at  $\delta$  3.91 ppm, 8 protons at b-position appearing as triplets at  $\delta$  3.67 ppm, and 8 protons at c-position appearing as multiplets at  $\delta$  2.42 ppm, as shown in Figure 1. Electrospray ionization mass spectrometry (ESI-MS) data revealed in a signal at 625.3356 m/z (M + Na)<sup>+</sup> of C<sub>29</sub>H<sub>52</sub>O<sub>12</sub>Na.



**Figure 1** <sup>1</sup>H-NMR spectrum of macroinitiator (4)

#### 3.2 Synthesis of Linear and Star-Shaped PCLs

Linear and star-shaped PCLs could be synthesized in high yield (> 90%) via ROP of CL using SnOct<sub>2</sub> in conjunction with 1-hexanol and pentaerythritol tetrakis(6'-hydroxyhexanoate) (4). The purified linear PCL was a white elastic solid but the star-shaped PCL was a pale yellow brittle solid. The GPC results (Table 1) showed that the number-average molecular weight ( $\bar{M}_n$ ) could be predicted and controlled by the monomer to initiator ratio (100:0.05 mol %). From dilute-solution viscometry results (Table 1), it was found that star-shaped PCL exhibited lower intrinsic viscosity, [ $\eta$ ] than linear PCL at the 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 PCL occupies a

smaller hydrodynamic volume in solution than the linear PCL at the same molecular weight.

The thermal properties of linear and star-shaped PCL were investigated by DSC as shown in Table 1. It was found that thermal properties and crystallinity can be controlled by the molecular architecture. The melting temperature ( $T_m$ ) and heat of melting ( $\Delta H_f$ ) of linear PCL was higher than star-shaped PCL, which could be attributed to the crystalline imperfection mainly due to the short chain length of the star-shaped PCL arms. Moreover, the branched structure of star-shaped PCL should make contribution to the crystalline imperfection. The globular structures of the star-shaped PCLs decreased the intermolecular interactions and the number of molecular conformations, which facilitated crystallization. The DSC results indicate that the thermal properties and crystallinity are affected when branching point are introduced into the polymer.

**Table 1** Characterization of linear and star-shaped PCLs.

Polymer	PCL 1-hexanol	PCL (4)
Yield (%)	90	96
GPC		
$\bar{M}_n$	16,240	13,510
Polydispersity	1.78	1.24
Viscometry		
Intrinsic viscosity*	1.28	1.24
$\bar{M}_v$	103,564	99,716
DSC		
$T_m$ (onset) (°C)	61.3	59.7
$\Delta H_f$ (J/g)	81.1	75.7

\* Measured at 30.0°C in chloroform solution

### 4. Conclusions

The synthesis of the star-core macroinitiator can be achieved via a sequence of simple reactions: methanolysis, alcohol protection, hydrolysis, esterification and deprotection, resulting in a moderate yield of the final product. The star-shaped PCL was successfully synthesized by ROP of CL using SnOct<sub>2</sub> and pentaerythritol tetrakis(6'-hydroxyhexanoate) as the initiating system. Thermal analysis and dilute-solution viscometry revealed that the star-shaped PCL possessed a lower melting point and intrinsic viscosity than linear PCL. The effects of molecular architecture on the mechanical and rheological properties and also on the *in vitro* biodegradabilities are currently being investigated.

### Acknowledgements

Financial support (for SK) from the Center for Innovation in Chemistry: Postgraduate Education and Research Program in Chemistry (PERCH-CIC), Commission on Higher Education, Ministry of Education, is gratefully acknowledged.

### References

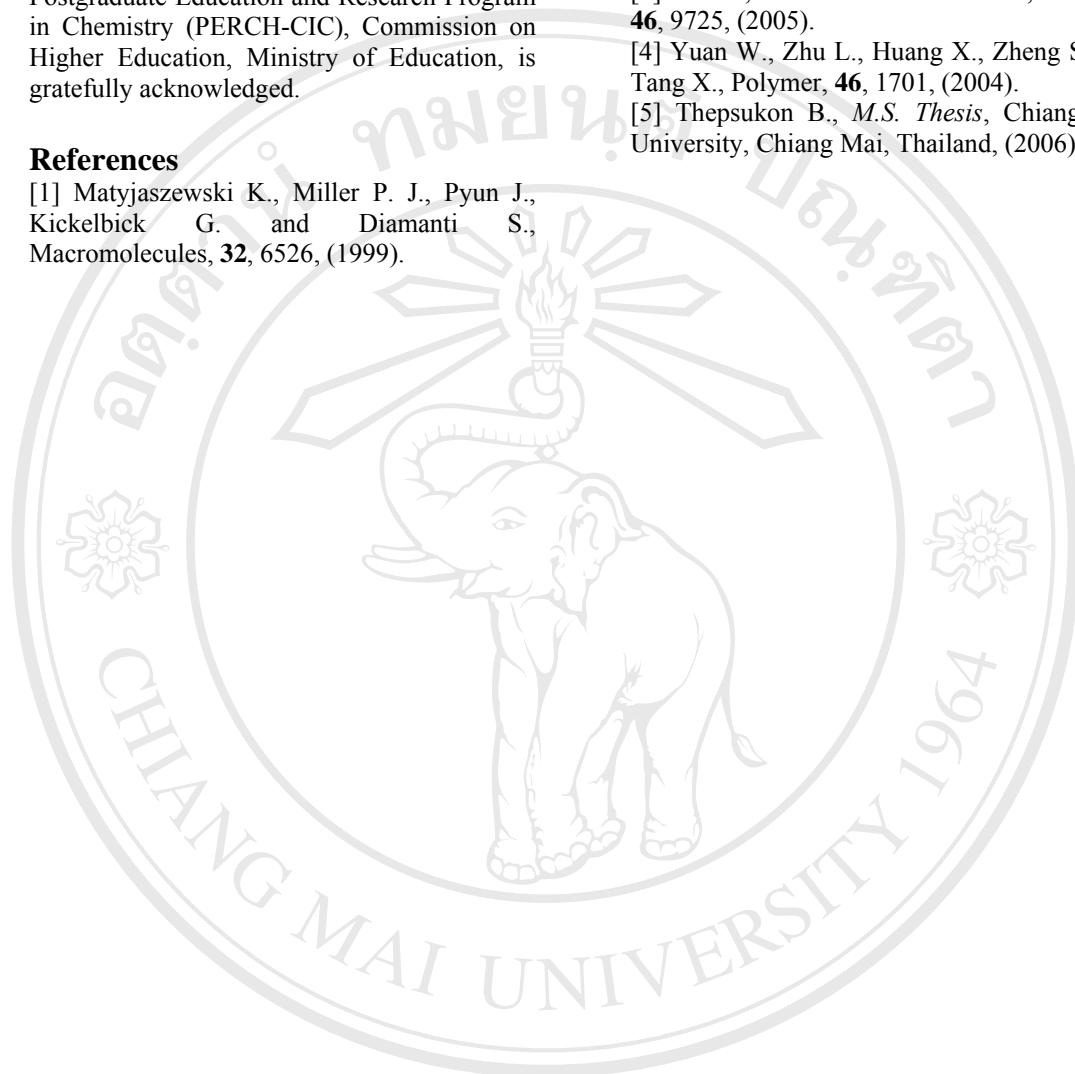
[1] Matyjaszewski K., Miller P. J., Pyun J., Kicelbick G. and Diamanti S., *Macromolecules*, **32**, 6526, (1999).

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**Sawitree Kathongthung**, Puttinan Meepowpan, Robert  
Molloy and Winita Punyodom

*“Synthesis and Characterization of Novel Star-Core  
Macroinitiator for Use in the Ring-Opening  
Polymerization of L-Lactide”*

**The 2<sup>nd</sup> International Conference on Advances in  
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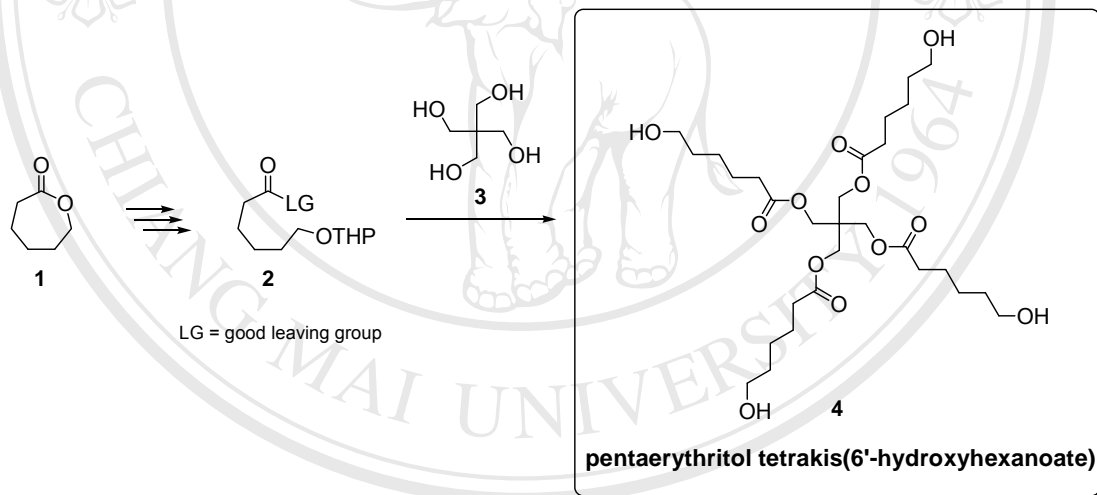
## SYNTHESIS AND CHARACTERIZATION OF NOVEL STAR-CORE MACROINITIATORS FOR USE IN THE RING-OPENING POLYMERIZATION OF L-LACTIDE

Sawitree Kathongthung, Puttinan Meepowpan\*, Winita Punyodom and Robert Molloy

Biochemical Polymers Technology Unit, Department of Chemistry, Faculty of Science, Chiang Mai University, Chiang Mai, 50200, Thailand; e-mail: \*puttinan@chiangmai.ac.th

### ABSTRACT

Novel pentaerythritol tetrakis(6'-hydroxyhexanoate) (**4**) has been synthesized from  $\epsilon$ -caprolactone (**1**) as a star-core macroinitiator for use in the ring-opening polymerization (ROP) of cyclic esters. Compound **2** was prepared by methanolysis of **1**, with the protection of the alcohol group by dihydro(2H)pyran, and hydrolysis to give the ether acid in high yield. The ether acid could then be reacted with pentaerythritol (PTOL, **3**) to give the star-core macroinitiator **4** in moderate yield which, in turn, could then be used to synthesize star-shaped poly(L-lactide) (PLL) via the ROP of L-lactide (LL) in bulk using stannous octoate as an initiator. The microstructure of the PLL obtained was characterized by means of  $^1\text{H-NMR}$ , dilute-solution viscometry and differential scanning calorimetry (DSC) and its properties compared with linear PLL synthesized using 1-hexanol instead of PTOL. The effect of chain architecture on polymer properties is discussed.



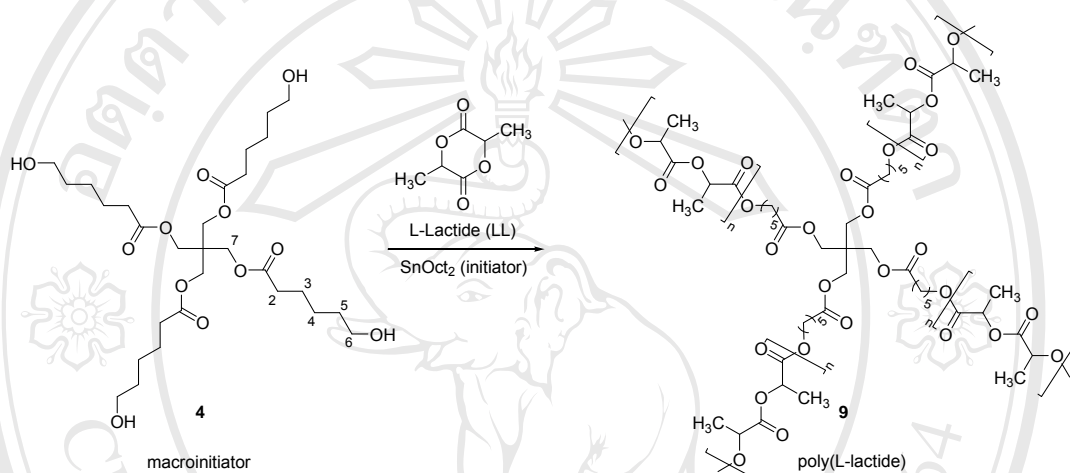
### 1. INTRODUCTION

Branched and star-shaped biodegradable aliphatic polyesters have gained widespread attention due to their unique properties, often differing significantly from their linear counterparts. Structure-property studies have shown that variations in the macromolecular architecture can have substantial effects on the morphological, thermal, rheological and physico-mechanical properties and also on the biodegradability of biomedical materials [1]. Poly(L-lactide), PLL, is one of the most widely used biomedical polymers because it has good biodegradability, high mechanical strength and excellent shaping and molding properties. However, the biomedical applications of PLL are limited because of the difficulties arising from its variable biodegradation, poor compatibility with soft tissue due to its high crystallinity, and induction of material defects based on the lability of its melt viscosity [2]. To control its crystallinity and biodegradation rate, many approaches have been used such as the introduction of branched structures into PLL [2-5]. Recently, a series of linear and star-shaped polyesters with variable number of arms were synthesized by ROP using alcohols with different numbers of hydroxyl groups (1-hexanol, 2,2-dimethyl-1,3-propanediol (DMP), 1,1,1-tris(hydroxymethyl)propane (TMP) and pentaerythritol (PTOL)) as initiators and the



effects of branching on polymer properties studied [2-5]. By introducing star-branched structures into linear polyesters, physical property changes such as lower crystallinity, decrease melting temperature and increasing biodegradation rate were observed. The drawback is that it is difficult to achieve the required molecular architecture without any imperfections because of the difficulty of dissolving the PTOL initiator in cyclic esters monomers. [5]

The main propose of this study is to synthesize star-shaped polymer using a novel pentaerythritol tetrakis(6'-hydroxyhexanoate) (**4**) star-core macroinitiator (Scheme 1). This macroinitiator is to be prepared using  $\epsilon$ -caprolactone (CL) to cap the OH groups of PTOL in a ratio of 1:1. The effects of differing molecular architecture on the thermal and morphological properties of linear and star-shaped PLLs will be investigated.

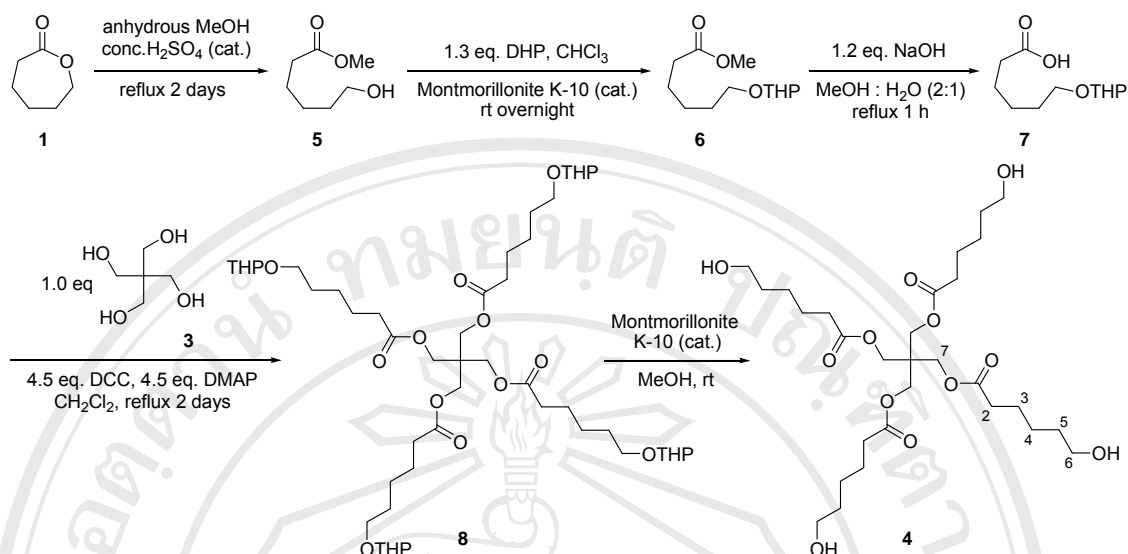


Scheme 1: Polymerization of L-lactide using a star-core macroinitiator (**4**).

## 2. EXPERIMENTAL

### 2.1 Synthesis of Pentaerythritol Tetrakis(6'-hydroxyhexanoate) (**4**)

Methyl 6-hydroxyhexanoate (**5**) was prepared by methanolysis of  $\epsilon$ -caprolactone (**1**) using concentrated sulfuric acid as a catalyst. The hydroxyl group of compound **5** was protected by dihydro(2H)pyran in chloroform using montmorillonite K-10. The methyl 6-(tetrahydro-2H-pyran-2-yloxy)hexanoate product (**6**) was hydrolyzed by sodium hydroxide to give 6-(tetrahydro-2H-pyran-2-yloxy)hexanoic acid (**7**) and then reacted with pentaerythritol (PTOL, **3**) in the presence of *N,N*-dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP) to yield compound **8**. Finally, the THP group of **8** was removed by stirring with montmorillonite K-10 in methanol to yield the star-core macroinitiator (**4**) as shown in Scheme 2.



Scheme 2: Synthesis of pentaerythritol tetrakis(6'-hydroxyhexanoate) (**4**).

## 2.2 Synthesis of Linear and Star-Shaped Poly(L-lactide)

Linear and star-shaped PLL were synthesized by ROP of LL in bulk at 120°C for 48 hours using SnOct<sub>2</sub> and either 1-hexanol (1-OH), PTOL (4-OH) or pentaerythritol tetrakis(6'-hydroxyhexanoate) as the initiating system. The number-average weight molecular weight ( $\overline{M}_n$ ) was controlled by the monomer to initiator ratio (100:1 mol %). The crude products were dissolved in chloroform and then precipitated in cold methanol. The polymers were dried under vacuum at 55°C to constant weight and characterized by <sup>1</sup>H-NMR, DSC and dilute-solution viscometry.

## 3. RESULTS AND DISCUSSION

### 3.1 Synthesis and Characterization of Pentaerythritol Tetrakis(6'-hydroxyhexanoate)

Pentaerythritol tetrakis(6'-hydroxyhexanoate) was successfully synthesized via methanolysis (79%), alcohol protection (92%), hydrolysis (75%), esterification and deprotection (43%) respectively. The star-core macroinitiator was characterized by IR, ESI-MS and <sup>1</sup>H-NMR spectroscopy. The IR spectrum shows the absorption peaks of C=O stretching (ester) at 1740 cm<sup>-1</sup> and O-H stretching (alcohol) at 3400 cm<sup>-1</sup>. The <sup>1</sup>H-NMR spectrum shows 8 protons at a-position appearing as multiplets at  $\delta$  3.91 ppm, 8 protons at b-position appearing triplets at  $\delta$  3.67 ppm, and 8 protons at c-position appearing multiplets at  $\delta$  2.42 ppm, as shown in figure 1. Electrospray ionization mass spectrometry (ESI-MS) data revealed in a signal at 625.3356 m/z ( $M + Na$ )<sup>+</sup> of C<sub>29</sub>H<sub>52</sub>O<sub>12</sub>Na.

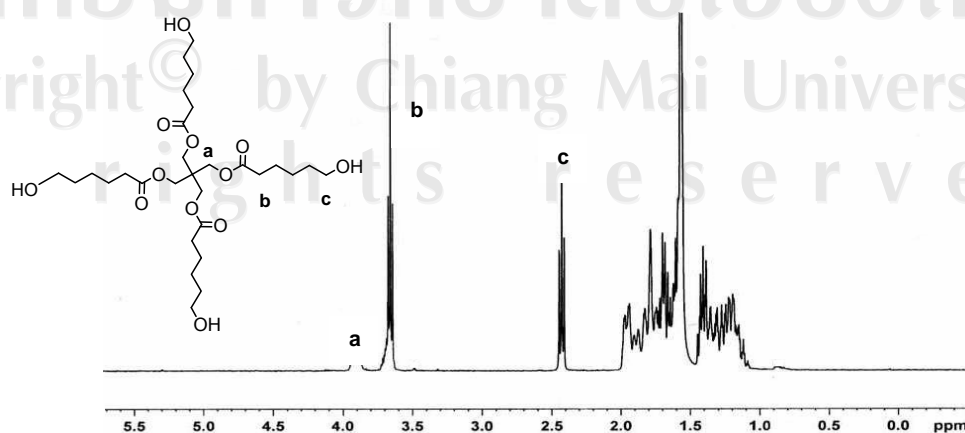


Figure 1: <sup>1</sup>H-NMR spectrum of pentaerythritol tetrakis(6'-hydroxyhexanoate) (**4**)

### 3.2 Synthesis of Linear and Star-Shaped Poly(L-lactide)

Linear and star-shaped PLLs could be synthesized in high yield (> 90%) via ROP of LL using stannous octoate in conjunction with 1-hexanol, PTOL and pentaerythritol tetrakis(6'-hydroxyhexanoate) (4). The purified linear PLL was a white rigid solid but the star-shaped PLLs were pale yellow brittle solids. The number-average molecular weight ( $\overline{M}_n$ ) could be predicted and controlled by the monomer to initiator ratio (100:1 mol %), as shown in Table 1.

Table 1: Characterization of linear and star-shaped PLLs synthesized using [monomer]:[initiator] = 100:1 mol %.

Polymers	% Yield	$\overline{M}_n$ theory	DSC(1 <sup>st</sup> run, 2 <sup>nd</sup> run)					Dilute-Solution Viscometry * [ $\eta$ ]
			T <sub>g</sub> (°C)	T <sub>c</sub> (peak) (°C)	T <sub>m</sub> (peak) (°C)	$\Delta H_m$ (J/g)	Degree of Crystallinity (%)	
PLL_hexanol	94.9	15,114	-, 47.9	105.6, 88.3	170.0, 167.3	56.6, 52.6	60.5, 56.2	0.42
PLL_PTOL	93.4	14,843	-, 53.2	104.6, 108.0	158.0, 157.0	48.0, 42.8	51.3, 45.7	0.36
PLL_(4)	91.5	15,005	-, 47.7	102.3, 98.6	155.3, 154.0	46.6, 49.7	49.8, 53.1	0.29

\* Measured at 30.0°C in chloroform solution

The DSC thermograms (1<sup>st</sup> run) (Figure 2 (a)) as showed that all PLL samples did not exhibit a glass transition (T<sub>g</sub>) peak but did show crystallization (T<sub>c</sub>) and melting (T<sub>m</sub>) peaks. This was due to their thermal histories. In contrast, the DSC thermograms (2<sup>nd</sup> run) (Figure 2 (b)) all exhibited T<sub>g</sub>, T<sub>c</sub> and T<sub>m</sub> transitions since all samples has been quenched from their melt states. Consequently very little crystallinity was present in the samples prior to the second heating scan. It was found that the T<sub>g</sub> of the linear PLL was lower than the star-shaped PLL synthesized from PTOL. This was due to the effect of chain microstructure. The higher T<sub>g</sub> of the star-shaped PLL showed that branching hinders segmental motion. It was also observed that the star-shaped PLLs possessed lower melting points (in the range of 155-170°C) and degrees of crystallinity (in the range of 47-57%) than the linear PLL, which could be attributed to crystal imperfections mainly due to the short chain lengths of the star-shaped polymers arms. It can also be seen clearly that the T<sub>c</sub> of linear PLL is lower than the star-shaped PLLs, attributable to relatively slow crystallization. The globular structures of the star-shaped PLLs decreased the intermolecular interactions and the number of molecular conformations, which facilitated crystallization. Meanwhile, it is noted that the PLLs have two melting peaks resulting from differences in crystallite size and/or shape. These DSC results indicate that the thermal properties and crystallinity are affected when branching point are introduced into the polymer.

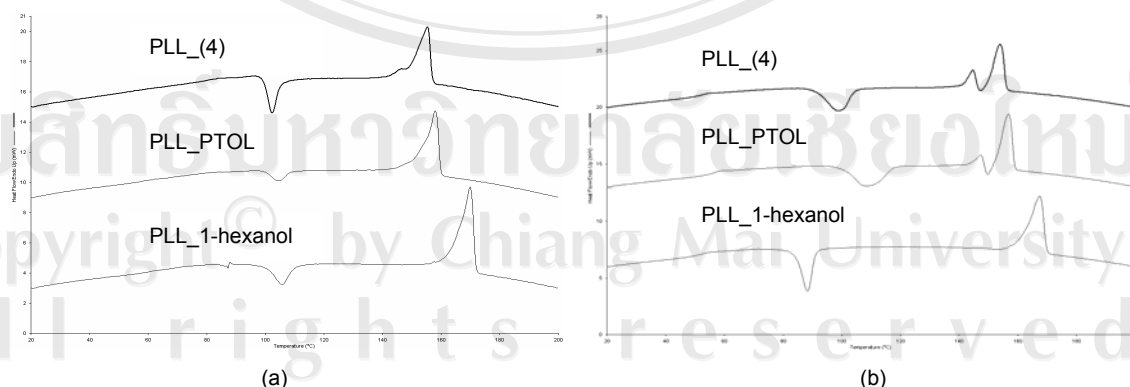


Figure 2: Comparison of the DSC thermograms of the linear and star-shaped PLLs (a) 1<sup>st</sup> run and (b) 2<sup>nd</sup> run.

From the dilute-solution viscometry results in Table 1, it was found that star-shaped PLLs exhibited lower intrinsic viscosities than those of linear PLL at same molecular weight ( $\overline{M}_n$ ), 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.

#### 4. CONCLUSIONS

The synthesis of the star-core pentaerythritol tetrakis(6'-hydroxyhexanoate) macroinitiator **4** has been achieved via a sequence of simple reactions: methanolysis, alcohol protection, hydrolysis, esterification and deprotection, resulting in a moderate yield of the final product. Star-shaped PLL could be synthesized by ROP of LL using stannous octoate and pentaerythritol tetrakis(6'-hydroxyhexanoate) as the initiating system. Thermal analysis and dilute-solution viscometry revealed that the star-shaped PLL possessed a lower melting point, crystallinity and intrinsic viscosity than linear PLL. The effects of molecular architecture on the mechanical and rheological properties and also on the *in vitro* biodegradabilities of the PLLs are currently being investigated.

#### ACKNOWLEDGEMENTS

Financial support (for SK) from the Center for Innovation in Chemistry: Postgraduate Education and Research Program in Chemistry (PERCH-CIC), Commission on Higher Education, Ministry of Education, is gratefully acknowledged.

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Punyodom and Robert Molloy

*“Synthesis and Characterisation of a Novel Star-Core*

*Macroinitiator for Use in the Ring-Opening*

*Polymerisation of  $\epsilon$ -Caprolactone”*

**The 6<sup>th</sup> PERCH Annual Scientific Congress**

**(PERCH-CIC CONGRESS VI)**

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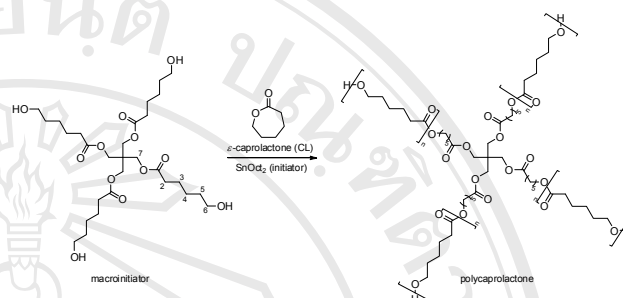
## Synthesis and Characterization of a Novel Star-Core Macroinitiator for Use in the Ring-Opening Polymerization of Cyclic Esters

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### Objective

The main purpose of this study is to synthesize well-defined star-shaped poly( $\epsilon$ -caprolactone), PCL, using a 4-arm macroinitiator with pentaerythritol (PTOL) at its core and OH-terminated arms of 6'-hydroxyhexanoate. The effects of differing molecular architecture on the polymer properties of linear and star-shaped PCLs are being investigated.



### Methods

Pentaerythritol tetrakis(6'-hydroxyhexanoate) for use as a star-core macroinitiator was synthesized and characterized. Linear and star-shaped PCLs were synthesized by the ring-opening polymerization (ROP) of  $\epsilon$ -caprolactone (CL) in bulk at 120°C using stannous octoate as initiator in conjunction with 1-hexanol, PTOL or pentaerythritol tetrakis(6'-hydroxyhexanoate). The microstructure and properties of the PCLs obtained were characterized by means of  $^1\text{H-NMR}$ , DSC, TG, mechanical and rheological properties.

### Results

The synthesis of the star-core macroinitiator can be achieved via a sequence of simple reactions: methanolysis, alcohol protection, hydrolysis, esterification and deprotection, resulting in a moderate yield of the final product. The chemical structure of the star-core macroinitiator was confirmed by IR,  $^1\text{H-NMR}$  and ESI-mass spectroscopy.

Low molecular weight PCLs (PCL\_hexanol, PCL\_PTOL and PCL\_macroinitiator) were synthesized and characterized to confirm their molecular architectures. The  $^1\text{H-NMR}$  results showed that the average number of OH groups initiating polymerization, as calculated from the average degree of the polymerization per arm ( $\text{DP}_n/\text{arm}$ ), was close to the actual OH functionalities. 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. This could be attributed to their shorter chain lengths and greater number of free chain ends which disrupts the orderly folded chain pattern in the crystal. Structure-property studies have shown that the variation in molecular architecture from linear to star-branched can have substantial effects on the thermal properties, crystallinity, mechanical and rheological properties of high molecular weight PCLs. The effect of chain architecture on polymer properties is discussed.

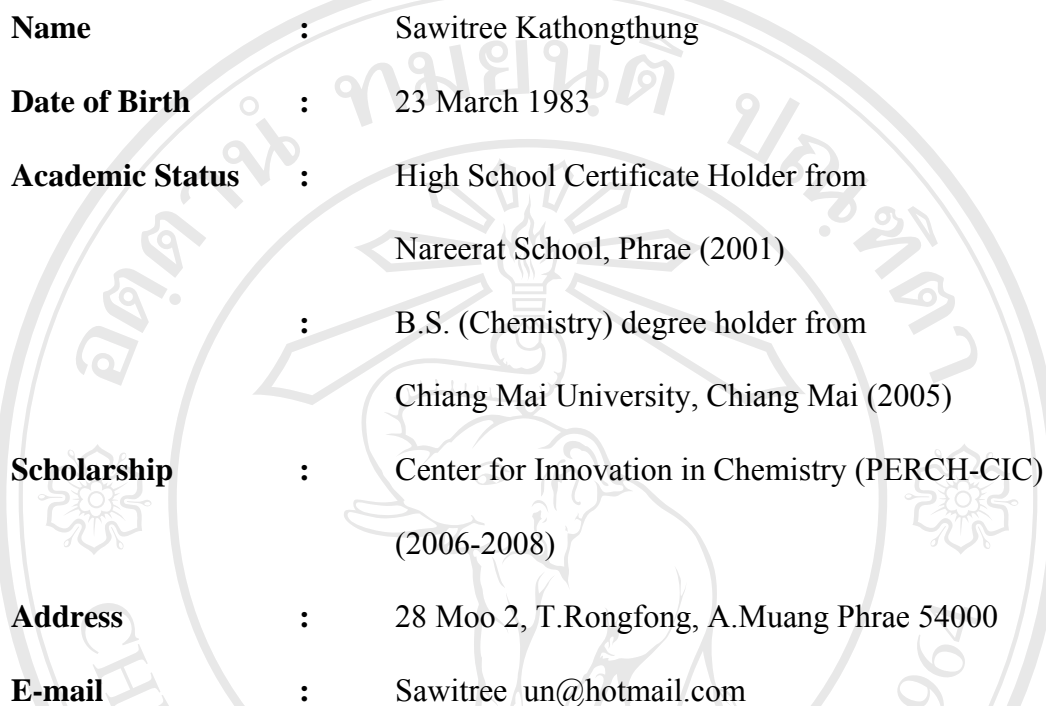
### Conclusions

A novel pentaerythritol tetrakis(6'-hydroxyhexanoate) star-core macroinitiator was prepared and obtained as a colorless oil in moderate yield (43%). The problem of the insolubility of PTOL in CL monomer 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.

**Keywords:** pentaerythritol, pentaerythritol tetrakis(6'-hydroxyhexanoate), star-shaped poly( $\epsilon$ -caprolactone)

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**VITA**The background of the page features a large, faint watermark of the Chiang Mai University seal. The seal is circular and contains the university's name in Thai script at the top and "CHIANG MAI UNIVERSITY 1964" in English at the bottom. In the center of the seal is an elephant standing on a base, with a sunburst or flame-like symbol above its head.

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