

**Sirindhorn International Institute of Technology
Thammasat University**

Thesis ChE-ME-2009-06

**SYNTHESIS AND CHARACTERIZATION OF PLA-BASED
ALIPHATIC- AROMATIC COPOLYESTERS: EFFECT OF DIOLS**

ชำนาญกหอสมุด

Montree Namkajorn

**SYNTHESIS AND CHARACTERIZATION OF PLA-BASED
ALIPHATIC- AROMATIC COPOLYESTERS: EFFECT OF DIOLS**

A Thesis Presented

by

Montree Namkajorn

Master of Engineering in
Chemical Engineering Program
Sirindhorn International Institute of Technology
Thammasat University
May 2010

Synthesis and Characterization of PLA-Based
Aliphatic-Aromatic Copolyesters: Effect of Diols

A Thesis Presented

By

Montree Namkajorn

Submitted to


Sirindhorn International Institute of Technology

Thammasat University


In partial fulfillment of the requirement for the degree of


MASTER OF ENGINEER IN ENGINEERING

Approved as to style and content by the Thesis Committee:

Advisor 
Asst. Prof. Pakorn Opaprakasit, Ph. D.

Co-Advisor 
Atitsa Petchsuk, Ph. D.

Chair and Member 
Assoc. Prof. Luckhana Lawtrakul, Dr.rer.nat.

Member 
Assoc. Prof. Alice Sharp, Ph. D.

External Examiner: Assoc.Prof. Supawan Tantayanon, Ph.D.

May 2010

Acknowledgement

I wish to express my deepest and sincere gratitude to my supervisor, Asst. Prof. Dr. Pakorn Opaprakasit for his supervision, valuable instructions, excellent suggestions, kindness and assistance on the preparation of this thesis. This accomplishment would not be possible without his help.

Moreover, I feel very thankful and grateful to Dr. Atitsa Petchsuk, Dr. Mantana Opaprakasit for their kindness and valuable discussion and comments on this thesis.

My appreciation is also extended to the staff of the School of Bio-Chemical Engineering and Technology and the department of Common and Graduate Studies, Sirindhorn International Institute of Technology (SIIT), Thammasat University.

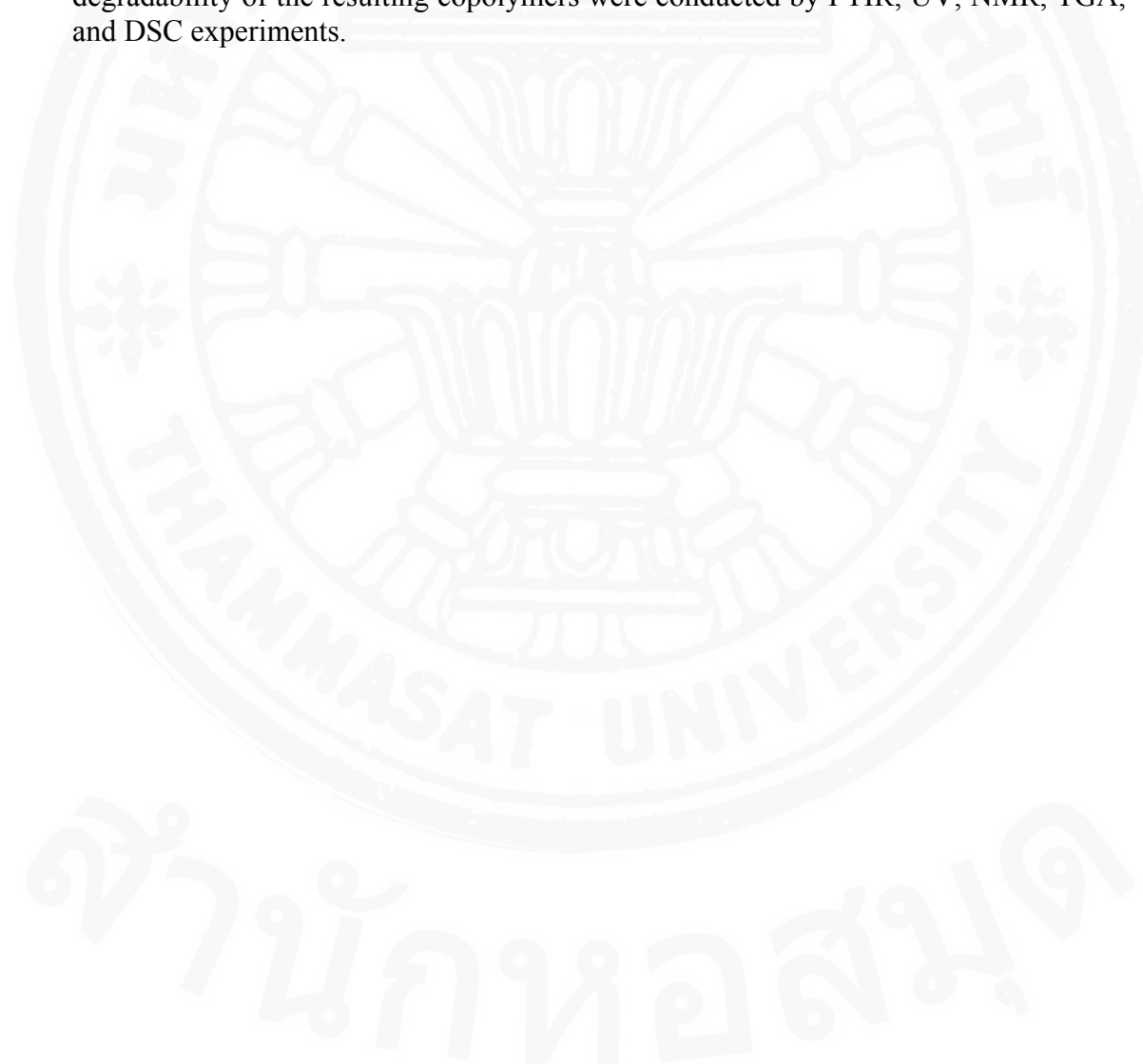
Unforgettably, this work was made possible by a financial support from the SIIT-NSTDA scholarship and partial support from the teaching assistant program.

I would like to thank all of my colleagues for great cooperation and the best wonderful relationship. Finally, thank you my lovely family for their love and encouragement.

Montree Namkajorn

Abstract

PLA-based aliphatic aromatic copolyesters have been synthesized and characterized in order to incorporate the degradability of PLA and good mechanical property of aromatic species. Synthesis of the copolymer was conducted by polycondensation of lactic acid with dimethyl terephthalate (DMT) and diols using Stannous(II)octoate as a catalyst. Four types of diols with different methylene length were employed, i.e., ethylene glycol (EG), propylene glycol (PG), 1, 4-butanediol (BD), 1,3-propanediol (PD). Effects of diols and comonomer ratio on the polycondensation and the molecular weight of resulting copolymers were investigated. Diacids and diol ratios of L-lactic acid (LLA), dimethyl terephthalate (DMT) and diol of 1/1/2, 1/2/4, and 2/1/2 were employed, respectively. Characterization of chemical property, molecular weight, thermal property and degradability of the resulting copolymers were conducted by FTIR, UV, NMR, TGA, and DSC experiments.



List of Contents

| Chapter Title | Page |
|--|------|
| Signature Page | i |
| Acknowledgment | ii |
| Abstract | iii |
| List of Contents | iv |
| List of Figures | v |
| List of Tables | viii |
| List of abbreviate | xi |
| 1. Introduction | 1 |
| 1.1 Introduction | 1 |
| 1.2 Concepts and significant | 3 |
| 1.3 Objective of study | 4 |
| 1.4 scope of study | 4 |
| 2. Literature Review | 6 |
| 2.1 Introduction | 6 |
| 2.2 Polymerization of lactic acid | 7 |
| 2.3 Polymerization of bis(hydroxyethyl) terephthalate | 7 |
| 2.4 Synthesis of PET- <i>co</i> -PLA | 8 |
| 2.5 Copolymerization of lactic acid | 8 |
| 2.6 Crosslinking | 10 |
| 2.7 Characterized structure of PET- <i>co</i> -PLA | 11 |
| 3. Methodology | 12 |
| 3.1 Materials | 12 |
| 3.2 Equipments | 12 |
| 3.3 Synthesis of PLA-based Aliphatic-Aromatic Copolyesters | 12 |
| 3.4 Characterizations of PLA-based Aliphatic-Aromatic Copolyesters | 15 |
| 3.5 Solubility test | 15 |
| 3.6 Degradability of PLA-based Aliphatic-Aromatic Copolyesters | 15 |
| 4. Results and Discussion | 17 |
| 5. Conclusion and Recommendations | 53 |
| 6. Reference | 55 |
| Appendix | 61 |

List of Figures

| Figure | Page |
|---|------|
| Figure 1.1 Life cycle of degradable PLA | 1 |
| Figure 1.2 Ring-open polymerization of lactide | 2 |
| Figure 1.3 PET synthesis reactions: (a) esterification reaction of terephthalic acid (b) trans-esterification reaction of dimethyl terephthalate. (c) condensation reaction | 3 |
| Figure 1.4 Summary of the synthesis reaction of aliphatic-aromatic copolyesters. | 5 |
| Figure 2.1 Overview of polymerization methods of high-molecular weight poly(lactic acid) | 7 |
| Figure 2.2 BHET synthesis start | 9 |
| Figure 3.1 The glassware setup for synthesis of the copolymers | 13 |
| Figure 3.2 A graphical illustration of the synthesis procedure | 14 |
| Figure 4.1 ^1H NMR spectrum of PET–PLLA copolyester | 17 |
| Figure 4.2 1,2-ethanediol (E), dimethyl terephthalate (T) and dimethyl sebacate (S) copolyesters | 19 |
| Figure 4.3 Possible E-centered triads and diads of the resulting copolyesters | 20 |
| Figure 4.4 ^1H NMR spectrum of EG212, EG112, EG124 | 21 |
| Figure 4.5 Atom numbering and assignments of EG group | 21 |
| Figure 4.6 ^1H NMR spectrum of PG212, PG112, PG124 | 24 |
| Figure 4.7 Atom numbering and assignments of PG group | 24 |
| Figure 4.8 ^1H NMR spectrum of PD 212, PD 112, PD 124 | 27 |
| Figure 4.9 Atom numbering and assignments of PD group | 27 |
| Figure 4.10 ^1H NMR spectrum of BD212, BD112, BD124 | 30 |

| Figure | Page |
|---|-------------|
| Figure 4.11 Atom numbering and assignments of BD group | 30 |
| Figure 4.12 FTIR spectra of copolymers derived from LA/DMT/EG | 34 |
| Figure 4.13 FTIR spectra of copolymers derived from LA/DMT/PG | 34 |
| Figure 4.14 FTIR spectra of copolymers derived from LA/DMT/PD | 35 |
| Figure 4.15 FTIR spectra of copolymers derived from LA/DMT/BD | 35 |
| Figure 4.16 DSC thermograms of copolymers derived from EG | 36 |
| Figure 4.17 DSC thermograms of copolymers derived from PG | 37 |
| Figure 4.18 DSC thermograms of copolymers derived from PD | 38 |
| Figure 4.19 DSC thermograms of copolymers derived from BD | 39 |
| Figure 4.20 TGA thermograms of EG212, EG112, and EG124 | 41 |
| Figure 4.21 TGA thermograms of PG212, PG112, and PG124 | 41 |
| Figure 4.22 TGA thermograms of PD212, PD112, and PD124 | 42 |
| Figure 4.23 TGA thermograms of BD212, BD112, and BD124 | 42 |
| Figure 4.24 Percentage of weight loss of EG212, EG112 and EG124 | 46 |
| Figure 4.25 Percentage of weight loss of PG212, PG112 and PG124 | 46 |
| Figure 4.26 Percentage of weight loss of BD212, BD 112 and BD 124 | 47 |
| Figure 4.27 Percentage of weight loss of PD 212, PD112 and PD 124 | 47 |
| Figure 4.28 UV spectra of DMT, BHET, LA and acetic acid | 49 |
| Figure 4.29 UV spectra of copolymer derived form EG, PG, PD and BD | 49 |

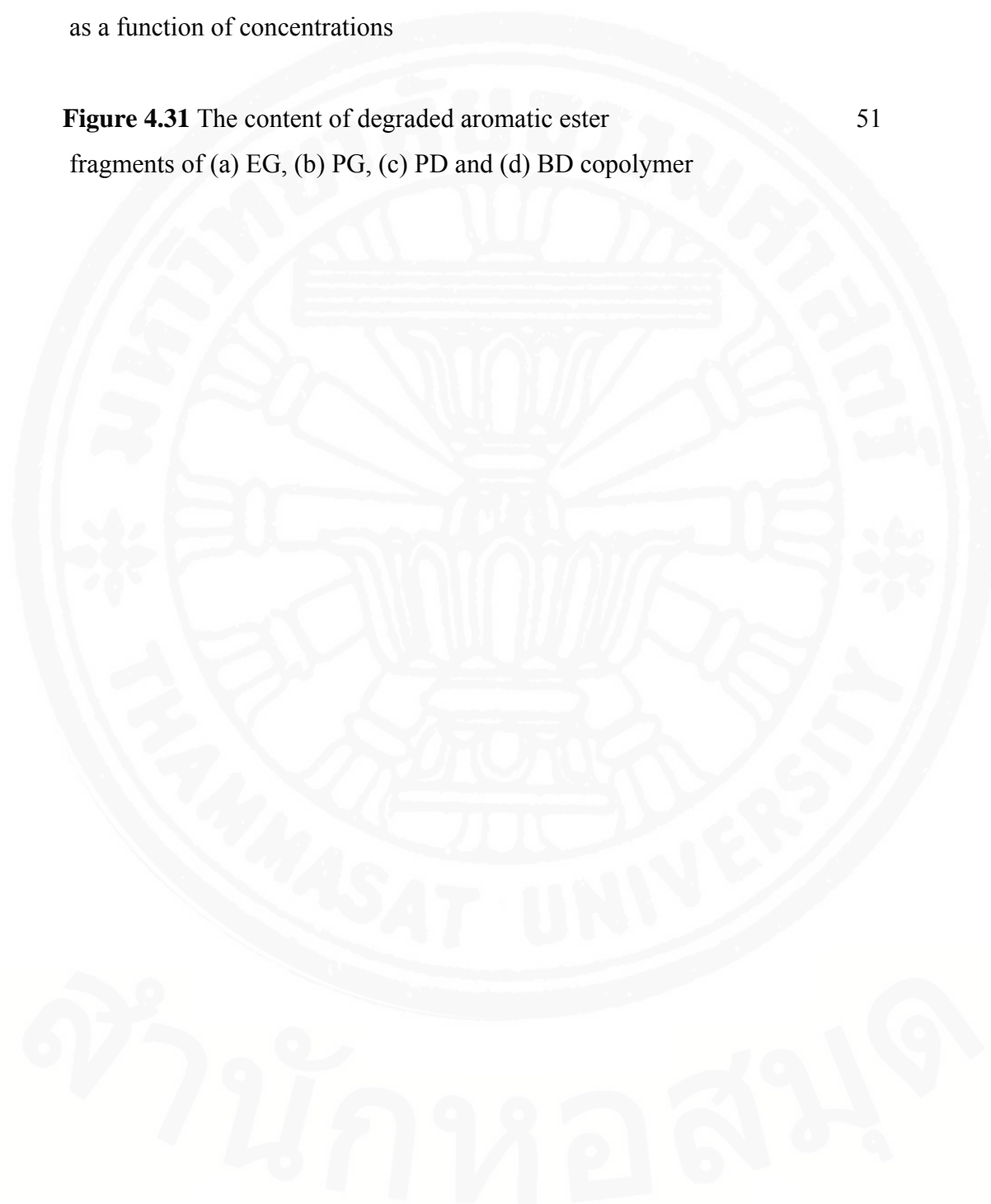
Figure**Page**

Figure 4.30 The standard curve constructed from absorbance of the 243 nm band of DMT solutions as a function of concentrations

50

Figure 4.31 The content of degraded aromatic ester fragments of (a) EG, (b) PG, (c) PD and (d) BD copolymer

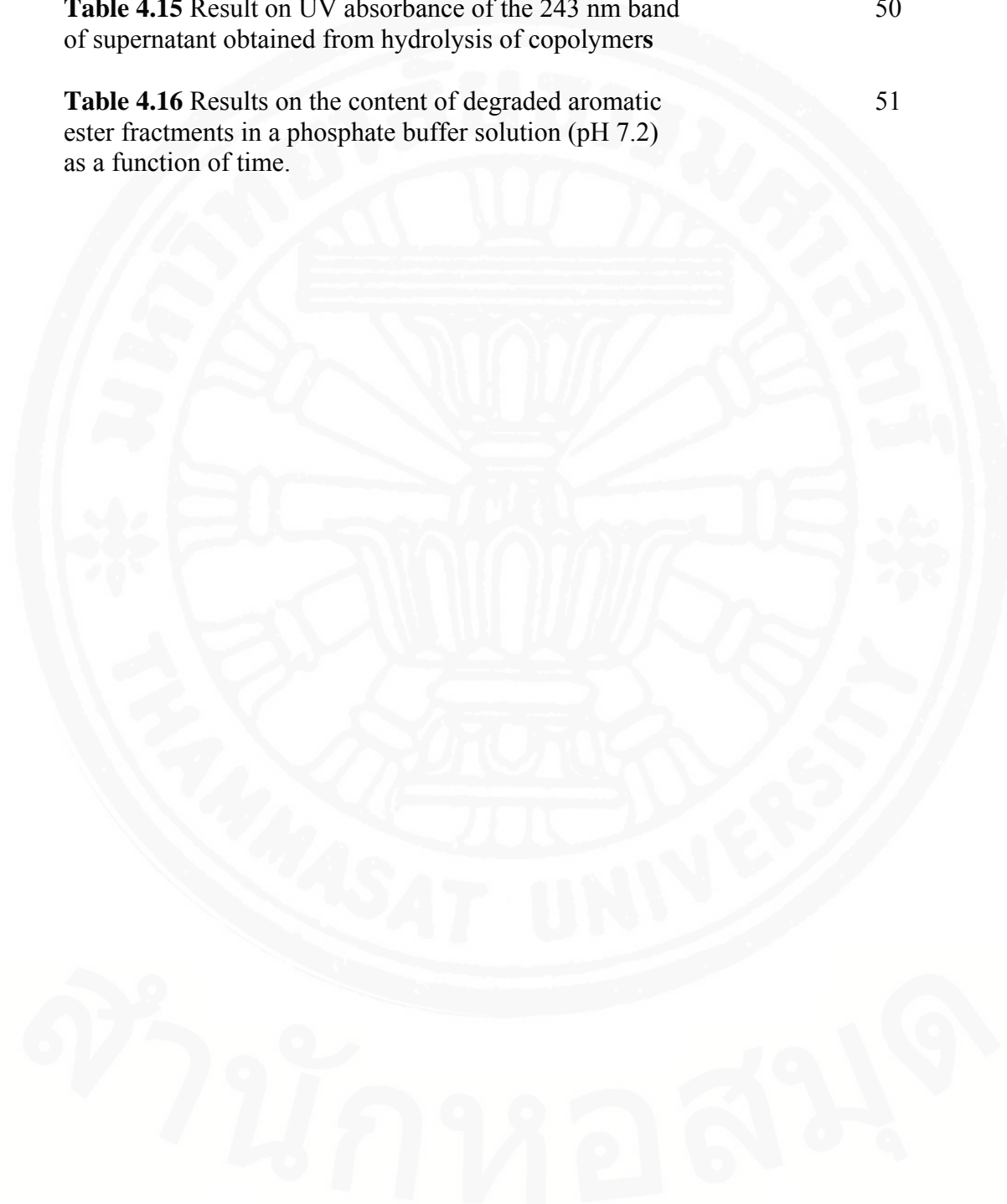
51



List of Tables

| Table | Page |
|---|------|
| Table 4.1 Proton signal assignments of ^1H NMR spectrum of PET-PLA copolymers | 17 |
| Table 4.2 Result on molecular weight and structural information: $Y_{(L)}$, $X_{(ET)}$, $L_{n(L)}$, $L_{n(ET)}$ and B of EG copolymer series | 23 |
| Table 4.3 Result on molecular weight and structural information: $Y_{(L)}$, $X_{(ET)}$, $L_{n(L)}$, $L_{n(ET)}$ and B of PG copolymer series | 26 |
| Table 4.4 Result on molecular weight and structural information : $Y_{(L)}$, $X_{(ET)}$, $L_{n(L)}$, $L_{n(ET)}$ and B of PD copolymer series | 29 |
| Table 4.5 Result on molecular weight and structural information: $Y_{(L)}$, $X_{(ET)}$, $L_{n(L)}$, $L_{n(ET)}$ and B of BD copolymer series | 32 |
| Table 4.6 The ratio of DMT: LA in the copolymer | 33 |
| Table 4.7 Effect of molar ratios of LA/DMT/EG monomers on the copolymers thermal properties | 36 |
| Table 4.8 Effect of molar ratio of LA/DMT/PG monomers on the copolymer thermal properties | 37 |
| Table 4.9 Effect of molar ratio of LA/DMT/PD monomers on the copolymer thermal properties | 38 |
| Table 4.10 Effect of molar ratio of LA/DMT/BD monomers on the copolymer thermal properties | 39 |
| Table 4.11 Summary on effect of type of diols and molar ratios of LA/DMT/diols on thermal properties of the copolymers | 40 |
| Table 4.12 Summary on thermal stability of the copolymers | 43 |
| Table 4.13 Solubility of the copolymers in CH_2Cl_2 and THF | 44 |

| Table | Page |
|--|-------------|
| Table 4.14 Percentage weight loss of copolymers as a function of submersing time | 45 |
| Table 4.15 Result on UV absorbance of the 243 nm band of supernatant obtained from hydrolysis of copolymers | 50 |
| Table 4.16 Results on the content of degraded aromatic ester fragments in a phosphate buffer solution (pH 7.2) as a function of time. | 51 |



List of abbreviate

| | |
|---------------------------------|--|
| LA | lactic acid |
| DMT | dimethyl terephthalate |
| T | terephthalate |
| EG | ethylene glycol |
| EG212 | synthesized copolymer with mol ratio 2/1/2 (LA/DMT/EG) |
| EG112 | synthesized copolymer with mol ratio 1/1/2 (LA/DMT/EG) |
| EG124 | synthesized copolymer with mol ratio 1/2/4 (LA/DMT/EG) |
| PG | propylene glycol |
| PG212 | synthesized copolymer with mol ratio 2/1/2 (LA/DMT/PG) |
| PG112 | synthesized copolymer with mol ratio 1/1/2 (LA/DMT/PG) |
| PG124 | synthesized copolymer with mol ratio 1/2/4 (LA/DMT/PG) |
| PD | 1,3-propane diol |
| PD212 | synthesized copolymer with mol ratio 2/1/2 (LA/DMT/PD) |
| PD112 | synthesized copolymer with mol ratio 1/1/2 (LA/DMT/PD) |
| PD124 | synthesized copolymer with mol ratio 1/2/4 (LA/DMT/PD) |
| BD | 1,4-butane diol |
| BD212 | synthesized copolymer with mol ratio 2/1/2 (LA/DMT/BD) |
| BD112 | synthesized copolymer with mol ratio 1/1/2 (LA/DMT/BD) |
| BD124 | synthesized copolymer with mol ratio 1/2/4 (LA/DMT/BD) |
| PLA | polylactic acid |
| PET | Poly(ethylene terephthalate) |
| TPA | terephthalic acid |
| BHET | bis(hydroxyethyl) terephthalate |
| DP | degree of polymerization |
| MW | molecular weight |
| η | intrinsic viscosity |
| T _g | glass transition temperature |
| T _m | melting temperature |
| HMDI | hexamethylene diisocyanate |
| BDI | 1,4-butane diisocyanate |
| IPDI | isophorone diisocyanate |
| MDI | diphenylmethane diisocyanate |
| BOX | 2,2'-bis(2-oxazoline) |
| DSC | Differential Scanning Calorimetry |
| TGA | Thermo Gravimetric Analysis |
| FTIR | Fourier-Transform Infrared |
| NMR | Nuclear Magnetic Resonance |
| CDCl ₃ | deuteriochloroform |
| B | degree of randomness |
| L _{n(L)} | the number-average sequence lengths of L |
| L _{n(ET)} | the number-average sequence lengths of ET |
| Y _(L) | probability of finding L next to another L |
| X _(ET) | probability of finding ET next to another ET |
| CH ₂ Cl ₂ | dichloromethane |
| THF | tetrahydrofuran |