

OLEFIN METATHESIS OF BIORENEWABLE RESOURCES-APPLICATION OF RUTHENIUM CATALYSTS

ΒY

MR. DUY LE

A DISSERTATION SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY (CHEMISTRY) DEPARTMENT OF CHEMISTRY FACULTY OF SCIENCE AND TECHNOLOGY THAMMASAT UNIVERSITY ACADEMIC YEAR 2019 COPYRIGHT OF THAMMASAT UNIVERSITY

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THAMASAT UNIVERSITY

FACULTY OF SCIENCE AND TECHNOLOGY

DISSERTATION

BY

MR. DUY LE

ENTITLED

OLEFIN METATHESIS OF BIORENEWABLE RESOURCES-APPLICATION OF RUTHENIUM CATALYSTS

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ABSTRACT

Concerns over the depleting fossil resources and increasing CO_2 emissions are driving a strong interest in utilizing bio-renewable resources in the production of valuable synthesis materials. This research focuses on the synthesis of polyfunctional compounds, polyesters, and thermoset polymers from vegetable oils and its derivatives via olefin metathesis reactions using ruthenium-carbene catalysts. The research can be divided into three parts as follows.

In the first part, cross-metathesis (CM) of unsaturated fatty acid methyl esters [methyl oleate (MO), methyl petroselinate (MP), and methyl erucate (ME), obtained from vegetable oils] with eugenol (obtained from clove oil) proceeded under green and mild conditions (in 2-propanol or ethanol at 50 °C) in the presence of a ruthenium-carbene catalyst (called a second-generation Grubbs catalyst, **G2**). These metathesis reactions archived high conversion (>90% of MO, MP) and selectivity (>98%) even with low catalyst loading (0.1 mol % Ru). It believes that the CM reactions of UG with unsaturated fatty acid methyl esters open the route for the synthesis of a variety of polyfunctional compounds from renewable feedstocks.

The second part is the development of bio-based polymers derived from vegetable oils via olefin metathesis polymerization. In this part, the renewable polyesters were synthesized by acyclic diene metathesis (ADMET) polymerization of α, ω -dienes, 4-allyl-2-methoxyphenyl 10-undecenoate (M1), prepared from bio-renewable eugenol and castor oil (undecenoate). The second-generation Grubbs catalyst (G2) afforded polymers with unimodal molecular weight distributions (M_n = 12700, M_w/M_n = 1.85). The polymerization of M1 in the presence of a triarm cross-linker, 5-formylbenzene-1,2,3-triyl tris(undec-10-enoate), also afforded polymers with certain uniform network structures. It thus believes that the present method approach is promising and should be applicable for the synthesis of polyesters from monomers prepared from bio-renewable resources.

In the third part, bio-based thermoset polymers from norbornenefunctionalized various plant oils (olive oil, rapeseed oil, and soybean oil) were prepared via ring-opening metathesis polymerization (ROMP) in the presence of **G2** catalyst. Two norbornene-based crosslinking agents included petroleum-based norbornene and biobased norbornene (norbornene-functionalized isosorbide, NB-IS) were used as crosslinkers. The catalyst loading determined to be most effective in this study was 0.5 %wt. The glass transition temperature (T_{o}) and storage modulus (E') of the resulting bio-based thermoset films increased dramatically upon increasing catalyst loading due to the enhanced the crosslink density. The number of norbornene rings per triglyceride in the norbornene-functionalized plant oils significantly influenced on the crosslink density. Moreover, the addition of crosslinkers increased considerably the Tg and E' values of all bio-based thermoset films. The results revealed that the bio-based norbornene crosslinker (NB-IS) is comparative to replace the petroleum-based norbornene in target to improve the thermo-mechanical properties of the bio-based thermoset films. These plant oil-based thermosets are potential promising environmentally friendly thermoset polymers.

Keywords: Renewable resources, Vegetable oils, Cross-metathesis (CM), Acyclic diene metathesis (ADMET), Ring-opening metathesis polymerization (ROMP), Polyfunctional compounds, Polyesters, Thermoset polymers, Ru-carbene catalysts.

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TABLE OF CONTENTS

	Page
ABSTRACT	(1)
ACKNOWLEDGEMENTS	(3)
LIST OF TABLES	(10)
LIST OF FIGURES	(11)
LIST OF SCHEMES	(15)
LIST OF ABBREVIATIONS	(17)
CHAPTER 1 INTRODUCTION	1
1.1 Motivation of the research	1
1.2 Dissertation organization	3
1.3 Research objectives	4
CHAPTER 2 BACKGROUND AND LITERATURE REVIEW	6
2.1 Olefin metathesis	6
2.1.1 Development of well-defined olefin metathesis catalyst	6
2.1.2 General mechanism of olefin metathesis using Ruthenium-	9
2.2 Ring-opening metathesis polymerization (ROMP)	10
2.2 Any opening metathesis polymerization (Nown)	12
2.4 Vegetable oils	14
	1-1

TABLE OF CONTENTS (continued)

	Page
2.4.1 Structure of vegetable oils	14
2.4.2 Metathesis of vegetable oil and its derivatives	16
2.5 Eugenol	25
2.6 Isosorbide	26
2.7 References	27
CHAPTER 3 EFFICIENT CONVERSION OF RENEWABLE UNSATURATED FATTY	34
ACID METHYL ESTERS BY CROSS METATHESIS WITH EUGENOL	
3.1 Introduction	34
3.2 Materials and Methods	36
3.2.1 Materials	36
3.2.2 Measurements and Characterization	37
3.2.3 The effective carbon number (ECN) of materials	39
3.2.4 General procedure for the cross-metathesis reaction of fatty	39
acid methyl esters (MO, MP, ME and MU) with eugenol (UG)	
3.3 Results and Discussion	40
3.3.1 Cross-metathesis of methyl oleate (MO) with eugenol (UG)	40
using ruthenium catalysts	
3.3.1.1 Effect of solvent and MO concentration in cross-	42
metathesis of MO with UG	
3.3.1.2 Effect of UG/MO molar ratio, reaction time and	44
temperature in cross-metathesis of MO with UG	
3.3.1.3 Effect of catalyst loading and different types of Ru-	46
carbene catalysts in cross-metathesis of MO with UG	
3.3.2 Structure characterization of CM products of MO with UG	48

	Page
3.3.3 Cross-metathesis of various methyl esters [methyl petroselinate (MP), methyl erucate (ME), and methyl 10- undecanoate (MU)] with UG	51
3.4 Conclusions	53
3.5 References	54
CHAPTER 4 SYNTHESIS OF NEW POLYESTERS BY ACYCLIC DIENE METATHESIS	61
Polymerization of bio-based α, ω -dienes prepared from	
EUGENOL AND CASTOR OIL (UNDECENOATE)	
4.1 Introduction	61
4.2 Materials and Methods	63
4.2.1 Materials	63
4.2.2 Measurements and Characterizations	63
4.2.3 Synthesis of 4-allyl-2-methoxyphenyl undec-10-enoate	64
monomer (M1)	
4.2.4 Synthesis of 5-hexen-1-yl 10-undecenoate monomer (M2)	65
4.2.5 Synthesis of 10-undecen-1-yl 10-undecenoate monomer	66
(M3)	
4.2.6 Synthesis of 5-formylbenzene-1,2,3-triyl tris(undec-10-	67
enoate) crosslinker (CL)	
4.2.7 General procedure for synthesis of polymers by acyclic	68
diene metathesis (ADMET) polymerization using ruthenium	
catalysts	
4.3 Results and Discussion	69
4.3.1 Structure characterization of monomers and crosslinker	69
4.3.2 ADMET polymerization of monomer M1	76
4.3.3 ADMET polymerization of monomers M2 and M3	81

TABLE OF CONTENTS (continued)

	Page
4.3.4. Effect of crosslinker on ADMET polymerization of M1	84
4.3.5 Thermal properties of the polymers	87
4.4 Conclusions	88
4.5 References	89
CHAPTER 5 SYNTHESIS OF RENEWABLE THERMOSET FILMS BY RING-OPENING	95
METATHESIS POLYMERIZATION (ROMP) OF NORBORNENE-	
FUNCTIONALIZED PLANT OILS	
5.1 Introduction	95
5.2 Materials and Methods	97
5.2.1 Materials	97
5.2.2 Synthesis of epoxidized plant oils [olive oil (OO), rapeseed	98
oil (RO) and soybean oil (SO)]	
5.2.3 Synthesis of norbornene-functionalized plant oils	100
5.2.4 Synthesis of norbornene-functionalized isosorbide (NB-IS)	101
5.2.5 Preparation of bio-based thermoset films via ROMP	103
5.2.6 Characterization of monomers and thermoset films	104
5.3 Results and Discussion	105
5.3.1 Structure characterization of norbornene-functionalized	105
plant oil monomers	
5.3.2 Structure characterization of norbornene-functionalized	108
isosorbide (NB-IS)	
5.3.3 Fourier Transform Infrared (FT-IR) spectroscopy of	110
norbornene-plant oil thermosets and norbornene-plant	
oil with crosslinkers thermosets	
5.3.4 ROMP of the norbornene-functionalized plant oils	112

TABLE OF CONTENTS (continued)

	Page
5.3.5 Dynamic mechanical analysis (DMA) of bio-based thermosets	115
films from norbornene-functionalized with different plant	
oils	
5.3.6 Dynamic mechanical analysis (DMA) of norbornene-	118
functionalized plant oils with different crosslinkers	
5.3.7 Thermogravimetric analysis (TGA) of the bio-based	122
thermoset films	
5.4 Conclusions	126
5.5 References	127
CHAPTER 6 GENERAL CONCLUSIONS	
6.1 General conclusions	132
6.2 Recommendations	134
APPENDICES	135
APPENDIX A	136
APPENDIX B	155
APPENDIX C	159

BIOGRAPHY

(9)

173

LIST OF TABLES

Tables	Page
2.1 Functional group tolerance of olefin metathesis catalyst	9
2.2 Fatty acid components and iodine value (IV) of the most common	16
vegetable oils	
3.1 ECN contributions of atoms or groups	39
3.2 Effect of solvent and MO concentration in CM of MO with UG by ${f G2}$	43
3.3 Effect of UG/MO molar ratio, reaction time and temperature in CM of	45
MO with UG by G2	
3.4 Effect of catalyst loading and different types of Ru-carbene catalysts in	46
CM of MO with UG	
3.5 CM of unsaturated fatty acid methyl esters (MP, ME and MU) with UG	53
by G2	
4.1 ADMET polymerization of 4-allyl-2-methoxyphenyl 10-undecenoate	78
(M1) by Ru catalysts	
4.2 ADMET polymerization of M2 and M3 by $G2$ catalyst	82
4.3 ADMET polymerization of M1 using G2 in the presence of cross-linker	85
(CL)	
5.1 Fatty acid compositions in the starting plant oils determined based on	98
GC-FID analysis	
5.2 Extraction data of the bio-based thermosets films at various catalyst	113
loading and different plant oils	
5.3 DMA analysis of the bio-based thermoset films at various catalyst	117
loading and different plant oils	
5.4 DMA analysis of the bio-based thermoset films for different plant oils	120
with various crosslinkers	
5.5 TGA data for the bio-based thermoset films	124

LIST OF FIGURES

Figures	Page
2.1 Generation of Grubb Ruthenium carbene catalysts	8
2.2 General structure of triglyceride and the most common fatty a	icids 15
obtained from various vegetable oils	
2.3 The chemical structure of eugenol (UG)	26
3.1 GC-FID chromatogram for the cross-metathesis reaction of me	thyl 41
oleate (MO) with eugenol (UG)	
3.2 ^1H NMR spectra (in CDCl $_3$ at 25 °C) of Dec-1-ene (CM1) with	n its 48
assignments	
3.3 ^{1}H NMR spectra (in CDCl_3 at 25 °C) of Methyl dec-9-enoate (CM2)	with 49
its assignments	
3.4 ^1H NMR spectra (in CDCl_3 at 25 °C) of 2-methoxy-4-(undec-2-e	n-1- 49
yl)phenol (CM3) with its assignments	
3.5 ^1H NMR spectra (in CDCl $_3$ at 25 °C) of Methyl 11-(4-hydrox	xy-3- 50
methoxyphenyl)undec-9-noate) (CM4) with its assignments	
3.6 1 H-NMR spectra (in CDCl $_{3}$ at 25 °C) of 4,4'-(but-2-ene-1,4-diyl)b	is(2- 56
methoxyphenol) (SM4) with its assignments	
4.1 Synthesis procedure of 4-allyl-2-methoxyphenyl undec-10-end	oate 65
monomer (M1)	
4.2 Synthesis procedure of 5-hexen-1-yl 10-undecenoate monomer (M	12) 66
4.3 Synthesis procedure of 10-undecen-1-yl 10-undecenoate mono	mer 67
(M3)	
4.4 Synthesis procedure of 5-formylbenzene-1,2,3-triyl tris(undec	:-10- 68
enoate) crosslinker (CL)	
4.5 ^1H NMR spectra (in CDCl $_3$ at 25 °C) of 4-allyl-2-methoxypheny	l 10 71
undecenoate (M1) with its peak assignments	
4.6 13 C NMR spectra (in CDCl $_3$ at 25 °C) of 4-allyl-2-methoxypheny	l 10 71
undecenoate (M1) with its peak assignments	

LIST OF FIGURES (continued)

Figures	Page
4.7 1 H NMR spectra (in CDCl $_3$ at 25 °C) of 5-formylbenzene-1,2,3-triyl	72
tris(undec-10-enoate) (CL) with its peak assignments	
4.8 13 C NMR spectra (in CDCl $_3$ at 25 °C) of 5-formylbenzene-1,2,3-triyl	72
tris(undec-10-enoate) (CL) with its peak assignments	
4.9 ^1H NMR spectra (in CDCl_3 at 25 °C) of 5-hexen-1-yl 10-undecenoate	73
(M2) with its peak assignments	
4.10 13 C NMR spectra (in CDCl $_3$ at 25 °C) of 5-hexen-1-yl 10-undecenoate	74
(M2) with its peak assignments	
4.11 ^1H NMR spectra (in CDCl $_3$ at 25 °C) of 10-undecen-1-yl 10-	75
undecenoate (M3) with its peak assignments	
4.12 13 C NMR spectra (in CDCl $_3$ at 25 °C) of 10-undecen-1-yl 10-	75
undecenoate (M3) with its peak assignments	
4.13 GPC traces of polymers (P1) in ADMET polymerization of M1 under	79
(a) effect of different G2 loading, and (b) effect of Ru catalysts.	
Detailed data are shown in Table 4.1	
4.14 1 H NMR spectra (in CDCl $_3$ at 25 °C) for (a) 4-allyl-2-methoxyphenyl	80
10-undecenoate (M1), and (b) the resultant polymer (P1) prepared	
by the ADMET polymerization (run 8)	
4.15 13 C NMR spectra (in CDCl $_3$ at 25 °C) for (a) 4-allyl-2-methoxyphenyl	81
10-undecenoate (M1), and (b) the resultant polymer (P1) prepared	
by the ADMET polymerization (run 8)	
4.16 ^1H NMR spectra (in CDCl $_3$ at 25 °C) for (a) 5-hexen-1-yl 10-	83
undecenoate (M2), and (b) the resultant polymer (P2) prepared by	
the ADMET polymerization (run 14)	
4.17 ^1H NMR spectra (in CDCl $_3$ at 25 °C) for (a) 10-undecen-1-yl 10-	84
undecenoate (M3), and (b) the resultant polymer (P3) prepared by	
the ADMET polymerization (run 19)	

LIST OF FIGURES (continued)

Figures	Page
4.18 GPC traces of polymers (PL1) in ADMET polymerization of M1 with	86
CL under effect of CL loading and polymerization time	
4.19 ^{1}H NMR spectra (in CDCl $_{3}$ at 25 °C) for (a) cross-linker (CL), (b) the	86
resultant polymer (P1) prepared by ADMET polymerization of M1	
(run 8), and (c) resultant polymer (PL1) prepared by the ADMET	
polymerization of M1 in the presence of CL (5.0 mol%, sample run	
24)	
4.20 DSC thermograms for (a) polymers P1 (sample run 8), PL1 (sample	87
run 24), and (b) polymers P2 (sample run 14), P3 (sample run 19),	
second heating cycle at a heating/cooling rate of 10 °C/min	
5.1 Epoxidation of triglycerides from plant oils (representative olive oil)	99
5.2 Illustration of norbornene-functionalized plant oils (representative	101
olive oil)	
5.3 The overall procedure for the synthesis of norbornene-functionalized	102
isosorbide (NB-IS)	
5.4 Schematic of the overall procedure for the synthesis of bio-based	104
thermoset films via ROMP	
5.5 ^{1}H NMR spectra (in CDCl_3 at 25 °C) of olive oil (OO), epoxidized olive	107
oil (EOO) and norbornene-functionalized olive oil (NB-OO)	
5.6 FT-IR spectra of olive oil (OO), epoxidized olive oil (EOO) and	108
norbornene functionalized olive oil (NB-OO)	
5.7 FT-IR spectra of isosorbide and norbornene-functionalized isosorbide	109
(NB-IS)	
5.8 (a) Synthesis scheme of norbornene-isosorbide (NB-IS) through the	110
coupling of 5-norbornene-2-carbonyl chloride to hydroxyl groups on	
isosorbide, (b) 1 H NMR spectrum (in CDCl $_3$ at 25 °C) of crosslinker (NB-	
IS)	

LIST OF FIGURES (continued)

Fig	gures	Page
	5.9 FT-IR spectra of (a) NB-OO, NB-OO film and NB-OO with CL, and (b)	111
	thermosets with different plant oils	
	5.10 $^1\mathrm{H}$ NMR spectra (in CDCl_3 at 25 °C) of the soluble materials of the	115
	NB-OO thermoset films at various catalyst loading	
	5.11 DMA thermograms for storage modulus and tan $\boldsymbol{\delta}$ curves as a	116
	function of temperature for NB-OO thermoset films at various	
	catalyst loading (1 Hz, 3 °C/min)	
	5.12 DMA thermograms for storage modulus and tan $\boldsymbol{\delta}$ curves as a	118
	function of temperature for the thermoset films of different plant	
	oils with 0.5 %wt G2 (1 Hz, 3 °C/min)	
	5.13 DMA thermograms for storage modulus and tan δ curves for (a) NB-	121
	OO, (b) NB-RO, and (c) NB-SO thermoset films with different	
	crosslinkers at 0.5%wt G2 (1 Hz, 3 °C/min)	
	5.14 (a) TGA and (b) DTG curves of the representative NB-OO thermoset	122
	film at various catalysts loading	
	5.15 (a) TGA and (b) DTG curves of bio-based thermoset polymer films	123
	from different plant oils (olive oil, rapeseed oil and soybean oil)	
	5.16 TGA curves of thermoset polymer films (a) NB-OO (b) NB-RO and (c)	125
	NB-SO with different crosslinkers	

LIST OF SCHEMES

Schemes	Page
2.1 Olefin metathesis reactions	6
2.2 Mechanism of olefin metathesis	7
2.3 Mechanism of olefin metathesis using $(PCy_3)_2Cl_2Ru=CHPh$	10
2.4 ROMP reaction of cyclopentene	10
2.5 Mechanism of G2 -catalyzed ROMP relied on Chauvin's Mechanism	11
2.6 ROMP of (a) 2,3-disubstituted norbornadiene and (b) 2-substituted	12
norborn-5-ene	
2.7 Generally mechanism of ADMET polymerization	13
2.8 Self-metathesis of methyl oleate	17
2.9 Self-metathesis of methyl 10-undecanoate	18
2.10 Self-metathesis of methyl linolenate	18
2.11 Cross-metathesis of methyl oleate with 3-hexene	19
2.12 Synthesis of saturated α, ω -diols and ω -functional aldehydes from	20
10-undecenal	
2.13 Different monomers obtained from self-metathesis/cross-metathesis	21
of fatty acid derivatives with methyl acrylate	
2.14 Cross-metathesis of methyl oleate with cyclododecene	22
2.15 Triblock copolymers by ROMP with sequential monomer addition	25
2.16 Reaction scheme of the conversion of starch to isosorbide	27
3.1 Typical unsaturated fatty acid methyl esters from plant oils or algae-	35
derived feedstocks, and eugenol obtained from biomass	
3.2 Cross-metathesis (CM) of eugenol (UG) with methyl oleate (MO) or	37
other unsaturated fatty acid methyl esters	
3.3 Proposed mechanism of CM between MO and UG.	41
3.4 Degradation of the first-generation Grubb catalyst G1 with ethanol	47
3.5 The second metathesis reactions of the CM products	47

LIST OF SCHEMES (continued)

Schemes	Page
3.6 CM of various methyl esters [Methyl petroselinate (MP),	51
Methylerucate (ME), and Methyl 10- undecanoate (MU)] with UG	
3.7 Proposed isomerization and CM of MU isomerization with UG	52
4.1 Reaction scheme of synthesizing monomer M1	64
4.2 Reaction scheme of synthesizing monomer M2	65
4.3 Reaction scheme of synthesizing monomer M3	66
4.4 Reaction scheme of synthesizing crosslinker (CL)	67
4.5 Synthesis of monomers (M1-M3)	69
4.6 Acyclic Diene Metathesis (ADMET) polymerization of M1 in the	76
presence of Ru-carbene catalysts	
4.7 Acyclic Diene Metathesis (ADMET) polymerization of M2 and M3 in the	82
presence of Ru-carbene catalyst (G2)	
4.8 Acyclic Diene Metathesis (ADMET) polymerization of 4-allyl-2-	84
methoxyphenyl 10-undecenoate (M1) in the presence of 5-	
formylbenzene-1,2,3-triyl tris(undec-10-enoate) (CL)	
5.1 In situ epoxidation of triglyceride with hydrogen peroxide and formic	100
acid	
5.2 Synthesis scheme of norbornene-functionalized plant oil	101
(representative olive oil) via epoxidized ring opening with	
norbornene carboxylic acid	
5.3 A schematic illustration of the formation of norbornene-isosorbide	103
(NB-IS) through the coupling of 5-norbornene-2-carbonyl chloride to	
hydroxyl (-OH) groups on isosorbide (IS)	
5.4 Synthesis scheme of norbornene-functionalized plant oils	106
(representative norbornene-olive oil, NB-OO)	
5.5 ROMP of norbornene-functionalized plant oils (representative NB-OO)	113

LIST OF ABBREVIATIONS

Symbols/Abbreviations	Terms
ADMET	Acyclic diene metathesis
APCI	Atmospheric pressure chemical ionization
ATMS	Allyltrimethylsilane
ATR-FTIR	Attenuated Total Reflectance Fourier
	Transform Infrared Spectrometer
BCO	Norbornene-functionalized castor oil
CL	Crosslinker
CL1	1,4-bis[dimethyl[2-(5-norbornen-2-
	yl)ethyl]silyl]benzene
СМ	Cross-metathesis
СО	cis-4-octene
СО	Cyclooctene
CS	<i>cis</i> -stilbene
DCM	Dichloromethane
DCPD	Dicyclopentadiene
DMA	Dynamic mechanical analysis
DMAP	4-dimethylaminopyridine
DMC	Dimethyl carbonate
DMF	N,N-Dimethylformamide
DSC	Differential scanning calorimetric
DTG	Derivative Thermogravimetry
E'	Storage modulus
E''	Loss modulus
ECN	Effective carbon number
ENB	Ethylidene-2-norbornene
EOO	Epoxidized olive oil

LIST OF ABBREVIATIONS (continued)

Symbols/Abbreviations	Terms
EPO	Epoxidized plant oil
ERO	Epoxidized rapeseed oil
ESO	Epoxidized soybean oil
FAME	Fatty acid methyl ester
G1	First-generation Grubbs catalyst
G2	Second-generation Grubbs catalyst
G3	Third-generation Grubbs catalyst
GC-FID	Gas chromatography Flame ionization detector
GC-MS	Gas Chromatography-Mass spectroscopy
GPC	Gel-permeation chromatography
Hex	5-hexene-1-ol
HG2	Second-generation Hoveyda-Grubbs catalyst
IS	Isosorbide
ME	Methyl erucate
MO	Methyl oleate
MP	Methyl petroselinate
MU	Methyl 10-undecanoate
NB	bicyclo[2.2.1]heptene-2
NBCA	5-norbornene-2-carboxylic acid
NB-IS	Norbornene-Isosorbide
NB-OO	Norbornene-Olive oil
NB-RO	Norbornene-Rapeseed oil
NB-SO	Norbornene-Soybean oil
NCA	Norbornenyl-functionalized castor oil alcohol
NBE	Norbornene
NBE	Norbornene

LIST OF ABBREVIATIONS (continued)

Symbols/Abbreviations	Terms
NCO	Norbornenyl-functionalized castor oil
NMR	Nuclear magnetic resonance
NPO	Norbornene palm olein
00	Olive oil
R	Universal gas constant
RCM	Ring-closing metathesis
RO	Rapeseed oil
ROMP	Ring-opening metathesis polymerization
SEM	Scanning electron microscopy
SO	Soybean oil
т	Absolute temperature
Tg	Glass transition temperature
T _m	Melting temperature
TEA	Triethylamine
TGA	Thermogravimetric Analysis
THBD	3,4,5-trihydroxybenzaldehyde
TLC	Thin layer chromatography
TMS	Tetramethylsilane
UDC	10-undecenoyl chloride
UDO	10-undecen-1-ol
v _e	Crosslink density
Δ	Tangent

CHAPTER 1 INTRODUCTION

1.1 Motivation of the research

The depletion of fossil resources and the impact of global warming are driving strong demand for an alternative to fossil feedstocks from renewable resources. However, the oleochemical industry is still strongly dependent on the utilization of petroleum-derived monomers. Vegetable oils (composed of predominantly of triglyceride with three fatty acid-based ester chains) are one of the most important and frequently used renewable resources to produce fine-chemicals and polymeric materials. Long-chain vegetable oils such as soybean oil, rapeseed oil (containing mainly unsaturated C18 chain) and palm oil (containing both C16 and unsaturated C18 chain) are especially highly utilized in the production of oleochemicals. Short and medium-chain vegetable oils such as coconut and palm oils consist mainly of lauric (C12) and myristic (C14) acid chains are important sources for the synthesis of cosmetics, detergents, soaps, and emulsifiers. Castor oil (containing 85–95% ricinoleic acid) is considered an important source of the oleochemicals industry. Besides, unsaturated fatty acid esters (vegetable oil derivatives) are usually obtained from the transesterification of vegetable oils with alcohol. They are also considered promising potential sources for producing chemical compounds and polymeric materials. More than 90% of all oleochemical reactions of unsaturated fatty acid esters are modified at the carboxy function for the conversion into fatty alcohols and fatty amines. Moreover, due to the inherent carbon-carbon double bond functionality, they offer the possibility of being transformed via several very efficient catalytic processes, such as hydrogenation, epoxidation, ozonolysis, and dimerization. Recently, the development of catalysts in olefin metathesis allows the chemist to directly polymerize or introduce a variety of functional groups to these renewable resources in an efficient manner. The utilization of bio-renewable materials such as vegetable oils and derivatives in the olefin metathesis has been considered as the promising subject in terms of both green chemistry and oleochemistry in recent years. For

example, cross-metathesis (CM) of unsaturated fatty acid esters with functionalized olefins to produce α, ω -bifunctional linear molecules, valuable monomers for synthesis of polyesters and polyamides, have been investigated. A couple of reports have recently appeared on the transformation by olefin metathesis of eugenol, another Eugenol, (UG, 4-allyl-2-methoxyphenol) interesting renewable resource. is representative of the kind of unsaturated compounds obtained from clove oil. Owing to its polyfunctional groups [hydroxyl (–OH), methoxy (–OCH₃) and allyl groups], UG can be used as starting material for synthesis of new compounds exemplified in designing polymer networks via thiol-ene coupling or bismaleimide networks. UG can also be transformed via olefin metathesis due to its inherent terminal olefin group. Recently, study on UG mainly focused on Ru-catalyzed olefin metathesis reactions such as direct self-metathesis and cross-metathesis with electron-deficient olefins. Thus, it is possible to prepare different types of functionalized phenol derivatives to develop new routes for synthesis of different multifunctional products from UG. Besides, olefin metathesis has been used to produce vegetable oil-based polymers, primarily by acyclic diene metathesis polymerization (ADMET) and ring-opening metathesis polymerization (ROMP). The ADMET and ROMP are considered as efficient methods for bio-based polymers synthesis because these polymerizations can be performed under environmentally benign conditions. Therefore, olefin metathesis with vegetable oil and their derivatives can contribute to a sustainable development of our future, since this approach has great potential for the substitution of currently used petrochemicals and a variety of value-added chemical intermediates, especially for the polymer industry.

In this research, utilization of ruthenium catalysts to transform renewable resources such as vegetable oil and their derivatives into valuable products (fine chemicals, polyfunctional compounds, bio-based polyesters and thermoset polymers) via cross-metathesis, ADMET polymerization and ROMP, respectively, were investigated. The research involves three main parts: The first part is to study CM of renewable unsaturated fatty acid methyl esters (obtained from vegetable oil) with eugenol (obtained from clove oil). These CM reactions were performed under mild conditions (in ethanol or 2-propanol at 50 °C) using low catalyst loading (0.1 %mol

Ru). The CM of unsaturated fatty acid esters with UG should thus afford several new and bio-sourced multifunctional phenol derivatives having the potential for the synthesis of polyesters.

The second part is to synthesis of bio-based polymers from vegetable oil derivatives. The renewable polyesters were synthesized via ADMET polymerization of α, ω -dienes, 4-allyl-2-methoxyphenyl 10-undecenoate (M1), prepared from derived bio-renewable eugenol and castor oil. Polyester with high molecular weight and unimodal molecular weight distribution have been obtained under optimized conditions. The crosslinked polyesters were also prepared by ADMET polymerization of monomer M1 in the presence of crosslinker. The third part focuses on the preparation and characterization of renewable thermoset films by ring opening metathesis polymerization (ROMP) of norbornene-functionalized plant oils (olive oil, rapeseed oil, and soybean oil). The thermoset polymers in the presence of bio-based norbornene as a crosslinker (obtained from norbornene-functionalized isosorbide) and petroleumbased norbornene crosslinker were also investigated.

1.2 Dissertation organization

The dissertation is divided into six chapters, in which Chapters 3, 4 and 5 are each manuscript that has either been published in or prepared for submission to scholarly journals. The detailed of the dissertation organization is shown below.

Chapter 1 gives the motivations of the research and organization of the dissertation as well as the objectives of the research

Chapter 2 provides general introduction that outlines the background olefin metathesis. It also includes a briefly introduction to the mechanism of CM, ADMET polymerization, and ROMP followed by a detailed olefin metathesis in vegetable oils and their derivatives. Finally, a brief discussion about structure of eugenol and isosorbide is also introduced.

Chapter 3 involves the cross-metathesis of eugenol (UG) with a series of unsaturated fatty acid methyl esters having an internal double bond, such as MO, methyl petroselinate (MP), and methyl erucate (ME), and that having a terminal double bond (methyl 10-undecanoate, MU), in the presence of Ru-carbene catalysts. The effect of reaction conditions (such as time, temperature, substrate concentration, and ratio of UG/substrate) toward both activity and selectivity were investigated and discussed in detail.

Chapter 4 involves synthesis of new polyester by ADMET polymerization of α , ω -dienes prepared from bio-renewable eugenol and castor oil (undecenoate). The ruthenium-carbene (called second generation Grubbs) catalyst afforded high molecular weight polymers with unimodal molecular weight distributions ($M_n = 12700$, $M_w/M_n = 1.85$). The polymerization in the presence of a triarm cross-linker, 5formylbenzene-1,2,3-triyl tris(undec-10-enoate), also afforded polymers with certain uniform network structures.

Chapter 5 includes the synthesis and characterization of bio-based thermoset polymer films by ROMP of norbornene-functionalized plant oils (olive oil, rapeseed oil, and soybean oil) in the presence of Ru catalyst. Norbornenefunctionalized isosorbide was synthesized and used as a renewable crosslinker to increase the glass transition temperature and storage modulus for the resulting thermoset films. A petroleum-based norbornene was also used as a crosslinker for a comparison. The overall thermal-mechanical properties of the resulting thermoset films were investigated in detail by dynamic mechanical analysis and thermogravimetric analysis

Chapter 6 provides general conclusions and suggestions of future works.

1.3 Research Objectives

The research target of the first topic is to study the efficient conversion of unsaturated fatty acid methyl esters (FAME) by CM with eugenol (UG) in order to produce bio-sourced polyfunctional compounds. A series of unsaturated FAME having an internal double bond, such as methyl oleate (MO), methyl petroselinate (MP), and methyl erucate (ME), and that having a terminal double bond (methyl 10-undecanoate, MU) were utilized as substrates to CM with UG in the presence of Ru-carbene catalysts. The effect of solvents (green solvent and chlorinated solvents), reaction time (5–30 min), reaction temperature (25–80 °C), substrate concentration (1.0–20 M), and

UG/substrate ratio (1.0–20 molar ratio) on catalyst activity and selectivity have been studied.

The research target for the second topic on the synthesis of renewable polymers is to develop bio-based polyester from castor oil derivative and eugenol. This attempt consists of two stages: (1) synthesis of bio-based α, ω -dienes monomer, 4-allyl-2-methoxyphenyl 10-undecenoate (M1), from castor oil derivative (undecenoate) and eugenol, (2) synthesis of new polyester by ADMET polymerization of monomer M1 in the presence of Ru-catalysts. The ADMET polymerization conditions such as catalyst loading (0.5–3.0 mol%), type of catalyst (G1, G2 and G3) and reaction time (3–18 h) were investigated and discussed in detail. The ADMET polymerization of M1 in the presence of triarm crosslinker, 5-formylbenzene-1,2,3-triyl tris(undec-10enoate) was also studied. Two aliphatic polyesters with linear aliphatic α, ω -dienes were also prepared for comparison. The thermal properties of the resultant polymers were characterized by differential scanning calorimetry (DSC).

The research target for the third topic on bio-renewable thermosets is to develop bio-based thermoset films from different plant oils. This effort is divided into three steps (1) Synthesis of norbornene-functionalized various plant oils (olive oil, rapeseed oil, and soybean oil) and norbornene-functionalized isosorbide (NB-IS) used as bio-based crosslinker, (2) preparation of bio-renewable thermoset films by ringopening metathesis polymerization (ROMP) using Grubbs second-generation catalyst, and (3) characterization of the bio-renewable thermoset films. The bio-based thermoset films were prepared by ROMP of norbornene-functionalized plant oils. The ROMP conditions such as catalyst loading (0.0625–0.5 %wt) and cured temperature (80 and 120 °C) were investigated. The influence of different crosslinkers (petroleum-based norbornene and norbornene-isosorbide) and crosslinkers contents (5-15 %wt) were also studied in detail. The characterization of the bio-based thermoset films focused on the thermal-mechanical properties, especially storage modulus (E') and glass transition temperature (T_e), which should clarify the possibility to the potential applications of the thermoset films. The thermal properties of the bio-based thermoset films were also investigated.

CHAPTER 2

BACKGROUND AND LITERATURE REVIEW

2.1 Olefin metathesis

Olefin metathesis reaction was first discovered in the mid-1950s,¹ and the term "olefin metathesis" is used to describe an exchange reaction between two olefins, in which there is an exchange of carbon atoms amid a pair of double bonds. The mechanism reaction highly depends on the nature of carbon-carbon double bonds in the reactants. The olefin metathesis is classified to four different reactions consisting of (1) Cross-metathesis (CM, an exchange between substituted double bonds creating an unsaturated organic molecule and ethylene), (2) Acyclic diene metathesis polymerization (ADMET, where a diene with terminal double bonds is polymerized by CM), (3) Ring-closing metathesis (RCM, in which a diene is closed to form a cyclic olefin and ethylene) and (4) Ring-opening metathesis polymerization (ROMP, where a cycloolefin is opened to create a linear polyunsaturated), as shown in Scheme 2.1. The mechanistic variability of the olefin metathesis makes it become an efficient tool for carbon-carbon double bonds transformation to produce valuable organic compounds and polymeric materials.²



Scheme 2.1 Olefin metathesis reactions.²

2.1.1 Development of well-defined olefin metathesis catalyst

The reaction of olefin metathesis is believed to occur through a metallacyclobutane intermediate formed between a metal alkylidene and an olefin as shown in Scheme 2.2.³ These systems consist of transition metal salts combined with main group organometallic reagents or deposited on solid supports such as WCl_6/Bu_4Sn , $WOCl_4/EtAlCl_2$, MoO_3/SiO_2 , and Re_2O_7/Al_2O_3 . These catalysts have been widely applied in olefin metathesis in the early years due to their low cost and facile synthesis.⁴



Scheme 2.2 Mechanism of olefin metathesis.³

However, the utilization of these catalysts was limited because they required harsh conditions and strong Lewis acids, which make them incompatible with most functional groups. Moreover, the reactions were hard to initiate and control because very small amount of the active species formed in the mixture of catalyst.⁴ Later on, Schrock *et al.*⁵ have developed highly reactive molybdenum and tungsten alkylidenes with a general formula (ArN)(R'O)₂M=CHR (where Ar =2,6-Prⁱ₂-C₆H₃, R =CMe₂-Ph, and R' =C(CH₃)(CF₃)₂). The outstanding of these catalysts is its high activity. Thus, they are able to react with both terminal and internal olefins and undergo ROMP with low-strain monomers, as well as undergo ring-closing metathesis with sterically demanding and electron-poor substrates. However, the utilization of these catalysts was limited because they are very sensitive to moisture and air because of the high oxophilicity of the metal centers.

In the mid-1990s, Grubbs and co-workers developed well-defined ruthenium alkylidenes via reaction of $RuCl_2(PPh_3)_3$ with phenyldiazomethane and tricyclohexylphosphine, named as the first-generation Grubbs catalyst $(PCy_3)_2Cl_2Ru=CHPh$ (G1).⁶ This catalyst is not only compatible with most functional groups but also stable to air and moisture, especially active towards olefin metathesis reactions. The mono-substitution of PCy₃ by N-heterocyclic carbene (NHC) ligand in the G1 catalyst structure formed the second-generation Grubbs catalyst (G2). This catalyst is not only having higher activity but also more tolerant with most functional groups as well as better thermal stability than the **G1** catalyst. Due to the outstanding properties, ruthenium-alkylidenes have been expanded application in olefin metathesis.⁷ The mono-substitution of PCy₃ by NHC remarkably improved the reaction rate and the activity of the catalyst. The rate of initiation, however, was still slower than the rate of propagation, producing polydisperse products. In the latest generation of the catalyst, the remaining PCy₃ in the **G2** catalyst was substituted with two 3bromopyridine ligands, resulted in third-generation Grubbs catalyst (**G3**) (Figure 2.1).⁸ This substitution increased the initiation rate to be commensurate with the rate of propagation, producing polymers with controlled molecular weights and narrow molecular weight distribution. The advances in metathesis catalysts have possibly allowed synthesizing a range of polymers with functionality and molecular weight control that previously were not possible via organometallic catalysts.



 $Cy = cyclohexyl, Ar = 2,4,6-Me_3C_6H_2$



The catalyst activity can be hampered by the functional groups in the substrate employed or solvent (comprising oxygen and water) according to various ways. Therefore, a suitable way to enhance the compatibility of functional group in olefin metathesis reactions is the development of a catalyst which reacts preferentially with olefins in the presence of heteroatomic functionalities. Ruthenium-alkylidenes react preferentially with olefinic double bonds compared to most other catalysts. This feature makes the Ru-catalysts highly stable towards alcohols, amides, aldehydes, and carboxylic acids as shown in Table 2.1.⁴ The development of the well-defined ruthenium-carbenes catalysts (such as **G1**, **G2**, and **G3**) has turned olefin metathesis becoming an efficient method for carbon-carbon transformation applied for the production of various organic compounds and polymeric materials over the past decade. Extensive mechanistic investigations of this catalyst system have been continuing to study to understand how they work and how they can be improved. **Table 2.1** Functional group tolerance of olefin metathesis catalyst.⁴

Titanium	Tungsten	Molybdenum	Ruthenium	*
Acids	Acids	Acids	<u>Olefins</u>	 ≩
Alcohols, water	Alcohols, water	Alcohols, water	Acids	activi
Aldehydes	Aldehydes	Aldehydes	Alcohols, water	sing a
Ketones	Ketones	<u>Olefins</u>	Aldehydes	JCrea
Esters, amides	<u>Olefins</u>	Ketones	Ketones	<u> </u>
<u>Olefins</u>	Esters, amides	Esters, amides	Esters, amides	

Increasing functional group tolerance ightarrow

2.1.2 General mechanism of olefin metathesis using Rutheniumcarbene catalyst

Initial mechanistic studies of catalyst **G1** and its analogs established that olefin metathesis reactions in these systems are inhibited by the addition of free phosphine. The mechanism of olefin metathesis is shown in Scheme 2.3. As shown in Scheme 2.3, the first step is olefin coordination to the transition metal center, assumedly *cis* to the alkylidene. In route (A), the dissociation of phosphine and rotation of alkylidene happen to form the 16-electron intermediate (1), where the olefin remains *cis* to the alkylidene. Then this intermediate undergoes metallocyclobutane formation *cis* to the bound phosphine, followed by the scission to release the metathesis products. In contrast, in route (B) involves the dissociation of phosphine and redistribution of the olefin *trans* to the remaining phosphine. Then this intermediate (2) undergo metallocyclobutane formation *trans* to the phosphine. Although route (B) was not initially preferred because of the considering of the reversible, it is currently being reevaluated in more detail. In addition, the mechanism in which both phosphines remain bound to the transition metal center seems to make an insignificant contribution to the overall activity.



Scheme 2.3 Mechanism of olefin metathesis using (PCy₃)₂Cl₂Ru=CHPh.⁴

2.2 Ring-opening metathesis polymerization (ROMP)

ROMP is a type of olefin metathesis chain-growth polymerization, in which a mixture of cyclic olefin is transformed into a linear unsaturated polymer as illustrated in Scheme 2.4.^{9,10} The main characteristic to distinguish ROMP with other olefin addition polymerizations (for example, ethylene \rightarrow polyethylene) is that in ROMP any unsaturation associated with the monomer is conserved when it is converted to polymer.



Scheme 2.4 ROMP reaction of cyclopentene.^{9,10}

The mechanism of ruthenium-catalyzed ROMP relies on the Chauvin's mechanism as shown in Scheme 2.5.¹¹ The first step involves the dissociation of 14electron complex from the metathesis initiator, followed by undergoing [2+2] cycloaddition to generate a metallacyclobutane intermediate. This intermediate then undergoes [2+2] cycloreversion to release a ring-opened product. Because of the reduction of the ring-strain of the initial monomer, this sequence is greatly thermodynamically favored. This intermediate bears the catalytically active Rualkylidene and undergoes further reactions until the monomer is completely converted. Subsequent quenching of the polymerization by adding excess ethyl vinyl ether yield a polymer and an alkoxycarbene complex.¹²



Scheme 2.5 Mechanism of G2-catalyzed ROMP relied on Chauvin's mechanism.¹¹

Like most olefin metathesis reactions, ROMP reactions are reversible. Thus, ROMP is equilibrium-controlled reactions, and the equilibrium position (monomer vs. polymer) can be predicted by considering the thermodynamics of the polymerization. Therefore, the ROMP reaction is force driven by the relief of the ring-strain in cyclic olefins. The cyclic olefins having high ring-strain (> 5 kcal/mol) such as cyclooctene, cyclobutene, norbornene and their derivatives are more favorable for the ROMP reactions. Low ring-strain cyclic olefins as cyclohexene cannot undergo ROMP due to having a very little enthalpic driving force.¹² In addition, the concentration and temperature factors also heavily influence the outcome of the ROMP reactions.¹² The most favorable conditions for a successful ROMP are high monomer concentration and low temperature.

The polymerization of cyclic olefins with strained ring by rutheniumalkylidenes of general formula $L_nM = CRR'$ (L = ligand, R, R' = H, alkyl, aryl) generates polymers by ring-opening of unsaturated double bonds in each repetitive unit. This polymerization reaction is named as "ring-opening metathesis polymerization, ROMP" because its mechanism relies on repetitive metathesis steps. Olefins with cyclic or bicyclic strained ring structures such as 2-norbornene or norbornadiene are required for the performance of ROMP (Scheme 2.6).¹³



Scheme 2.6 ROMP of (a) 2,3-disubstituted norbornadiene and (b) 2-substituted 5norbornene.¹³

2.3 Acyclic diene metathesis (ADMET) polymerization

Acyclic diene metathesis (ADMET) polymerization is a step-growth polymerization forced driven by the release of ethylene.¹⁴ ADMET polymerization is typically conducted on terminal dienes (α , ω -dienes) in order to form the precise linear unsaturated polymers.

The mechanism of ADMET polymerization is illustrated in Scheme 2.7.¹⁵ Initially, olefin coordinates to the transition metal center followed by undergoing [2+2] cycloaddition to generate a metallacyclobutane intermediate (1). This intermediate rapidly undergoes the cleavage to form a metathesis active alkylidene complex (2). Then reacts with the double bond of another monomer to produce the metallacyclobutane ring (3), which subsequently results in the formation of a polymer. The cycle proceeds with the coordination of another diene or growing polymer, followed by cleavage of product, and release of ethylene. Because all the species involved in this catalytic cycle are in equilibrium, thus, ethylene formed in the ADMET polymerization is usually removed from the reaction mixture in order to shift the reaction toward the polymer side. Ethylene is often removed either by applying a vacuum or using a constant flow of inert gases like argon or nitrogen.



Scheme 2.7 Generally mechanism of ADMET polymerization.¹⁵

Like any other step-growth polymerization, ADMET polymerization is preferably conducted in bulk in order to avoid the formation of cyclic oligomers. During the polymerization, however, the molecular weight of the polymer and the viscosity increased leading to hampering stirring and making removal of ethylene difficult. Therefore, depending on the property of monomers, the utilization of solvents is probably necessary to obtain high conversion. The non-volatile solvents such as toluene or *o*-xylene are favorably in these cases. The earliest reports on ADMET revealed that the ADMET polymerization of non-functionalized α, ω -diene can be conducted under mild reaction conditions as the main advantage of this method. Recently, the development of olefin metathesis catalysts which are robust and versatile allows the ADMET polymerization of a wide range of functionalized α, ω dienes at a low temperature. It is necessary for the success of ADMET polymerization in order to hamper side reactions. This can be resolved by selecting an appropriate catalyst and optimal reaction conditions. However, ADMET polymerization does not always generate well-defined polymeric architectures due to the competing of the isomerization with olefin metathesis.^{16,17} Therefore, double bond isomerization sidereactions have been subjected to extensive research. During ADMET polymerization, the double bonds can migrate along the polymer backbone or monomer. As a result, the repeat unit structure of the resulting polymer can become irregular with respect to carbon chain length and double bond position.

The discovery and application of the Schrock and Grubbs catalysts in ADMET polymerization have opened the way for the synthesis of different polymers with well-defined functionalities and architectures.¹⁸⁻²⁰ Consequently, through ADMET polymerization a variety of novel polymers with designed architectures can be synthesized that would be not accessible by other methods. Several telechelic polymers have been synthesized, both directly and via the ADMET depolymerization of unsaturated polymers.²¹ Some of these were applied for synthesizing segmented and ABA-type block copolymers. Moreover, ADMET polymerization allows the synthesis of perfectly linear unsaturated polymer and various alkyl branched as well as functionalized polymers with precisely placed pendant groups into the hydrocarbon backbone.²² Graft copolymers with "perfect comb" structures are also synthesized via ADMET polymerization.

2.4 Vegetable oils

2.4.1 Structure of vegetable oils

Vegetable oils are considered one of the most plentiful biorenewable resources extracted from various plants. Vegetable oils are usually named according to their biological sources such as olive oil, soybean oil, and palm oil. Vegetable oils are composed of triglyceride molecules with three fatty acid-based ester chains formed.²³ Fatty acids account for 95% of the total weight of triglycerides and their content is featuring for each vegetable oil. The structures of the most common fatty acids are shown in Figure 2.2. Most fatty acids are long straight-chain aliphatic compounds with an even number of carbons. The carbon-carbon double bonds in most of the unsaturated fatty acids possess a *cis*-configuration. The unsaturated fatty acids are considered as promising renewable resources for monomers and polymers
synthesis because the carbon-carbon double bond allows for further chemical modification. Besides carbon-carbon double bonds, some fatty acid chains like ricinoleic and vernolic also possess extra functional groups such as hydroxyl group (-OH) and epoxy group (C-O-C). The physical properties of vegetable oils strongly depend on the character and the distribution of the fatty acids, and they are usually in liquid state at room temperature. Generally, vegetable oils contain longer fatty acid chains with a lower number of carbon-carbon double bonds, and a *trans*-configuration and conjugation of the carbon-carbon double bonds have higher melting point temperatures.





Different types of vegetable oils contain different fatty acids components which highly depend on the plant sources and the growing conditions.²⁴ The fatty acid components of the most common vegetable oils are shown in Table 2.2.^{25,26} The chemical and physical properties of vegetable oils are also strongly

affected by the degree of unsaturation, which is usually estimated by measuring the iodine value (IV). The IV value is the amount of iodine (mg) reacting with the carbon-carbon double bonds in 100 g of vegetable oil. Table 2.2 shows the IV values of some common vegetable oil.^{25,26} The higher IV value reveals more carbon-carbon double bonds per vegetable oil triglyceride. Consequently, vegetable oils are classified into three types including drying oils (IV > 130), semi-drying oils (100 < IV < 130), and non-drying oils (IV < 100).

 Table 2.2 Fatty acid components and iodine value (IV) of the most common vegetable
 oils.^{25,26}

	Daulala	le dine velveb	Fatty acid (%)									
Plant oil	bond ^a	(mg/100 g)	Palmitic	Stearic	Oleic	Linoleic	Linolenic					
Palm	1.7	44-58	42.8	4.2	40.5	10.1	-					
Olive	2.8	75-94	13.7	2.5	71.1	10.0	0.6					
Groundnut	3.4	80-106	11.4	2.4	48.3	31.9	-					
Rapeseed	3.8	94-120	4.0	2.0	56.0	26.0	10.0					
Sesame	3.9	103-116	9.0	6.0	41.0	43.0	1.0					
Cottonseed	3.9	90-119	21.6	2.6	18.6	54.4	0.7					
Corn	4.5	102-130	10.9	2.0	25.4	59.6	1.2					
Soybean	4.6	117-143	11.0	4.0	23.4	53.3	7.8					
Sunflower	4.7	110-143	5.2	2.7	37.2	53.8	1.0					
Linseed	6.6	168-204	5.5	3.5	19.1	15.3	56.6					

^aThe average number of carbon-carbon double bonds per triglyceride

^bThe amount of iodine (mg) reacts with the carbon-carbon double bonds in 100 g of vegetable oil

2.4.2. Metathesis of vegetable oils and its derivatives

Over the past decade, olefin metathesis was considered as an important and powerful tool for carbon-carbon transformation applied for monomers synthesis and polymer chemistry. Olefin metathesis provide a useful, environmentally friendly and highly selective way to various chemical compounds and polymeric materials by directly or through only few reaction steps. For example, self-and crossmetathesis have been widely applied for producing of various organic compounds and monomers as well as multifunctional products. Besides, olefin metathesis has been employed to synthesis of bio-based polymers, primarily through acyclic diene metathesis polymerization (ADMET) and ring-opening metathesis polymerization (ROMP). The ADMET and ROMP are attractive methods for synthesis of bio-based polymers because these methods can be conducted under mild and environmentally benign conditions. One of the potential applications of olefin metathesis is the utilization of bio-renewable resources such as vegetable oil and their derivatives.^{27,28}

Self-metathesis (SM)

SM of unsaturated fatty acid methyl esters (FAME), vegetable oil derivatives, has been widely used for producing of various monomers and organic compounds. For example, SM of methyl oleate (MO, methyl *cis*-9-octadecenoate), to produce diesters (C18) and the alkene (C18), has been reported by Elevance *et al.* Also, Zelin *et al.* have reported the efficient production of 9-octadecene and 9-octadecene-1,18-dioate (9-OD) via SM of MO (Scheme 2.8).³³ The reactions were conducted in liquid-phase in the presence of silica-supported Hoveyda-Grubbs catalysts (**HG2**/SiO₂) (0.43-6.0 wt.% **HG2**). Self-metathesis of other unsaturated FAME [such as methyl palmitoleate (methyl *cis*-9-hexadecenoate), methyl erucate (methyl *cis*-13-docosenoate) and methyl petroselenate (methyl *cis*-6-octadecenoate)] with high conversion and selectivity obtained has also been described.³⁴



Scheme 2.8 Self-metathesis of methyl oleate.³³

Another example is SM of ω -unsaturated FAME (methyl 10undecenoate) afforded a long-chain unsaturated dicarboxylic acid ester as available monomer for synthesis of polyesters and polyamides. The SM of methyl 10undecenoate (obtained by pyrolysis of methyl ricinoleate from castor oil) was completely proceeded by removal of co-product ethene during the reaction (Scheme 2.9).²⁹





SM of unsaturated FAME, such as methyl linoleate and methyl linolenate afforded several reaction products. Three main obtained products were including dicarboxylic esters, monocarboxylic esters and polyenes. The distribution of the product at equilibrium corresponds to a random scrambling of carboxy-alkylidene and alkylidene moieties resulting in a 1:2:1 molar ratio of the three main obtained products. In addition, the cyclic hydrocarbons like cyclopolyenes and 1,4-cyclohexadiene were also obtained due to the secondary intramolecular metathesis reactions, as illustrated for methyl linolenate in Scheme 2.10.



Scheme 2.10 Self-metathesis of methyl linolenate.³⁵

Cross-metathesis (CM)

CM of unsaturated FAME with a short-chain olefin generates more desirable ester homologs and greatly expands the flexibility of the metathesis reaction in the oleo-chemistry field. Unsaturated FAME, predominantly obtained from vegetable oils, have a chain length ranged from C16 to C22 atoms. These long-chain unsaturated FAME can be shortened by CM with short-chain alkenes to produce less abundant medium-chain FAME, such as highly-demanded detergent ranged in C12-C14 acid esters. For instance, CM of methyl oleate (MO) with 3-hexene afforded methyl 9-dodecenoate and 3-dodecene (Scheme 2.11).³⁵ Using a large excess of 3-hexene can shift the reaction toward the product formation as well as suppress the formation of self-metathesis of the ester.



Scheme 2.11 Cross-metathesis of methyl oleate with 3-hexene.³⁵

CM reaction is also a very useful tool for producing bi-functional compounds, that could not be accessible obtain by other methods, or only after multiple reactions steps. For instance, Dixneuf *et al.* have reported CM of fatty acid-derived unsaturated esters, acids, and aldehydes with acrylonitrile and fumaronitrile using **HG2** catalyst.³² The obtained α, ω -bifunctional compounds can be easily converted into valuable monomers such as amino esters, amino acids, and amino alcohols, via simple reduction method. Another example from the same group demonstrated the synthesis of saturated C20 and C12 diols from castor oil derived 10-undecenal through either SM or CM with methyl acrylate, acrylic acid, acrolein and acrylonitrile, followed by hydrogenation in tandem catalytic reactions (Scheme 2.12).³⁶





Recently, Rybak and Meier have reported CM of fatty acid methyl esters derived from vegetable oils [Methyl oleate (1), methyl 10-undecenoate (2), methyl erucate (3) and methyl petroselinate (4)] with methyl acrylate.²⁹ These CM reactions performed with both high conversion (>97%) and selectivity of CM product (92%) in the presence of **G2** and **HG2** catalysts. A series of unsaturated α, ω -diesters with chain lengths of C8, C11, C12, and C15 (CM products 5-8) and C12, C18, C20 and C26 (SM products 9-12) were obtained as shown in Scheme 2.13. The obtained products are valuable monomers for the production of polyesters or polyamides.



Scheme 2.13 Different monomers obtained from self-metathesis/cross-metathesis of fatty acid derivatives with methyl acrylate.²⁹

Moreover, Abel *et al.* described CM of MO with allyl cyanide and homoallyl cyanide for the synthesis of methyl 12-aminododecanoate and 13-aminotridecanoate, as valuable precursors for producing nylon 12 and $13.^{37}$ The optimized CM was performed at 110 °C for 4 h using HG2 (2.0 mol%) in chlorobenzene at 5.0 equiv. of allyl cyanide. The MO conversion was 87% with 55% yield of desired products.

Also, Behr and Toepell have reported CM of methyl oleate and methyl 10-undecenoate with allyl acetate and *cis*-1,4-diacetoxy-2-butene using different Ru-catalysts.³⁸ The optimized CM were conducted at 80 °C in toluene for 2 h using 1.0 mol% catalyst with 3 equivalents of monomer to achieve high conversion and yield. The obtained products are interesting intermediates for polymers synthesis. Recently, Bonin *et al.* reported CM of FAME with acrolein in the presence of **G2** catalyst.³⁹ The obtained bifunctional formyl-esters are useful compounds for further transform into polymer precursors. Highly efficient conversion with low catalyst loading (TONs= 1000) was obtained when thermally pre-treated FAME.

Very recently, Awang *et al.* have reported CM of MO with a series of internal olefins (*cis*-4-octene (CO), *cis*-stilbene (CS), *cis*-1,4-diacetoxy-2-butene) and terminal olefins containing different substituents (allyltrimethylsilane, allyl glycidyl ether, vanillylidenacetone) using Ru catalysts.⁴⁰ The results demonstrated that the MO conversion and selectivity of CM products were significantly influenced by the molar ratio and characteristic of the substituent in the internal and terminal olefins as well as the reaction time. High MO conversion and selectivity of CM products were obtained under high molar ratio.

Additionally, long-chain linear *di*-unsaturated esters were synthesized by CM of an unsaturated FAME with a cyclic olefin. For example, 1triacontanol was obtained by CM of MO with cyclododecene (Scheme 2.14), then the obtained unsaturated ester was hydrogenated.³⁵





Ring opening metathesis polymerization (ROMP)

Ring-opening metathesis polymerization (ROMP), featuring the characteristics of a living polymerization, is a useful method for the preparation of precision polymers.⁴¹ However, ROMP is not the most suitable method for synthesis of

polymers when fatty acid was used as feedstock due to the low ring strain of the ensuing unsaturated cyclic monomers. In order to utilize vegetable oil in ROMP, it is necessary to modify fatty acid chains by coupling with cyclic olefins building blocks.⁴² Norbornene and its functionalized derivatives are usually used in ROMP due to commercial availability, low cost, and easy to undergo ROMP. Vegetable oils and their derivative have been extensively employed for preparing polymers via ROMP.

For instance, Larock *et al.*⁴³ have first studied ROMP of fatty acid derivatives. Castor oil was functionalized with 5-norbornene-2,3-dicarboxylic anhydride then co-polymerizing with cyclooctene via ROMP to produce thermoset polyesters. The T_g values of thermosets was in the range -14 to 1 °C. An increasing the amount of modified castor oil in the feed ratio led to increase in the extracted (unreacted or oligomeric) components in the thermoset. Dynamic mechanical analysis (DMA) and TGA of the extracted samples indicated that the free fatty acid chains and soluble portions incorporated into the polymer networks plays as plasticizers and make increasing in thermal stability. TGA results showed that all the thermosets were thermally stable below 200 °C.

Also, Larock *et al.*⁴⁴ have reported the fabrication of plant oil-based thermosets by ROMP of Dilulin (cyclopentadiene functionalized linseed oil)⁴⁵ and dicyclopentadiene, which was used as a matrix for composites with glass fiber. The resins and the corresponding composites showed increasing in the T_g , tensile strength, storage modulus (E'), and toughness when increasing dicyclopentadiene content.

A several norbornene-functionalized fatty acids with different chain lengths (C6-C18), were prepared and polymerized by ROMP using **G3**.⁴⁶ The obtained polymers had molecular weights up to 126 kDa with PDI in the range from 1.05 to 1.26 depending on the polymerization conditions. The thermal properties of the polymers were highly affected by the length of the fatty acid chain. As a result, the T_g value decreased from 102 to 32 C as increasing chain length from C6 to C18. In addition, only the polymers having chains length from C14 to C18 were able to crystallize, and the T_m value decreased from 30 °C to 6 °C corresponding to the increased chain length. TGA analyses revealed that the polymers were thermal stable below 325 °C. Recently, Xia *et al.*⁴⁷ have reported the synthesis of castor oil-based thermosets with various crosslink densities via ROMP. Two monomers were prepared including norbornenyl-functionalized castor oil (NCO), and norbornenyl-functionalized castor oil alcohol (NCA). The monomers were polymerized via ROMP in the present of **G2** (0.125 wt%) catalyst and resulted in bio-renewable plastic with different physical states from the rubbery to the rigid with crosslink densities in the range from 318 to 6028 mol/m³.

Very recently, Fernandes *et al.*⁴⁸ have reported a monomer norbornene palm olein (NPO). Palm oil was functionalized with 5-norbornene-2carboxilic acid and submitted to ROMP with **G2** catalyst. The ROMP was not undergone without co-monomer norbornene (NBE). In contrast, ROMP of NPO and co-monomer free NBE at 30 °C with different NPO/NBE ratios resulted in products with different physical states from viscous liquid to soft solids and brittle solids. The soft solids were insoluble in water, acetic acid, and typical organic solvents, but swollen in slightly polar organic solvents like chloroform at 30 °C. The resulting plant oil-based polymer showed thermal stability up to 300 °C.

Very recently, Ganewatta et al. synthesized high molecular weight renewable homopolymers and block copolymers derived from natural rosin (Scheme 2.15).⁴⁹ Monomers with high renewable content (70 %wt) were prepared by a simple esterification reaction between dehydroabietic alcohol and 5-exonorbornenecarboxylic acid. The monomers were submitted to ROMP in the presence of G3 and HG2 catalysts to obtain polymers with molecular weight up to 500 kg/mol. The T_g values were varied from 110 to 55 °C via hydrogenation or by controlling the spacer between the polymer backbone and the bulky dehydroabietic acid moiety. These homopolymers exhibit excellent thermal stabilities, and thermoplastic properties. In addition, the dehydroabietic-based homopolymer was chain extended by copolymerizing with soybean oil-derived norbornene monomer to obtain triblock copolymers via living ROMP.



Scheme 2.15 Triblock copolymers by ROMP with sequential monomer addition.⁴⁹

2.5 Eugenol

Eugenol (UG, 4-allyl-2-methoxyphenol shown in Figure 2.3) is an interesting renewable compound. UG (featuring a renewable phenolic compound) is typically extracted from clove oil. For instance, UG comprises approximately 70-90% of clove oil from Eugenia caryophyllata and occurs widely as a main component of essential oils.⁵⁰ UG has been widely used not only in the production of cosmetics, perfumes, soaps, and even food, but also in the medical and pharmaceutical fields as antibiotic and antihypertensive agents.⁵⁰ In addition, UG can also be considered as a lignin derivative and be potentially extracted from lignocellulosic biomass.⁵¹ Owing to its functional groups [hydroxyl (-OH), methoxy (-OCH₃) and allyl groups], UG can be easily converted to many types of chemicals. Thus, UG is considered interest as starting material for the synthesis of new compounds exemplified in designing polymer networks via thiol-ene coupling^{52,53} or bismaleimide networks.^{54,55} Recently, study on UG mainly focused on Ru-catalyzed olefin metathesis reactions such as selfmetathesis^{56,57} and cross-metathesis with either electron-deficient olefins^{58,59} or unsaturated fatty acid methyl esters⁶⁰ due to presence of the terminal olefin group. Therefore, it is possible to prepare different types of functionalized phenol derivatives to develop new routes for synthesis of different multifunctional products from UG.^{61,62} Additionally, UG structure, which contains an aromatic ring, has the potential

alternative to petroleum-based phenolic monomers, which are widely used nowadays in the field of polyesters. For instance, a wide variety of polyesters based on UG and α,ω -diols have been prepared by polycondensation and thiol-ene click reactions.^{63,64} The above-mentioned characteristics reveal that UG is a promising renewable feedstock for the synthesis and development of new polymeric materials.



Figure 2.3 The chemical structure of eugenol (UG).

2.6 Isosorbide

Isosorbide (IS) is another interesting renewable resource with high availability. IS is derived from glucose, which is typically obtained by the depolymerization of biomass-based such as starch and cellulose.^{65,66} IS can be produced in large scale from starch through three main chemical reactions (Scheme 2.16).⁶⁶ Firstly, starch is hydrolyzed to glucose and then hydrogenated to sorbitol. Finally, sorbitol is dehydrated to isosorbide. IS is a V-shaped diol with a unique bicyclic ring structure consisting of two *cis*-fused tetrahydrofuran rings and two secondary (-OH) groups in the 2- and 5- positions,⁶⁷ which imparts a degree of rigidity to polymers. Its inherent unique molecular structure, high thermal stability, biodegradability and nontoxicity makes it a promising monomer and monomer precursor for potential replacing petroleum-based derived polymers. The outstanding features of IS have motivated numerous studies on the synthesis of isosorbide-based polymers with high mechanical and thermal properties including polyesters, polyurethanes, and

poly(meth)acrylates.^{68,69} Moreover, the rigid, bicyclic structure of isosorbide tends to impart a high glass transition temperature (T_{g}) and modulus in the resulting materials. Therefore, isosorbide was considered as a green alternative to bisphenol A for the production of bio-based thermoset polymers. In addition, because the distinctive properties of IS such as attractive price, molecular rigidity, biodegradability, renewability, and non-toxicity, a numerous research has focused on exploring new isosorbide-based derivatives (monomers) to prepare high-performance materials for a wide range of applications.



Scheme 2.16 Reaction scheme of the conversion of starch to isosorbide.⁶⁶

2.7 References

- 1. Banks, R. L.; Bailey, G. C., Olefin Disproportionation. A New Catalytic Process. *I&EC Product Research and Development* 1964, 3, 170-173.
- 2. Front Matter, Volume 1: Catalyst Development and Mechanism. In *Handbook of Metathesis*, pp I-XVII.
- Hérisson, P. J. L.; Chauvin, Y., Catalyse de transformation des oléfines par les complexes du tungstène. II. Télomérisation des oléfines cycliques en présence d'oléfines acycliques. *Die Makromolekulare Chemie* 1971, 141, 161-176.
- 4. Trnka, T. M.; Grubbs, R. H., The Development of L₂X₂RuCHR Olefin Metathesis Catalysts: An Organometallic Success Story. *Acc. Chem. Res.* 2001, 34, 18-29.
- 5. Schrock, R. R.; Czekelius, C., Recent Advances in the Syntheses and Applications of Molybdenum and Tungsten Alkylidene and Alkylidyne Catalysts for the Metathesis of Alkenes and Alkynes. *Adv. Synth. Catal.* 2007, 349, 55-77.

- Schwab, P.; Grubbs, R. H.; Ziller, J. W., Synthesis and Applications of RuCl₂(CHR⁺)(PR₃)₂: The Influence of the Alkylidene Moiety on Metathesis Activity. *J. Am. Chem. Soc.* 1996, 118, 100-110.
- Scholl, M.; Ding, S.; Lee, C. W.; Grubbs, R. H., Synthesis and Activity of a New Generation of Ruthenium-Based Olefin Metathesis Catalysts Coordinated with 1,3-Dimesityl-4,5-dihydroimidazol-2-ylidene Ligands. *Org. Lett.* 1999, 1, 953-956.
- Love, J. A.; Morgan, J. P.; Trnka, T. M.; Grubbs, R. H., A Practical and Highly Active Ruthenium-Based Catalyst that Effects the Cross Metathesis of Acrylonitrile. *Angew. Chem. Int. Ed.* 2002, 41, 4035-4037.
- 9. Calderon, N., Ring-Opening Polymerization of Cycloolefins. J. Macromol. Sci. Polymer Rev. 1972, 7, 105-159.
- 10. Bielawski, C. W.; Grubbs, R. H., Living ring-opening metathesis polymerization. *Prog. Polym. Sci.* 2007, 32, 1-29.
- Jean-Louis Hérisson, P.; Chauvin, Y., Catalyse de transformation des oléfines par les complexes du tungstène. II. Télomérisation des oléfines cycliques en présence d'oléfines acycliques. *Die Makromolekulare Chemie* 1971, 141, 161-176.
- Sanford, M. S.; Ulman, M.; Grubbs, R. H., New Insights into the Mechanism of Ruthenium-Catalyzed Olefin Metathesis Reactions. *J. Am. Chem. Soc.* 2001, 123, 749-750.
- Li, F.; Larock, R. C., New soybean oil-Styrene-Divinylbenzene thermosetting copolymers—IV. Good damping properties. *Polym. Advan. Technol.* 2002, 13, 436-449.
- Baughman, T. W.; Wagener, K. B., Recent Advances in ADMET Polymerization. In Metathesis Polymerization: Buchmeiser, M. R., Ed. Springer Berlin Heidelberg: Berlin, Heidelberg, 2005; pp 1-42.
- 15. Wagener, K. B.; Boncella, J. M.; Nel, J. G., Acyclic diene metathesis (ADMET) polymerization. *Macromolecules* 1991, 24, 2649-2657.
- 16. Schmidt, B., In situ conversion of a Ru metathesis catalyst to an isomerization catalyst. *Chem. Commun.* 2004, (6), 742-743.

- Schmidt, B., Catalysis at the Interface of Ruthenium Carbene and Ruthenium Hydride Chemistry: Organometallic Aspects and Applications to Organic Synthesis. *Eur. J. Org. Chem.* 2004, (9), 1865-1880.
- Mutlu, H.; de Espinosa, L. M.; Meier, M. A. R., Acyclic diene metathesis: a versatile tool for the construction of defined polymer architectures. *Chem. Soc. Rev.* 2011, 40, 1404-1445.
- Watson, M. D.; Wagener, K. B., Tandem Homogeneous Metathesis/Heterogeneous Hydrogenation: Preparing Model Ethylene/CO₂ and Ethylene/CO Copolymers. *Macromolecules* 2000, 33, 3196-3201.
- 20. Hopkins, T. E.; Wagener, K. B., ADMET Synthesis of Polyolefins Targeted for Biological Applications. *Macromolecules* 2004, 37, 1180-1189.
- Marmo, J. C.; Wagener, K. B., Acyclic diene metathesis (ADMET) depolymerization. Synthesis of mass-exact telechelic polybutadiene oligomers. *Macromolecules* 1993, 26, 2137-2138.
- Opper, K. L.; Wagener, K. B., ADMET: Metathesis polycondensation. J. Polym. Sci. Pol. Chem. 2011, 49, 821-831.
- 23. Montero de Espinosa, L.; Meier, M. A. R., Plant oils: The perfect renewable resource for polymer science? *Eur. Polym. J.* 2011, 47, 837-852.
- 24. Meier, M. A. R.; Metzger, J. O.; Schubert, U. S., Plant oil renewable resources as green alternatives in polymer science. *Chem. Soc. Rev.* 2007, 36, 1788-1802.
- 25. Lu, Y.; Larock, R. C., Novel Polymeric Materials from Vegetable Oils and Vinyl Monomers: Preparation, Properties, and Applications. *Chem. Sus. Chem* 2009, 2, 136-147.
- 26. Xia, Y.; Larock, R. C., Vegetable oil-based polymeric materials: synthesis, properties, and applications. *Green Chem.* 2010, 12, 1893-1909.
- Biermann, U.; Bornscheuer, U.; Meier, M. A. R.; Metzger, J. O.; Schäfer, H. J., Oils and Fats as Renewable Raw Materials in Chemistry. *Angew. Chem. Int. Ed.* 2011, 50 (17), 3854-3871.
- Meier, M. A. R., Metathesis with Oleochemicals: New Approaches for the Utilization of Plant Oils as Renewable Resources in Polymer Science. *Macromol. Chem. Phys.* 2009, 210, 1073-1079.

- Rybak, A.; Meier, M. A. R., Cross-metathesis of fatty acid derivatives with methyl acrylate: renewable raw materials for the chemical industry. *Green Chem.* 2007, 9, 1356-1361.
- 30. Rybak, A.; Meier, M. A. R., Cross-metathesis of oleyl alcohol with methyl acrylate: optimization of reaction conditions and comparison of their environmental impact. *Green Chem.* 2008, 10, 1099-1104.
- 31. Quinzler, D.; Mecking, S., Renewable resource-based poly(dodecyloate) by carbonylation polymerization. *Chem. Commun.* 2009, (36), 5400-5402.
- Malacea, R.; Fischmeister, C.; Bruneau, C.; Dubois, J.-L.; Couturier, J.-L.; Dixneuf, P.
 H., Renewable materials as precursors of linear nitrile-acid derivatives via crossmetathesis of fatty esters and acids with acrylonitrile and fumaronitrile. *Green Chem.* 2009, 11, 152-155.
- 33. Zelin, J.; Trasarti, A. F.; Apesteguía, C. R., Self-metathesis of methyl oleate on silica-supported Hoveyda–Grubbs catalysts. *Catal. Commun.* 2013, 42, 84-88.
- Mol, J. C., Metathesis of unsaturated fatty acid esters and fatty oils. *J. Mol. Catal.* 1994, 90, 185-199.
- 35. Mol, J. C., Application of olefin metathesis in oleochemistry: an example of green chemistry. *Green Chem.* 2002, 4, 5-13.
- 36. Miao, X.; Fischmeister, C.; Bruneau, C.; Dixneuf, P. H., A Direct Route to Bifunctional Aldehyde Derivatives via Self- and Cross-Metathesis of Unsaturated Aldehydes. *Chem. Sus. Chem* 2009, 2, 542-545.
- 37. Ameh Abel, G.; Oliver Nguyen, K.; Viamajala, S.; Varanasi, S.; Yamamoto, K., Crossmetathesis approach to produce precursors of nylon 12 and nylon 13 from microalgae. *RSC Adv.* 2014, 4, 55622-55628.
- Behr, A.; Toepell, S., Comparison of Reactivity in the Cross Metathesis of Allyl Acetate-Derivatives with Oleochemical Compounds. *J. Am. Oil Chem. Soc.* 2015, 92 603-611.
- 39. Bonin, H.; Keraani, A.; Dubois, J.-L.; Brandhorst, M.; Fischmeister, C.; Bruneau, C., Cross-metathesis of fatty acid methyl esters with acrolein: An entry to a variety of bifunctional compounds. *Eur. J. Lipid Sci. Tech.* 2015, 117, 209-216.

- Awang, N. W.; Tsutsumi, K.; Hustakova, B.; Yusoff, S. F. M.; Nomura, K.; Yamin, B. M., Cross metathesis of methyl oleate (MO) with terminal, internal olefins by ruthenium catalysts: factors affecting the efficient MO conversion and the selectivity. *RSC Adv.* 2016, 6, 100925-100930.
- Leitgeb, A.; Wappel, J.; Slugovc, C., The ROMP toolbox upgraded. *Polymer* 2010, 51, 2927-2946.
- 42. Mutlu, H.; Meier, M. A. R., Ring-opening metathesis polymerization of fatty acid derived monomers. *J. Polym. Sci. Pol. Chem.* 2010, 48, 5899-5906.
- 43. Henna, P. H.; Larock, R. C., Rubbery Thermosets by Ring-Opening Metathesis Polymerization of a Functionalized Castor Oil and Cyclooctene. *Macromol Mater. Eng.* 2007, 292, 1201-1209.
- 44. Mauldin, T. C.; Haman, K.; Sheng, X.; Henna, P.; Larock, R. C.; Kessler, M. R., Ringopening metathesis polymerization of a modified linseed oil with varying levels of crosslinking. *J. Polym. Sci. Pol. Chem.* 2008, 46, 6851-6860.
- 45. Henna, P. H.; Kessler, M. R.; Larock, R. C., Fabrication and Properties of Vegetable-Oil-Based Glass Fiber Composites by Ring-Opening Metathesis Polymerization. *Macromol. Mater. Eng.* 2008, 293, 979-990.
- 46. Mutlu, H.; Meier, M. A. R., Ring-opening metathesis polymerization of fatty acid derived monomers. *J. Polym. Sci. Pol. Chem.* 2010, 48, 5899-5906.
- Xia, Y.; Larock, R. C., Castor oil-based thermosets with varied crosslink densities prepared by ring-opening metathesis polymerization (ROMP). *Polymer* 2010, 51 (12), 2508-2514.
- 48. Fernandes, H.; Souza Filho, R. M.; Silva Sá, J. L.; Lima-Neto, B. S., Bio-based plant oil polymers from ROMP of norbornene modified with triglyceride from crude red palm olein. *RSC Adv.* 2016, 6, 75104-75110.
- Ganewatta, M. S.; Ding, W.; Rahman, M. A.; Yuan, L.; Wang, Z.; Hamidi, N.; Robertson, M. L.; Tang, C., Biobased Plastics and Elastomers from Renewable Rosin via "Living" Ring-Opening Metathesis Polymerization. *Macromolecules* 2016, 49, 7155-7164.

- 50. Rojo, L.; Vazquez, B.; Parra, J.; López Bravo, A.; Deb, S.; San Roman, J., From Natural Products to Polymeric Derivatives of "Eugenol": A New Approach for Preparation of Dental Composites and Orthopedic Bone Cements. *Biomacromolecules* 2006, 7, 2751-2761.
- Kotake, T.; Kawamoto, H.; Saka, S., Pyrolysis reactions of coniferyl alcohol as a model of the primary structure formed during lignin pyrolysis. *J. Anal. Appl. Pyrol.* 2013, 104, 573-584.
- 52. Yoshimura, T.; Shimasaki, T.; Teramoto, N.; Shibata, M., Bio-based polymer networks by thiol–ene photopolymerizations of allyl-etherified eugenol derivatives. *Eur. Polym. J.* 2015, 67, 397-408.
- 53. Guzmán, D.; Ramis, X.; Fernández-Francos, X.; De la Flor, S.; Serra, A., New biobased materials obtained by thiol-ene/thiol-epoxy dual curing click procedures from eugenol derivates. *Eur. Polym. J.* 2017, 93, 530-544.
- 54. Shibata, M.; Tetramoto, N.; Imada, A.; Neda, M.; Sugimoto, S., Bio-based thermosetting bismaleimide resins using eugenol, bieugenol and eugenol novolac. *React. Funct. Polym.* 2013, 73, 1086-1095.
- 55. Neda, M.; Okinaga, K.; Shibata, M., High-performance bio-based thermosetting resins based on bismaleimide and allyl-etherified eugenol derivatives. *Mater. Chem. Phys.* 2014, 148, 319-327.
- 56. Alexander, K. A.; Paulhus, E. A.; Lazarus, G. M. L.; Leadbeater, N. E., Exploring the reactivity of a ruthenium complex in the metathesis of biorenewable feedstocks to generate value-added chemicals. *J. Organomet. Chem.* 2016, 812, 74-80.
- 57. Taber, D. F.; Frankowski, K. J., Grubbs' Catalyst in Paraffin: An Air-Stable Preparation for Alkene Metathesis. *J. Org. Chem.* 2003, 68, 6047-6048.
- Moïse, J.; Arseniyadis, S.; Cossy, J., Cross-Metathesis between α-Methylene-γbutyrolactone and Olefins: A Dramatic Additive Effect. *Org. Lett.* 2007, 9, 1695-1698.
- 59. Bilel, H.; Hamdi, N.; Zagrouba, F.; Fischmeister, C.; Bruneau, C., Eugenol as a renewable feedstock for the production of polyfunctional alkenes via olefin cross-metathesis. *RSC Adv.* 2012, 2, 9584-9589.

- 60. Le, D.; Samart, C.; Tsutsumi, K.; Nomura, K.; Kongparakul, S., Efficient Conversion of Renewable Unsaturated Fatty Acid Methyl Esters by Cross-Metathesis with Eugenol. *ACS Omega* 2018, 3, 11041-11049.
- 61. Thirukumaran, P.; Shakila, A.; Muthusamy, S., Synthesis and characterization of novel bio-based benzoxazines from eugenol. *RSC Adv.* 2014, 4, 7959–7966.
- Harvey, B. G.; Sahagun, C. M.; Guenthner, A. J.; Groshens, T. J.; Cambrea, L. R.; Reams, J. T.; Mabry, J. M., A High-Performance Renewable Thermosetting Resin Derived from Eugenol. *ChemSusChem* 2014, 7, 1964-1969.
- Hu, K.; Zhao, D.; Wu, G.; Ma, J., Synthesis and properties of polyesters derived from renewable eugenol and α,ω-diols via a continuous overheating method. *Polym. Chem.* 2015, 6, 7138-7148.
- 64. Hu, K.; Zhao, D.; Wu, G.; Ma, J., Polyesters derived from bio-based eugenol and 10-undecenoic acid: synthesis, characterization, and structure–property relationships. *RSC Adv.* 2015, 5, 85996-86005.
- 65. Hong, J.; Radojčić, D.; Ionescu, M.; Petrović, Z. S.; Eastwood, E., Advanced materials from corn: isosorbide-based epoxy resins. *Polym. Chem.* 2014, 5, 5360-5368.
- 66. Wang, B.-T.; Lu, F.-D.; Xu, F.; Li, Y.-Z.; Kessler, M. R., Synthesis of renewable isosorbide-based monomer and preparation of the corresponding thermosets. *Chinese Chem. Lett.* 2016, 27, 875-878.
- 67. Rose, M.; Palkovits, R., Isosorbide as a Renewable Platform chemical for Versatile Applications—Quo Vadis? *Chem. Sus. Chem.* 2012, 5, 167-176.
- Kristufek, T. S.; Kristufek, S. L.; Link, L. A.; Weems, A. C.; Khan, S.; Lim, S.-M.; Lonnecker, A. T.; Raymond, J. E.; Maitland, D. J.; Wooley, K. L., Rapidly-cured isosorbide-based cross-linked polycarbonate elastomers. *Polym. Chem.* 2016, 7, 2639-2644.
- 69. Wang, B.; Mireles, K.; Rock, M.; Li, Y.; Thakur, V. K.; Gao, D.; Kessler, M. R., Synthesis and Preparation of Bio-Based ROMP Thermosets from Functionalized Renewable Isosorbide Derivative. *Macromol. Chem. Phys.* 2016, 217, 871-879.

CHAPTER 3

EFFICIENT CONVERSION OF RENEWABLE UNSATURATED FATTY ACID METHYL ESTERS BY CROSS METATHESIS WITH EUGENOL

3.1 Introduction

Olefin metathesis has been known as an efficient method for synthesis of various intermediates and fine chemicals,¹⁻¹⁶ both cross metathesis (CM) and ring closing metathesis (RCM) have been employed especially for the purpose.¹⁻¹¹ One of the recent promising applications in the olefin metathesis is the utilization of renewable bio-source materials to complement or replace petroleum-based specialty chemicals.¹²⁻¹⁶ In particular, CM of unsaturated fatty acid esters (shown in Scheme 3.1), which are obtained from plant oils or algae-derived feedstocks, 1-3,17-20 has been considered as the promising subject in terms of both green chemistry and oleochemistry.^{12-16,21-41} Methyl oleate (MO) is the predominant component of fatty acid methyl esters of the triglycerides in many vegetable oils such as olive, canola oil or Jatropha oil,¹⁷⁻²⁰ and is usually obtained from the transesterification of vegetable oils with alcohol. Therefore, considerable attention has been paid for utilization of MO as the starting materials for the production of intermediates and polymer precursors via CM.³⁰⁻⁴¹ For instance, CM of MO with functionalized olefins, such as allyl chloride,³² methyl acrylate,^{33,34} acrylonitrile,^{35,36} allyl acetate,³⁷ allyl glycidyl ether, and allyltrimethylsilane (ATMS),⁴¹ has been studied to obtain renewable α, ω -bifunctional compounds.

Eugenol (UG), featuring a phenolic allyl benzene (shown in Scheme 3.1), is also an interesting bio-based compound. UG is typically obtained from clove oil and has been widely used not only in foods, perfumes, antioxidants but also in the medical and pharmaceutical fields, due to its unique properties in reducing blood sugar, triglyceride, and cholesterol.⁴² UG can also be considered as a lignin derivative and be extracted potentially from lignocellulosic biomass. Moreover, UG can be easily converted to many types of chemicals owing to its bifunctional nature. The aliphatic chain and methoxy group (-OCH₃) affect the physical properties of polymers derived from UG,⁴³⁻⁴⁵ whereas the hydroxyl (-OH) group and the terminal olefin provides further chemical modification exemplified in designing polymer networks via thiol-ene coupling^{46,47} or bismaleimide networks,^{48,49} particularly for performing metathesis reaction.⁵⁰ Therefore, reports concerning self-metathesis (SM)^{50,51} and CM of UG with symmetrical internal olefins^{13,52,53} and electron deficient terminal olefins (such as methyl acrylate, methyl methacrylate, acrylonitrile, and with acrylamides)^{50,52} have been known in the presence of ruthenium catalysts.

The CM of unsaturated fatty acid methyl esters with UG should thus afford multifunctional products having hydrophobic (long alkyl chain length) and hydrophilic (phenolic group) properties/or olefinic double bonds. These suggest that UG is the promising candidate as substrate for the CM reaction with fatty acid methyl esters; however, comprehensive studies of CM (shown in Scheme 3.1) still have not been conducted.





In this chapter, we wish to introduce our explored results for CM of UG with a series of unsaturated fatty acid methyl esters having an internal double bond, such as MO, methyl petroselinate (MP), and methyl erucate (ME), and that having a terminal double bond (methyl 10-undecanoate, MU), in the presence of ruthenium-carbene catalysts (Scheme 3.2). We herein present that these CM reactions proceed efficiently in ethanol, isopropanol and dimethyl carbonate (DMC) (environmentally benign solvent) under sustainable conditions, although these reactions are often conducted either in chlorinated solvents (dichloromethane (DCM) and 1,2-

dichloroethane)⁵⁴ or aromatic solvents (toluene, benzene and chlorobenzene).^{36,51} The influence of reaction conditions such as time (5–30 min), temperature (25–80 °C), substrate concentration (1.0–20 M), and ratio of UG/substrate (1.0–20 molar ratio) toward both activity and selectivity has been investigated in detail.

3.2 Materials and Methods

3.2.1 Materials

All experiments were carried out under a nitrogen atmosphere unless otherwise specified. All chemicals used were of reagent grade and were purified by the standard purification procedures. Anhydrous grade dichloromethane (DCM, >99.5 %) and n-hexane (Kanto Chemical Co., Inc.) were transferred into a bottle containing molecular sieves (mixture of 3A 1/16, 4A 1/8 and 13X 1/16) in the drybox. Ethanol dehydrated (>99.5%), 2-propanol dehydrated (>99.7%) were supplied by Kanto Chemical Co., Inc. Methyl oleate (MO, >60%), methyl 10-undecanoate (MU, >96.0%), methyl erucate (ME, methyl cis-13-docosenoate, >90.0%), methyl petroselinate (MP, methyl cis-6-octadecenoate, >98.0%), eugenol (UG, >99.0%) and dimethyl carbonate dehydrated (DMC, >98.0%) were obtained from Tokyo Chemical Industry, Co., Ltd. and were used as received without purification. Thin layer chromatography (PLC Silica gel 60 F254, 0.5 mm) was purchased from Merck KGaA. RuCl2(PCy3)2(CHPh) [called firstgeneration Grubbs catalyst (G1); Cy = cyclohexyl], $RuCl_2(PCy_3)(H_2IMes)(CHPh)$ [called (G2); second-generation Grubbs catalyst IMesH₂ = 1,3-bis(2,4,6trimethylphenyl)imidazolin-2-ylidene], RuCl₂(IMesH₂)(CH-2-OⁱPr-C₆H₄) [called secondgeneration Hoveyda-Grubbs catalyst (HG2)] and $RuCl_2(PCy_3)(IMesH_2)(CHPh)(3-BrC_5H_4N)_2$ [called third-generation Grubbs catalyst (G3)] were used in the dry-box as received (Aldrich Chemical Co.). Methyl heptadecanoate (C17, GC standard, >99.0%), used as the internal standard (IS) for GC analyses, was also purchased from Aldrich.



Scheme 3.2 Cross Metathesis (CM) of eugenol (UG) with methyl oleate (MO) or other unsaturated fatty acid methyl esters.

3.2.2 Measurements and Characterization

Analytical GC characterization of mixtures was performed on GC-2025, Shimadzu equipped with a DB-1 column (30 m x 0. 25 mm x 0.25 μ m), using a

flame ionization detection. Nitrogen gas was used as a carrier gas at a flow rate of 2.0 mL/min. The oven temperature program profile was: initial temperature 50 °C, hold for 10 min, ramp at 15 °C/min to 200 °C, hold for 55 min (hold for 100 min for analyzing products of MU with UG).

The quantitative analyses were performed by comparing the peak area of the products with known amount of methyl heptadecanoate as an internal standard. Calibration coefficient was determined by analyzing the mixtures of substrates (MO, MP, ME and MU) and the internal standard with different mass ratios. The amount of substrates (MO, MP, ME and MU) was calculated by normalizing using the internal standard method with the calibration coefficient. The conversion of substrates (MO, MP, ME and MU) was obtained from the comparison of peak areas before and after the reactions. The effective carbon number (ECN) concept for GC-FID analyses was used to calculate the yields of products.⁵⁵⁻⁵⁸

GC-MS analysis was carried out on Shimadzu GC-17A gas chromatography directly coupled to the mass spectrometer system (MS) of Shimadzu GCMS QP5050, equipped with a DB-1 column (30 m x 0.25 mm x 0.25 µm, with polyethylene glycol stationary phase). Helium gas was used as a carrier gas at a flow rate of 2.0 mL/min. The oven temperature program profile was: initial temperature 50 °C, hold for 10 min; ramp at 15 °C/min to 200 °C, hold for 55 min (hold for 100 min for analyzing products of MU with UG).

Thin layer chromatography (TLC) was carried out on glass-backed silica plates PLC Silica gel 60 F_{254} , 0.5 mm (dimension 20 cm x 20 cm). The reaction products were identified by visualizing the plates under UV light (wavelength 254 nm). Silica gel column chromatography was carried out using dry silica (size 20-60 μ m).

¹H and ¹³C NMR spectra were obtained by dissolving the samples in CDCl₃ and recording the spectra using Bruker AV500 NMR spectrometer (500 MHz for ¹H and 125 MHz for ¹³C). All spectra were obtained in the solvent indicated at 25 °C unless otherwise noted. Chemical shifts (δ) were reported as parts per million (ppm) with tetramethylsilane (TMS) as the internal standard (δ 0.00 ppm, ¹H, ¹³C). The coupling constants are given in Hz.

For characterization by the NMR spectra, the metathesis products of MO with UG were purified by column chromatography on silica gel (ethyl acetate/hexane mixtures) followed by thin layer chromatography (TLC, ethyl acetate/n-hexane = 2:8 v/v mixtures).

3.2.3 The effective carbon number (ECN) of materials

The ECN concept for GC-FID analyses was used to calculate the yields of products.⁵⁵⁻⁵⁸ Methyl heptadecanoate (C17) was used as the internal standard. Contributions to the effective carbon number are summarized in Table 3.1. ECN of starting materials and products for both self and cross-metathesis reactions are shown in Figure A3.1-3.4 in Appendix A.

Туре	Atom	ECN contribution
Aliphatic	С	1.0
Olefinic	С	0.95
Ester C	С	1.0
Ester group	000	-1.49
носна		5.2

 Table 3.1 ECN contributions of atoms or groups.

3.2.4 General procedure for the cross-metathesis reaction of fatty acid methyl esters (MO, MP, ME and MU) with eugenol (UG)

A typical procedure (Table 3.2, run 8) is as follows. The secondgeneration Grubbs catalyst $RuCl_2(PCy_3)(H_2IMes)(CHPh)$ (0.0017 g, 0.1 mol%, 0.0020 mmol) was weighed in 10 mL vial under nitrogen atmosphere. Fatty acid methyl esters (MO, 0.593 g, 2.00 mmol) or (ME, 0.706 g, 2.00 mmol) or (MP, 0.593 g, 2.00 mmol) or (MU, 0.397 g, 2.00 mmol) and eugenol (UG, 3.284 g, 20.0 mmol, 10 equiv.) were dissolved in solvent, and then quickly transferred to the catalyst vial. The mixture was stirred at 50 °C for 10 min, then the resulting mixture was passed through a packed column of Celite to remove the catalyst. Methyl heptadecanoate (IS, 10 mg) as an internal standard for GC analyses was added into the obtained filtrate. Afterward, the mixture was analyzed using the gas chromatograph with FID detector (GC-FID) and the gas chromatograph mass spectrometer (GC/MS). GC-FID and GC/MS spectra are shown in Figure A3.5-3.16 (Appendix A).

For NMR characterization, after solvent evaporated the metathesis products of MO with UG were purified by column chromatography on silica gel (ethyl acetate/hexane mixtures) followed by thin layer chromatography (TLC, ethyl acetate/n-hexane = 2:8 v/v mixtures).

3.3 Results and Discussion

3.3.1 Cross-metathesis of Methyl Oleate (MO) with Eugenol (UG) using Ruthenium catalysts

Methyl oleate (MO) has been chosen as a model substrate in this cross-metathesis (CM) with eugenol (UG) using Ru-carbene catalysts (shown in Scheme 3.2, G1, G2, G3, and HG2). Greener solvents such as dimethyl carbonate (DMC), ethanol and 2-propanol were used for purpose of environmentally benign conditions, although dichloromethane (DCM) or toluene was often used with these Ru catalysts. As shown in the Scheme 3.2, four types of CM products (expressed as CM1, CM2, CM3, and CM4), as well as self-metathesis (SM) products can be considered in the reaction. The CM of MO with UG produced fine chemicals and polyfunctional compounds. The highly expected compounds from CM of MO and UG are CM3 and CM4 which are able use as monomers for preparing polyesters. Note that the distribution of CM product in the CM reaction of MO with UG is 1:1 for (CM1+CM3)/(CM2+CM4) based on the theory of CM reaction. However, since the CM products can react (cross-metathesis) together, thus, utilizing a high UG/MO ratio is necessary in order to achieve high selectivity of CM products. The mechanism of CM reaction between MO and UG is shown in Scheme 3.3. The GC-FID chromatography of the CM reaction of MO with UG is shown in Figure 3.1.



Scheme 3.3 Proposed mechanism of CM between MO and UG.



Figure 3.1 GC-FID chromatogram for the cross-metathesis reaction of methyl oleate (MO) with eugenol (UG).

3.3.1.1 Effect of solvent and MO concentration in cross-metathesis of MO with UG

The CM reaction of MO with UG were first carried out at 50 °C for 10 min using G2 catalyst at 0.1 mol % to study influence of solvent and MO concentration. The selected results are shown in Table 3.2. It was found that the high conversions of MO have been attained under mild conditions (50 °C) even for a short reaction period (10 min), when the reaction was conducted in the presence of G2 (Table 3.2, runs 1-4). Importantly, the MO conversion carried out in DCM was relatively close to those carried out in DMC and 2-propanol. Moreover, the selectivity of CM and SM products (defined as select.(2)) in DMC, ethanol and, 2-propanol is almost identical to that in DCM; the selectivity of CM and SM products reached almost 98%. The catalytic activities evaluated as turnover number (TON) values on the basis of metathesis products are higher than those in the CM reactions of MO with cis-4-octene (CO), cis-1,4-diacetoxy-2-butene (DAB), and allyltrimethylsilane (ATMS) reported previously (conducted under similar conditions);⁴¹ the selectivity of CM products (defined as select.(2)) is close to those in the CM reactions with ATMS, CO, and DAB.⁴¹ It also turned out that the CM reaction of MO with UG proceeded without solvent (Table 3.2, run 5), although the conversion of MO was rather low. This is due to high viscosity of the reactant mixture (MO and UG) that would be probably affect to the dispersion of catalyst. These facts thus clearly indicate that the CM can be performed in environmentally friendly solvents (such as DMC, 2-propanol and ethanol) without decreasing the catalyst efficiency.

On basis of the above results, DMC, 2-propanol, and ethanol were chosen for optimization of the reaction conditions (at 50 °C, the same catalyst loading, reaction time in Table 3.2). Note that the MO conversion carried in ethanol was improved significantly upon increasing MO concentration from 1.0 to 4.0 M (runs 3 vs 7) and then no significant changes in both the MO conversion and selectivity of CM products (defined as select.(1)) were observed upon increasing the MO concentration (runs 7-10). In contrast, both MO conversion and the selectivity in DMC (run 6) decreased upon increasing the MO concentration. This could be explained due to the different in polarity of the solvents which probably significant impact on the initiation rates of the catalysts.

		ЦG	MO	МО			Met	Select.	Select.						
run	Solvent		conc.	conv.	CM1	CM2	CM3	CM4	SM1	SM1	SM2	SM2	(1)	(2)	TON^h
		(equiv)	(M)c	(%) ^d					trans	cis	Trans	Cis	(%) ^f	(%) ^g	
1	CH ₂ Cl ₂	10	1.0	70	21	20	17	10	1	0	0	0	62	00	440
1	(DCM)	10	1.0	10	21	30	17	19	1	0	0	0	05	90	440
2	DMC	10	1.0	82	23	34	17	21	1	0	1	0	59	98	480
3	ethanol	10	1.0	60	14	23	15	18	1	0	0	0	61	98	370
4	2-propanol	10	1.0	94	34	46	16	19	1	0	1	0	63	98	590
5	none ⁱ	10	-	41	12	16	11	12	1	0	0	0	63	98	260
6	DMC	10	4.0	42	8	13	9	10	1	0	0	0	48	97	200
7	ethanol	10	4.0	90	27	41	17	21	1	0	1	0	61	98	550
8	ethanol	10	10.0	91	31	48	17	21	1	0	1	0	65	98	590
9	ethanol	10	20.0	91	35	45	17	20	1	0	1	0	65	98	590
10	2-propanol	10	4.0	95	43	57	17	19	1	0	1	0	73	98	690
11	2-propanol	10	10.0	84	33	43	19	22	1	0	1	0	71	98	600
12	2-propanol	10	20.0	85	34	44	19	22	1	0	1	0	71	98	600

Table 3.2 Effect of solvent and MO concentration in CM of MO with UG by G2.^a

^aConditions: 2.00 mmol of MO, catalyst (**G2**) 0.002 mmol (0.1 mol %), temperature 50 °C, reaction time 10 min. ^bBased on MO. ^cInitial MO conc. in solvent. ^dConversion of MO estimated by gas chromatography (GC) using an internal standard (IS). ^eGC yield estimated according to the effect of carbon number (ECN) rule. ^fSelectivity of CM1–4 and SM1,2 based on the conversion of MO. ^gSelectivity of CM products (%) = (CM1 + CM2 + CM3 + CM4)/(CM1 + CM2 + CM3 + CM4 + SM1 + SM2). CM1: dec-1-ene, CM2: methyl dec-9-enoate, CM3: 2-methoxy-4-(undec-2-en-1-yl)phenol, CM4: methyl 11-(4-hydroxy-3-methoxyphenyl)undec-9-noate, SM1: octadec-9-ene, SM2: dimethyl octadec-9-enedioate. ^hTurnover number (TON) = molar amount of metathesis product from MO (on the basis of MO conv. and select.(1))/Ru (mol). ⁱConducted without solvent (MO and UG). Detailed analysis data are shown in the Appendix A.

Moreover, the polarity of solvents could also influence the ability to dissolve the reactants (MO and UG). Note that the reactants are non-polar substrates, thus, the mixture of the reactants with solvents play significant role in dispersion of catalyst. For instance, ethanol has higher polarity than 2-propanol, therefore, at low MO concentration at 1.0 M the 2-propanol solvent has better dissolve with reactant mixture than ethanol resulted in higher MO conversion. The results revealed that the CM reaction conducted in ethanol under high MO concentration (10 or 20 M), which was similar to that in 2-propanol with 4.0 M in terms of both MO conversion and selectivity (runs 8, 9 vs 10), seems to be thus appropriate for the further study.

3.3.1.2 Effect of UG/MO molar ratio, reaction time and temperature in cross-metathesis of MO with UG

Based on the above results, the CM reaction of MO with UG were further proceed at 10 M MO concentration in ethanol to study effect of UG/MO molar ratio (1.0-10 molar ration), reaction time (5-30 min) and temperature (25-80 °C). The obtained results are shown in Table 3.3.

As shown in Table 3.3, the MO conversion in the CM slightly increased over time course (runs 8, 13, 14), and the conversion reached 96 % after 30 min (from 91 % after 10 min). However, a longer reaction time led to an increase in the percentage of the SM product of UG (SM4, from 4 to 12 %) as well as the degree of isomerization (UG to isoeugenol) in the reaction mixture (observed on the GC chromatogram, Figure C5.7 and Table A3.1, Appendix A), as reported previously.⁴¹ Hence, extension of the reaction time (after 10 min) is not beneficial under these conditions.

Moreover, it turned out that the UG/MO molar ratio (10 equiv. of UG to MO) plays an important role in obtaining the CM products with high selectivity (defined as select.(2), runs 8, 15-17), whereas high MO conversion could be attained even with 1 equiv. of UG (run 15). The high UG/MO ratio is crucial due to low reactivity of UG, and this would be mostly considered in ordinary CM (with terminal olefins) of this type.^{4-11,41} Consistently, formation of the SM products was considerably reduced at a high UG/MO molar ratio, thereby confirming that the SM of MO was inhibited upon increasing the UG concentration. Further UG addition led to a decrease in the MO conversion (20 equiv., run 17), probably due to the increased degree of isomerization of UG observed on the GC chromatogram (Figure A3.8, Appendix A).

	ЦG	Taman	Time	MO			Met		Select.	Select.					
run (eq) ^c (°C	(°C)	(min)	conv. (%) ^d	CM1	CM2	CM3	CM4	SM1 trans	SM1 <i>Cis</i>	SM2 Trans	SM2 <i>cis</i>	(1) (%) ^f	(2) (%) ^g	TON ^h	
13	10	50	5	72	31	36	17	18	1	0	1	0	72	98	520
8	10	50	10	91	31	48	17	21	1	0	1	0	65	98	590
14	10	50	30	96	44	60	15	17	1	0	1	0	72	98	690
15	1.0	50	10	92	34	29	13	21	4	1	8	3	61	86	560
16	5.0	50	10	95	33	44	14	19	1	0	2	0	60	97	570
17	20	50	10	81	28	39	13	10	1	0	0	0	56	99	450
18	10	25	10	48	15	20	10	9	1	0	0	0	56	98	270
19	10	80	10	91	35	47	14	11	1	0	1	0	61	98	560

Table 3.3 Effect of UG/MO molar ratio, reaction time and temperature in CM of MO with UG by **G2**.^{a,b}

^aEffect of UG/MO molar ratio, reaction time, and temperature. ^bConditions: 2.00 mmol of MO, solvent ethanol, MO concentration 10.0 M, catalyst (**G2**) 0.002 mmol (0.1 mol %). ^cBased on MO. ^dConversion of MO estimated by GC using an internal standard. ^eGC yield estimated according to the effect of carbon number (ECN) rule. ^fSelectivity of CM1–4 and SM1,2 based on the conversion of MO. ^gSelectivity of CM products (%) = (CM1 + CM2 + CM3 + CM4)/(CM1 + CM2 + CM3 + CM4 + SM1 + SM2). CM1: dec-1-ene, CM2: methyl dec-9-enoate, CM3: 2-methoxy-4-(undec-2-en-1-yl)phenol, CM4: methyl 11-(4-hydroxy-3-methoxyphenyl)undec-9-noate, SM1: octadec-9-ene, SM2: dimethyl octadec-9-enedioate. ^hTON = molar amount of metathesis product from MO (on the basis of MO conv. and select.(1))/Ru (mol). Detailed analysis data are shown in the Appendix A.

It also turned out that the reaction temperature affected both reaction rate and selectivity in this catalysis. The MO conversion at 50 °C reached 90 % with exclusive CM selectivity (>98 %, defined as select.(2), run 8), but the MO conversion was low at room temperature (25 °C, run 18). No significant improvements in both MO conversion and CM selectivity were, however, observed at 80 °C, and the degree of isomerization of UG increased instead (ca. 5 times compared to that at 50 °C, on the basis of the GC chromatogram, Figure A3.9 and Table A3.2, Appendix A). Isomerization of terminal olefin (to internal olefin) is often observed in olefin metathesis in the presence of ruthenium catalysts,^{4–11,59–62} probably due to catalyst decomposition. These results revealed that the CM at 50 °C seems to be thus the appropriate condition in this catalysis.

3.3.1.3 Effect of catalyst loading and different types of Ru-carbene catalysts in cross-metathesis of MO with UG

In order to study effect of various Ru-carbene catalysts (shown in Scheme 3.2), the CM of MO with UG was performed under the optimized conditions (conducted as run 8, in ethanol at 50 °C). The results are summarized in Table 3.4.

Table 3.4 Effect of catalyst loading and different types of Ru-carbene catalysts in CM of MO with UG.^{a,b}

C; run mol	Cat	UG (eq) ^c	MO conv. (%) ^d			Met	Select.	Select.						
	mol (%)			CM1	CM2	СМ3	CM4	SM1 trans	SM1 <i>cis</i>	SM2 trans	SM2 <i>cis</i>	(1) (%) ^f	(2) (%) ^g	TON ^h
20	G2 (0.05)	10	58	20	26	12	12	1	0	0	0	62	98	720
8	G2 (0.1)	10	91	31	48	17	21	1	0	1	0	65	98	590
21	G1 (0.1)	10	8	1	1	1	1	0	0	0	0	28	84	22
22	G3 (0.1)	10	16	3	4	2	2	0	0	0	0	31	93	50
23	HG2 (0.1)	10	32	12	14	5	2	1	0	1	0	53	96	170

^aEffect of catalyst loading and different types of Ru-carbene catalysts. ^bConditions: 2.00 mmol of MO, MO concentration 10.0 M, temperature 50 °C, reaction time 10 min. ^cBased on MO. ^dConversion of MO estimated by GC using an internal standard. ^eGC yield estimated according to the effect of carbon number (ECN) rule. ^fSelectivity of CM1–4 and SM1,2 based on the conversion of MO. ^gSelectivity of CM products (%) = (CM1 + CM2 + CM3 + CM4)/(CM1 + CM2 + CM3 + CM4 + SM1 + SM2). CM1: dec-1-ene, CM2: methyl dec-9-enoate, CM3: 2-methoxy-4-(undec-2-en-1-yl)phenol, CM4: methyl 11-(4-hydroxy-3-methoxyphenyl)undec-9-noate, SM1: octadec-9-ene, SM2: dimethyl octadec-9-enedioate. ^hTON = molar amount of metathesis product from MO (on the basis of MO conv. and select.(1))/Ru (mol). Detailed analysis data are shown in the Appendix A.

It turned out that the catalyst **G2** (called a second-generation Grubbs catalyst) showed exceptionally better catalyst performance and higher MO conversion in the CM than **G1** and **G3** (runs 21, 22). The reason for the observed low activity by **G1** would be due to the catalyst decomposition, because **G1** is known to react with ethanol to form Ru-hydride species $Ru(H)(Cl)(CO)(PCy_3)$ (see Scheme 3.4),⁶³ which is active in olefin isomerization catalysts. Indeed, the reaction with **G1** led to the isomerization of UG predominantly (10%, Figure A3.10, Appendix A). The higher

activity of **G2** catalyst than **G1** is due to the mono-substitution of PCy_3 with N-heterocyclic carbenes (NHC). The presence of the NHC group help to protect the ruthenium active species from functional group resulted in higher activity and better thermal stability as well as stable to moisture and air. Moreover, the conversion of MO and selectivity of CM products (defined as select.(1)) by **HG2** was lower than those by **G2** (Table 3.4, runs 8, 23). This would be probably due to further reactions (second metathesis etc.) with the products. For instance, the cross-metathesis of the products (CM1 vs. CM4) and (CM2 vs. CM3) could convert back to the starting materials (MO and UG) as illustration in Scheme 3.5. An apparent increase in the activity (TONs on the basis of Ru) was not observed when the CM by **G2** was conducted at low catalyst loading (from 0.1 to 0.05 mol%, runs 8, 20). Moreover, an apparent decrease in the selectivity was not observed under these conditions.



Scheme 3.4 Degradation of the first-generation Grubb catalyst G1 with ethanol.⁶³





In summary, CM of MO with UG has been performed with both high MO conversion and high selectivity of CM products using the **G2** catalyst in ethanol (green solvent). Effects of the UG/MO molar ratio, reaction temperature (50 °C), initial MO concentration and others (catalyst, time etc.) play a role in obtaining the desired product in an efficient manner.

3.3.2 Structure Characterization of CM products of MO with UG

The CM reaction of MO with UG afforded four types of CM products involving dec-1-ene (CM1, m/z 140), methyl dec-9-enoate (CM2, m/z 184), 2-methoxy-4-(undec-2-en-1-yl)phenol (CM3, m/z 276) and methyl 11-(4-hydroxy-3methoxyphenyl)undec-9-noate (CM4, m/z 320). After completed reaction, the mixture was purified by column chromatography on silica gel followed by thin layer chromatography (TLC, ethyl acetate/n-hexane = 2:8 v/v mixtures). The structure of CM products was identified by ¹H NMR (Figure 3.2–3.6) and ¹³C NMR spectroscopy (Figure A3.17-3.21, Appendix A).^{50,64-66} The NMR spectroscopy of CM products indicated that the CM products were successfully obtained from CM reaction of MO with UG. It thus believes that it is possible to generate renewable monomers with bifunctional from CM of MO with UG.

Dec-1-ene (CM1)

¹H NMR (500 MHz, CDCl₃, ppm): δ 0.88 (s, 3H, CH₃) 1.26-1.31 (s, 10H, CH₂), 1.36 (s, 2H, CH₂), 2.02-2.06 (s, 2H, CH₂), 4.94-5.01 (m, 2H, CH₂=CH), 5.77-5.85 (m, 1H, CH₂=CH). (*: trace amount of impurity).



Figure 3.2 ¹H NMR spectra (in $CDCl_3$ at 25 °C) of Dec-1-ene (CM1) with its peak assignments.

Methyl dec-9-enoate (CM2): ¹H NMR (500 MHz, CDCl₃): δ 1.28 (s, 8H, CH₂), 1.61 (s, 2H, CH₂), 2.04 (d, 2H, CH₂), 2.30 (t, 2H, CH₂), 3.65 (s, 3H, CH₃), 4.90-4.99 (m, 2H, CH=CH₂), 5.8 (m, 1H, CH=CH₂). *: a trace amount impurity



Figure 3.3 ¹H NMR spectra (in CDCl₃ at 25 °C) of Methyl dec-9-enoate (CM2) with its peak assignments.

2-methoxy-4-(undec-2-en-1-yl)phenol (CM3): ¹H NMR (500 MHz, CDCl₃): δ 0.88 (s, 3H, CH₃), 1.29 (s, 10H, CH₂), 1.31 (s, 2H, CH₂), 2.10 (s, 2H, CH₂), 3.21 (s, 2H, CH₂), 3.83 (s, 3H, CH₃), 5.41 (m, 3H, CH₂=CH), 6.62-6.72 (m, 2Har, CH), 6.84 (m, 1Har, CH).



Figure 3.4 ¹H NMR spectra (in CDCl₃ at 25 °C) of 2-methoxy-4-(undec-2-en-1-yl)phenol (CM3) with its assignments.

Methyl 11-(4-hydroxy-3-methoxyphenyl)undec-9-noate) (CM4): ¹H NMR (500 MHz, CDCl₃, ppm): δ 1.29 (s, 8H, CH₂), 1.62 (2H, CH₂), 2.03 (2H, CH₂), 2.31 (2H, CH₂), 3.24 (2H, CH₂), 3.66 (3H, CH₃), 3.86 (3H, CH₃), 5.5 (1H, CH), 6.66-6.67 (2Har, CH), 6.82 (1Har, CH). *: peak of solvent acetone



Figure 3.5 ¹H NMR spectra (in CDCl₃ at 25 °C) of Methyl 11-(4-hydroxy-3-methoxyphenyl)undec-9-noate) (CM4) with its assignments.

4,4'-(but-2-ene-1,4-diyl)bis(2-methoxyphenol) (SM4): ¹H NMR (500 MHz, CDCl₃, ppm): δ 3.30 (d, 2H, *CH*₂), 3.83-3.85 (m, 6H, *CH*₃), 5.55 (m, 1H, *CH*), 5.64-5.71 (m, 1H, *CH*), 6.69-6.73 (m, 3Har, *CH*), 6.83-6.85 (m, 3H, *CH*). *: peaks of solvent ethyl acetate remaining during separation processing



Figure 3.6 ¹H-NMR spectra (in CDCl₃ at 25 °C) of 4,4'-(but-2-ene-1,4-diyl)*bis*(2-methoxyphenol) (SM4) with its assignments.
3.3.3 Cross-metathesis of various methyl esters [methyl petroselinate (MP), methyl erucate (ME), and methyl 10-undecanoate (MU)] with UG

On the basis of the above results from the CM of MO with UG, CM of the other unsaturated fatty acid methyl esters such as methyl petroselinate (MP), methyl erucate (ME), and methyl 10-undecanoate (MU) with UG was conducted in ethanol in the presence of **G2** (Scheme 3.6, conditions: Ru 0.1 mol % at 50 °C for 10 min, UG/substrate = 10 (molar ratio)). The selected results are summarized in Table 3.4. As shown in Scheme 3.6 (as well as explained in Scheme 3.2), the CM of internal olefins (MP and ME) affords 4 types of CM products (expressed as CM1, CM2, CM3, and CM4), in addition to SM products. CM of MU with UG should afford one CM product (expressed as CM1).





It should be noted that the CM of MP with UG proceeded with both high activity (920 turnovers after 10 min, high MP conversion) and the exclusive selectivity (>98 %, defined as select.(2), run 24). In contrast, the CM of ME with UG only reached 55 % under the same conditions (run 25, 390 turnovers). However, high ME conversion (95%), maintaining the exclusive selectivity of CM product (>99 %, defined as select.(2)), could be achieved upon increasing **G2** loading (0.2 mol%, run 26), although the percentage of one CM product (defined CM3), however, decreased upon increasing the catalyst loading probably due to second metathesis. These results clearly indicate that these CM reactions (of MO, MP and ME) with UG can be achieved in ethanol in an efficient manner in the presence of **G2**. The results also revealed that the catalyst performance was affected by the substrate employed, in the order of MP> MO> ME. It thus seems likely that olefinic double bonds relatively close to the methyl ester showed better performance in the CM reaction with UG. This can be explained because of the effect of steric hinderance of the methyl ester groups in the formation of the ruthenacyclobutane intermediate during the cross-metathesis of UG with the unsaturated fatty acid methyl esters.

In contrast, unfortunately, attempted CM of MU (terminal olefins) with UG, conducted under the same conditions as those in the CM of MO (UG/MU = 10, molar ratio), afforded negligible MU conversion (Table 3.5, run 27). Further attempts conducted under different MU/UG molar ratios with high **G2** loading improved the MU conversion (up to 83 %, run 29), but the yields of the desired CM products were very low (Table 3.5, runs 28, 29), probably due to the subsequent isomerization of MU *in situ* leading to another metathesis reactions (Scheme 3.7). In fact, the formation of the isomerized product of MU (methyl undec-9-enoate) and methyl 11-(4-hydroxy-3-methoxyphenyl)undec-9-enoateand (CM1'), which should be formed by the subsequent CM with UG, in addition to dimethyl octadec-9-enedioate (SM1') as the SM product was observed on the GC chromatogram and Figure A3.15-3.16 (Appendix A).



Scheme 3.7 Proposed isomerization and CM of MU isomerization with UG.

	Substrate	UG (eq.) ^b	Cat. mol (%)		Metathesis products (%) ^d						Select	Select.			
run				Conv. (%) ^c	CM1	CM2	CM3	CM4	SM1 trans	SM1 <i>Cis</i>	SM2 Trans	SM2 Cis	.(1) (%) ^e	(2) (%) ^f	TON ^g
24	MP	10	0.1	93	80	74	18	24	2	0	0	2	>99	98	920
25	ME	10	0.1	55	30	29	19	0	0	0	0	0	71	99	390
26	ME	10	0.2	95	78	70	8	0	1	0	0	0	83	99	390
27	MU	10	0.1	0	0	N/A	N/A	N/A	0	0	N/A	N/A	0	0	0
28	MU	5.0	0.5	47	4	N/A	N/A	N/A	2	0	N/A	N/A	7	67	7
29	MU	1.0	1.0	83	18	N/A	N/A	N/A	10	0	N/A	N/A	17	65	14

Table 3.5 CM of unsaturated fatty acid methyl esters (MP, ME and MU) with UG by **G2**.^a

^aConditions: 2.00 mmol of substrates (MP, ME, MU), solvent ethanol, substrate concentration 10.0 M, catalyst (**G2**), temperature 50 °C, time 10 min. ^bBased on substrates. ^cConversion of substrates estimated by GC using an internal standard. ^dGC yield estimated according to the effect of carbon number (ECN) rule. ^eSelectivity of CM1–4 and SM1,2 based on the conversion of substrates. ^fSelectivity of CM products (%) = (CM1 + CM2 + CM3 + CM4)/(CM1 + CM2 + CM3 + CM4 + SM1 + SM2). CM1: tridec-1-ene (from MP), dec-1-ene (from ME), methyl 12-(4-hydroxy-3-methoxyphenyl)dodec-10-enoate (from MU), CM2: methyl hept-6-enoate (from MP), methyl tetradec-13-enoate (from ME), CM3: 2-methoxy-4-(tetradec-2-en-1-yl)phenol (from MP), 2-methoxy-4-(undec-2-en-1-yl)phenol (from ME), CM4: methyl 8-(4-hydroxy-3-methoxyphenyl)oct-6-enoate (from MP), methyl 15-(4-hydroxy-3-methoxyphenyl)pentadec-13-enoate (from ME), SM1: tetracos-12-ene (from MP), octadec-9-ene (from ME), dimethyl icos-10-enedioate (from MU), SM2: dimethyl dodec-6-enedioate (from MP), dimethyl hexacos-13-enedioate (from ME). N/A: not applicable. [§]TON = molar amount of metathesis product from MO (on the basis of MO conv. and select.(1))/Ru (mol). Detailed analysis data are shown in the Appendix A.

3.4 Conclusions

We have shown that CM reactions of various renewable unsaturated fatty acid methyl esters (MO, MP, and ME) with UG successfully conducted by Ru-carbene catalyst (**G2**, shown in Scheme 3.2) under environmentally benign conditions (in isopropanol and ethanol at 50 °C). The reaction conditions could be optimized to reach high substrate conversion with high CM selectivity, particularly for CM of MO with UG. It turned out that both the MO conversion and selectivity of CM products were highly affected by initial MO concentration, UG/MO molar ratio, and reaction temperature. The catalyst performance was also affected by the substrate employed (in the order of MP> MO> ME); it seems that olefinic double bond relatively close to the methyl ester showed better performance in the CM reaction with UG. It was also revealed that the subsequent isomerization of either UG or fatty acid methyl esters *in situ* significantly affect the CM and the SM products yields.

3.5 References

- Selected Book (refs 1–3) Handbook of Metathesis; Grubbs, R. H., Ed.; Wiley-VCH: Weinheim, Germany, 2003.
- Olefin Metathesis: *Theory and Practice*; Grela, K., Ed.; John Wiley & Sons, Inc.: Hoboken, NJ, 2014.
- 3. *Handbook of Metathesis*, 2nd ed.; Grubbs, R. H., Wenzel, A. G., Eds.; Wiley-VCH: Weinheim, Germany, 2015; Vol. 1.
- 4. For example (refs 4–11) Fürstner, A. Olefin Metathesis and Beyond. *Angew. Chem., Int. Ed.* 2000, 39, 3012–3043.
- 5. Trnka, T. M.; Grubbs, R. H. The Development of $L_2X_2Ru = CHR$ Olefin Metathesis Catalysts: An Organometallic Success Story. *Acc. Chem. Res.* 2001, 34, 18–29.
- Schrock, R. R.; Hoveyda, A. H. Molybdenum and Tungsten Imido Alkylidene Complexes as Efficient Olefin-Metathesis Catalysts. *Angew. Chem., Int. Ed.* 2003, 42, 4592–4633.
- 7. Chatterjee, A. K. In *Handbook of Metathesis*; Grubbs, R. H., Ed.; Wiley-VCH: Weinheim, Germany, 2003; Vol. 2, p 246.
- Samojzowicz, C.; Bieniek, M.; Grela, K. Ruthenium-Based Olefin Metathesis Catalysts Bearing N-Heterocyclic Carbene Ligands. *Chem. Rev.* 2009, 109, 3708–3742.

- 9. Vougioukalakis, G.; Grubbs, R. H. Ruthenium-Based Heterocyclic Carbene-Coordinated Olefin Metathesis Catalysts. *Chem. Rev.* 2010, 110, 1746–1787.
- Monfette, S.; Fogg, D. Equilibrium Ring-Closing Metathesis. *Chem. Rev.* 2009, 109, 3783–3816.
- 11. Clavier, H.; Grela, K.; Kirschning, A.; Mauduit, M.; Nolan, S. P. Sustainable Concepts in Olefin Metathesis. *Angew. Chem., Int. Ed.* 2007, 46, 6786–6801.
- For examples (refs 12–16) Biermann, U.; Bornscheuer, U.; Meier, M. A. R.; Metzger, J. O.; Schafer, H. J. Oils and Fats as Renewable Raw Materials in Chemistry. *Angew. Chem., Int. Ed.* 2011, 50, 3854–3871.
- de Espinosa, L. M.; Meier, M. A. R. In *Organometallics and Renewables*; Meier, M. A. R., Weckjusen, B. M., Bruijnincx, P. C. A., Eds.; Springer-Verlag: Berlin Heidelberg, Germany, 2012; p 1.
- Nickel, A.; Pederson, R. L. In Olefin Metathesis: *Theory and Practice*; Grela, K., Ed.;
 John Wiley & Sons, Inc.; Hoboken, NJ, 2014; p 335.
- Philips, J. H. In *Handbook of Metathesis*, 2nd ed.; Grubbs, R. H., Wenzel, A. G.,
 O'Leary, D. J., Khosravi, E., Eds.; Wiley-VCH: Weinheim, Germany, 2015; Vol. 3, p
 357.
- Meier, M. A. R. Metathesis with Oleochemicals: New Approaches for the Utilization of Plant Oils as Renewable Resources in Polymer Science. *Macromol. Chem. Phys.* 2009, 210, 1073–1079.
- For examples (refs 17–20) Achten, W. M. J.; Verchot, L.; Franken, Y. J.; Mathijs, E.; Singh, V. P.; Aerts, R.; Muys, B. Jatropha bio-diesel production and use. *Biomass Bioenerg.* 2008, 32, 1063–1082.
- 18. Behr, A.; Westfechtel, A.; Pérez Gomes, J. Catalytic Processes for the Technical Use of Natural Fats and Oils. *Chem. Eng. Technol.* 2008, 31, 700–714.
- 19. Mata, T. M.; Martins, A. A.; Caetano, N. S. Microalgae for biodiesel production and other applications: A review. *Renew. Sust. Energ. Rev.* 2010, 14, 217–232.
- 20. Murzin, D. Y.; Maki-Arvela, P.; Aranda, D. A. G. Processing microalgae: beyond lipids. *Biofuels* 2014, 5, 29–32.

- Self-metathesis and ethenolysis of unsaturated fatty acid esters (exemplified by methyl oleate, MO, refs 21–31) Burdett, K. A.; Harris, L. D.; Margl, P.; Maughon, B. R.; Mokhtar-Zadeh, T.; Saucier, P. C.; Wasserman, E. P. Renewable Monomer Feedstocks via Olefin Metathesis: Fundamental Mechanistic Studies of Methyl Oleate Ethenolysis with the First-Generation Grubbs Catalyst. *Organometallics* 2004, 23, 2027–2047.
- Forman, G. S.; McConnell, A. E.; Hanton, M. J.; Slawin, A. M. Z.; Tooze, R. P.; van Rensburg, W. J.; Meyer, W. H.; Dwyer, C.; Kirk, M. M.; Serfontein, D. W. A Stable Ruthenium Catalyst for Productive Olefin Metathesis. *Organometallics* 2004, 23, 4824–4827.
- 23. Thurier, C.; Fischmeister, C.; Bruneau, C.; Olivier-Bourbigou, H.; Dixneuf, P. H. Ethenolysis of Methyl Oleate in Room-Temperature Ionic Liquids. *Chem. Sus. Chem.* 2008, 1, 118–122.
- Anderson, D. R.; Ung, T.; Mkrtumyan, G.; Bertrand, G.; Grubbs, R. H.; Schrodi, Y. Kinetic Selectivity of Olefin Metathesis Catalysts Bearing Cyclic (Alkyl)(Amino)Carbenes. *Organometallics* 2008, 27, 563–566.
- Schrodi, Y.; Ung, T.; Vargas, A.; Mkrtumyan, G.; Lee, C. W.; Champagne, T. M.; Pederson, R. L.; Hong, S. H. Ruthenium Olefin Metathesis Catalysts for the Ethenolysis of Renewable Feedstocks. *Clean Soil Air Water* 2008, 36, 669–673.
- 26. Marinescu, S. C.; Schrock, R. R.; Muller, P.; Hoveyda, A. H. Ethenolysis Reactions Catalyzed by Imido Alkylidene Monoaryloxide Monopyrrolide (MAP) Complexes of Molybdenum. *J. Am. Chem. Soc.* 2009, 131, 10840–10841.
- Mutlu, H.; Hofsa; Montenegro, R. E.; Meier, M. A. R. Self-metathesis of fatty acid methyl esters: full conversion by choosing the appropriate plant oil. *RSC Adv.* 2013, 3, 4927–4934.
- Nickel, A.; Ung, T.; Mkrtumyan, G.; Uy, J.; Lee, C. W.; Stoianova, D.; Papazian, J.; Wei, W.-H.; Mallari, A.; Schrodi, Y.; Pederson, R. L. A Highly Efficient Olefin Metathesis Process for the Synthesis of Terminal Alkenes from Fatty Acid Esters. *Top. Catal.* 2012, 55, 518–523.
- 29. Ohlmann, D. M.; Tschauder, N.; Stockis, J.-P.; Gooßen, K.; Dierker, M.; Gooßen, L.J. Isomerizing Olefin Metathesis as a Strategy to Access Defined Distributions of

Unsaturated Compounds from Fatty Acids. J. Am. Chem. Soc. 2012, 134, 13716–13729.

- 30. Ullah, A.; Arshad, M. Remarkably Efficient Microwave-Assisted Cross-Metathesis of Lipids under Solvent-Free Conditions. *Chem. Sus. Chem.* 2017, 10, 2167–2174.
- 31. Jin, L.; Geng, K.; Arshad, M.; Ahmadi, R.; Ullah, A. Synthesis of Fully Biobased Polyesters from Plant Oil. *ACS Sustain. Chem. Eng.* 2017, 5, 9793–9801.
- 32. Examples for cross metathesis of unsaturated fatty acid esters (MO, refs 32–41) Jacobs, T.; Rybak, A.; Meier, M. A. R. Cross-metathesis reactions of allyl chloride with fatty acid methyl esters: Efficient synthesis of α, ω -difunctional chemical intermediates from renewable raw materials. *Appl. Catal. A* 2009, 353, 32–35.
- Rybak, A.; Meier, M. A. R. Cross-metathesis of fatty acid derivatives with methyl acrylate: renewable raw materials for the chemical industry. *Green Chem.* 2007, 9, 1356–1361.
- Biermann, U.; Meier, M. A. R.; Butte, W.; Metzger, J. O. Cross-metathesis of unsaturated triglycerides with methyl acrylate: Synthesis of a dimeric metathesis product. *Eur. J. Lipid Sci. Technol.* 2011, 113, 39–45.
- 35. Miao, X.; Malacea, R.; Fischmeister, C.; Bruneau, C.; Dixneuf, P. H. Rutheniumalkylidene catalysed cross-metathesis of fatty acid derivatives with acrylonitrile and methyl acrylate: a key step toward long-chain bifunctional and amino acid compounds. *Green Chem.* 2011, 13, 2911–2919.
- Abel, G. A.; Nguyen, K. O.; Viamajala, S.; Varanasi, S.; Yamamoto, K. Crossmetathesis approach to produce precursors of nylon 12 and nylon 13 from microalgae. *RSC Adv.* 2014, 4, 55622–55628.
- Behr, A.; Pérez Gomes, J. The cross-metathesis of methyl oleate with cis-2butene-1,4-diyl diacetate and the influence of protecting groups. *Beilstein J. Org. Chem.* 2011, 7, 1–8.
- Abbas, M.; Slugovc, C. Optimized reaction conditions for the cross-metathesis of methyl oleate and oleylamine with ethyl acrylate. *Monatsh. Chem.* 2012, 143, 669–673.
- 39. Kajetanowicz, A.; Sytniczuk, A.; Grela, K. Metathesis of renewable raw materialsinfluence of ligands in the indenylidene type catalysts on self-metathesis of

methyl oleate and cross-metathesis of methyl oleate with (Z)-2-butene-1,4-diol diacetate. *Green Chem.* 2014, 16, 1579–1585.

- 40. Winkler, M.; Meier, M. A. R. Olefin cross-metathesis as a valuable tool for the preparation of renewable polyesters and polyamides from unsaturated fatty acid esters and carbamates. *Green Chem.* 2014, 16, 3335–3340.
- Awang, N. W.; Tsutsumi, K.; Hustakova, B.; Yusoff, S. F. M.; Nomura, K.; Yamin, B. M. Cross metathesis of methyl oleate (MO) with terminal, internal olefins by ruthenium catalysts: factors affecting the efficient MO conversion and the selectivity. *RSC Adv.* 2016, 6, 100925–100930.
- Peppas, N. A.; Am Ende, D. J. Controlled release of perfumes from polymers. II. Incorporation and release of essential oils from glassy polymers. *J. Appl. Polym. Sci.* 1997, 66, 509–513.
- Harvey, B. G.; Guenthner, A. J.; Lai, W. W.; Meylemans, H. A.; Davis, M. C.; Cambrea,
 L. R.; Reams, J. T.; Lamison, K. R. Effects of o-Methoxy Groups on the Properties and Thermal Stability of Renewable High-Temperature Cyanate Ester Resins. *Macromolecules* 2015, 48, 3173–3179.
- Hu, K.; Zhao, D.; Wu, G.; Ma, J. Synthesis and properties of polyesters derived from renewable eugenol and α,ω-diols via a continuous overheating method.
 Polym. Chem. 2015, 6, 7138–7148.
- 45. Britt, P. F.; Buchanan, A. C.; Cooney, M. J.; Martineau, D. R. Flash Vacuum Pyrolysis of Methoxy-Substituted Lignin Model Compounds. *J. Org. Chem.* 2000, 65, 1376–1389.
- 46. Yoshimura, T.; Shimasaki, T.; Teramoto, N.; Shibata, M. Biobased polymer networks by thiol-ene photopolymerizations of allyletherified eugenol derivatives. *Eur. Polym. J.* 2015, 67, 397–408.
- 47. Guzmán, D.; Ramis, X.; Fernández-Francos, X.; De la Flor, S.; Serra, A. New biobased materials obtained by thiol-ene/thiol-epoxy dual curing click procedures from eugenol derivates. *Eur. Polym. J.* 2017, 93, 530–544.
- 48. Shibata, M.; Tetramoto, N.; Imada, A.; Neda, M.; Sugimoto, S. Bio-based thermosetting bismaleimide resins using eugenol, bieugenol and eugenol novolac. *React. Funct. Polym.* 2013, 73, 1086–1095.

- 49. Neda, M.; Okinaga, K.; Shibata, M. High-performance biobased thermosetting resins based on bismaleimide and allyl-etherified eugenol derivatives. *Mater. Chem. Phys.* 2014, 148, 319–327.
- 50. Bilel, H.; Hamdi, N.; Zagrouba, F.; Fischmeister, C.; Bruneau, C. Eugenol as a renewable feedstock for the production of polyfunctional alkenes via olefin cross-metathesis. *RSC Adv.* 2012, 2, 9584–9589.
- 51. Alexander, K. A.; Paulhus, E. A.; Lazarus, G. M. L.; Leadbeater, N. E. Exploring the reactivity of a ruthenium complex in the metathesis of biorenewable feedstocks to generate value-added chemicals. *J. Organomet. Chem.* 2016, 812, 74–80.
- Vieille-Petit, L.; Clavier, H.; Linden, A.; Blumentritt, S.; Nolan, S. P.; Dorta, R. Ruthenium Olefin Metathesis Catalysts with N-Heterocyclic Carbene Ligands Bearing N-Naphthyl Side Chains. Organometallics 2010, 29, 775–788.
- Broggi, J.; Urbina-Blanco, C. A.; Clavier, H.; Leitgeb, A.; Slugovc, C.; Slawin, A. M. Z.; Nolan, S. P. The Influence of Phosphane Ligands on the Versatility of Ruthenium–Indenylidene Complexes in Metathesis. *Chem. Eur. J.* 2010, 16, 9215–9225.
- 54. Yapa Mudiyanselage, A.; Viamajala, S.; Varanasi, S.; Yamamoto, K. Simple Ring-Closing Metathesis Approach for Synthesis of PA11, 12, and 13 Precursors from Oleic Acid. *ACS Sustain. Chem. Eng.* 2014, 2, 2831–2836.
- 55. Kállai, M.; Balla, J. The effect of molecular structure upon the response of the flame ionization detector. *Chromatographia* 2002, 54, 357–360.
- 56. *Modern Practice of Gas Chromatography*; Grob, R. L., Barry, E. F., Eds.; Wiley-Interscience: NY, 2004; pp 302–305.
- 57. Kállai, M.; Veres, Z.; Balla, J. Response of flame ionization detectors to different homologous series. *Chromatographia* 2001, 54, 511–517.
- Scanlon, J. T.; Willis, D. E. Calculation of Flame Ionization Detector Relative Response Factors Using the Effective Carbon Number Concept. *J. Chromatogr. Sci.* 1985, 23, 333–340.
- 59. Jinesh, C. M.; Sen, A.; Ganguly, B.; Kannan, S. Microwave assisted isomerization of alkenyl aromatics over solid base catalysts: an understanding through theoretical study. *RSC Adv.* 2012, 2, 6871–6878.

- 60. Lastra-Barreira, B.; Crochet, P. Ruthenium-catalyzed estragole isomerization: high trans-selective formation of anethole. *Green Chem.* 2010, 12, 1311–1314.
- 61. Lastra-Barreira, B.; Francos, J.; Crochet, P.; Cadierno, V. Ruthenium(iv) catalysts for the selective estragole to trans-anethole isomerization in environmentally friendly media. *Green Chem.* 2011, 13, 307–313.
- 62. Trita, A. S.; Over, L. C.; Pollini, J.; Baader, S.; Riegsinger, S.; Meier, M. A. R.; Gooßen,
 L. J. Synthesis of potential bisphenol A substitutes by isomerising metathesis of renewable raw materials. *Green Chem.* 2017, 19, 3051–3060.
- 63. Dinger, M. B.; Mol, J. C. Degradation of the First-Generation Grubbs Metathesis Catalyst with Primary Alcohols, Water, and Oxygen. Formation and Catalytic Activity of Ruthenium (II) Monocarbonyl Species. *Organometallics* 2003, 22, 1089–1095.
- Schotten, C.; Plaza, D.; Manzini, S.; Nolan, S. P.; Ley, S. V.; Browne, D. L.; Lapkin,
 A. Continuous Flow Metathesis for Direct Valorization of Food Waste: An Example
 of Cocoa Butter Triglyceride. ACS Sustain. Chem. Eng. 2015, 3, 1453–1459.
- 65. Naoum, R.; Séguin, J. P.; Trant, J. F.; Frampton, M. B.; Hudlický, T.; Zelisko, P. M. A chemoenzymatic route to chiral siloxanes. Tetrahedron 2016, 72, 4027–4031.
- 66. Witt, T.; Haußler, M.; Kulpa, S.; Mecking, S. Chain Multiplication of Fatty Acids to Precise Telechelic Polyethylene. *Angew. Chem., Int. Ed.* 2017, 56, 7589–7594.

CHAPTER 4

SYNTHESIS OF NEW POLYESTERS BY ACYCLIC DIENE METATHESIS POLYMERIZATION OF BIO-BASED α, ω -DIENES PREPARED FROM EUGENOL AND CASTOR OIL (UNDECENOATE)

4.1 Introduction

Polyesters are widely used in our daily life and attract considerable attention due to their tunable mechanical properties and potential biodegradability.¹⁻ ⁵ Most polyesters are currently prepared from compounds derived from petroleumbased resources (especially from fossil resources). Synthesis of polyesters from bioderived monomers is thus of great interest for research and development on high performance and sustainable materials.⁶ In this context, various raw materials from renewable resources such as plant oils,^{7,8} lignin,⁹ polysaccharides,¹⁰ sugars,^{11,12} and terpenes¹³ have been investigated. Among them, plant oils exemplified castor oil,¹⁴ which generally convert to fatty acids or fatty acid methyl esters by chemical modifications, are useful feedstock for synthesis of polymers.¹⁵ Acyclic diene metathesis (ADMET) polymerization is very useful for the synthesis of a wide variety of linear polymers and polymer architectures that are not available using the other polymerization methods.^{16,17} Recently, numerous studies have concentrated on the ADMET polymerization of fatty acids and its derivatives to obtain polyesters.¹⁸ Castor oil derivative, ω -undecenoate, containing both olefinic double bond and carboxylate at the termini is an ideal substance for synthesis of high purity α, ω -dienes as valuable monomers for preparing polyesters via ADMET polymerization. For instance, ADMET polymerizations of castor oil-based α, ω -dienes (undecenyl-undecenoate) using second generation Grubbs-type ruthenium catalysts resulted in high molecular weight unsaturated polyesters have been investigated by Meier et al.¹⁹ The ADMET polymerization of α, ω -dienes prepared from castor-oil derivative with hydroxyl-bearing unsaturated compounds, diols and diamine have also been studied.^{18,20,21}

Eugenol (UG, 4-allyl-2-methoxyphenol) is an interesting renewable resource obtained from clove oil. UG has been widely used not only in the production of cosmetics, perfumes, soaps, and even food, but also in the medical and pharmaceutical fields as antibiotic and antihypertensive agents.²² Owing to its functional groups [hydroxyl (-OH), methoxy (-OCH₃) and allyl groups], UG can be used as starting material for synthesis of new compounds exemplified in designing polymer networks via thiol-ene coupling^{23,24} or bismaleimide networks.^{25,26} Recently, study on UG mainly focused on Ru-catalysed olefin metathesis reactions such as self-metathesis^{27,28} and cross-metathesis with either electron-deficient olefins^{29,30} or unsaturated fatty acid methyl esters³¹ due to presence of the terminal olefin group. Therefore, it is possible to prepare different types of functionalized phenol derivatives to develop new routes for the synthesis of different multifunctional products from UG.^{32,33} Additionally, UG structure, which contains an aromatic ring, has the potential alternative to petroleum-based phenolic monomers, which are widely used nowadays in the field of polyesters. For instance, a wide variety of polyesters based on UG and α, ω -diols have been prepared by polycondensation and thiol-ene click reactions.^{34,35} However, there are no reports had been published till date about using UG as a precursor for the synthesis of novel α, ω -dienes monomers incorporating with aliphatic chain (undecenoate) to produce polyesters via ADMET polymerization, although there is one report for ADMET polymerization of dieugenol derived from UG affording amorphous polymer with high molecular weight.36

In this chapter, we wish to present a simple preparation of α, ω -diene monomer M1, derived from bio-renewable UG and castor oil, for synthesis of polyesters P1 by ADMET polymerization. The ADMET polymerization conditions in term of catalyst loading, type of catalyst and reaction time, have been investigated in detail. The ADMET polymerization of M1 in the presence of triarm cross-linker, 5-formylbenzene-1,2,3-triyl tris(undec-10-enoate) was also studied. Two aliphatic polyesters with linear aliphatic α, ω -dienes were also prepared for comparison.

4.2 Materials and Methods

4.2.1 Materials

All experiments were carried out under nitrogen atmosphere or using standard Schlenk techniques unless otherwise specified. Anhydrous grade dichloromethane and toluene (>99.5 %, Kanto Chemical Co., Inc.) were transferred into a bottle containing molecular sieves (mixture of 3A 1/16, 4A 1/8 and 13X 1/16) in the drybox. RuCl₂(PCy₃)₂(CHPh) (called first-generation Grubbs catalyst (**G1**); Cy = cyclohexyl), RuCl₂(PCy₃)(H₂IMes)(CHPh) [called second-generation Grubbs catalyst (**G2**); IMesH₂ = 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene] and RuCl₂(IMesH₂)(CH-2-O[']Pr-C₆H₄) [called second-generation Hoveyda-Grubbs catalyst (**HG2**)] were purchased from Aldrich Chemical Co., and were used as received. Chemicals of reagent grades such as Eugenol (UG, >99.0 %, Tokyo Chemical Industry, Co., Ltd.), 10-undecenoyl chloride (UDC, >99 %), 10-undecen-1-ol (UDO, >98 %), 5-hexene-1-ol (Hex), 3,4,5-trihydroxybenzaldehyde (>98 %) and triethylamine (NEt₃, >99 %) were obtained from Tokyo Chemical Industry, Co., Ltd., and were used as received. Ethyl vinyl ether (>98%) and Celite® were purchased from Wako Pure Chemical Industries, Ltd.

4.2.2 Measurements and Characterizations

All ¹H and ¹³C NMR spectra were recorded using a Bruker AV500 spectrometer (500 MHz for ¹H, 125 MHz for ¹³C). All chemical shifts were reported in parts per million (ppm) with referenced to SiMe₄ (TMS) at 0.00 ppm. Obvious multiplicities and routine coupling constants are usually not listed, and all spectra were obtained in the solvent indicated at 25 °C unless otherwise noted. Molecular weights and the molecular weight distributions of the resultant polymers were measured by gel-permeation chromatography (GPC). GPC measurements were performed at 40 °C on a Shimadzu SCL-10A using a RID-10A detector (Shimadzu Co., Ltd.) in THF (containing 0.03 wt % of 2,6-*di-tert*-butyl-*p*-cresol, flow rate 1.0 mL/min). HPLC grade THF (Wako Pure Chemical Ind., Inc.) was used as the eluent with a flow rate of 1.0 mL/min and was degassed prior to use. GPC columns (ShimPAC GPC-806,

804 and 802, 30 cm × 8.0 mm diameter, spherical porous gel made of styrene/divinylbenzene copolymer, ranging from < 10^2 to 2×10^7 MW) were calibrated versus polystyrene standard samples. Differential scanning calorimetric (DSC) data for polymer were measured using a Hitachi DSC 7020 analyzer. Nitrogen was used as purge gas and all samples (approx. of 5-7 mg) were placed in standard aluminium pans. Polymer samples were first heated from 25 to 250 °C then cooled to -100 °C. The glass transition (T_g) and melting (T_m) temperature were determined upon second heating cycle. All runs were performed at a rate of 10 °C/min. Atmospheric pressure chemical ionization (APCI) mass spectrometry was performed on Bruker MicrOTOF II-SDT1.

4.2.3 Synthesis of 4-allyl-2-methoxyphenyl undec-10-enoate monomer (M1)

10-undecenoyl chloride (UDC, 3.04 g, 15 mmol) was added dropwise into a toluene solution (15.0 mL) containing eugenol (2.46 g, 15 mmol) and triethylamine (2.51 mL, 18 mmol) over 30 min at 0 °C. The mixture was then warmed to room temperature and was stirred for 4 h (Scheme 4.1). After the reaction was reached to completion, by confirmation of consumption of 10-undecenoyl chloride by TLC, the reaction mixture was then neutralized with 2N HCl, and was washed with 5% NaHCO₃ (15 mL x 3 times), deionized water (15 mL x 4 times), was then with brine (15 mL x 2 times). The solution was dried over anhydrous MgSO₄, and was then filtered through a Celite pad, and the filtrate was evaporated under reduced pressure. The crude product was purified by column chromatography using hexane/ethyl acetate (9/1) as an eluent to yield M1 as colorless oil (3.87 g, 78% yield). The overall synthesis procedure of monomer M1 is shown in Figure 4.1.



Scheme 4.1 Reaction scheme of synthesizing monomer M1.



Figure 4.1 Synthesis procedure of 4-allyl-2-methoxyphenyl undec-10-enoate monomer (M1).

4.2.4 Synthesis of 5-hexen-1-yl 10-undecenoate monomer (M2)

10-undecenoyl chloride (UDC, 3.04 g, 15 mmol) was added dropwise into a toluene solution (20.0 mL) containing 5-hexen-1-ol (5-Hex, 1.50 g, 15 mmol) and triethylamine (2.51 mL, 18 mmol) over 30 min at 0 °C. The mixture was then warmed to room temperature and was stirred for 2.5 h (Scheme 4.2). After the reaction was reached to completion, by confirmation of consumption of 10-undecenoyl chloride by TLC, the reaction mixture was then neutralized with 2N HCl, and was washed with 5% NaHCO₃ (15 mL x 3 times), deionized water (15 mL x 4 times), was then with brine (15 mL x 2 times). The solution was dried over anhydrous MgSO₄, and was then filtered through a Celite pad, and the filtrate was evaporated under reduced pressure. The crude product was purified by column chromatography using hexane/ethyl acetate (9/1) as an eluent to yield M2 as a colorless oil (3.24 g, 81% yield). The overall synthesis procedure of monomer M2 is shown in Figure 4.2.



Scheme 4.2 Reaction scheme of synthesizing monomer M2.



Figure 4.2 Synthesis procedure of 5-hexen-1-yl 10-undecenoate monomer (M2).

4.2.5 Synthesis of 10-undecen-1-yl 10-undecenoate monomer (M3)

10-undecenoyl chloride (3.04 g, 15 mmol) was added dropwise into a toluene solution (20.0 mL) containing 10-undecen-1-ol (UDO, 2.55 g, 15 mmol) and triethylamine (2.51 mL, 18 mmol) over 30 min at 0 °C. The mixture was then warmed to room temperature and was stirred for 2.5 h (Scheme 4.3). After the reaction was reached to completion, by confirmation of consumption of 10-undecenoyl chloride by TLC, the reaction mixture was then neutralized with 2N HCl, and was washed with 5% NaHCO₃ (15 mL x 3 times), deionized water (15 mL x 4 times), was then with brine (15 mL x 2 times). The solution was dried over anhydrous MgSO₄, and was then filtered through a Celite pad, and the filtrate was evaporated under reduced pressure. The crude product was purified by column chromatography using hexane/ethyl acetate (9/1) as an eluent to yield M3 as a colorless oil (4.26 g, 85% yield). The overall synthesis procedure of monomer M3 is shown in Figure 4.3.



Scheme 4.3 Reaction scheme of synthesizing monomer M3.



Figure 4.3 Synthesis procedure of 10-undecen-1-yl 10-undecenoate monomer (M3).

4.2.6 Synthesis of 5-formylbenzene-1,2,3-triyl tris(undec-10-enoate) crosslinker (CL)

10-undecenoyl chloride (UDC, 1.98 g, 9.8 mmol) was added dropwise into a THF solution (15.0 mL) containing 3,4,5-trihydroxybenzaldehyde (THBD, 508 mg, 3.3 mmol) and triethylamine (2.1 mL, 14.6 mmol) over 20 min at -30 °C. The mixture was then warmed to room temperature and was stirred for 14 h (Scheme 4.4). After the reaction was completed, the reaction mixture was passed through a Celite pad (two times), and the filtrate was evaporated under reduced pressure to yield CL as a yellow oil (2.0 g, 94% yield). The overall synthesis procedure of monomer CL is shown in Figure 4.4.



Scheme 4.4 Reaction scheme of synthesizing crosslinker (CL).



Figure 4.4 Synthesis procedure of 5-formylbenzene-1,2,3-triyl tris(undec-10-enoate) crosslinker (CL).

4.2.7 General procedure for synthesis of polymers by acyclic diene metathesis (ADMET) polymerization using ruthenium catalysts

A typical procedure for synthesis of polymer (P1) by ADMET polymerization (Table 4.1, run 8, page 83) is as follows. The monomer (M1, 330 mg, 1.0 mmol) was loaded into a 25 mL sealed Schlenk-type tube. The second-generation Grubbs catalyst G2, RuCl₂(PCy₃)(H₂IMes)(CHPh)) (0.0127 g, 1.5 mol%) was dissolved in 0.4 mL of dichloromethane and transferred into a sealed Schlenk-type tube. The reaction mixture was magnetically stirred in an oil bath set at 50 °C under nitrogen atmosphere for 30 min. The mixture was then placed into a liquid nitrogen bath to remove ethylene gas from the reaction medium by opening the valve connected to the vacuum line for a short period time (approx. 1 min), and then closed the valve and placed into the oil bath to continue the reaction. The procedure removing ethylene was repeated with a certain period (30 min for the first time then every 1.0 h). The polymerization mixture was then cooled to room temperature and was guenched with excess ethyl vinyl ether while stirring for 1.0 h. The resultant solution was then dissolved in chloroform (2.0 mL) for dilution, and the solution was added dropwise into the cold methanol (50 mL). The solution was stirred for 1.0 h, and the precipitates were then collected by filtration and dried *in vacuo* to yield P1 as rubbery solids (0.299 g, 91% yield). A similar polymerization protocol was used for polymerization of M2 (266 mg, 1.0 mmol) and M3 (336 mg, 1.0 mmol) to yield polymers P2 and P3, respectively. The ¹H NMR and ¹³C NMR spectra of obtained polymers with detailed peak assignments are shown in the Appendix B.²⁴

4.3 Results and Discussion

4.3.1 Structure characterization of monomers and crosslinker

In this research, 10-undecenoyl chloride (a derivative commercially available from undecenoic acid that can be obtained as a major component from castor oil)¹⁴ has been chosen to prepare α, ω -diene monomer with eugenol (UG, obtained from clove oil). 5-Hexen-1-ol and 10-undecen-1-ol¹⁹ instead of UG were also chosen for comparison. These monomers (expressed as M1-M3 in Scheme 4.5) were prepared in toluene in the presence of triethylamine according to the reported procedure.³⁷ The resultant compounds were purified by column chromatography and were identified by ¹H NMR and ¹³C NMR spectra and APCI mass spectrometry (shown in the Appendix B).³⁸



Scheme 4.5 Reaction scheme of synthesizing monomers (M1-M3).

 1 H NMR spectrum (in CDCl₃ at 25 °C) of the monomer, 4-allyl-2methoxyphenyl 10-undecenoate (M1, Figure 4.5), shows characteristic resonances at 4.92–5.02 and 5.92–6.0 ppm, and 5.08–5.13 and 5.78–5.86 ppm ascribed to olefinic protons in terminal position. ¹³C NMR spectrum of the monomer M1 shows characteristic resonances at 114.3 and 116.2 ppm, 139.3 and 137.2 ppm corresponded to the olefinic carbons in terminal position as shown in Figure 4.6. The formation of M1 was further identified by ACPI mass spectroscopy, which revealed a molecular ion [M+H]⁺ peak at 331.0 (Figure B4.1, Appendix B).³⁸ All results demonstrate that the target monomer (M1) was successfully synthesized.

Similarly, reaction of 3,4,5-trihydroxybenzaldehyde with 10undecenoyl chloride in THF in the presence of excess triethylamine afforded the corresponding ester, 5-formylbenzene-1,2,3-triyl tris(undec-10-enoate) (CL), employed as the cross-linker in this study. CL was also identified by ¹H NMR and ¹³C NMR spectra and APCI mass spectrometry. Figure 4.7 shows ¹H NMR spectrum (in CDCl₃ at 25 °C) for 5-formylbenzene-1,2,3-triyl tris(undec-10-enoate) (CL). Characteristic resonances at 5.01 and 5.8 ppm ascribed to olefinic protons in terminal position belong to 10-undecenoyl chloride. Resonances at 9.92 and 7.64 ppm were attributed to aldehyde and aromatic protons, respectively, belong to the 3,4,5 trihydroxybenzaldehyde. All other peaks are match well with the protons of the CL. ¹³C NMR spectrum of the CL is shown in Figure 4.8. Resonances ascribed to the carbons in terminal position belong to 10undecenoyl chloride are also observed at 114.3 and 139.2 ppm, while the resonance ascribed to carbon of aldehyde in 3,4,5 trihydroxybenzaldehyde was observed at 189.4 ppm. The formation of CL was further confirmed by ACPI mass spectroscopy, which revealed a molecular ion $[M+H]^+$ peak at 652.4 (Figure B4.2, Appendix B).³⁸ All the results thus clearly indicate the successful synthesis of triarm crosslinker (CL).

¹H NMR (CDCl₃): δ 1.33 (s, 10H, 5CH₂) 1.75-1.79 (quint, *J*=7.5 Hz, 2H, CH₂), 2.03-2.07 (quart, *J*=7.5 Hz, 2H, CH₂CH=CH₂), 2.55-2.58 (t, *J*=7.5 Hz, 2H, -CH₂COO-), 3.37-3.38 (d, *J*=6.8 Hz, 2H, Ar-CH₂), 3.81 (s, 3H, OCH₃), 4.92-5.02 (m, 2H, Ar-CH₂CH=CH₂), 5.08-5.13 (2H, -CH=CH₂), 5.78-5.86 (m, *J*=6.68, 6.68 and 6.77 Hz, 1H, -CH=CH₂), 5.92-6.0 (m, *J*=6.75, 6.75 and 6.79 Hz, 1H, Ar-CH₂CH=CH₂), 6.75-6.79 (m, 1HAr, CH), 6.93-6.94 ppm (m, 2HAr, 2CH).



Figure 4.5 ¹H NMR spectra (in CDCl₃ at 25 °C) of 4-allyl-2-methoxyphenyl 10undecenoate (M1) with its peak assignments.

¹³C NMR (CDCl₃): δ 25.1 (s, CH₂), 29.0 (s, CH₂), 29.1 (s, CH₂), 29.3 (s, CH₂), 29.4 (s, CH₂), 33.9 (s, CH₂COO-), 34.1 (s, CH₂), 40.2 (s, Ar-CH₂), 55.9 (s, OCH₃), 112.8 (s, CH), 114.3 (s, CH=CH₂), 116.2 (s, Ar-CH₂CH=CH₂), 120.7 (s, CH), 122.6 (s, CH), 137.2 (s, Ar-CH₂CH=CH₂), 138.2 (s, C), 138.9 (s, C), 139.3 (s, CH=CH₂), 151.0 (s, C), 172.1 ppm (s, - COO-). APCI-MS: calculated for C₂₁H₃₀O₃ [M + H]⁺ 331.2; found 331.2.



Figure 4.6 13 C NMR spectra (in CDCl₃ at 25 °C) of 4-allyl-2-methoxyphenyl 10undecenoate (M1) with its peak assignments.

¹H NMR (500 MHz, CDCl₃, ppm): **\delta** 1.32-1.40 (s, 30H, 15CH₂) 1.70-1.76 (quint, *J*=7.5 Hz, 6H, 3CH₂), 2.02-2.06 (quart, *J*=7.0 Hz, 6H, 3CH₂CH=CH₂), 2.53-2.56 (t, *J*=7.5 Hz, 6H, 3CH₂COO-), 4.92-5.01 (m, *J*=10.2 and 17.1 Hz, 6H, 3CH=CH₂), 5.77-5.85 (m, *J*=16.7, 16.8 and 17.0 Hz, 3H, 3CH=CH₂), 7.64 (s, 2HAr, 2CH), 9.92 ppm (s, 1H, -COH).



Figure 4.7 ¹H NMR spectra (in CDCl₃ at 25 °C) of 5-formylbenzene-1,2,3-triyl tris(undec-10-enoate) (CL) with its peak assignments.

¹³C NMR (125 MHz, CDCl₃, ppm): δ 24.9 (s, CH₂), 29.0 (s, CH₂), 29.1 (s, CH₂), 29.2 (s, CH₂), 29.3 (s, CH₂), 29.4 (s, CH₂), 33.8 (s, CH₂), 114.3 (s, CH=CH₂), 121.7 (s, CH), 134.0 (s, C), 139.2 (s, CH=CH₂), 139.9 (s, C), 144.5 (s, C), 170.5 (s, -COO-), 189.5 ppm (s, -COH). APCI-MS: calculated for C₄₀H₆₀O₇ [M + H]⁺ 652.43; found 652.4.



Figure 4.8 ¹³C NMR spectra (in CDCl₃ at 25 °C) of 5-formylbenzene-1,2,3-triyl tris(undec-10-enoate) (CL) with its peak assignments.

The reaction of 10-undecenoyl chloride with 5-Hexen-1-ol and 10-undecen-1-ol instead of UG were also chosen for comparison. The ¹H NMR spectrum of monomer M2 in Figure 4.9 shows the characteristic resonances of olefinic protons around 5.0 ppm (external olefin) and 5.7 ppm (internal olefin). The purity of M2 was also verified by ¹³C NMR spectrum. Characteristic resonance ascribed to the terminal carbons (-CH=CH₂) are also observed around 114 and 139 ppm as shown in Figure 4.10. Similarly, the ¹H NMR spectrum of M3 shows the characteristic resonances of olefinic protons around 4.9 and 5.7 ppm; corresponding resonances ascribed to the carbons are also observed at 114 and 139 ppm as shown in Figure 4.11 and 4.12. The ACPI mass spectroscopy of M2 and M3 show the molecular ion [M+H]⁺ peak at 266.2 and 336.3, respectively (Figure B4.3-4.4, Appendix B).³⁸ These results indicate that the monomers M2 and M3 were successfully synthesized.

¹H NMR (500 MHz, CDCl₃, ppm): **\delta** 1.28-1.36 (s, 10H, 5CH₂), 1.44 (m, 2H, CH₂), 1.61-1.64 (m, 4H, 2CH₂), 2.02-2.08 (m, *J*=15.2 and 16.9 Hz, 4H, 2CH₂CH=CH₂), 2.26-2.29 (t, *J*=7.4 Hz, 2H, -CH₂COO-), 4.06 (t, *J*=6.5 Hz, 2H, -COOCH₂-), 4.91-5.02 (m, *J*=8.8 and 14.0 Hz, 4H, 2CH₂=CH-), 5.77-5.80 ppm (m, *J*=1.4 and 11.6 Hz, 2H, 2CH₂=CH-).



Figure 4.9 ¹H NMR spectra (in CDCl₃ at 25 °C) of 5-hexen-1-yl 10-undecenoate (M2) with its peak assignments.

¹³C NMR (125 MHz, CDCl₃, ppm): **δ** 25.1 (s, CH₂), 25.3 (s, CH₂), 28.2 (s, CH₂), 29.0 (s, CH₂), 29.2 (s, CH₂), 29.3 (s, CH₂), 29.4 (s, CH₂), 33.4 (s, CH₂), 33.9 (s, CH₂), 34.5 (s, CH₂), 64.2 (s, -COOCH₂-), 114.3 (s, CH=CH₂), 139.3 (s, CH=CH₂), 174.1 ppm (s, -COO-).



APCI-MS: calculated for $C_{17}H_{30}O_2$ [M + H]⁺ 267.2; found 267.2.

Figure 4.10 ¹³C NMR spectra (in CDCl₃ at 25 °C) of 5-hexen-1-yl 10-undecenoate monomer (M2) with its peak assignments.

¹H NMR (500 MHz, $CDCl_{3}$, ppm): **\delta** 1.27-1.36 (s, 22H, 11CH₂), 1.60 (s, 4H, 2CH₂), 2.02-2.03 (d, *J*=6.4 Hz, 4H, 2CH₂CH=CH₂), 2.26-2.29 (t, *J*=7.4 Hz, 2H, -CH₂COO-), 4.03-4.05 (t, J=6.6 Hz, 2H, -COOCH₂-), 4.90-4.99 (m, *J*=9.3 and 17.1 Hz, 4H, 2CH₂=CH-), 5.76-5.81 ppm (d, *J*=6.8 Hz, 2H, 2CH₂=CH-).



Figure 4.11 ¹H NMR spectra (in $CDCl_3$ at 25 °C) of 10-undecen-1-yl 10undecenoate (M3) with its peak assignments.

¹³C NMR (125 MHz, CDCl₃, ppm): **δ** 26.0 (s, CH₂), 28.8 (s, CH₂), 29.0 (s, CH₂), 29.1 (s, CH₂), 29.2 (s, CH₂), 29.3 (s, CH₂), 29.4 (s, CH₂), 29.5 (s, CH₂), 29.6 (s, CH₂), 33.9 (s, CH₂), 34.5 (s, CH₂), 64.5 (s, -COOCH₂-), 114.2 (s, CH=CH₂), 139.2 (s, CH=CH₂), 174.0 ppm (s, -COO-).¹¹ APCI-MS: calculated for C₂₂H₄₀O₂ [M + H]⁺ 337.3; found 337.3.



Figure 4.12 ¹³C NMR spectra (in CDCl₃ at 25 °C) of 10-undecen-1-yl 10undecenoate (M3) with its peak assignments.

4.3.2 ADMET polymerization of monomer M1

Acyclic diene metathesis (ADMET) polymerizations of M1 were conducted in CH_2Cl_2 using a sealed Schlenk tube equipped with a high-vacuum valve in the presence of ruthenium catalyst (Scheme 4.6). The reactions were conducted in an oil bath heated at 50 °C under nitrogen atmosphere initially for a certain period (30 min), and the mixture was then placed *in vacuo* to remove ethylene formed in this condensation polymerization (experimental details are described in the Experimental Section),^{39,40} as conducted in synthesis of all-*trans* poly(9,9-n-alkyl fluorene-2,7vinylene)s by the ADMET polymerization.^{41,42} The ruthenium catalysts were chosen to achieve polymerization as they tend to display more functional group tolerance than Mo-based metathesis catalysts. Dichloromethane (CH_2Cl_2), previously reported as a preferred solvent to achieve high polymerization degrees in ADMET,⁴³ was used as solvent for ADMET polymerizations. The ADMET polymerization were carried out at mild temperature (50 °C) in order to increase the lifetime of the active catalyst as well as decreases the amount of double bond migration and isomerization by **G2**.⁴⁴ The results for ADMET polymerization of M1 are summarized in Table 4.1.



Scheme 4.6 Acyclic Diene Metathesis (ADMET) polymerization of M1 in the presence of Ru-carbene catalysts.

As shown in Table 4.1 that the ADMET polymerization of M1 using called second-generation Grubbs catalyst (**G2**) afforded polymers with unimodal molecular weight distributions ($M_n = 7100, 8100; M_w/M_n = 1.74, 2.05$, respectively, runs 1,2). Efficient removal of ethylene formed in this condensation polymerization seems beneficial for obtainment of high molecular weight polymers, because the M_n value seemed decreasing with increasing the initial reaction time under nitrogen [$M_n, M_w/M_n = 7100, 1.87$ (1.0 h under N₂ instead of 30 min); $M_n, M_w/M_n = 6900, 1.96$ (4.0 h under N₂)] or the M_n value increased when ethylene was removed repeatedly after the initial reaction under nitrogen atmosphere [$M_w/M_n = 8100, 2.05, run 2$]. These results clearly demonstrated that the removal of by-product (ethylene), which is released during the metathesis reaction, from the reaction mixture at the first stage to shift the reaction equilibrium are very important factors for obtaining the high molecular weight polymers.

To further increase the molecular weight of the obtained polyesters, screening of polymerization parameters (catalyst loading, type of catalysts and reaction time) were investigated to identify the best conditions. The Grubbs second-generation catalyst (G2), with loading varying from 0.2 to 3.0 mol%, was employed to study effect of catalyst loading on the molecular weight of polyester. It was also revealed that the $M_{\rm p}$ value was also affected by the amount of ruthenium catalyst loaded (G2, runs 3-5, 8, 12, 13, Figure 4.9a), and the polymerization in the presence of low Ru loading (0.2 mol%) afforded low molecular weight oligomer with broad molecular weight distributions (PDI) $(M_n=3200, M_w/M_n= 3.63, run 3, Figure 4.13a)$. Moreover, the M_n value in the resultant polymer increased by increasing the Ru loading $[M_n = 7500 (0.5 \text{ mol}\%)]$ run 4) vs M_n = 12700 (1.5 mol%, run 8)], and the GPC traces became unimodal upon increasing the Ru loading as clearly demonstrated in Figure 4.13a. It thus turned out that the optimized conditions concerning the amount of Ru are 1.5 or 2.0 mol% (based on M1, runs 8 and 12) for obtainment of high molecular weight polymers with unimodal molecular weight distributions.

Run	Ru cat. (mol %) ^b	Time / h	<i>M</i> n ^c / g/mol	$M_{\rm w}/M_{\rm n}^{\rm c}$	yield ^d / %
1	G2 (1.0)	12	7100	1.74	86
2 ^e	G2 (1.0)	12	8100	2.05	88
3	G2 (0.2)	12	3200	3.63	55
4	G2 (0.5)	12	7500	2.09	79
5	G2 (1.0)	12	8100	2.05	88
6	G2 (1.5)	3	9400	1.97	87
7	G2 (1.5)	6	10300	1.95	87
8	G2 (1.5)	12	12700	1.85	91
9	G2 (1.5)	18	12400	1.64	87
10	G1 (1.5)	12	5500	1.87	81
11	HG2 (1.5)	12	4500	1.63	79
12	G2 (2.0)	12	12500	1.84	91
13	G2 (3.0)	12	7900	1.93	81

Table 4.1 ADMET polymerization of 4-allyl-2-methoxyphenyl 10-undecenoate(M1) by Ru catalysts.^a

^aConditions: Ru catalyst (shown in Scheme 4.6), monomer M1 (330 mg, 1.0 mmol), CH₂Cl₂ 0.4 mL (initial monomer concentration 2.50 M), 50 °C. The sealed reaction tube was placed *in vacuo* after 30 min. ^bMol % based on monomer M1. ^cGPC data in THF vs polystyrene standards. ^dIsolated yield by precipitation as the methanol insoluble fraction. ^eThe tube was placed in *vacuo* twice at the first time (30 min).

The M_n value was also affected by the reaction time (runs 6-9), and no significant increase in the M_n value was observed after 12 h (runs 8, 9). It also turned out, under the above optimized conditions (run 8), that the other ruthenium catalysts (expressed as **G1**, and **HG2** in Scheme 4.6) afforded polymers with rather low molecular weights (runs 10, 11, respectively, Figure 4.13b). This would be probably because of low reactivity of **G1** toward olefins in this ADMET polymerization.⁴⁵⁻⁴⁷ It also seems likely that rather low catalyst efficiency by **HG2** compared to **G2** might be considered for the explanation under these conditions. Therefore, **G2** seems to be the most suitable in terms of synthesis of high molecular weight polymers with unimodal molecular weight distributions.



Figure 4.13 GPC traces of polymers (P1) in ADMET polymerization of M1 under (a) effect of different **G2** loading, and (b) effect of Ru catalysts. Detailed data are shown in Table 4.1.

In addition to GPC, NMR spectrometry were also performed not only to confirm the polymers structures but also to reveal potential undesired side reactions such as ring-closing metathesis (RCM) or olefin isomerization. Figure 4.14 shows ¹H NMR spectrum (in CDCl₃ at 25 °C) for 4-allyl-2-methoxyphenyl 10undecenoate (M1, Figure 4.14a) and the resultant polymer (P1, Figure 4.14b) prepared by ADMET polymerization (sample run 8). Resonances ascribed to protons of terminal olefins (at 4.92–5.02 and 5.92–6.0 ppm, and 5.08–5.13 and 5.78–5.86 ppm) disappeared and resonances ascribed to protons assigned to internal olefins (at 5.35–5.67 and 6.15– 6.45 ppm, placed as dashed circle in Figure 4.14b) were observed, whereas the other resonances were remained. It was also observed that the formation of cyclic oligomers is unlikely to occur during the ADMET polymerization of M1, as monomers with chain lengths exceed ten atoms are disfavored to undergo this type of side reactions.¹⁶ The results thus clearly indicate formation of polymers by the ADMET polymerization.^{39,40,45-} ⁴⁷ As also suggested by the NMR spectra (broad and several resonances ascribed to olefinic protons), the resultant polymers do not have regular structures in almost certainly but are probably a mixture of head-to-head, head-to-tail, and tail-to-tail arrangement of the repeat unit containing *cis* and *trans* double bonds. This can also be suggested by ¹³C NMR spectrum in P1 (resonances ascribed to internal olefinic carbons at 128-141 ppm as shown in Figure 4.15). The fact might also explain additional resonances in the aliphatic region (marked with *) compared to M1 in Figure 4.14b.

P1 (sample run 8). ¹H NMR (CDCl₃): **δ** 1.33, 1.75-1.79, 2.03-2.07, 2.55-2.58, 3.37-3.38, 3.81, 5.39-5.67, 6.15-6.44, 6.75-6.79, 6.93-6.94. ¹³C NMR (CDCl₃): **δ** 25.1, 26.8, 29.0, 29.1, 29.3, 29.4, 32.6, 33.9, 34.1, 39.1, 55.9, 112.8, 120.7, 122.6, 128.6, 132.5, 138.2, 138.9, 151.0, 172.1.



Figure 4.14 ¹H NMR spectra (in $CDCl_3$ at 25 °C) for (a) 4-allyl-2-methoxyphenyl 10undecenoate (M1), and (b) the resultant polymer (P1) prepared by the ADMET polymerization (run 8).



Figure 4.15 ¹³C NMR spectra (in CDCl₃ at 25 °C) for (a) 4-allyl-2-methoxyphenyl 10undecenoate (M1), and (b) the resultant polymer (P1) prepared by the ADMET polymerization (run 8).

4.3.3 ADMET polymerization of monomers M2 and M3

The ADMET polymerization of monomers M2 and M3¹⁹ were also conducted in the presence of Ru-carbene catalyst (**G2**, Scheme 4.7). under the same conditions with M1. The ADMET polymerization of M2 yielded polymer P2 as white solid, whereas the polymerization of M3 produce polymer P3 as rubbery. The results for ADMET polymerization of M2 and M3 are summarized in Table 4.2. It was revealed that the polymerizations of M2 afforded polymers with unimodal molecular weight distributions (ex. $M_n = 8300 M_w/M_n = 1.52$, run 14) under optimized conditions. As observed in the ADMET polymerization of M1, in the polymerization of M2, the M_n value was affected by the amount of ruthenium catalyst charged, and the M_n value in the resultant polymer (P2) increased by increasing the Ru loading [$M_n = 8300$ (2.0 mol%, run 14) vs $M_n =$ 7300 (0.5 mol%, run 16)]. In contrast, in the polymerization of M3,¹⁹ the optimized conditions seem 0.5 mol% (run 19) for obtainment of high molecular weight polymer (P3) with unimodal molecular weight distribution. It thus turned out that the utilization of different α , ω -Dienes monomers (M1-M3) in ADMET polymerization could archive a variety of polyesters with different structure and molecular weight as well as morphology.

Run	Monomer	G2 / mol% ^b	<i>M</i> n ^c / g/mol	$M_{\rm w}/M_{\rm n}^{\rm c}$	yield ^d / %
14	M2	2.0	8300	1.52	71
15	M2	1.0	7700	1.49	71
16	M2	0.5	7300	1.44	72
17	M3	2.0	6200	1.50	78
18	M3	1.0	6900	1.53	78
19	M3	0.5	8500	1.64	84
20	M3	0.2	7200	1.55	83

Table 4.2 ADMET polymerization of M2 and M3 by G2 catalyst.^a

^aConditions: Monomer M2 (266 mg, 1.0 mmol) or M3 (336 mg, 1.0 mmol), $CH_2Cl_2 0.4$ mL (initial monomer concentration 2.5 M), 50 °C, 12 h. The sealed reaction tube was placed *in vacuo* after 30 min. ^bMol % based on monomer. ^cGPC data in THF vs polystyrene standards. ^dIsolated yield by precipitation as the methanol insoluble fraction.



Scheme 4.7 Acyclic Diene Metathesis (ADMET) polymerization of M2 and M3 in the presence of Ru-carbene catalyst (**G2**).

Both ¹H and ¹³C NMR spectra clearly support formation of polymers by the ADMET polymerization. The resonances ascribed to protons of terminal olefins at 5.0 and 5.8 ppm disappeared and resonances assigned to protons internal olefins around 5.4 ppm as shown in Figure 4.16 and 4.17; corresponding resonances ascribed to the carbons are also observed around 130 ppm (Figure B4.5 and B4.6, Appendix B). The results thus clearly indicate formation of polymers P2 and P3 by the ADMET polymerization.

P2 (sample run 14). ¹H NMR (CDCl₃): δ 1.27-1.28, 1.38-1.41, 1.60-1.63, 1.95-2.04, 2.26-2.29, 4.06, 5.33-5.42. ¹³C NMR (CDCl₃): δ 25.2, 25.9, 28.3, 29.2, 29.3, 29.4, 29.5, 32.3, 32.7, 32.8, 34.5, 64.3, 130.4, 174.1.

P3 (sample run 19). ¹H NMR (CDCl₃): δ 1.29, 1.61, 1.96, 2.28, 4.05, 5.38.
¹³C NMR (CDCl₃): δ 25.2, 26.0, 28.3, 29.3, 29.4, 29.5, 29.6, 29.7, 29.8, 29.9, 32.7, 34.5, 64.5, 130.5, 174.1.



Figure 4.16 ¹H NMR spectra (in CDCl₃ at 25 °C) for (a) 5-hexen-1-yl 10-undecenoate (M2), and (b) the resultant polymer (P2) prepared by the ADMET polymerization (run 14).



Figure 4.17 ¹H NMR spectra (in $CDCl_3$ at 25 °C) for (a) 10-undecen-1-yl 10-undecenoate (M3), and (b) the resultant polymer (P3) prepared by the ADMET polymerization (run 19).

4.3.4 Effect of crosslinker on ADMET polymerization of M1

In order to demonstrate a possibility of synthesis of cross-linked polymers (often employed to improve mechanical properties etc.), ADMET polymerizations of 4-allyl-2-methoxyphenyl 10-undecenoate (M1) were conducted in the presence of cross-linker, CL (2.5–5.0 mol%) with reaction time in the range 12–24h, prepared by reaction of 3,4,5-trihydroxybenzaldehyde with 10-undecenoyl chloride in this study (Scheme 4.8). The results are summarized in Table 4.3.



Scheme 4.8 Acyclic Diene Metathesis (ADMET) polymerization of 4-allyl-2methoxyphenyl 10-undecenoate (M1) in the presence of 5-formylbenzene-1,2,3triyl tris(undec-10-enoate) (CL). It was revealed that M_n value in the resultant polymer (P1) slightly increased in the presence of CL [M_n = 12700 (run 8) vs 13300 (run 21), reaction 12 h, CL 2.5 mol%], and further stirring afforded polymer with low PDI (M_w/M_n) value (run 22, reaction 18 h). Increasing the amount of CL (from 2.5 to 5.0 mol%) afforded the polymers with rather broad molecular weight distributions even after 18 h (runs 23, 24), and no significant increase in the M_n values were observed (runs 21-24). However, as shown in Figure 4.18, GPC traces in the resultant polymers, it seems that the molecular weight distributions became unimodal after 18 h; the PDI value became low upon increasing the Ru loading (run 25). It turned out that increase of Ru loading (run 25), addition of CL after the initial ADMET polymerization did not affect the increase of M_n value in the resultant polymers.

Run	CL / mol% ^b	Time / h	<i>M</i> n ^c / g/mol	$M_{\rm w}/M_{\rm n}^{\rm c}$	yield ^d /%
8	1	12	12700	1.85	91
21	2.5	12	13300	2.58	88
22	2.5	18	13600	2.28	89
23	5.0	12	11500	3.95	88
24	5.0	18	13500	3.48	88
25 ^e	5.0	18	13800	2.80	90
26 ^f	5.0	18	10200	2.05	81
27 ^f	5.0	24	11800	2.59	86

Table 4.3 ADMET polymerization of M1 using G2 in the presence of cross-linker (CL).^a

^aConditions: Monomer M1 (330 mg, 1.0 mmol), Ru catalyst (**G2**) 1.5 mol%, cross-linker (CL), CH₂Cl₂ 0.4 mL (initial monomer concentration 2.50 M), 50 °C. The sealed reaction tube was placed in *vacuo* after 30 min. ^bMol % based on monomer M1. ^cGPC data in THF vs polystyrene standards. dIsolated yield by precipitation as the methanol insoluble fraction. ^eRu 2.0 mol%. ^fCross-linker (CL, 5.0 mol%) was added after 30 min.



Figure 4.18 GPC traces of polymers (PL1) in ADMET polymerization of M1 with CL under effect of CL loading and polymerization time.

PL1 (sample run 24). ¹H NMR (CDCl₃): δ 1.32, 1.75, 1.97-2.03, 2.56, 3.31-3.35, 3.80, 5.36-5.68, 6.18-6.44, 6.77, 6.92, 7.64, 9.92. ¹³C NMR (CDCl₃): δ 25.2, 26.8, 29.0, 29.1, 29.3, 29.4, 32.6, 33.9, 34.1, 39.1, 55.9, 112.8, 120.7, 122.6, 128.6, 132.5, 138.2, 138.9, 144.5, 151.2, 170.5, 172.2, 189.5.





Figure 4.19 shows ¹H NMR spectra (in CDCl₃ at 25 °C) of P1 (sample run 8) and PL1 (sample run 24). As observed in P1 (Figure 4.15b), protons assigned to terminal olefins in M1 and CL were disappeared, and resonances ascribed to protons

86
in the internal olefins were observed (placed as dashed circle in Figures 4.15b and c). Moreover, resonances ascribed to CL (in particular protons corresponding to aldehyde and aromatic proton marked as * in Figure 4.19a and c) were clearly observed. The results clearly demonstrate that it is possible to obtain high molecular weight aromaticaliphatic polyesters from ADMET polymerization of α, ω -diene monomers derived from renewable eugenol and castor oil derivative. Therefore, the polymers discussed within this contribution are not only renewable but also do not interfere with food or feed supply as clove oil and castor oil are non-edible plant oils.

4.3.5 Thermal properties of the polymers

The glass transition temperature (T_g) and other thermal behaviors of the resultant polyesters were studied by DSC at a 10 °C/min heating and cooling rate. The second heating DSC curves of the resultant polyesters are shown in Figure 4.20. As observed from DSC thermogram curves (sample run 8) as shown in Figure 4.20a, the resultant polymer (P1) possesses glass transition temperature (T_g) at -9.6 °C and no melting. While DSC thermograms in the resultant polymer (PL1) show a glass transition temperature (T_g) at -10.5 °C, which is relatively close to that in P1 ($T_g = -9.6$ °C).



Figure 4.20 DSC thermograms for (a) polymers P1 (sample run 8), PL1 (sample run 24), and (b) polymers P2 (sample run 14), P3 (sample run 19), second heating cycle at a heating/cooling rate of 10 °C/min.

These results thus probably suggest that PL1 possesses a certain network structure consisting of P1 and CL (with low degree of cross-linking) with uniform composition. The resultant polymer sample (PL1) was hardly soluble in CDCl₃ (30 mg/2.0 mL) at room temperature but became completely soluble overnight (stirred for 24 h), whereas the sample is easily soluble in THF for GPC measurement.

In contrast, DSC thermograms in the resultant polymers (P2, P3) show a melting temperature (T_m) at 14.3 °C (P2, sample run 14), 51.5 °C (P3, sample run 19), respectively, as observed in long-chain aliphatic polyesters (Figure 4.16b). $^{18,19,48\text{-}51}$ In general, the melting temperature (T_m value) in the polyester increases with increasing hydrocarbon chain length, 5^{2} and the T_{m} value in the polyester consisting of two types of methylene units also affected the distribution.⁵³This can be justified by considering that the ester groups present along the chain act as defects influencing the crystallization of the polymers. As the distance between two ester groups lengthens, the number of defects decreases, more perfect crystals can be formed, resulting in an increasing melting temperature. Therefore, increase in the T_m value from P2 to P3 would be due to increase of methylene chain length. However, observed T_m values might be rather low probably due to that microstructure in the resultant polymers are a mixture of head-to-tail, head-to-head and tail-to-tail repeat units. In contrast, placing phenyl group into the polymer main chain in P1 afforded the amorphous materials. The different in thermal properties of these resultant polymers is likely due to the different in the morphology structure of the polymers. The polymer P2 and P3 (aliphatic polyesters) are more symmetric structure as compared to structure of P1 which contains an aromatic group in the repeating unit. The existence of methoxy group (-OCH₃) adjacent to benzyl ring in M1 impede the structural symmetry resulting in the structural defection. In addition, the random configuration of polymer P1 was also unfavorable for regular crystal chains packing according to their steric hindrance.

4.4 Conclusions

In this study, we have shown that synthesis of new polyesters by ADMET polymerization of α, ω -dienes, 4-allyl-2-methoxyphenyl 10-undecenoate (M1),

prepared from bio-renewable eugenol (obtained from clove oil) and 10-undecenoic acid derivative (obtained from castor oil). Ruthenium-carbene (called secondgeneration Grubbs) catalyst afforded polymers with unimodal molecular weight distributions ($M_n = 12700$, $M_w/M_n = 1.85$). The polymerization of M1 in the presence of triarm cross-linker, 5-formylbenzene-1,2,3-triyl tris(undec-10-enoate), also afforded certain network polymers, suggested by NMR spectra and DSC thermogram. Since 9decenoate obtained from the other vegetable oil (e.g. methyl oleate) by ethenolysis, should be used in place of 10-undecenoate, also since, as described in the introductory, further chemical modification can be possible from functional group (methoxy group) in the resultant polymers (P1, PL1), we thus believe that the present approach is promising and should be applicable for synthesis of polyesters from monomers prepared from bio-renewable resources.

4.5 References

- 1. Lillie, L. M.; Tolman, W. B.; Reineke, T. M. Structure/property relationships in copolymers comprising renewable isosorbide, glucarodilactone, and 2,5-bis(hydroxymethyl)furan subunits. *Polym. Chem.* 2017, 8, 3746-3754.
- 2. Nasiri, M.; Reineke, T. M. Sustainable glucose-based block copolymers exhibit elastomeric and adhesive behavior. *Polym. Chem.* 2016, 7, 5233-5240.
- 3. Gallagher, J. J.; Hillmyer, M. A.; Reineke, T. M. Isosorbide-based Polymethacrylates. *ACS Sustain. Chem. Eng.* 2015, 3, 662-667.
- 4. Hillmyer, M. A.; Tolman, W. B. Aliphatic Polyester Block Polymers: Renewable, Degradable, and Sustainable. *Acc. Chem. Res.* 2014, 47 (8), 2390-2396.
- Coulembier, O.; Degée, P.; Hedrick, J. L.; Dubois, P. From controlled ring-opening polymerization to biodegradable aliphatic polyester: Especially poly(β-malic acid) derivatives. *Prog. Polym. Sci.* 2006, 31, 723-747.
- 6. Mülhaupt, R. Green Polymer Chemistry and Bio-based Plastics: Dreams and Reality. *Macromol. Chem. Phys.* 2013, 214, 159-174.
- 7. Meier, M. A. R.; Metzger, J. O.; Schubert, U. S. Plant oil renewable resources as green alternatives in polymer science. *Chem. Soc. Rev.* 2007, 36, 1788-1802.

- Biermann, U.; Bornscheuer, U.; Meier, M. A. R.; Metzger, J. O.; Schäfer, H. J. Oils and Fats as Renewable Raw Materials in Chemistry. *Angew. Chem. Int. Ed.* 2011, 50, 3854-3871.
- Zakzeski, J.; Bruijnincx, P. C. A.; Jongerius, A. L.; Weckhuysen, B. M. The Catalytic Valorization of Lignin for the Production of Renewable Chemicals. *Chem. Rev.* 2010, 110, 3552-3599.
- 10. Kobayashi, H.; Fukuoka, A. Synthesis and utilisation of sugar compounds derived from lignocellulosic biomass. *Green Chem.* 2013, 15, 1740-1763.
- Shearouse, W. C.; Lillie, L. M.; Reineke, T. M.; Tolman, W. B. Sustainable Polyesters Derived from Glucose and Castor Oil: Building Block Structure Impacts Properties. *ACS Macro Lett.* 2015, 4, 284-288.
- Fenouillot, F.; Rousseau, A.; Colomines, G.; Saint-Loup, R.; Pascault, J. P. Polymers from renewable 1,4:3,6-dianhydrohexitols (isosorbide, isomannide and isoidide): A review. *Prog. Polym. Sci.* 2010, 35, 578-622.
- 13. Wilbon, P. A.; Chu, F.; Tang, C. Progress in Renewable Polymers from Natural Terpenes, Terpenoids, and Rosin. *Macromol. Rapid Commun.* 2013, 34, 8-37.
- 14. Mutlu, H.; Meier, M. A. R. Castor oil as a renewable resource for the chemical industry. *Eur. J. Lipid Sci. Technol.* 2010, 112, 10-30.
- Gandini, A.; Lacerda, T. M. Monomers and Polymers from Chemically Modified Plant Oils and their Fatty Acids, *Polymers from Plant Oils*, John Wiley & Sons, Inc., Hoboken, NJ, USA, and Scrivener Publishing LLC, Beverly, MA, USA, 2nd edition, 2019, pp. 33–82.
- 16. Schwendeman, J. E.; Church, A. C.; Wagener, K. B. Synthesis and Catalyst Issues Associated with ADMET Polymerization. *Adv. Synth. Catal.* 2002, 344, 597-613.
- Gandini, A.; Lacerda, T. M. Metathesis Reactions Applied to Plant Oils and Polymers Derived from the Ensuing Products, *Polymers from Plant Oils*, John Wiley & Sons, Inc., Hoboken, NJ, USA, and Scrivener Publishing LLC, Beverly, MA, USA, 2nd edn, 2019, pp. 83–108.
- Dannecker, P.-K.; Biermann, U.; Sink, A.; Bloesser, F. R.; Metzger, J. O.; Meier, M. A.
 R. Fatty Acid–Derived Aliphatic Long Chain Polyethers by a Combination of

Catalytic Ester Reduction and ADMET or Thiol-Ene Polymerization. *Macromol. Chem. Phys.* 2019, 220, 1800440.

- Rybak, A.; Meier, M. A. R. Acyclic Diene Metathesis with a Monomer from Renewable Resources: Control of Molecular Weight and One-Step Preparation of Block Copolymers. *Chem. Sus. Chem.* 2008, 1, 542-547.
- Lebarbé, T.; Neqal, M.; Grau, E.; Alfos, C.; Cramail, H. Branched polyethylene mimicry by metathesis copolymerization of fatty acid-based α,ω-dienes. *Green Chem.* 2014, 16, 1755-1758.
- 21. Mutlu, H.; Meier, M. A. R. Unsaturated PA X,20 from Renewable Resources via Metathesis and Catalytic Amidation. *Macromol. Chem. Phys.* 2009, 210, 1019-1025.
- 22. Rojo, L.; Vazquez, B.; Parra, J.; López Bravo, A.; Deb, S.; San Roman, J. From Natural Products to Polymeric Derivatives of "Eugenol": A New Approach for Preparation of Dental Composites and Orthopedic Bone Cements. *Biomacromolecules* 2006, 7, 2751-2761.
- 23. Yoshimura, T.; Shimasaki, T.; Teramoto, N.; Shibata, M. Bio-based polymer networks by thiol–ene photopolymerizations of allyl-etherified eugenol derivatives. *Eur. Polym. J.* 2015, 67, 397-408.
- 24. Guzmán, D.; Ramis, X.; Fernández-Francos, X.; De la Flor, S.; Serra, A. New biobased materials obtained by thiol-ene/thiol-epoxy dual curing click procedures from eugenol derivates. *Eur. Polym. J.* 2017, 93, 530-544.
- 25. Shibata, M.; Tetramoto, N.; Imada, A.; Neda, M.; Sugimoto, S. Bio-based thermosetting bismaleimide resins using eugenol, bieugenol and eugenol novolac. *React. Funct. Polym.* 2013, 73, 1086-1095.
- 26. Neda, M.; Okinaga, K.; Shibata, M. High-performance bio-based thermosetting resins based on bismaleimide and allyl-etherified eugenol derivatives. *Mater. Chem. Phys.* 2014, 148, 319-327.
- 27. Alexander, K. A.; Paulhus, E. A.; Lazarus, G. M. L.; Leadbeater, N. E. Exploring the reactivity of a ruthenium complex in the metathesis of biorenewable feedstocks to generate value-added chemicals. *J. Organomet. Chem.* 2016, 812, 74-80.

- 28. Taber, D. F.; Frankowski, K. J. Grubbs' Catalyst in Paraffin: An Air-Stable Preparation for Alkene Metathesis. *J. Org. Chem.* 2003, 68, 6047-6048.
- Moïse, J.; Arseniyadis, S.; Cossy, J. Cross-Metathesis between α-Methylene-γbutyrolactone and Olefins: A Dramatic Additive Effect. *Org. Lett.* 2007, 9, 1695-1698.
- 30. Bilel, H.; Hamdi, N.; Zagrouba, F.; Fischmeister, C.; Bruneau, C. Eugenol as a renewable feedstock for the production of polyfunctional alkenes via olefin cross-metathesis. *RSC Adv.* 2012, 2, 9584-9589.
- 31. Le, D.; Samart, C.; Tsutsumi, K.; Nomura, K.; Kongparakul, S. Efficient Conversion of Renewable Unsaturated Fatty Acid Methyl Esters by Cross-Metathesis with Eugenol. *ACS Omega* 2018, 3, 11041-11049.
- 32. Thirukumaran, P.; Shakila, A.; Muthusamy, S. Synthesis and characterization of novel bio-based benzoxazines from eugenol. *RSC Adv.* 2014, 4, 7959-7966.
- Harvey, B. G.; Sahagun, C. M.; Guenthner, A. J.; Groshens, T. J.; Cambrea, L. R.; Reams, J. T.; Mabry, J. M. A High-Performance Renewable Thermosetting Resin Derived from Eugenol. *Chem. Sus. Chem.* 2014, 7, 1964-1969.
- Hu, K.; Zhao, D.; Wu, G.; Ma, J. Synthesis and properties of polyesters derived from renewable eugenol and α,ω-diols via a continuous overheating method. *Polym. Chem.* 2015, 6, 7138-7148.
- 35. Hu, K.; Zhao, D.; Wu, G.; Ma, J. Polyesters derived from bio-based eugenol and 10-undecenoic acid: synthesis, characterization, and structure-property relationships. *RSC Adv.* 2015, 5, 85996-86005.
- 36. Llevot, A.; Grau, E.; Carlotti, S.; Grelier, S.; Cramail, H. ADMET polymerization of bio-based biphenyl compounds. *Polym. Chem.* 2015, 6, 7693-7700.
- Nomura, K.; Takahashi, S.; Imanishi, Y. Synthesis of Poly(macromonomer)s by Repeating Ring-Opening Metathesis Polymerization (ROMP) with Mo(CHCMe₂Ph)(NAr)(OR)₂ Initiators. *Macromolecules* 2001, 34, 4712-4723.
- Selected NMR spectra of monomers (M1–M3), cross-linker (CL) and polymers (P1– P3, PL1) are shown in the Appendix B.

- For example, selected review in ADMET polymerization (refs 39-40). Berda, E. B.;
 Wagener, K. B., in *Polymer Science: A Comprehensive Reference*, ed. K.
 Matyjaszewski and K. Mullen, Elsevier BV, Amsterdam, 2012, vol. 5, pp. 195–216.
- 40. Berda, E. B.; Wagener, K. B., in *Synthesis of Polymers; New Structures and Methods*, ed. D. Schluter, C. Hawker and J. Sakamoto, Wiley-VCH, Weinheim, Germany, 2012, pp. 587–600
- Related experimental procedure for synthesis of all-trans poly(9,90-dialkyl-fluorene-2,7-vinylene)s by ADMET polymerization (refs 41-42). Nomura, K.; Morimoto, H.; Imanishi, Y.; Ramhani, Z.; Geerts, Y. Synthesis of high molecular weight trans-poly(9,9-di-n-octylfluorene-2,7-vinylene) by the acyclic diene metathesis polymerization using molybdenum catalysts. *J. Polym. Sci. Part A: Polym. Chem.* 2001, 39, 2463-2470.
- 42. Nomura, K.; Yamamoto, N.; Ito, R.; Fujiki, M.; Geerts, Y. Exclusive End Functionalization of all-trans-Poly(fluorene vinylene)s Prepared by Acyclic Diene Metathesis Polymerization: Facile Efficient Synthesis of Amphiphilic Triblock Copolymers by Grafting Poly(ethylene glycol). *Macromolecules* 2008, 41, 4245-4249.
- 43. Schulz, M. D.; Wagener, K. B. Solvent Effects in Alternating ADMET Polymerization. ACS Macro Lett. 2012, 1, 449-451.
- 44. Fokou, P. A.; Meier, M. A. R. Use of a Renewable and Degradable Monomer to Study the Temperature-Dependent Olefin Isomerization during ADMET Polymerizations. *J. Am. Chem. Soc.* 2009, 131, 1664-1665.
- 45. For example (refs 45-47). *Handbook of Metathesis*, ed. Grubbs, R. H., Wiley-VCH, Weinheim, Germany, 2003
- 46. *Olefin Metathesis: Theory and Practice*, ed. Grela, K., John Wiley & Sons, Inc., Hoboken, New Jersey, USA, 2014
- 47. *Handbook of Metathesis*, ed. Grubbs, R. H.; Wenzel, A. G., Wiley-VCH, Weinheim, Germany, 2nd edition, 2015, vol. 1
- For examples (refs 18,19, 48-50). Gaines, T. W.; Nakano, T.; Chujo, Y.; Trigg, E. B.;
 Winey, K. I.; Wagener, K. B. Precise Sulfite Functionalization of Polyolefins via ADMET Polymerization. ACS Macro Lett. 2015, 4, 624-627.

- 49. Parkhurst, R. R.; Balog, S.; Weder, C.; Simon, Y. C. Synthesis of poly(sulfonate ester)s by ADMET polymerization. *RSC Adv.* 2014, 4, 53967-53974.
- 50. Türünç, O.; Meier, M. A. R. Thiol-ene vs ADMET: a complementary approach to fatty acid-based biodegradable polymers. *Green Chem.* 2011, 13, 314-320.
- 51. Synthesis of long-chain aliphatic polyesters (refs 18,51). Stempfle, F.; Ritter, B. S.; Mülhaupt, R.; Mecking, S. Long-chain aliphatic polyesters from plant oils for injection molding, film extrusion and electrospinning. *Green Chem.* 2014, 16, 2008-2014.
- 52. Stempfle, F.; Ortmann, P.; Mecking, S. Long-Chain Aliphatic Polymers to Bridge the Gap between Semicrystalline Polyolefins and Traditional Polycondensates. *Chem. Rev.* 2016, 116, 4597-4641.
- 53. V. V. Korshak, V. V.; Vinogradova, S. V. *Polyesters*, Pergamon Press, Oxford, UK, 1965.



CHAPTER 5

SYNTHESIS OF RENEWABLE THERMOSET FILMS BY RING-OPENING METATHESIS POLYMERIZATION (ROMP) OF NORBORNENE-FUNCTIONALIZED PLANT OILS

5.1 Introduction

Concerns of depleting fossil resources and growing on environmental problems are driving strong demand for replacing unsustainable petroleum-based materials. Therefore, the utilization of renewable resources for producing polymeric materials appears to be increasingly important in both the economic and environmental viewpoints.¹⁻³ A wide range of bio-renewable polymers have been developed utilizing renewable resources such as plant oils,⁴⁻⁷ polysaccharides,⁸ lignin,⁹ sugars,^{10,11} cellulose,^{12,13} and rosin.¹⁴⁻¹⁶ Among that, plant oils are considered as the most promising starting material for the synthesis of polymers due to their inherent biodegradability and low toxicity. Recently, the utilization of plant oils as renewable feedstocks for producing bio-based thermosetting has attracted much attention in both academics and industrials.¹⁷⁻²⁰

Thermoset polymers are important matrices in fiber-reinforced composites due to their attractive qualities such as outstanding in thermal and chemical resistances as well as good physical and mechanical properties. Utilizing plant oils for producing bio-based thermosets is employed by several techniques such as co-polymerization to obtain epoxy thermosets^{21,22} or polyurethanes,^{23,24} free radical homo-polymerization,^{7,25,26} and cationic polymerization.^{27,28} Besides, olefin metathesis have also been employed as an efficient method for developing strong and tough thermosets derived from plant oils, primarily through ADMET^{4,29} and ROMP.^{30,31} For instance, three kinds of plant oil-based ROMP thermoset polymers were explored by copolymerizing of norbornene-functionalized castor oil (BCO) with cyclooctene (CO)³¹, Dilulin (a commercially available norbornene-functionalized linseed oil) with dicyclopentadiene (DCPD)³⁰ and Dilulin with bicyclic norbornene-based crosslinkers (Bicyclo[2.2.1]hepta-2,5-diene)³² using second-generation Grubbs catalyst. However,

phase separations were observed in these thermosets due to the difference in reactivity between the plant oil-based monomers and the petroleum-based comonomers, resulting in decreasing mechanical properties. The phase separation has also been observed in system of vegetable oil-based thermosets from castor oil³¹ and palm oil³³ with petroleum based-norbornene as comonomer. To address the phase separation, it is necessary to reduce vegetable oil triglycerides into fatty alcohols then functionalized with norbornene groups such as 5-norbornene-2,3-dicarboxylate anhydride or 5-norbornene-2-carbonyl chloride.^{34,35} These norbornene-functionalized bio-renewable monomers were easily undergo ROMP without the need of comonomers, leading to enhance storage modulus and T_g of the resultant thermosets.³⁶

In other hand, plant oil- based thermosets usually show low $T_{\rm g}$ and thermal properties due to highly flexible chains of triglyceride, thus low room temperature mechanical strength. In order to enhance the T_g of the plant oil-based thermoset polymers, plant oil monomers are primarily copolymerized with a petroleum-based norbornene monomer or crosslinker such as dicyclopentadiene (DCPD), 5-ethylidene-2-norbornene (ENB) and norbornene (NB, bicyclo[2.2.1]heptene-2) as aforementioned. The utilization of petroleum-based norbornene as comonomers or crosslinkers can easily undergo ROMP to form thermosets with good thermomechanical properties in the presence of Ru catalysts. However, the rigid structure, relatively slow in-situ polymerization rate, large amount of required catalyst, and nonrenewable characteristic restrict petroleum-based norbornene application in thermoset polymer materials. Thus, considering of using bio-based materials in industrial applications and attempts to move toward sustainability, it is necessary to explore new norbornene-containing monomers, especially those derived from biobased resources with high reactivity and low melting point as co-monomer or crosslinkers to substitute for the nonrenewable-based norbornene such as (DCPD, NB, CO) in preparing plant oil-based thermosets via ROMP.

Isosorbide (IS) is an interesting renewable resource with high availability. IS is derived from glucose and typically obtained from the depolymerization of cellulose and starch.^{37,38} IS is a V-shaped diol with a unique bicyclic ring structure consisting of

two *cis*-fused tetrahydrofuran rings and two secondary hydroxyl groups in the 2- and 5- positions,³⁹ which imparts a degree of rigidity to polymers. Its inherent unique molecular structure, high thermal stability, biodegradability and nontoxicity makes it a promising monomer and monomer precursor for potential replacing petroleum-based derived polymers. ^{40,41} Take advantage of isosorbide as a platform and incorporated high reactive norbornene functional group into isosorbide backbone to synthesize one novel bio-based norbornene-functionalized isosorbide use as crosslinker in ROMP of norbornene-functionalized plant oils.

In this chapter, several thermoset polymer films were synthesized via ROMP of norbornene-functionalized various plant oils including olive oil, rapeseed oil and soybean oil. The structure of plant oil-based monomers and bio-based crosslinker was determined by NMR spectroscopy and Fourier transform infrared spectroscopy (FTIR). The ROMP reactions were carried out at 40 °C and ambient pressure using **G2** catalyst. The ROMP conditions such as catalyst loading (0.0625–0.5 %wt) and cured temperature (80 and 120 °C) were studied. Thermo-mechanical properties, in term of storage modulus (E'), glass transition temperature (T_g), and crosslink density were characterized by dynamic mechanical analysis (DMA). Thermal properties measured by thermogravimetric analysis (TGA) was also discussed. The thermo-mechanical properties of the resultant thermoset films depending on the norbornene-functionalized isosorbide (as bio-based crosslinker) content and plant oil sources were discussed. For comparison, thermoset polymer films from norbornene-functionalized plant oils with petroleum-based norbornene, a crosslinker 1,4-*bis*[dimethyl[2-(5-norbornen-2-yl)ethyl]silyl]benzene, were also prepared and discussed.

5.2 Materials and Methods

5.2.1 Materials

Dichloromethane dehydrated (>99.5 %) obtained from Carlo ERBA was transferred into a bottle containing molecular sieves (mixture of 3A 1/16, 4A 1/8 and 13X 1/16) in the drybox. The second-generation Grubbs catalyst, $RuCl_2(PCy_3)(H_2IMes)(CHPh)$ [G2, $IMesH_2 = 1,3$ -*bis*(2,4,6-trimethylphenyl)imidazolin-2-

ylidene] and 4-*bis*[dimethyl[2-(5-norbornen-2-yl)ethyl]silyl]benzene as crosslinker (CL1) were purchased from Sigma-Aldrich. 5-norbornene-2-carboxylic acid, a mixture of *endo-* and *exo* (NBCA, >98.0%), isosorbide (IS, >98%), *N*,*N* Dimethylformamide (DMF, >99.5%), oxalyl chloride (>98%), 4-dimethylaminopyridine (DMAP >90%) and triethylamine (Et₃N, >99%) were obtained from Tokyo Chemical Industry, Co., Ltd. Hydrogen peroxide (30%) was supplied by QRëC. Formic acid (90%) was purchased from Ajax Finechem. Ethyl acetate (99.9%) was obtained from Thermo Fisher Scientific.

Plant oils were purchased in a local supermarket: Olive oil (Cotoliva, Extra Virgin, 100 g (ρ = 0.89 g/mL) contains 15 g saturated, 75 g monounsaturated, and 10 g polyunsaturated fatty acids), rapeseed oil (Mackintosh, Cold pressed, 100 g (ρ = 0.89 g/mL) contains 6.96 g saturated, 54.9 g monounsaturated, and 29.34 g polyunsaturated fatty acids), and soybean oil (UPC Morakot, 100 mL (ρ = 0.90 g/mL) contains 16.7 g saturated, 23.3 g monounsaturated, and 60 g polyunsaturated fatty acids). The fatty acid composition in the starting plant oils is shown in Table 5.1 (see Figure C5.1-5.2, Appendix C).

Table 5.1. Fatty acid compositions in the starting plant oils determined based on GC-FID analysis.

	Fatty acid (%)						
Plant oil	Palmitic	Stearic	Oleic	Linoleic	Linolenic		
	C16:0	C18:0	C18:1	C18:2	C18:3		
Olive	10.6	0	73.6	15.1	0.7		
Rapeseed	2.9	0	56.4	29.1	11.6		
Soybean	6.7	3.0	25.6	58.2	6.5		

5.2.2 Synthesis of epoxidized plant oils [olive oil (OO), rapeseed oil (RO) and soybean oil (SO)]

Plant oils (OO, RO or SO) and formic acid (HCOOH 90%) were introduced into a three-necked round bottom flask equipped with an additional funnel and a condenser at room temperature (27±0.5 °C). The mixture was stirred and purged nitrogen gas for 20 min. Hydrogen peroxide (H₂O₂) was added dropwise (1.5 mL/min) while stirring at room temperature (H₂O₂/HCOOH/double bond average number = 20/2/1 molar ratio). The temperature was gradually increased to 60 °C, and the mixture was stirred for 4 h to produce a white color biphasic solution. After the reaction completed, the mixture was transferred to a separatory funnel and was then extracted with ethyl acetate (30 ml). The organic layer containing the epoxidized plant oils (EPO) was washed with 10% (w/w) NaHCO₃ (30 mL x 4 times) and then with brine (30 mL x 3 times). The obtained product was dried over anhydrous Na₂SO₄ and was filtered, and the filtrate was evaporated under reduced pressure to yield epoxidized plant oils (EPO) as viscous oils (see Figure C5.3, Appendix C).⁴² The procedure for synthesizing epoxidized plant oils is shown in Figure 5.1, and the *in situ* epoxidation of triglyceride with hydrogen peroxide and formic acid is displayed in Scheme 5.1.



Figure 5.1 Epoxidation of triglycerides from plant oils (representative olive oil).



Scheme 5.1 In situ epoxidation of triglyceride with hydrogen peroxide and formic acid.

5.2.3 Synthesis of norbornene-functionalized plant oils

A typical procedure for synthesis of norbornene-functionalized olive oil (NB-OO) is as follows. Epoxidized olive oil (EOO, 15 g) and TEA (90 µL) were introduced into a three-necked round bottom flask equipped with an additional funnel and a condenser. The mixture was stirred and purged nitrogen gas for 30 min. After that, NBCA (4.4 g) was slowly added into the mixture and was stirred at 160 °C for 24 h. The NBCA stoichiometry was 1:1 in relation to the oxirane rings present in the EOO. After the reaction completed, the mixture was quenched with 5% (w/w) Na₂CO₃ solution (350 mL) to convert unreacted NBCA into the corresponding carboxylate salt. The mixture was stirred for 12 h at room temperature (27±0.5 °C). After that, the mixture was transferred to a separatory funnel and then was extracted with ethyl acetate (100 mL), dried over anhydrous Na_2SO_4 and was filtered. The filtrate was evaporated under reduced pressure to yield NB-OO as viscous brown oil (see Figure C5.3, Appendix C). The average number of norbornene rings present in the NB-OO was determined by the integrated intensity of the signals in the ¹H NMR spectrum. A similar protocol was used for synthesis of norbornene-functionalized rapeseed oil (NB-RO) and soybean oil (NB-SO). The procedure for the synthesis of norbornene-functionalized

plant oil is shown in Figure 5.2, and the illustration of epoxidized ring opening with norbornene carboxylic acid is displayed in Scheme 5.2.



Figure 5.2 Illustration of norbornene-functionalized plant oils (representative olive oil).





Scheme 5.2 Synthesis scheme of norbornene-functionalized plant oil (representative olive oil) via epoxidized ring opening with norbornene carboxylic acid.

5.2.4 Synthesis of norbornene-functionalized isosorbide (NB-IS)

Oxalyl chloride (1.4 mL, 16 mmol) was added dropwise into an anhydrous dichloromethane solution (25 mL) containing 5-norbornene-2-carboxylic acid (NBCA) (1.33 mL, 10.85 mmol, a mixture of *endo* and *exo*) and *N,N* dimethylformamide (DMF, 171 μ L) over 15 min at 0 °C (cooled in ice baht). The mixture was then warm to room temperature and was stirred for 6 h under N₂ atmosphere. After the reaction was completed, the excess oxalyl chloride and solvent were

removed under reduced pressure. 5-Norbornene-2-carbonyl chloride was re-dissolved in anhydrous DCM (3.0 mL) and was added dropwise into an anhydrous DCM solution (50 mL) containing isosorbide (IS, 0.79 g, 5.4 mmol), DMAP (0.1 mL, 0.82 mmol) and trimethylamine (2.49 mL, 18 mmol) over 15 min at 0 °C (cooled in ice baht). The mixture was then warm to room temperature and stirred overnight (12 h). After the reaction was completed, the reaction mixture was passed through a Celite pad, and the filtrate was extracted with saturated NH₄Cl solution. The organic layer was subsequently separated and dried over anhydrous Na₂SO₄ and was then filtered through a filter paper. The filtrate was evaporated under reduced pressure to yield NB-IS as a black viscous oil (1.90 g, 91% yield) see Figure C5.4, Appendix C. The procedure for the synthesis of NB-IS is shown in Figure 5.3, and a schematic illustration of the formation of norbornene-isosorbide (NB-IS) through the coupling of 5-norbornene-2carbonyl chloride to hydroxyl (-OH) groups on isosorbide (IS) is displayed in Scheme 5.3.



Figure 5.3 The overall procedure for the synthesis of norbornene-functionalized isosorbide (NB-IS).



Scheme 5.3 A schematic illustration of the formation of norbornene-isosorbide (NB-IS) through the coupling of 5-norbornene-2-carbonyl chloride to hydroxyl (-OH) groups on isosorbide (IS).

5.2.5 Preparation of bio-based thermoset films via ROMP

A typical procedure for the preparation of bio-based thermoset films ROMP is follows. The second-generation Grubbs by as catalyst G2, RuCl₂(PCy₃)(H₂IMes)(CHPh)) (0.0625- 0.5 %wt based on the entire monomer and crosslinker) dissolved in 0.4 mL CH₂Cl₂ was added to the mixture of monomer (NB-OO, NB-RO or NB-SO, 2.0 g) and crosslinker (5-15 %wt) in CH₂Cl₂ (1.0 mL of per 1000 mg of total monomer and crosslinker) which had been cooled to 0 °C in advanced in an ice bath. The mixture was vigorously stirred in a 20 mL glass vial for 30 s to obtain a homogeneous solution. The solution was casted into a mold, and was then placed in an oven, and cured for 1 h at 40 °C and then post-cure at 120 °C for 12 h. The resulting thermoset films are rubbery and slightly transparent with retaining the monomers' original. The overall of the procedure for the preparation of bio-based thermoset film via ROMP is shown in Figure 5.4.



Figure 5.4 Schematic of the overall procedure for the synthesis of bio-based thermoset films via ROMP.

5.2.6 Characterizations of monomers and thermoset films

All ¹H and ¹³C NMR spectra were recorded on Bruker Avance III HD 600 MHz NMR spectrometer. All chemical shifts were reported in parts per million (ppm) with referenced to tetramethylsilane (TMS) at 0.00 ppm. Obvious multiplicities and routine coupling constants are usually not listed, and all spectra were obtained in the solvent indicated at 25 °C unless otherwise noted. Fourier transform infrared spectroscopy (FTIR) were recorded on Perkin Elmer Spectrum 100 FT-IR spectrometer with attenuated total reflectance (ATR) techniques at the range of wavenumber between 4000 and 600 cm^{-1} and the resolution of 4 cm⁻¹ with 32 scans. Thermogravimetric analysis (TGA) were performed on a Mettler-Toledo TGA/DSC3+ thermogravimetric analyzer. An approximately 10 mg specimen was heated under N₂ atmosphere from 30 to 700 °C at a heating rate 20 °C/min with nitrogen flow 30 mL/min. Dynamic mechanical analysis (DMA) were recorded on a Mettler Toledo DMA1 analyzer using three points bending mode at 1.0 Hz. Samples were cut into rectangular shapes with a dimension of 10 mm x 5 mm x 1 mm (length x width x thickness). Each sample was cooled to -70 °C and held isothermally at that temperature for 3 min. The samples were then heated at 3 °C/min to 150 °C.

Soxhlet extraction of thermoset films were carried out by Soxhlet extractor using methylene chloride as a solvent. A rectangular sample with a dimension of 10 mm x 10 mm x 1 mm (length x width x thickness) (approx. weight of 140-150 mg) was extracted with 200 mL of methylene chloride (CH_2Cl_2) at 60 °C for 24 h. After extraction, the insoluble portion was dried in oven at 60 °C for 12 h and weighed. The resulting solution was concentrated under reduced pressure and dried in *vacuo*. The solution portion of all thermoset films were calculated according to the following equation, Eq. (1).

Soluble portion (%) =
$$[1 - (m_1/m_0)] \times 100$$
 (1)

where, m_0 is the initial weight and m_1 is the dry weight after extraction.

5.3 Results and Discussion

5.3.1 Structure characterization of norbornene-functionalized plant oil monomers

In this study, three different norbornene-functionalized plant oil monomers were designed and synthesized though simple reactions including epoxidation of olefin groups and ring-opening of epoxide groups (shown in Scheme 5.4). The olefin groups in the triglycerides from plant oil (representative triglyceride from olive oil) were converted into oxirane rings by in situ performic acid method, resulting in epoxidized olive oil (EOO), as indicated by the 1 H NMR spectra (Figure 5.4). The resonances ascribed to protons of olefin (a), inter-olefin (b), and α -olefin (d) (at 5.3, 2.8, and 2.0 ppm, respectively) vanished and resonances assigned to protons of oxirane and α -oxirane rings (at 2.90-3.10 ppm range and 1.50 ppm) were observed. The absence of the resonance at 5.3 ppm indicates that double bonds conversion has been completed. The results clearly indicate the formation of epoxidized olive oil (EOO). Similar ¹H NMR spectroscopy results were also obtained for the epoxidized rapeseed oil (ERO) and epoxidized soybean oil (ESO), as shown in Figure C5.5-5.6 (Appendix C). From the integrated intensity of the resonances in the ¹H NMR spectra, an average number of oxirane rings per EOO, ERO and ESO unit were calculated to be 1.3, 1.8 and 1.7 oxirane rings, respectively (see Figure C5.7, Appendix C).



Scheme 5.4 Synthesis scheme of norbornene-functionalized plant oils (representative norbornene-olive oil, NB-OO).

The presence of the norbornene unit in the norbornenefunctionalized olive oil (NB-OO) monomer, from the reaction between NBCA and the oxirane rings in the EOO, was verified by the ¹H NMR spectrum (Figure 5.5c). The resonances attributed to oxirane ring protons at 2.9-3.1 ppm decreased, and the resonances at 5.9-6.3 ppm corresponded to the norbornene protons appeared. The resonances ascribed to the proton in the carbon attached to the norbornene (NB) (at 4.8 ppm) and to the proton in the carbon attached to the hydroxyl group (at 3.6 ppm) from the opening of the oxirane ring were observed. The remaining of resonances attributed to the protons in the glycerol unit (α and β), indicates the triglyceride structure remains after reactions. The successful synthesis of the monomers was also confirmed by ¹³C NMR spectroscopy (Figure C5.8, Appendix C). The results thus clearly indicated that the norbornene molecules were successfully grafted onto the olive oil triglycerides. The similar ¹H and ¹³C NMR spectroscopy results were also observed for norbornene-functionalized rapeseed oil (NB-RO) and soybean oil (NB-SO) as shown in Figure C5.9-5.10 (Appendix C). From the integrated intensity of the resonances in the ¹H NMR spectra, an average number of norbornene molecule per NB-OO, NB-RO and NB-SO unit were calculated to be 1.0, 1.3 and 1.5 norbornene rings, respectively (Appendix C).



Figure 5.5 ¹H NMR spectra (in CDCl₃ at 25 °C) of olive oil (OO), epoxidized olive oil (EOO) and norbornene-functionalized olive oil (NB-OO).

The successfully norbornene-functionalized olive oil was further verified by FTIR spectra shown in Figure 5.6. The disappearance of the peak at 3005 cm⁻¹ in EOO indicated the complete conversion of olefinic group while the appearance of the peak at 845 cm⁻¹ in EOO indicated the formation of oxirane ring. In addition, the transmittance increases at 3500 cm⁻¹ and decrease at 845 cm⁻¹ in NB-OO indicated the formation of epoxy groups, respectively. Moreover, the appearance of peaks at 3060 cm⁻¹ in NB-OO related to the olefinic bonds vibration in the norbornene groups was also observed. These results thus clearly demonstrated that the norbornene-functionalized olive oil monomer was successfully synthesized. Similar FT-IR spectra results were also attained for the norbornene-functionalized rapeseed oil (NB-RO) and soybean oil (NB-SO), as shown in Figure C5.11-5.12 (Appendix C).



Figure 5.6 FT-IR spectra of olive oil (OO), epoxidized olive oil (EOO) and norbornenefunctionalized olive oil (NB-OO).

5.3.2 Structure characterization of norbornene-functionalized isosorbide (NB-IS)

A novel renewable bio-based norbornene crosslinker (NB-IS) was designed and synthesized through the coupling of 5-norbornene-2-carbonyl chloride to hydroxyl (-OH) groups on isosorbide (IS). The 5-norbornene-2-carbonyl chloride (NBCC) was obtained by reacting of norbornene carboxylic acid with oxalyl chloride and DMF in dichloromethane at room temperature (Scheme 5.3). IS, readily obtained from starch,³⁷ was chosen for the synthesis of bio-based norbornene crosslinker (NB-IS) due to its robust bicycling structure,³⁹ which has a potentially enhancing the glass transition temperature (T_g) to the resulting polymers. Moreover, functionalizing isosorbide via incorporation of NBCC allows to potential degradation back to isosorbide, resulting in an environmentally friendly product. For comparison, a petroleum-based norbornene, 4-*bis*[dimethyl[2-(5-norbornen-2-yl)ethyl]silyl]benzene was selected as a crosslinker (CL1), because it not only owned the crucial functional

group, high reactive norbornenyl group but also contained rigid aromatic structure, which could also enhance the T_g of the resulting polymers. The chemical compositions and structures of the crosslinker NB-IS were identified by FT-IR and ¹H NMR spectroscopy. To verify the successful synthesis of the crosslinker (NB-IS), FT-IR was first employed to characterize the crosslinker. The FT-IR spectra of IS and NB-IS were illustrated in Figure 5.7. The spectrum of IS exhibited the characteristic peaks of -OH stretching vibration (3364 cm⁻¹), -CH₂- stretching vibration (2867 and 2937 cm⁻¹) and C-O or C-H stretching vibration (1050, 1071 and 1117 cm⁻¹). Compared with that of IS, the spectrum of NB-IS demonstrated news peaks at 1730 cm⁻¹ and 3060 cm⁻¹, which were corresponded to C=O and C=C stretching vibration of norbornene group. The complete disappearance of the -OH group accompanied by the formation of C=O and C=C bonds on NB-IS proved that the norbornene groups have been successfully coupled with hydroxyl (-OH) groups on the IS.



Figure 5.7 FT-IR spectra of isosorbide and norbornene-functionalized isosorbide (NB-IS)

To further determine the structure of the NB-IS crosslinker, ¹H NMR of NB-IS was conducted as shown in Figure 5.8. The characteristic resonances at 5.88-6.26 ppm ascribed to the vinyl protons on the norbornene groups, while the resonances range (3.44-5.2 ppm) assigned to the eight protons of two fused rings of

isosorbide moieties. All other resonances match well with the protons of the NB-IS crosslinker as shown in Figure 5.8b. The molar ratio of NB/IS estimated by integrating intensity of the resonances in the ¹H NMR spectra was 2.2:1 (see Figure 5.13 and calculated in Appendix C). This value is relatively close to the structure of the NB-IS 2:1. The results thus clearly demonstrate that the target bio-based crosslinker (NB-IS) was successfully synthesized.



Figure 5.8 (a) Synthesis scheme of norbornene-isosorbide (NB-IS) through the coupling of 5-norbornene-2-carbonyl chloride to hydroxyl groups on isosorbide, (b) ¹H NMR spectrum (in CDCl₃ at 25 °C) of crosslinker (NB-IS).

5.3.3 Fourier Transform Infrared (FT-IR) spectroscopy of norborneneplant oil thermosets and norbornene-plant oil with crosslinkers thermosets

FTIR spectra of the starting monomers and the thermoset films (representative thermoset films of NB-OO) were characterized to demonstrate the successfully happened of ROMP. Bio-based thermoset film at 0.5 %wt catalyst **G2** were exemplarily selected for discussing (Figure 5.9a). The peak at 3060 cm⁻¹ in NB-OO disappeared indicates the transformation of olefinic of norbornene ring. The appearance of peak at 968 cm⁻¹ in the NB-OO film ascribed to the ring-opened of norbornene unit of the NB-OO.⁴⁵ This peak (not observed in the NB-OO monomer),



could be corresponded to a *trans* double bond in the metathesized backbone of the bio-based thermoset.

Figure 5.9 FT-IR spectra of a) NB-OO monomer, NB-OO film and NB-OO with CL films b) bio-based thermoset films of different plant oils at 0.5 %wt **G2** catalyst.

FTIR spectra of the bio-based thermoset films from different plant oils show marginal differences in the fingerprint region (Figure 5.9b). The intensity of the peaks at 3475 cm⁻¹ and 968 cm⁻¹ corresponding to the hydroxyl (-OH) groups and H-C=C-H deformation vibration increases from olive oil to rapeseed oil to soybean oil. This is likely due to the increase in the number of norbornene rings per triglyceride in the monomer structure, which increases in the same order. The ATR-FTIR results of the bio-based thermoset films proved the ROMP reaction efficiency.

5.3.4 ROMP of the norbornene-functionalized plant oils

The bio-based thermoset films were prepared by ROMP curing of norbornene-functionalized with various plant oils (olive oil, rapeseed oil and soybean oil) in the presence of second-generation Grubbs catalyst (G2) (see Scheme 5.5 for a representative NB-OO). The ROMP of the norbornene-functionalized plant oils was conducted in dichloromethane at 40 °C and ambient pressure in an oven for 1 h. Thus, homogenous films with comparable thicknesses around 1.0 ±0.1 mm were formed and cured at different temperatures under ambient pressure. Catalyst loading varying from 0.0625 to 0.5 %wt were firstly investigated to determine the optimum catalyst loading for the ROMP of the norbornene-functionalized plant oils. The obtained bio-based thermoset films are flexible and slightly transparent with sand-like color (see Figure. C5.14, Appendix C). To investigate the influence of catalyst loading on the ROMP reaction efficiency, all thermoset films were subjected to Soxhlet extraction to remove the soluble materials present in the bio-based thermoset films. Table 5.2 shows the Soxhlet extraction of the resultant bio-based thermoset films with varying amounts of catalyst loading. It turned out that the percent soluble material, oligomeric NB-OO or unreacted triglyceride oil components, decreases from 60 to 9 %wt soluble material upon increasing catalyst loading from 0.0625 to 0.5 %wt (runs 1-5). This is due to the increasing of ROMP reactivity resulted in more crosslinked insoluble polymer network is formed. Similar results were also observed for NB-RO and NB-SO thermoset films in which the soluble portion decreases from 53 %wt to 4 %wt, and from 28 %wt to 3 %wt, respective for NB-RO and NB-SO thermoset films when increasing catalyst loading from 0.0625 to 0.5 %wt (see Table C5.1, Appendix C).



Scheme 5.5 ROMP of norbornene-functionalized plant oils (representative NB-OO).

Entry	Polymer	Cat. (G2) (%wt)	Cured temp. (°C)	Soluble (%wt)	Insoluble (%wt)
1	NB-OO	0.0625	120	60	40
2	NB-OO	0.125	120	34	66
3	NB-OO	0.125	80	47	53
4	NB-OO	0.25	120	19	81
5	NB-OO	0.5	120	9	91
6	NB-RO	0.5	120	4	96
7	NB-SO	0.5	120	3	97

Table 5.2 Extraction data of the bio-based thermoset films at various catalyst loadingand different plant oils.

* soluble materials: unreacted triglyceride oil or oligomers of the norborneneplant oil component.

As also shown in Table 5.2, at 0.5 %wt **G2**, about 9 %wt of NB-OO film was soluble while both NB-RO and NB-SO afforded only 4 %wt and 3 %wt of

soluble materials, respectively (runs 5-7). The NB-OO film displays higher percent of soluble portion compared to that of the NB-RO and NB-SO films. This is likely because the NB-OO bears only one norbornene ring per triglyceride lead to restrict the happening of ROMP steps due to a large steric hindrance. Moreover, the NB-OO structure has two long-chain fatty acids without containing norbornene groups which hinder the coordination between the olefinic C=C and the catalyst. This result thus reveals that the extra norbornene rings (a larger norbornene ring density) play an important role in increasing the crosslink densities of the resulting films. In order to investigate the influence of curing temperature, the curing was performed at 80 °C and 120 °C for 12 h in an oven for the thermoset films with 0.125 %wt **G2** catalyst. It was observed that the thermoset film cured at 80 °C shows a significantly higher percent soluble portion (13 %wt) compared to the film cured at 120 °C. The lower percentage of the soluble portion in the thermoset film at higher curing temperature indicates a higher crosslinking density due to the higher activity of the catalyst.

Figure 5.10 shows the ¹H NMR spectra of the soluble portions of the representative NB-OO thermoset films at various catalyst loading. It was found that resonances at 1.25, 1.95 and 5.35 ppm corresponding to portions of the unreacted triglyceride oil or oligomers of the NB-OO component. The resonance at 2.3 ppm is possibly attributed to the residual catalyst (G2). The soluble portion in the NB-OO films at 0.0625 %wt and 0.125 %wt of catalyst loading show more unreacted triglyceride and oligomeric NB-OO component as evidenced by the presence of the resonances at 4.1, 4.3 ppm, and 6.2 ppm which correspond to protons assigned to the glycerol moiety in triglyceride, and norbornene rings in the NB-OO films. As increasing catalyst loading, the intensity of the resonances ascribed to the protons of norbornene ring significantly reduced in the soluble portions. This revealed that almost all the norbornene rings underwent ROMP. Since 0.5 %wt G2 shows the lowest presence of unreacted norbornene rings in the soluble portion, this amount of catalyst loading seems to be thus the optimum value for the obtainment of high insoluble thermoset films.



Figure 5.10 ¹H NMR spectra (in CDCl₃ at 25 °C) of the soluble materials of the NB-OO thermoset films at various catalyst loading.

5.3.5 Dynamic mechanical analysis (DMA) of bio-based thermosets films norbornene-functionalized with different plant oils

The thermo-mechanical properties, in terms of storage modulus (E') and glass transition temperature (T_g) as well as the crosslink densities of the bio-based thermoset films were studied by DMA. Figure 5.11 shows the representative storage modulus (E') and tan δ curves as a function of temperature for the NB-OO thermoset films at various catalyst loading. It turned out that all NB-OO thermoset films show the rubbery state at room temperature. The storage modulus (E') decreased slightly when the temperature increased from -70 to -35 °C. Then a substantial decrease in the E' value is observed for all NB-OO thermoset films in a range of temperature between - 20 °C and 0 °C. This corresponds to the primary relaxation (T α) peak related to energy dissipation, where a maximum is observed in the tan δ curve. At high temperatures after the α -relaxation, a plateau was observed in the storage modulus curves, which is evidence for the existence of the crosslinked network in the thermoset films.



Figure 5.11 DMA thermograms for storage modulus and tan δ curves as a function of temperature for NB-OO thermoset films at various catalyst loading (1 Hz, 3 °C/min).

The crosslink density (v_e) values were calculated at temperature 40 °C above the T_g in the rubbery plateau of the storage modulus curve, using the rubbery theory of elasticity according to the equation below, Eq. (2):^{42,43}

$$v_e = \frac{E'}{3RT} \tag{2}$$

where, v_e is the crosslink density, E' (Pa) is the storage modulus at $T_g + 40$ °C in the rubbery plateau, R is the universal gas constant 8.31 J.mol⁻¹.K⁻¹ and T is the absolute temperature (K) at $T_g + 40$ °C. The calculated crosslink density for the thermoset films is summarized in Table 5.3. It was revealed that the crosslink density values of the NB-OO films increased by increasing catalyst loading [$v_e = 38 \text{ mol/m}^3$ (0.0625 %wt, run 1) vs. $v_e = 657 \text{ mol/m}^3$, run 4). This indicates that increasing catalyst loading has led to more efficient ROMP of NB-OO. The T_g value of the thermoset films was determined by the temperature at the maximum peak height of the tan δ curve. Table 5.3 (runs 1-4) shows the T_g values of the NB-OO thermoset films. It was found that the T_g values of the NB-OO films considerably increased from -23 to -8 °C when the catalyst loading increased from 0.0625 %wt to 0.5 %wt due to the increased degree of crosslinking and the crosslink density that restrict the mobility of the polymer.

Table 5.3 (runs 1-4) also shows the storage modulus (E') values at room temperature for the NB-OO thermoset films. It was revealed that, the E' values of the NB-OO films sustainably increased upon increasing catalyst loading [E' = 0.26 MPa (0.0625 %wt, runs 1 vs. E' = 5.0 MPa (0.5 %wt, run 4)]. This is because when molecular motions became more restricted due to the increased crosslink density upon increasing catalyst loading (runs 1-4), the amount of energy that can be dissipated throughout the polymer sample significantly decreased. Thus, the E' value at room temperature was dramatically enhanced when increasing catalyst loading. Meanwhile, the tan δ peak shifts to a higher temperature and the value decreased upon increasing catalyst loading. The tan δ values of all the NB-OO thermoset films ranged from 0.73 to 1.59.

Run Poly	Delvineer	Cat. (G2)	E' at 25 ℃	Τ _g	v _e	tan δ
	Polymer	(%wt)	(MPa) ^a	(°C) ^b	(mol/m ³) ^c	
1	NB-OO	0.0625	0.26	-23	38	1.59
2	NB-OO	0.125	1.26	-19	172	1.14
3	NB-OO	0.25	3.11	-13	414	0.84
4	NB-OO	0.5	5.00	-8	657	0.73
5	NB-RO	0.5	27.9	21	880	0.62
6	NB-SO	0.5	40.0	24	895	0.68

Table 5.3 DMA analysis of the bio-based thermoset films at various catalyst loadings and different plant oils.

^a Storage modulus at 25 °C

^b Glass transition temperature determined by DMA

 $^{\rm c}$ Crosslink density was calculated at temperature 40 $^{\circ}$ C above the T $_{
m g}$

The tendency of the E' at room temperature, T_g and crosslink density for variation of catalyst loading is comparable for all norbornene-functionalized plant oils (for detailed value, see Table C5.2-5.3 and Figure C5.15-5.16, Appendix C). However, the absolute values different depending on the nature of the plant oil. The trend can be observed where the E' and T_g values increased from NB-OO to NB-RO to NB-SO thermoset films (Table 5.2, runs 1, 5, 6 and Figure 5.12). For instance, at 0.5 %wt **G2**, the E' at room temperature increased from 5 to 28 to 40 MPa, and the T_g from -8 to 21 to 24 °C for NB-OO, NB-RO, and NB-SO thermoset films, respectively as shown in Figure 5.12. Likewise, the crosslink density values also increased from 657 to 880 to 895 mol.m⁻³ for NB-OO, NB-RO and NB-SO thermoset films, respectively (Table 5.3, runs 1, 5, 6). In the same order, the amount of polyunsaturated fatty acid intimately related to the average number of norbornene rings per triglyceride of plant oil increases from 1.0 to 1.3 to 1.5 for NB-OO, NB-RO, and NB-SO, respectively. These results revealed that the extra reactive norbornene rings exist in the monomer structure are effectively incorporated into the thermoset film networks, resulting in higher crosslinked thermoset films. Tan δ values of thermoset films were also presented in Table 5.3. It turned out that all three NB-OO, NB-RO and NB-SO thermoset films (at 0.5%wt **G2**) have tan δ values greater 0.3 over a temperature range of approximately 60 °C, making these films have a great potential in damping applications.⁴⁴



Figure 5.12 DMA thermograms for storage modulus and tan δ curves as a function of temperature for thermoset films of different plant oils with 0.5%wt G2 (1 Hz, 3 °C/min).

5.3.6 Dynamic mechanical analysis (DMA) of norbornenefunctionalized plant oils with different crosslinkers

To enhance the crosslinking of the thermoset films resulted in improving T_g values, the ROMP of norbornene-functionalized plant oils was conducted in the presence of crosslinkers. Two different crosslinkers include petroleum-based

norbornene (expressed as CL1) and bio-based norbornene prepared from norbornenefunctionalized isosorbide (NB-IS, expressed as CL2) were applied. DMA analysis for the thermoset films with crosslinkers is shown in Table 5.4 and Figure 5.13. Figure 5.13 shows the storage modulus (E') and tan δ as a function of temperature for plant oilbased thermoset films with different loadings of crosslinkers. Note that no significant changes in both storage modulus (E') and crosslink density of all plant oil-based thermoset films were observed when adding 5 %wt CL1. However, the E' values were an increase of 1.4, 10 and 7.0 times that of neat NB-OO, NB-RO and NB-SO thermoset films, respectively when increasing the amount of CL1 (from 5 to 10 %wt). Similarly, the crosslink densities were also increased by 1.3, 1.3 and 1.9 times that of the neat NB-OO, NB-RO, and NB-SO films, respectively. This revealed that addition of CL1 in the thermoset films results in a more crosslinked polymer network that improves the thermosets' rubbery modulus. Corresponding to the shift of E' increase, T_g values of plant oil-based films at 10 %wt CL1 loading significantly increased from -8, 21 and 24 °C to -2, 34 and 40 °C for NB-OO-CL1, NB-RO-CL1, and NB-SO-CL1, respectively. Further raising the CL1 loading (over 10 %wt CL1) led to brittle material films, which broke during preparation (see Figure 5.13 Appendix C). This would probably be due to the existence of an aromatic ring in the structure of CL1 making the thermoset films become more rigid at a high amount of CL1 loading.

In contrast, both storage modulus (E') and crosslink density as well as T_g values of all plant oil-based thermoset films were dramatically improved in the presence of CL2 even at 5% wt CL2 loading. For instance, the E' at room temperature of NB-OO-CL2, NB-RO-CL2 and NB-SO-CL2 films at 5 %wt CL2 loading is 9.1, 116 and 149 MPa, respectively, an increase of 1.8, 4.2, and 3.7 times that of the neat NB-OO, NB-RO and NB-SO films, respectively. The T_g values of the plant oil-based thermoset films also increased significantly from -8, 21 and 24 °C to 2, 32 and 35 °C for NB-OO-CL2, NB-RO-CL2, and NB-SO-CL2 films, respectively. This is due to the increasing of crosslink density. Increasing the amount of CL2 (from 5 to 10 %wt) in the NB-OO film improved the E' and crosslink density values up to 12.9 MPa and 1167 mol/m³, respectively. Further raising the amount of CL2 loading in the NB-OO film led to brittle material films, which broke during preparation (see Figure C5.17 Appendix C). In contrast, no specimens for DMA could be prepared at 10 %wt CL2 for the NB-RO and NB-SO films because the sample are too brittle and broke during preparation (see Figure C5.13, Appendix C).

 Table 5.4 DMA analysis of the bio-based thermoset films for different plant oils with various crosslinkers.

run ^a	Polymer	E' at 25 ℃	Τ _g	v_e	tan ${f \delta}$	Soluble	Insoluble
		(MPa) ^b	(°C) ^c	(mol/m ³) ^d		(%wt)	(%wt)
1	NB-OO	5.00	-8	657	0.73	9	91
2	NB-OO-5CL1	4.98	-8	658	0.72	10	90
3	NB-OO-10CL1	7.03	-2	878	0.67	9	91
4	NB-OO-5CL2	9.1	2	1055	0.63	6	94
5	NB-OO-10CL2	12.9	7	1167	0.55	6	94
6	NB-RO	27.9	21	880	0.62	4	96
7	NB-RO-5CL1	44.4	26	884	0.66	3	97
8	NB-RO-10CL1	294	34	1112	0.58	3	97
9	NB-RO-5CL2	116	32	1010	0.50	4	96
10	NB-SO	40.0	24	895	0.68	3	97
11	NB-SO-5CL1	41.4	25	1000	0.66	4	96
12	NB-SO-10CL1	278	40	1720	0.59	3	97
13	NB-SO-5CL2	149	35	1408	0.59	4	96

^areactions were conducted at 0.5 %wt G2

^b Storage modulus at 25 °C

^c Glass transition temperature determined by DMA

 $^{
m d}$ Crosslink densities were calculated at temperature 40 °C above the T $_{
m g}$

In comparing the T_g of the plant oil-based thermoset film adding CL1 compared to that one adding CL2, it was found that the T_g values of thermoset films with CL2 were much higher than that of CL1. For example, at 5 %wt crosslinker loading, T_g increase from -8 to 2 °C for NB-OO-CL1 and NB-OO-CL2, respectively. This is due to the relatively short and more rigid of isosorbide in the CL2 lead to the difficulty in chain motions. This result clearly revealed that the bio-based norbornene crosslinker (NB-IS) could replace petroleum-based norbornene as a crosslinker in the polymer network via ROMP.



Figure 5.13 DMA thermograms for storage modulus and tan δ curves for (a) NB-OO, (b) NB-RO, and (c) NB-SO thermoset films with different crosslinkers at 0.5%wt G2 (1 Hz, 3 °C/min).

5.3.7 Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was carried out for measuring thermal stability and degradation behaviors of the thermoset films under N_2 atmosphere. Figure 5.14 shows the representative TGA and DTG curves of NB-OO thermoset films, and the results are summarized in Table 5.5. The degradation temperature for 5% weight loss (T_5) and the maximum degradation temperature (T_{max}) was regarded as the indicators to appraise the thermal stabilities of the thermoset films. TGA curves of the NB-OO thermoset films displays two decomposition stages (Figure 5.14a). The first stage of thermal degradation (250–350 °C) is attributed to evaporation and decomposition of the soluble components (unreacted monomer and oil fragments) in the thermoset films.⁴⁵ The weight loss (%) in the first stage of these thermoset films decreased upon increasing catalyst loading. This is probably due to more effective crosslinking in the thermoset films. Corresponding to this peak in DTG curves (Figure 5.14b) the intensity decreases with increasing catalyst loading indicating less soluble components and oligomers in the thermoset films. This result is consistent with the Soxhlet extraction data. The second stage from 350 to 500 °C is the fastest degradation stage. It represents the main chain degradation of the polymer backbone in the thermoset films such as the cleavage of C=C double bonds and ester groups.



Figure 5.14 (a) TGA and (b) DTG curves of the representative NB-OO thermoset films at various catalysts loading.
As shown in Table 5.5, the T₅ values of the NB-OO films increased when increasing catalyst loading [T₅ = 314 °C, (run 1, 0.0625 %wt **G2**) vs. T₅ = 362 °C (run 4, 0.5 %wt **G2**)]. This is due to the high crosslinked insoluble of the NB-OO films upon increasing catalyst loading. However, all NB-OO thermoset films have approximately the same T_{max} values, around 490 °C. The similar profiles were also observed for thermoset films of NB-RO and NB-SO at various catalyst loadings as shown in Figure C5.18-5.19 (Appendix C).

TGA degradation curve of bio-based thermoset films from different plant oils (olive, rapeseed and soybean oil) with the same catalyst loading (0.5 %wt) presented the same profiles with two main degradation stages as shown in Figure 5.15. The main difference is the degradation process at 5% weight loss. The T₅ value of NB-OO film (T₅ = 362 °C) was much higher than that of NB-RO and NB-SO films (T₅ = 341 °C and 344 °C). This can be explained by the fact that the NB-RO and NB-SO structures have more oxirane (C-O-C) and hydroxyl (-OH) groups on structure than that of NB-OO. The higher number of these groups on the main network of the thermoset films would be probably subjected to the debonding and oxidization at early elevated temperature. However, the T_{max} values of three thermoset films from different plant oils are approximately the same which are around 490 °C. It is worth noting that all thermoset films from different plant oils showed good thermal stability since they all have T₅ temperature higher than 340 °C.



Figure 5.15 (a) TGA and (b) DTG curves of bio-based thermoset polymer films from different plant oils (olive oil, rapeseed oil and soybean oil).

Polymer	T₅ ^a (°⊂)	Т ₅₀ ^ь (°С)	T _{max} ^c (°C)	
NB-OO _{0.5}	362	419	490	
NB-OO _{0.25}	355	418	489	
NB-OO _{0.125}	335	418	487	
NB-OO _{0.0625}	314	414	486	
NB-OO-5CL1	359	419	484	
NB-OO-10CL1	363	424	524	
NB-OO-5CL2	350	418	482	
NB-OO-10CL2	346	419	482	
NB-RO	341	416	486	
NB-RO-5CL1	341	419	486	
NB-RO-10CL1	347	423	484	
NB-RO-5CL2	325	413	480	
NB-SO	344	418	484	
NB-SO-5CL1	330	418	505	
NB-SO-10CL1	347	424	507	
NB-SO-5CL2	314	415	486	

Table 5.5 TGA data for the bio-based thermoset films.

^a Temperature at 5% weight loss

^b Temperature at 50% weight loss

^c Maximum thermal degradation temperature



Figure 5.16 TGA curves of thermoset polymer films (a) NB-OO (b) NB-RO and (c) NB-SO with different crosslinkers.

Figure 5.16 shows TGA degradation curves of thermoset films with different crosslinkers. It turned out that the addition of 5 %wt CL1 decrease the thermoset films initial thermal stability compared to the neat thermoset. However, addition of 10 %wt CL1 led to slightly improve the initial thermal stability of the thermoset films as illustrated in the inserted graph. For example, with 10 %wt CL1 resulting in a 1, 6 and 3 °C increased compared to the neat NB-OO, NB-RO, and NB-SO, respectively. The reason can be due to the formation of pronounced heterogeneity in the polymer network at low CL1 content 5 %wt. In contrast, at higher crosslinker content 10 %wt CL1 the aromatic rings in CL1 structure help to improve the thermal stability of thermoset films. The addition of CL2 (NB-IS) led to a reduction in initial thermal stability, for instance, with 5% CL2 resulting in a 12, 16 and 20 °C decrease compared to the neat NB-OO, NB-RO and NB-SO, respectively. In general, incorporation NB-IS into norbornene plant oil macromolecular chain would decrease the high temperature performances of obtained thermoset films due to the less thermal stability of NB-IS.⁴¹ However, the addition of CL2 did not significant alter the T_{max} values of all thermoset films from different plant oils as shown in Table 5.5 and Figure 5.16.

5.4 Conclusions

Bio-based thermoset films were successfully prepared by ring-opening metathesis polymerization (ROMP) of norbornene-functionalized different plant oils (olive oil, rapeseed oil, and soybean oil) in the presence of **G2** catalyst. An increasing catalyst loading led to increase considerably the storage modulus (E') and glass transition temperature (T_g) as well as decrease extracted components (unreacted or oligomeric polymers) in the resultant thermoset films due to the enhanced the crosslink density. The catalyst loading determined to be most effective was 0.5 %wt. Comparing different plant oil, the amount of polyunsaturated fatty acids in the plant oil structure related to the number of norbornene rings per triglyceride influences the material properties significantly. The higher number of norbornene rings in the starting material afforded a more efficient ROMP and thus improved crosslink density, result in higher E' and T_g values. In general, the thermoset films showed thermal stability up to

340 °C. Addition of renewable norbornene-isosorbide crosslinker (NB-IS) led to increase significantly the T_g and E' values of all bio-based plant oil films, however, the initial thermal stability T_5 was slightly reduced. It thus believes that the renewable norbornene crosslinker (NB-IS) is comparative to alternative petroleum-based norbornene in target to improve the thermo-mechanical properties of thermoset polymers.

5.5 References

- 1. Xia, Y.; Larock, R. C., Vegetable oil-based polymeric materials: synthesis, properties, and applications. *Green Chem.* 2010, 12, 1893-1909.
- 2. Gandini, A., Polymers from Renewable Resources: A Challenge for the Future of Macromolecular Materials. *Macromolecules* 2008, 41, 9491-9504.
- 3. Gandini, A.; Lacerda, T. M., From monomers to polymers from renewable resources: Recent advances. *Prog. Polym. Sci.* 2015, 48, 1-39.
- Le, D.; Samart, C.; Kongparakul, S.; Nomura, K., Synthesis of new polyesters by acyclic diene metathesis polymerization of bio-based α,ω-dienes prepared from eugenol and castor oil (undecenoate). *RSC Adv.* 2019, 9, 10245-10252.
- Lu, Y.; Larock, R. C., Novel Polymeric Materials from Vegetable Oils and Vinyl Monomers: Preparation, Properties, and Applications. *Chem. Sus. Chem.* 2009, 2, 136-147.
- Zhang, C.; Garrison, T. F.; Madbouly, S. A.; Kessler, M. R., Recent advances in vegetable oil-based polymers and their composites. *Prog. Polym. Sci.* 2017, 71, 91-143.
- 7. Liu, K.; Madbouly, S. A.; Kessler, M. R., Biorenewable thermosetting copolymer based on soybean oil and eugenol. *Eur. Polym. J.* 2015, 69, 16-28.
- 8. Gandini, A.; Lacerda, T. M.; Carvalho, A. J. F.; Trovatti, E., Progress of Polymers from Renewable Resources: Furans, Vegetable Oils, and Polysaccharides. *Chem. Rev.* 2016, 116, 1637-1669.

- 9. Over, L. C.; Hergert, M.; Meier, M. A. R., Metathesis Curing of Allylated Lignin and Different Plant Oils for the Preparation of Thermosetting Polymer Films with Tunable Mechanical Properties. *Macromol. Chem. Phys.* 2017, 218, 1700177.
- Shearouse, W. C.; Lillie, L. M.; Reineke, T. M.; Tolman, W. B., Sustainable Polyesters Derived from Glucose and Castor Oil: Building Block Structure Impacts Properties. ACS Macro. Lett. 2015, 4, 284-288.
- 11. Galbis, J. A.; García-Martín, M. d. G.; de Paz, M. V.; Galbis, E., Synthetic Polymers from Sugar-Based Monomers. *Chem. Rev.* 2016, 116, 1600-1636.
- Shaghaleh, H.; Xu, X.; Wang, S., Current progress in production of biopolymeric materials based on cellulose, cellulose nanofibers, and cellulose derivatives. *RSC Adv.* 2018, 8, 825-842.
- Le, D.; Kongparakul, S.; Samart, C.; Phanthong, P.; Karnjanakom, S.; Abudula, A.;
 Guan, G., Preparing hydrophobic nanocellulose-silica film by a facile one-pot method. *Carbohyd. Polym.* 2016, 153, 266-274.
- Ganewatta, M. S.; Ding, W.; Rahman, M. A.; Yuan, L.; Wang, Z.; Hamidi, N.; Robertson, M. L.; Tang, C., Biobased Plastics and Elastomers from Renewable Rosin via "Living" Ring-Opening Metathesis Polymerization. *Macromolecules* 2016, 49, 7155-7164.
- Rahman, M. A.; Lokupitiya, H. N.; Ganewatta, M. S.; Yuan, L.; Stefik, M.; Tang, C., Designing Block Copolymer Architectures toward Tough Bioplastics from Natural Rosin. *Macromolecules* 2017, 50, 2069-2077.
- 16. Ma, Q.; Liu, X.; Zhang, R.; Zhu, J.; Jiang, Y., Synthesis and properties of full biobased thermosetting resins from rosin acid and soybean oil: the role of rosin acid derivatives. *Green Chem.* 2013, 15, 1300-1310.
- 17. Feedstocks for the Future, Copyright, Foreword. In Feedstocks for the Future, American Chemical Society: 2006; Vol. 921, pp i-v.
- Biermann, U.; Friedt, W.; Lang, S.; Lühs, W.; Machmüller, G.; Metzger, J. O.; Rüsch gen. Klaas, M.; Schäfer, H. J.; Schneider, M. P., New Syntheses with Oils and Fats as Renewable Raw Materials for the Chemical Industry. *Angew. Chem. Int. Ed.* 2000, 39, 2206-2224.

- 19. Meier, M. A. R.; Metzger, J. O.; Schubert, U. S., Plant oil renewable resources as green alternatives in polymer science. *Chem. Soc. Rev.* 2007, 36, 1788-1802.
- 20. Montero de Espinosa, L.; Meier, M. A. R., Plant oils: The perfect renewable resource for polymer science?! *Eur. Polym. J.* 2011, 47, 837-852.
- Jian, X.-Y.; An, X.-P.; Li, Y.-D.; Chen, J.-H.; Wang, M.; Zeng, J.-B., All Plant Oil Derived Epoxy Thermosets with Excellent Comprehensive Properties. *Macromolecules* 2017, 50, 5729-5738.
- 22. Mashouf Roudsari, G.; Mohanty, A. K.; Misra, M., Study of the Curing Kinetics of Epoxy Resins with Biobased Hardener and Epoxidized Soybean Oil. *ACS Sustain. Chem. Eng.* 2014, 2, 2111-2116.
- 23. Zhang, C.; Madbouly, S. A.; Kessler, M. R., Biobased Polyurethanes Prepared from Different Vegetable Oils. *ACS Appl. Mater. Inter.* 2015, 7, 1226-1233.
- 24. Tanaka, R.; Hirose, S.; Hatakeyama, H., Preparation and characterization of polyurethane foams using a palm oil-based polyol. *Bioresour. Technol.* 2008, 99, 3810-3816.
- 25. Valverde, M.; Andjelkovic, D.; Kundu, P. P.; Larock, R. C., Conjugated lowsaturation soybean oil thermosets: Free-radical copolymerization with dicyclopentadiene and divinylbenzene. *J. Appl. Polym. Sci.* 2008, 107, 423-430.
- 26. Henna, P. H.; Andjelkovic, D. D.; Kundu, P. P.; Larock, R. C., Biobased thermosets from the free-radical copolymerization of conjugated linseed oil. *J. Appl. Polym. Sci.* 2007, 104, 979-985.
- 27. Andjelkovic, D. D.; Valverde, M.; Henna, P.; Li, F.; Larock, R. C., Novel thermosets prepared by cationic copolymerization of various vegetable oils-synthesis and their structure–property relationships. *Polymer* 2005, 46, 9674-9685.
- 28. Sharma, V.; Banait, J. S.; Larock, R. C.; Kundu, P. P., Morphological and Thermal Characterization of Linseed-Oil Based Polymers from Cationic and Thermal Polymerization. *J. Polym. Environ*. 2010, 18, 235-242.
- 29. Rybak, A.; Meier, M. A. R., Acyclic Diene Metathesis with a Monomer from Renewable Resources: Control of Molecular Weight and One-Step Preparation of Block Copolymers. *Chem. Sus. Chem.* 2008, 1, 542-547.

- Henna, P.; Larock, R. C., Novel thermosets obtained by the ring-opening metathesis polymerization of a functionalized vegetable oil and dicyclopentadiene. J. Appl. Polym. Sci. 2009, 112, 1788-1797.
- Henna, P. H.; Larock, R. C., Rubbery Thermosets by Ring-Opening Metathesis Polymerization of a Functionalized Castor Oil and Cyclooctene. *Macromol. Mater. Eng.* 2007, 292, 1201-1209.
- 32. Mauldin, T. C.; Haman, K.; Sheng, X.; Henna, P.; Larock, R. C.; Kessler, M. R., Ringopening metathesis polymerization of a modified linseed oil with varying levels of crosslinking. *J. Polym. Sci. Pol. Chem.* 2008, 46, 6851-6860.
- 33. Fernandes, H.; Souza Filho, M. R.; Silva Sa, R. M.; Lima-Neto, S. B. Bio-based plant oil polymers from ROMP of norbornene modified with triglyceride from crude red palm olein. RSC Adv., 2017, 6, 75104–75110.
- 34. Xia, Y.; Lu, Y.; Larock, R. C., Ring-opening metathesis polymerization (ROMP) of norbornenyl-functionalized fatty alcohols. *Polymer* 2010, 51, 53-61.
- 35. Xia, Y.; Larock, R. C., Castor oil-based thermosets with varied crosslink densities prepared by ring-opening metathesis polymerization (ROMP). *Polymer* 2010, 51, 2508-2514.
- 36. Ding, R.; Xia, Y.; Mauldin, T. C.; Kessler, M. R., Biorenewable ROMP-based thermosetting copolymers from functionalized castor oil derivative with various cross-linking agents. *Polymer* 2014, 55, 5718-5726.
- Hong, J.; Radojčić, D.; Ionescu, M.; Petrović, Z. S.; Eastwood, E., Advanced materials from corn: isosorbide-based epoxy resins. *Polym. Chem.* 2014, 5, 5360-5368.
- 38. Wang, B.-T.; Lu, F.-D.; Xu, F.; Li, Y.-Z.; Kessler, M. R., Synthesis of renewable isosorbide-based monomer and preparation of the corresponding thermosets. *Chinese Chem. Lett.* 2016, 27, 875-878.
- 39. Rose, M.; Palkovits, R., Isosorbide as a Renewable Platform chemical for Versatile Applications—Quo Vadis? *Chem. Sus. Chem.* 2012, 5, 167-176.
- 40. Kristufek, T. S.; Kristufek, S. L.; Link, L. A.; Weems, A. C.; Khan, S.; Lim, S.-M.; Lonnecker, A. T.; Raymond, J. E.; Maitland, D. J.; Wooley, K. L., Rapidly-cured

isosorbide-based cross-linked polycarbonate elastomers. *Polym. Chem.* 2016, 7, 2639-2644.

- 41. Wang, B.; Mireles, K.; Rock, M.; Li, Y.; Thakur, V. K.; Gao, D.; Kessler, M. R., Synthesis and Preparation of Bio-Based ROMP Thermosets from Functionalized Renewable Isosorbide Derivative. *Macromol. Chem. Phys.* 2016, 217, 871-879.
- 42. Ravve, A., Physical Properties and Physical Chemistry of Polymers. In *Principles of Polymer Chemistry*, Ravve, A., Ed. Springer New York: New York, NY, 2012; pp 17-67.
- 43. Rubber-Like Elasticity. In *Mechanical Properties of Solid Polymers*, pp 61-85.
- 44. Li, F.; Larock, R. C., New soybean oil-Styrene-Divinylbenzene thermosetting copolymers—IV. Good damping properties. *Polym. Adv. Technol.* 2002, 13, 436-449.
- 45. Andjelkovic, D. D.; Larock, R. C., Novel Rubbers from Cationic Copolymerization of Soybean Oils and Dicyclopentadiene. 1. Synthesis and Characterization. *Biomacromolecules* 2006, 7, 927-936.

CHAPTER 6 GENERAL CONCLUSIONS

6.1 General conclusions

In this research, a variety of example of the utilization of renewable resources exemplified vegetable oil derivatives for the synthesis of organic building blocks and polymers have been described. The olefin metathesis has been shown as a suitable chemical transformation for monomers synthesis via cross-metathesis (CM) and for the polymerization of renewable monomers via ADMET and ROMP in the presence of ruthenium-based catalysts. The detailed results are described as follows:

The first topic reported on cross-metathesis (CM) of various renewable unsaturated fatty acid methyl esters (MO, MP, and ME) in the vegetable oils with eugenol (UG). These CM reactions were successfully conducted by ruthenium-carbene catalyst (**G2**) under environmentally benign conditions (in isopropanol and ethanol at 50 °C). The reaction conditions could be optimized to reach high substrate conversion with high CM selectivity, particularly for CM of MO with UG. It turned out that both the MO conversion and selectivity of CM products were highly affected by initial MO concentration, UG/MO molar ratio, and reaction temperature. The catalyst performance was also affected by the substrate employed (in the order of MP> MO> ME); it seems that olefinic double bond relatively close to the methyl showed better performance in the CM reaction with UG. It was also revealed that the subsequent isomerization of either UG or fatty acid methyl esters *in situ* significantly affect the CM and the SM products yields. The obtained CM products exemplified CM2 and CM4 can be used as precursors for the synthesis of polyesters.

The second topic described a simple way to synthesis of new polyesters by ADMET polymerization of α, ω -dienes, 4-allyl-2-methoxyphenyl 10-undecenoate (M1), prepared from bio-renewable eugenol (obtained from clove oil) and 10undecenoic acid derivative (obtained from castor oil). Ruthenium-carbene (called second generation Grubbs) catalyst afforded polymers with unimodal molecular weight distributions (M_n = 12700, M_w/M_n = 1.85). The polymerization of M1 in the presence of triarm cross-linker, 5-formylbenzene-1,2,3-triyl tris(undec-10-enoate), also afforded certain network polymers, suggested by NMR spectra and DSC thermogram. Since 9-decenoate obtained from the other vegetable oil (e.g. methyl oleate) by ethenolysis, should be used in place of 10-undecenoate, also since, as described in the introductory, further chemical modification can be possible from functional group (methoxy group) in the resultant polymers (P1, PL1), it thus believes that the present approach is promising and should be applicable for synthesis of polyesters from monomers prepared from bio-renewable resources.

The third topic focused on the synthesis of bio-based thermoset films via ring-opening metathesis polymerization (ROMP) of norbornene-functionalized different plant oils (olive oil, rapeseed oil, and soybean oil) in the presence of a rutheniumcarbene (called second-generation Grubbs) catalyst. An increasing catalyst loading led to increase considerably the storage modulus (E') and glass transition temperature (T_{ρ}) as well as decrease extracted (unreacted or oligomeric) components in the resultant thermoset films due to the enhanced the crosslink density. The catalyst concentration determined to be most effective in this study was 0.5 %wt. Comparing different plant oil, the amount of polyunsaturated fatty acids in the plant oil structure related to the number of norbornene rings per triglyceride influences the material properties significantly. The higher number of norbornene rings in the starting material afforded a more efficient ROMP and thus improved crosslink density, result in higher E' and T_e values. Addition of renewable norbornene-isosorbide crosslinker led to increase significantly the glass transition temperature and storage modulus properties of all biobased plant oil films. It thus believes that the renewable norbornene crosslinker (NB-IS) is comparative to alternative petroleum-based norbornene in target to improve the thermo-mechanical properties of thermoset polymers. These plant oil-based thermosets represent another promising route to environmentally friendly thermoset polymers.

The results summarized above demonstrate the attempt dedicated to the development of environmentally friendly methodologies for the synthesis of organic compounds, precursor monomers, and polymers from bio-renewable resources. All procedures display some interesting advantages over the conventional synthetic ways

within the minimization of waste production and the concomitant benefit of using starting materials from bio-renewable resources. Therefore, through this research, we have contributed to the production of monomers and polymers by sustainable reactions with vegetable oil derivatives.

6.2 Recommendations

We considered that the works in this research can be further investigated to both improve current sustainable approaches and develop final products in some aspects as follows.

In the first topic, the CM reactions of unsaturated fatty acid methyl esters with eugenol afforded high conversion and CM selectivity by using excess of UG. It should be further study of recovery and reusability of eugenol in the CM reaction. On the order hand, the CM products (e.g. CM2 and CM4) can be further used as starting material for preparing various monomer precursors potential to produce polyesters.

In the second topic, the utilization of 9-decenoate obtained from the other vegetable oil (e.g. methyl oleate) by ethenolysis can be further study to replace 10undecenoate for synthesis of α, ω -dienes. The further chemical modification can be possible from functional group (methoxy group) in the resultant polymers.

In the third topic, the various norbornene functionalized plant oils and isosorbide can be further study as a binder for application in batteries synthesis.



APPENDICES

APPENDIX A EFFICIENT CONVERSION OF RENEWABLE UNSATURATED FATTY ACID METHYL ESTERS BY CROSS METATHESIS WITH EUGENOL





(i) The effective carbon number (ECN) of materials

Figure A3.1 ECN of the starting material and products for the cross-metathesis of methyl oleate (MO) with eugenol (UG).



Figure A3.2 ECN of the starting material and products for the cross-metathesis of methyl petroselinate (MP) with eugenol (UG).







Figure A3.4 ECN of the starting material and products for the cross-metathesis of methyl 10-undecanoate (MU) with eugenol (UG).

(ii) GC-FID and GC-MS chromatogram for cross-metathesis reaction of methyl esters (MO, MP, ME and MU) with eugenol (UG)

2.1 Cross-metathesis of methyl oleate (MO) with eugenol (UG) using ruthenium catalysts

Cross-metathesis reaction of MO with UG afforded four types of CM products involving dec-1-ene (CM1, m/z 140), methyl dec-9-enoate (CM2, m/z 184), 2-methoxy-4-(undec-2-en-1-yl)phenol (CM3, m/z 276) and methyl 11-(4-hydroxy-3-methoxyphenyl)undec-9-noate (CM4, m/z 320), which were observed at retention time of 12.6 (CM1), 17.5 (*cis*-CM2), 17.6 (*trans*-CM2), 32.1 (*cis*-CM3), 31.9 (*trans*-CM3) and 55.5 (*cis*-CM4), 55.2 (*trans*-CM4) min, respectively (Figure A3.5). In addition, self-metathesis products consisting of 9-octadecene (SM1, m/z 252), dimethyl octadec-9-enedioate (SM2, m/z 340) appeared at 22.5 (*cis*-SM1), 22.6 (*trans*-SM1) and 47.3 (*cis*-SM2), 48.0 (*trans*-SM2) min, respectively. The self-metathesis of eugenol (SM4, m/z 300) was observed at 63.3 min, while MO, SM3, m/z 296 which is the starting material methyl oleate appeared at 29.3 (*cis*), 29.5 (*trans*) min on GC chromatogram. The peak appeared at retention time of 18.96 min was assigned to isomerization of UG (isoeugenol, m/z 164) (Figure A3.5). GC-MS chromatogram and the mass fragmentation of patterns of each peak are shown in Figure A3.6.



Figure A3.5 GC-FID chromatogram for the CM reaction of MO with UG.





Figure A3.6 (a) GC-MS chromatogram for the CM reaction of MO with UG and (b) MS fragmentation patterns of the cross-metathesis products.



Cross-metathesis of MO with UG: Study of reaction time

Figure A3.7 Overlay GC-FID for CM of MO with UG at various reaction times by G2 (MO = 2.0 mmol, T= 50 °C, UG/MO= 10 eq., solvent ethanol, MO concentration of 10 M).

Table A3.	1 Cross-metathe	sis of MO wit	th UG by C	52 – yield	of self-met	athesis	product
(SM4) and	isoeugenol/euge	enol ratio (iso	oUG/UG). ^a				

		Metathesis products (%) ^c									
run	Time (min)	MO conv. (%) ^b	CM1	CM2	CM3	CM4	SM1	SM2	SM3	SM4	isoUG/UG ratio ^d x10 ²
13	5	72	31	36	17	18	1	1	23	4	0.6
8	10	91	31	48	17	21	1	1	7	9	1.3
14	30	96	44	60	15	17	1	1	3	12	1.4

^aConditions: 2.00 mmol of methyl oleate, solvent ethanol, MO concentration 10.0 M, UG/MO = 10/1, catalyst (**G2**) 0.002 mmol, temperature 50 °C. ^bConversion of MO estimated by GC using internal standard. ^cGC yield estimated according to the effect of carbon number (ECN) rule. ^disoeugenol/eugenol ratio.



Cross-metathesis of MO with UG: Study of UG/MO molar ratios





Cross-metathesis of MO with UG: Study of reaction temperature

Figure A3.9 Overlay GC-FID for CM of MO with UG at various reaction temperature by G2 (MO = 2.0 mmol, time = 10 min, UG/MO= 10 eq., solvent ethanol, MO concentration of 10.0 M).

Table A3.2 Content of UG isomerization (isoeugenol) in CM of MO with UG: Effect of reaction temperature.^{*a*}

Te run (Temp	MO conv. (%) ^b	Metathesis products (%) ^c								isoUG/UG
	(°C)		CM1	CM2	CM3	CM4	SM1	SM2	SM3	SM4	ratio ^d x10 ²
18	25	48	15	20	10	9	1	0	41	2	0.9
8	50	91	31	48	17	21	1	1	7	9	1.3
19	80	91	35	47	14	11	1	1	8	1	7.5

^aConditions: 2.00 mmol of methyl oleate, solvent ethanol, MO concentration 10.0 M, UG/MO = 10/1, catalyst (**G2**) 0.002 mmol, time 20 min. ^bConversion of MO estimated by GC using internal standard. ^cGC yield estimated according to the effect of carbon number (ECN) rule. ^disoeugenol/eugenol ratio.



Cross-metathesis of MO with UG: Study of different types of ruthenium catalysts

Figure A3.10 Overlay GC-FID for CM of MO with UG at different types of catalysts (MO = 2.0 mmol, T= 50 ° C, UG/MO= 10 eq., solvent ethanol, MO concentration of 10.0 M).

2.2 Cross metathesis of Methyl petroselinate (MP) with Eugenol (UG)

Cross-metathesis reaction of MP with UG afforded four CM products involving tridec-1-ene (CM1, m/z 182), methyl hept-6-enoate (CM2, m/z 142), 2methoxy-4-(tetradec-2-en-1-yl)phenol (CM3, m/z 319) and methyl 8-(4-hydroxy-3methoxyphenyl)oct-6-enoate (CM4, m/z 278), which were observed at retention time of 17.5 (CM1), 12.7 (CM2), 53.6 (CM3) and 32.0 (*trans*-CM4), 32.2 (*cis*-CM4) min, respectively. The self-metathesis products consisting of tetracos-12-ene (SM1, m/z 337) and dimethyl dodec-6-enedioate (SM2, m/z 256) appeared at 44.9 (*cis*-SM1), 45.8 (*trans*-SM1) and 22.7 (SM2) min, respectively, while (MP, SM3, m/z 296) which is the starting material MP appeared at 29.1 (*cis*) and 29.3 (*trans*) min on GC chromatogram (Figure A3.11). GC-MS chromatogram and the mass fragmentation of patterns of each peak are shown in Figure A3.12.









Figure A3.12 (a) GC-MS chromatogram for the CM reaction of MP with UG and (b) MS fragmentation patterns of the CM products.

2.3 Cross-metathesis of Methyl erucate (ME) with Eugenol (UG)

Cross-metathesis reaction of ME with UG created four types of CM products including dec-1-ene (CM1, m/z 140), methyl tetradec-13-enoate (CM2, m/z 240), 2-methoxy-4-(undec-2-en-1-yl)phenol (CM3, m/z 276) and methyl 15-(4-hydroxy-3-methoxyphenyl)pentadec-13-enoate (CM4, m/z 376), which were observed at retention time of 12.5 (CM1), 21.6 (*trans*-CM2), 21.7 (*cis*-CM2), 31.7 (*trans*-CM3), 31.9 (*cis*-CM3) min, respectively. The SM product consisting of octadec-9-ene (SM1, m/z 252) appeared at 22.5 (*cis*-SM1) and 22.6 (*trans*-SM1) min, while (ME, SM3, m/z 353) which is the starting material methyl erucate appeared at 57.4 (*cis*) and 58.5 (*trans*) min on GC chromatogram (Figure A3.13). GC-MS chromatogram and the mass fragmentation of patterns of each peak are shown in Figure A3.14.



Figure A3.13 GC-FID chromatogram for the CM reaction of ME with UG.



Figure A3.14 (a) GC-MS chromatogram for the CM reaction of ME with UG and (b) MS fragmentation patterns of the cross-metathesis products.

2.4 Cross-metathesis of methyl 10-undecanoate (MU) with eugenol

(UG)

Cross-metathesis reaction of MU with UG afforded Methyl 12-(4hydroxy-3-methoxyphenyl)dodec-10-enoate (CM1, m/z 334) product, which was observed at 69.1 (CM1) min. The SM products consisting of dimethyl icos-10-enedioate (SM1, m/z 369) and 4,4'-(but-2-ene-1,4-diyl)bis(2-methoxyphenol) (SM2, m/z 300) appeared at 75.5 (SM1) and 61.8 (SM2) min, respectively on GC chromatogram (Figure A3.15). GC-MS chromatogram and the mass fragmentation of patterns of each peak are shown in Figure A3.16.



Figure A3.15 GC-FID chromatogram for the CM reaction of MU with UG.





Figure A3.16 (a) GC-MS chromatogram for the CM reaction of MU with UG and MS fragmentation patterns of the cross-metathesis products.

(iii) ¹³C NMR spectroscopy of cross-metathesis products of MO with UG

Dec-1-ene (CM1): ¹³C NMR (125 MHz, CDCl₃, ppm): **δ** 14.1 (s, CH₃), 22.7 (s, CH₂), 28.9 (s, CH₂), 29.1 (s, CH₂), 29.3 (s, CH₂), 29.4 (s, CH₂), 31.9 (s, CH₂), 33.8 (s, CH₂), 114.0 (s, CH₂), 139.2 (s, CH).



Figure A3.17 ¹³C-NMR spectra (in CDCl₃ at 25 °C) of dec-1-ene (CM1).

Methyl dec-9-enoate (CM2): ¹³C NMR (125 MHz, CDCl₃, ppm): δ 24.9 (s, CH₂), 29.0 (s, CH₂), 29.4 (s, CH₂), 29.6 (s, CH₂), 29.7 (s, CH₂), 33.7 (s, CH₂), 34.1 (s, CH₂), 51.3 (s, CH₃), 114.1 (s, CH₂), 139.0 (s, CH), 174.2 (s, C).





2-methoxy-4-(undec-2-en-1-yl)phenol (CM3): ¹³C NMR (125 MHz, CDCl₃, ppm): **δ** 14.1 (s, CH₂), 22.7 (s, CH₂), 29.3 (s, CH₂), 29.7 (s, 2CH₂), 29.9 (s, CH₂), 31.9 (s, CH₂), 33.7 (s, CH₂), 39.4 (s, CH₂), 56.1 (s, CH₃), 111.3 (s, CH), 115.5 (s, CH), 122.7 (s, CH), 126.1 (s, CH), 132.1 (s, CH), 133.5 (s, C), 145.7 (s, C), 147.4 (S, C).



Figure A3.19 ¹³C NMR spectra of 2-methoxy-4-(undec-2-en-1-yl)phenol (CM3)

Methyl 11-(4-hydroxy-3-methoxyphenyl)undec-9-noate) (CM4): ¹³C NMR (125 MHz, CDCl₃, ppm): δ 24.9 (s, CH₂), 29.0 (s, CH₂), 29.3 (s, CH₂), 29.5 (s, CH₂), 32.3 (s, CH₂), 33.0 (s, CH₂), 34.0 (s, CH₂), 38.6 (s, CH₂), 51.4 (s, CH₃), 55.7 (s, CH₃), 111.0 (s, CH), 114.1 (s, CH), 120.9 (s, CH), 129.1 (s, CH), 131.7 (s, CH), 132.9 (s, C), 143.6 (s, C), 146.3 (s, C), 174.3 (C).





4,4'-(but-2-ene-1,4-diyl)bis(2-methoxyphenol) (SM4): ¹³C NMR (125 MHz, CDCl₃, ppm): δ 38.5 (s, CH₂), 55.7 (s, CH₃), 111.0 (s, CH), 114.1 (s, CH), 120.9 (s, CH), 130.5 (s, CH), 132.6 (s, C), 143.7 (s, C), 146.3 (s, C).



Figure A3.21 ¹³C NMR spectra (in CDCl₃ at 25 °C) of 4,4'-(but-2-ene-1,4-diyl)bis(2-methoxyphenol) (SM4).

APPENDIX B

Synthesis of New Polyesters by acyclic diene metathesis polymerization of Bio-Based α, ω -Dienes prepared from Eugenol and Castor Oil (Undecendate)



(i) Atmospheric pressure chemical ionization (APCI) mass spectra of monomers and crosslinker



Figure B4.1 APCI mass spectrum of 4-allyl-2-methoxyphenyl 10-undecenoate (M1).



Figure B4.2 APCI mass spectrum of 5-formylbenzene-1,2,3-triyl tris(undec-10-enoate) **(CL)**.



Figure B4.3 APCI mass spectrum of 5-hexen-1-yl 10-undecenoate (M2)



Figure B4.4 APCI mass spectrum of 10-undecen-1-yl 10-undecenoate (M3).

(ii) ¹³C NMR spectroscopy of polymers

Polymer P2 (sample run 14): ¹³C NMR (125 MHz, CDCl₃, ppm): δ 25.2 (CH₂), 25.9 (CH₂), 28.3 (CH₂), 29.2 (CH₂), 29.3 (CH₂), 29.4 (CH₂), 29.5 (CH₂), 32.3 (CH₂), 32.7 (CH₂), 32.8 (CH₂), 34.5 (CH₂), 64.3 (-COOCH₂-), 130.4 (-CH=CH-), 174.1 ppm (-COO-).



Figure B4.5 13 C NMR spectrum (in CDCl₃ in 25 °C) for (a) monomer (M2) and (b) polymer (P2).

Polymer P3 (sample run 19). ¹³C NMR (125 MHz, CDCl₃, ppm): δ 25.2 (CH₂), 26.1 (CH₂), 28.8 (CH₂), 29.3 (CH₂), 29.4 (CH₂), 29.5 (CH₂), 29.6 (CH₂), 29.7 (CH₂), 29.8 (CH₂), 29.9 (CH₂), 32.7 (CH₂), 34.5 (CH₂), 64.5 (-COOCH₂-), 130.5 (-CH=CH-), 174.1 ppm (-COO-).



Figure B4.6 ¹³C NMR spectrum (in CDCl₃ in 25 °C) for (a) monomer (M3) and (b) polymer (P3).
APPENDIX C SYNTHESIS OF RENEWABLE THERMOSET FILMS BY RING-OPENING METATHESIS POLYMERIZATION (ROMP) OF NORBORNENE-FUNCTIONALIZED PLANT OILS





Figure C5.1 GC-MS chromatogram of derivatized soybean oil.





Figure C5.2 MS fragmentation patterns of derivatized soybean oil.



Figure C5.3 Photo of plant oils (olive oil, rapeseed oil, soybean oil) and their epoxidized plant oil and norbornene-plant oil.



Figure C5.4 Photo of norbornene functionalized isosorbide (NB-IS).



Figure C5.5 1 H NMR spectra (in CDCl₃ at 25 °C) of rapeseed oil (RO), epoxidized rapeseed oil (ERO) and norbornene-functionalized rapeseed oil (NB-RO).



Figure C5.6 ¹H NMR spectra (in CDCl₃ at 25 °C) of soybean oil (SO), epoxidized soybean oil (ESO) and norbornene-functionalized soybean oil (NB-SO).



Figure C5.7 ¹H NMR spectrum (in CDCl₃ at 25 °C) of epoxidized olive oil (EOO).

Integrated from ¹H NMR of EOO:

The average number of oxirane rings per triglyceride was calculated by total peaks area of oxirane (I + j) divided to peak area of triglyceride (α)

Total peaks area of oxirane was calculated by Sum of peaks area (i + j) to be 2.9375 Total peaks area of triglyceride was calculated by Sum of peak area (α) to be 2.2403 The average number of oxirane rings per triglyceride is 2.9375/2.2403= 1.31



Figure C5.8 13 C NMR spectra (in CDCl₃ at 25 °C) of (a) olive oil (OO) and (b) norbornene-functionalized olive oil (NB-OO).



Figure C5.9 13 C NMR spectra (in CDCl₃ at 25 °C) of (a) rapeseed oil (RO) and (b) norbornene-functionalized rapeseed oil (NB-RO).



Figure C5.10 13 C NMR spectra (in CDCl₃ at 25 °C) of (a) soybean oil (SO) and (b) norbornene-functionalized soybean oil (NB-SO).



Figure C5.11 FT-IR spectra of soybean oil (RO), epoxidized soybean oil (ERO), norbornene-functionalized soybean oil (NB-RO) and thermoset polymer film NB-RO.



Figure C5.12 FT-IR spectra of soybean oil (SO), epoxidized soybean oil (ESO), norbornene-functionalized soybean oil (NB-SO) and thermoset polymer film NB-SO.



Figure C5.13 1 H NMR spectrum (in CDCl₃ at 25 °C) of crosslinker (NB-IS).

Integrated from ¹H NMR of NB-IS:

Total peaks area of IS was calculated by Sum of peaks area (a + b + c + d + e + f + g) to be 7.342

Total peaks area of NB was calculated by Sum of peaks area (1 + 2 + 4 + 5 + 6 + 6') to be 3.2342

Area ratio of IS/NB = 7.3487/3.2342= 2.27



Figure C5.14 Photo of NB-OO thermoset films with various catalyst loading from 0.0625 to 0.5 %wt **G2**.

Polymer	Cat. (G2)	Cured temp.	Soluble	Insoluble
	(%wt)	(°C)	(%wt)	(%wt)
NB-RO	0.5		4	96
	0.25	120	13	87
	0.125	120	29	71
	0.0625		53	47
NB-SO	0.5	556	3	97
	0.25	120	14	86
	0.125	120	24	76
	0.0625		28	72

Table C5.1 Extraction data of bio-based thermoset films (NB-RO and NB-SO) for various catalyst loadings.



Figure C5.15 DMA thermograms for storage modulus and tan δ curves as function of catalyst concentration for NB-RO thermoset films (1 Hz, 3 °C/min).

Polymer	Cat. (G2) (%wt)	E' at 25 °C (MPa)ª	T _g (℃) ^b	v_e (mol/m ³) ^c	tan δ
	0.5	27.9	21	880	0.62
NB-RO	0.25	4.69	11	415	0.90
	0.125	1.93	3	217	1.28

Table C5.2 DMA analysis of the bio-based NB-RO thermoset films at various catalystloadings.

^a Storage modulus at 25 °C

 $^{\text{b}}$ Glass transition temperature determined by DMA at the maximum of the tan δ curves

^c Crosslink densities were calculated at temperature 40 °C above the T_g



Figure C5.16 DMA thermograms for storage modulus and tan δ curves as function of temperature for NB-SO thermoset films (1 Hz, 3 °C/min).

Polymer	Cat. (G2)	E' at 25 ℃	Τ _g	v_e	top 8
	(%wt)	(MPa) ^a	(°C) ^b	(mol/m ³) ^c	
NB-SO	0.5	40.0	24	895	0.68
	0.25	7.27	13	594	0.88
	0.125	2.72	5	326	1.06
	0.0625	2.70	4	287	1.13

Table C5.3 DMA analysis of the bio-based NB-SO thermoset films at various catalystloadings.

^a Storage modulus at 25 °C

 $^{\text{b}}$ Glass transition temperature determined by DMA at the maximum of the tan δ curves

 $^{\rm c}$ Crosslink densities were calculated at temperature 40 °C above the $\rm T_g$



Figure C5.17 Photo bio-based thermoset films from plant oil-norbornene with different crosslinkers (CL1 and CL2) broken during the preparation.



Figure C5.18 (a) TGA and (b) DTG curves of NB-RO polymer film thermoset at various catalysts loading.



Figure C5.19 (a) TGA and (b) DTG curves of NB-SO polymer film thermoset at various catalysts loading.

BIOGRAPHY

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Publications

- 1. <u>Duy, L</u>., Chanatip, S., Suwadee, K., Kotohiro, N. Preparation of Renewable Thermoset Films by Ring-Opening Metathesis Polymerization of Norbornene-Functionalized Plant Oils. Manuscript prepared., 2019.
- <u>Duy, L</u>., Chanatip, S., Suwadee, K., Kotohiro, N. Synthesis of new polyesters by acyclic diene metathesis polymerization of bio-based α,ω-dienes prepared from eugenol and castor oil (undecenoate). *RSC Adv.*, 2019, 9, 10245- 10252.

- 3. <u>Duy, L</u>., Chanatip, S, Ken, T., Kotohiro, N., Suwadee, K. Efficient Conversion of Renewable Unsaturated Fatty Acid Methyl Esters by Cross-Metathesis with Eugenol. *ACS Omega*, 2018, 9, 11041-11049.
- Jittrapon, S., <u>Duy, L</u>., Chanatip, S., Hideo, S., Masakazu, N., Narong, C., Suwadee, K., Suda, K. Superhydrophobic Coating from Fluoroalkylsilane Modified Natural Rubber Encapsulated SiO₂ Composites for Self-Driven Oil/Water Separation. *Appl. Surf. Sci.*, 2018, 462, 164-174.
- Duy, L., Suwadee, K., Chanatip, S., Patchiya P., Surachai. K., Abuliti, A., Guoqing,
 G. One-Pot Fabrication of Hydrophobic Nanocellulose-Silica Film for Water Resistant Packaging Application. *Journal of the Japan Institute of Energy*, 2017, 8, 261-265.
- <u>Duy, L</u>., Chanatip, S., Boonyawan, Y. Suwadee, K. A One-Step Latex Compounding Method for Producing Composites of Natural Rubber/Epoxidized Natural Rubber/Aminosilane Functionalized Montmorillonite; Enhancement of Tensile Strength and Oil Resistance, *Polym. Int.*, 2017, 66, 1064-1073.
- Suwadee, K., Saktip, K., Porapak, S., <u>Duy, L</u>., Chanatip, S., Nuanphun, C., Pattarapan, P., Guoqing, G. Self-healing Hybrid Nanocomposite Anticorrosive Coating from Epoxy/Modified Nanosilica/Perfluorooctyl Triethoxysilane. *Prog. Org. Coat.*, 2017, 104, 173-179.
- <u>Duy, L</u>., Suwadee, K., Chanatip, S., Patchiya, P., Surachai, K., Abuliti, A., Guoqing,
 G. Preparing Hydrophobic Nanocellulose-Silica Film by a Facile One-Pot Method. *Carbohydr. Polym.*, 2016, 153, 266-274.
- Duy, L., Chanatip, S., Boonyawan, Y., Suwadee, K. Preparation and Properties of Natural Rubber/Epoxidized Natural Rubber/Montmorillonite Composites. *Thammasat International Journal of Science and Technology*, 2015, 23, 224-233.

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