

**Peroxide-initiated Modification of  
Polylactic acid (PLA) and Poly(3-hydroxyalkanoates) (PHAs)  
in the Presence of Allylic and Acrylic Coagents**

by

Karolina Aleksandra Dawidziuk

A thesis submitted to the Department of Chemical Engineering

in conformity with the requirements for the

Degree of Master of Applied Science

Queen's University

Kingston, Ontario, Canada

(January 2018)

Copyright © Karolina Aleksandra Dawidziuk, 2018

## Abstract

This thesis investigates the fundamentals of modification of polylactic acid (PLA) and poly(3-hydroxyalkanoates) (PHAs), focusing on improving the understanding of the reactivity of these polymers in the presence of peroxide and multifunctional coagents. The first objective was to examine the effects these modifications had on PLA and to compare them to a well understood polyolefin system, ethylene octene copolymer (EOC). The linear viscoelastic (LVE) properties and molecular weight distributions showed that in the presence of peroxide and coagent these systems were able to produce long-chain branched structures, with allylic coagents being more effective at altering the chain architecture. These reactions were found to proceed through a radical mechanism as oppose to other forms of ionic chemistry. Evaluation of the abstraction efficiencies (AE) and graft propagation of monofunctional coagents showed that PLA is a poor hydrogen donor and the effectiveness of the allylic coagents is likely a result of solubility between the polymer and coagent in the melt.

The second objective was to investigate the chemical modification of poly(3-hydroxyalkanoates) (PHAs), with different lengths of side chains. Medium-chain-length PHAs (MCL-PHAs) showed an affinity for both allylic and acrylic coagents with increases in viscosity, the appearance of shear thinning, and bimodal molecular weight distributions. On the other hand, the short-chain-length PHAs (SCL-PHAs), poly(3-hydroxybutyrate) PHB, performed very similar to what was observed with PLA, where allylic coagents outperformed the acrylate coagents. The AE of these materials gave significant insight into the reactivity. As the alkane side chain length was increased from SCL-PHAs to MCL-PHAs, the number of methylene groups increased and as a result more hydrogen abstraction sites became available, thus resulting in higher AE. This implies there is a greater probability for coagents to graft onto the polymer backbone and therefore the promotion of branched structures.

## **Acknowledgements**

I would like to express my thanks to Dr. Marianna Kontopoulou and Dr. J. Scott Parent, my research supervisors, for their patient guidance, understanding and support during my recovery from operations, and critiques of this work. Without their assistance I would not have been able to complete my research to the level of professionalism that was accomplished.

Special thanks to my lab mates: Praf, Heather, Mike, Rob, and the rest of the Kontopoulou and Parent research group, both current and past, for making my time in the lab more enjoyable. This experience would not have been complete without all the events the Chemical Engineering Graduate Association (CEGSA) continuously organized and all my friends have I made during my times at Queen's. I would like to especially thank my friends: Kelli, Brad, Connor, Ryan, Shannon, and Josh for their overwhelming support during this journey. These last few years have left a mark on me which will always be remembered.

Finally, this experience would not have been possible without the love and continuous support of my parents.

# Table of Contents

Abstract .....	ii
Acknowledgements.....	iii
List of Tables .....	vi
List of Figures.....	vii
Nomenclature.....	viii
List of Schemes.....	x
Chapter 1: Introduction and Literature Review .....	1
1.1 Biobased/Biodegradable Polymers .....	1
1.3 Poly(3-hydroxyalkanoates) (PHAs).....	3
1.4 PLA and PHAs Applications and Limitations .....	3
1.5 Literature on Branching .....	5
1.5.1 PLA Branching .....	5
1.5.2 PHA Branching.....	7
1.6 Existing Polymer Free-radical Mechanisms .....	8
1.6.1 Peroxide Initiated Mechanism .....	8
1.6.2 Coagent Grafting.....	9
1.6.3 Abstraction Efficiency (AE) .....	10
1.6.4 Graft Yields.....	11
1.7 Thesis Objective.....	11
1.8 Thesis Organization .....	11
1.9 References.....	13
Chapter 2: Peroxide-initiated Graft Modification of Polylactic acid (PLA): Introduction of Long-Chain Branching.....	24
2.1 Introduction.....	24
2.2 Materials and Methods.....	25
2.2.1 Materials .....	25
2.2.2 Compounding.....	26
2.2.3 Rheology .....	27
2.2.4 Gel Permeation Chromatography (GPC) .....	27
2.2.5 Gel Content .....	27
2.2.6 Nuclear Magnetic Resonance (NMR) Spectroscopy .....	28

2.2.7 Abstraction Efficiency (AE) .....	28
2.3 Results and Discussion .....	28
2.3.1 Long Chain Branching Efficiency of Coagent-based PLA Modifications .....	28
2.3.2 Contribution of Ionic Reactions to PLA Modification .....	33
2.3.3 Abstraction Efficiency and Monofunctional Coagent Graft Modification .....	33
2.3.4 Solubility Considerations for PLA Branching .....	37
2.4 Conclusion .....	38
2.5 References.....	39
Chapter 3: Peroxide-initiated Modification of Poly(3-hydroxyalkanoates) (PHAs) with Tri-functional Allylic and Acrylic Coagents.....	44
3.1 Introduction.....	44
3.2 Materials and Methods.....	46
3.2.1 Materials .....	46
3.2.2 Compounding.....	47
3.2.3 Rheology .....	47
3.2.4 Gas Permeation Chromatography (GPC).....	48
3.2.5 Gel Content .....	48
3.2.6 Nuclear Magnetic Resonance (NMR) Spectroscopy .....	48
3.2.7 Abstraction Efficiency (AE) .....	49
3.3 Results and Discussion .....	49
3.3.1 PHO Modification using Allylic and Acrylate Coagents.....	49
3.3.2 PHB Modification using Allylic and Acrylate Coagents .....	52
3.3.3 Abstraction Efficiency and Monofunctional Graft Modifications .....	54
3.4 Conclusions.....	57
3.5 References.....	58
Chapter 4: Thesis Overview.....	63
4.1 Thesis Conclusions .....	63
4.2 Future Work.....	63
Appendix A: Effect of amount of TAM and TAC coagents on PLA (Rheology) .....	65
Appendix B: PHO <sup>1</sup> H NMR.....	66
Appendix C: Cross-model Fit .....	669

## List of Tables

Table 2.1: Gel content and molecular weight data for unmodified polymers and their derivatives. ....	31
Table 2.2: Grafted amounts of allyl benzoate (AB) and butyl acylate (BA) to EOC and PLA. ....	36
Table 3.1: Molecular weight data, and Cross-model parameters for PHO formulations.....	49
Table 3.2: AE, functional group content, and graft yeilds of various polymers. ....	55

## List of Figures

Figure 2.1: (a,d) complex viscosity and (b,e) storage modulus as a function of frequency, (c,f) van Gulp-Palmen plot for PLA and EOC formulations, respectively. ....	29
Figure 2.2: (a,c) molecular weight distribution and (b,d) GPC light scattering detector response for EOC and PLA samples respectively. ....	32
Figure 3.1: (a) Molecular weight distribution and (b) light scattering analysis of PHO modified with coagent loadings of $24.2 \mu\text{mol}\cdot\text{g}^{-1}$ of coagent. ....	50
Figure 3.2: (a) Complex viscosity and (b) storage modulus versus frequency and (c) van Gulp-Palmen plot at $60^\circ\text{C}$ with coagent loading of $24.2 \mu\text{mol}\cdot\text{g}^{-1}$ . ....	51
Figure 3.3: (a) Complex viscosity and (b) storage modulus versus frequency, and (c) van Gulp-Palmen plot at $180^\circ\text{C}$ with coagent loadings of $12.1 \mu\text{mol}\cdot\text{g}^{-1}$ . ....	53
Figure 3.4: Abstraction efficiency as a function of reaction temperature. The $150^\circ\text{C}$ melting point of PHB precluded an AE measurement at this temperature obtained. ....	55
Figure A.1: (a,d) Complex viscosity and (b,e) storage modulus versus frequency, and (c,f) van Gulp-Palmen plot at $180^\circ\text{C}$ with various loadings of allylic coagents, TAM and TAC respectively. ....	65
Figure B.1: $^1\text{H}$ NMR spectra of PHO with grafted AB. Since there are more un-grafted PHO chains in the polymer, this results in small peaks from the coagent. The internal standard used for calculations was TMS, the solvent was chloroform and are represented by the peaks at 0.00 ppm and 7.26 ppm respectively. ....	66
Figure B.2: $^1\text{H}$ NMR spectra of PHO with grafted BA. Since there are more un-grafted PHO chains in the polymer, this results in small peaks from the coagent. The internal standard used for calculations was TMS, the solvent was chloroform and are represented by the peaks at 0.00 ppm and 7.26 ppm respectively. ....	67
Figure C.1: Output of the Cross-model fit for neat PHO applying equations 3.1. ....	69

## Nomenclature

### Nomenclature

a	Mark-Houwink constant
$\bar{D}$	dispersity
$G'$	storage (elastic) modulus (Pa)
$G''$	loss (viscous) modulus (Pa)
$G^*$	complex modulus (Pa)
$M_n$	number average molecular weight ( $\text{kg}\cdot\text{mol}^{-1}$ )
$M_w$	weight average molecular weight ( $\text{kg}\cdot\text{mol}^{-1}$ )
$M_z$	z average molecular weight ( $\text{kg}\cdot\text{mol}^{-1}$ )
T	temperature ( $^{\circ}\text{C}$ )
t	time (s)
wt·%	weight percent (%)

### Greek

$\delta$	phase degree ( $^{\circ}$ )
$\mu\text{mol}$	micromoles
$\eta^*$	complex viscosity ( $\text{Pa}\cdot\text{s}$ )
$\eta_0$	zero shear viscosity ( $\text{Pa}\cdot\text{s}$ )
$\lambda$	relaxation time (s)
$\omega$	angular frequency ( $\text{rad}\cdot\text{s}^{-1}$ )

### Abbreviations

AE	abstraction efficiency
ASTM	American Society for Testing Materials
AB	allyl benzoate
BA	butyl acrylate
BDE	bond dissociation energy
d- $\text{CHCl}_3$	deuterated chloroform
DCP	dicumyl peroxide
dn/dc	differential refractive index
EOC	ethylene octene copolymer
GC	gas chromatography
GPC	gel permeation chromatography
H-atom	hydrogen atom
hr	hour
LCB	long chain branching
LDPE	low density polyethylene
LVE	linear viscoelastic
MCL	medium chain length
MFI	melt flow index
min	minute
mL	milliliters



MMD	molecular weight dispersity
MWD	molecular weight distribution
NMR	nuclear magnetic spectroscopy
PHA	poly(3-hydroxyalkanoates)
PBS	polybutylene succinate
PCL	polycaprolactone
PGA	polyglycolic acid
PHB	poly(3-hydroxybutyrate)
PHD	poly(3-hydroxydecanoate)
PHN	poly(3-hydroxynonanoate)
PHO	poly(3-hydroxyoctanoate)
PLA	polylactic acid
RPM	rotations per minute
SCL	short chain length
TAC	triallyl cyanurate
TAM	triallyl trimesate
THF	tetrahydrofuran
TMS	tetramethylsilane
TMPTA	trimethylolpropane triacrylate

## List of Schemes

Scheme 1.1: Monomers of lactic acid, adapted from Lee et al. 1996 [6].	2
Scheme 1.2: Reaction scheme to produce PLA, adapted from Rascal et al. 2010 [6].	2
Scheme 1.3: Chemical structure of poly(3-hydroxyalkanoates). R is variable, usually with various lengths of alkane chains. This Scheme is adapted from Nerkar et al. 2013 [10].	3
Scheme 1.4: Structures of various branch architecture adapted from Nouri et al. 2015 [37].	5
Scheme 1.5: Idealized mechanism for peroxide initiated curing of polyethylene, adapted from Molloy et al. 2014 [74].	9
Scheme 1.6: Byproduct formed from the thermolysis of DCP accompanied by the AE formula adapted from Garret et al. 2014 [85].	100
Scheme 2.1: Monomers for PLA and EOC graft modification.	26
Scheme 2.2: Byproducts of the thermolysis of DCP accompanied by abstraction efficiency (AE) formula and results for EOC and PLA, respectively.	34
Scheme 3.1: Chemical structure of coagents used in the present work.	46

# Chapter 1: Introduction and Literature Review

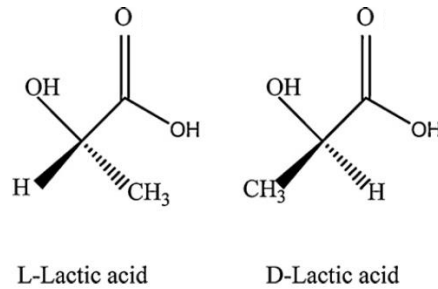
## 1.1 Biobased/Biodegradable Polymers

The current generation lives in a take-make-dispose world; one where we extract from our environment, produce and use goods, and then dispose of them [1]. With an increase in demand for plastics since the 1950s, finding more sustainable alternatives is crucial to reduce the environmental impact of these products, which ultimately end up in landfills, oceans, and other ecosystems. This makes substitution of traditional petroleum-based plastics with bioplastics increasingly pertinent [2].

The term bioplastics refers to materials which are biodegradable, biobased, or both. Biodegradation of a polymer is defined as the change in chemical structure and loss of mechanical and physical properties. These changes result in the production of compounds like water, carbon dioxide, minerals, and intermediate byproducts that naturally exist in the environment, such as biomass and humic material [3]. On the other hand, biobased plastics are synthesized from living organisms (polysaccharides, cellulose, bacteria, or proteins) or renewable resources (corn, sugarcane, rice, etc.). There are plenty of examples of bioplastics including poly(3-hydroxyalkanoates) (PHAs), polybutylene succinate (PBS), polycaprolactone (PCL), polyglycolic acid (PGA), and polylactic acid (PLA) [4]. Two aliphatic polyesters that are amongst the most promising bioplastics are PLA and PHAs. This chapter will review the production, properties, main uses, and modification approaches of these polymers.

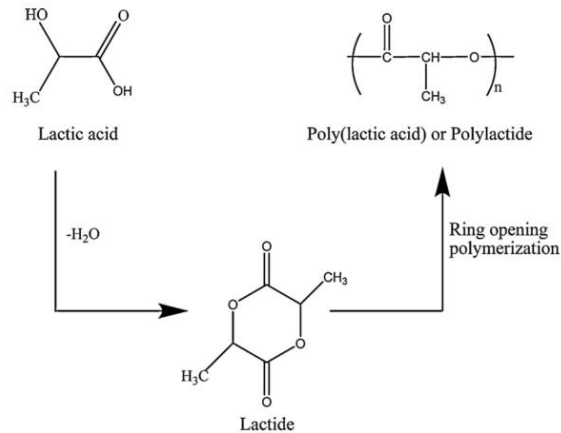
## 1.2 Polylactic Acid (PLA)

Lactide, the precursor to PLA, is a chiral molecule that can dimerize to produce three possible stereoisomers: the D,D-lactide, L,L-lactide (optically active), and the L,D or D,L lactide, referred to as meso-lactide (optically inactive) [5]. These structures are depicted in Scheme 1.1.



Scheme 1.1: Monomers of lactic acid, adapted from Lee et al. 1996 [6].

A simplification of the steps for converting lactic acid into PLA can be found in Scheme 1.2.



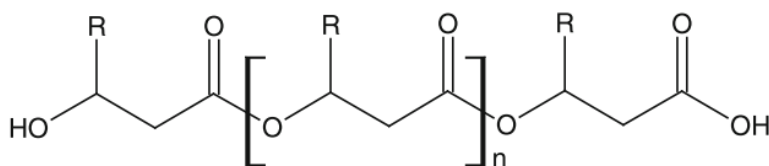
Scheme 1.2: Reaction scheme to produce PLA, adapted from Rascal et al. 2010 [6].

The stereochemistry of PLA can be controlled during the polymerization process; a high content of L-lactide is used to produce semi-crystalline polymers while materials with a high D-lactide content are more amorphous [7]. The wide array of properties which can be thus achieved make PLA an extremely versatile material. PLAs with a high meso content (> 7%) are used for films and packaging, including clam shells and cups, as these polymers exhibit low durability. Decreasing the meso content (< 7%) increases durability, with applications ranging from mobile

phone housings, bottles, and biofoams. Stereocomplex PLA exhibits improved heat resistance, which significantly improves the performance of the material [5].

### 1.3 Poly(3-hydroxyalkanoates) (PHAs)

Another group of biodegradable polymers which are of interest are poly(3-hydroxyalkanoates) (PHAs); a group of polyesters which can be classified into two main groups: short-chain-length PHAs (SCL-PHAs) with side chains ranging from 3-5 carbons and medium-chain-length PHAs (MCL-PHAs) which have side chains between 6-14 carbons [8]. PHAs are produced through bacterial fermentation of sugars or lipids [9]. The chain length is dependent on the family of bacteria used, with *alcaligenes eutrophus* and *pseudomonas oleovorans* being the most commonly used to produce SCL-PHAs and MCL-PHAs, respectively [8].



Scheme 1.3: Chemical structure of poly(3-hydroxyalkanoates). R is variable, usually with various lengths of alkane chains. This Scheme is adapted from Nerkar et al. 2013 [10].

PHAs have many characteristics which are sought after in commercial products. The PHA family is known for its water insolubility [11], making it resistant to hydrolytic degradation; it is soluble in chlorinated hydrocarbons, biocompatible, and nontoxic [12]. In particular SCL-PHAs are brittle and have a high melting point, whereas MCL-PHAs show low crystallinity, do not break easily, and exhibit elastomeric behaviour [13].

### 1.4 PLA and PHAs Applications and Limitations

PLA and PHAs are both suitable for a wide array of applications in biomedicine, due to their biocompatibility and bioresorbability. For instance, they have been applied as resorbable sutures, drug delivery vehicles, cardiovascular stents, porous scaffolds for cellular applications, and in

nerve and soft tissue repair [3][14][13]. Commercially, PLA is used in films and thermoformed packaging products and has been found to provide mechanical properties superior to polystyrene and comparable to polyethylene terephthalate. In fact, PLA has become the material of choice in the emerging industry of 3D printing [14]. On the other hand, PHAs were first used for packaging with single use application (razors, utensils, shampoo bottles, etc.) and as a moisture resistant barrier for products such as milk cartons and sanitary towels [8][13][15]. More recently, due to the biodegradability of PHAs, they have become a popular and environmentally friendly material for the encapsulation of insecticides and herbicides [11].

In spite of the many potential applications of PLA and PHAs, advances have been limited by their low melt-strength and slow crystallization kinetics. These deficiencies mainly stem from the linear chain architecture of these polymers, and their chain conformation. The processability and mechanical properties can be improved through copolymerization or blending [16]–[20] or by implementation of chemical modifications such as chain extension, cross-linking, and functionalization [21]–[25]. With a continued focus on producing these materials more economically, improving both their mechanical and physical properties, implementing sustainable large-scale production facilities, and efficient end-of-life disposal; the potential exists to one day replace commodity plastics such as polyethylene, polypropylene, and polystyrene [11][14]–[16].

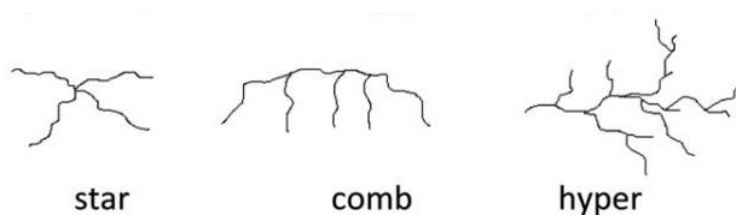
Significant research has been conducted on methods to improve the physical and mechanical properties of polymers. Polymer blending, the use of chain extenders, and introduction of radical and/or multi-functional coagents are some of the many ways which have been used to successfully modify polymers architectures. The next sections aim to examine the current literature regarding these methods.

## 1.5 Literature on Branching

### 1.5.1 PLA Branching

One of the most effective ways to increase melt-strength is to modify the chain architecture by introducing branches onto the polymer; this approach has been studied excessively in thermoplastics, such as polyolefins [26]–[31] and polyesters.

In polyesters common methods to introduce branching include end group chemistry, use of chain extenders, and reactive melt processing through the introduction of free radicals [22][32]–[36]. Depending upon the method, various branch types such as star, comb, or hyper branched (branch on branch) can be introduced to the polymer. Scheme 1.4 illustrates the structures of these topographies. Long chain branching (LCB) promotes shear thinning, improves extensional strain hardening (melt-strength), and enhanced crystallization [22][36]–[38].



Scheme 1.4: Structures of various branch architecture adapted from Nouri et al. 2015 [37].

Chain extenders are used extensively to promote branched or cross-linked structures and obtain increased viscosity and molecular weight [36][39]–[45]. One of the most well-known chain extenders is the epoxy-functionalized oligomeric allylic copolymer known as Joncryl<sup>®</sup>. Al-Itry et al. [45] studied the mechanism for the reaction between PLA and Joncryl. Joncryl has the ability to react with both the hydroxyl and carbonyl groups of PLA. This allows for the reaction to progress through hydroxyl end-group chemistry accompanied by an epoxy ring-opening reaction to create covalent bonds. There is a complex balance between concurrent degradation, chain extension, and branching mechanisms [45].

The effect of peroxide-initiated reactions on PLA has been studied by various research groups. Takamura et al. [46][47] concluded that peroxide decomposition is a localized reaction, resulting in partial cross-linking, making the overall degree of crystallinity dependent on the entanglement density and number of branch points. Carlson et al. [32] and Signori et al. [48] saw that in the presence of peroxide there was a decrease in molecular weight of the samples likely due to chain scission from a radical mechanism, backbiting, and thermolysis reaction.

The introduction of radicals can be achieved either through hydrogen abstraction from the methyl group/tertiary carbon or cleavage of C-C bonds in PLA. In the absence of peroxide, these radicals can be induced through various methods including electron beam irradiation, gamma ray irradiation, or ultraviolet irradiation [49]–[56]. With all irradiation methods PLA showed signs of degradation attributed to random chain scission from the polymer backbone [49][50]. This was evident by a decrease in molecular weight and reduction in viscosity. With the addition of a multifunctional coagent trimethylolpropane triacrylate (TMPTA), the presence of branched or cross-linked structures was evident. Improvement in the rheological properties, such as increased complex viscosity, appearance of shear thinning, and longer relaxation times, were also observed [53][54].

Similar results were seen by You et al. [22], who reacted PLA with dicumyl peroxide (DCP) and pentaerythritol triacrylate (PETA). They speculated that comb-like branch architecture was formed. This resulted in a decrease in cold crystallization temperature as branching levels increased, and improvements in the nucleation density.

The Kontopoulou group has done a significant amount of work on PLA modified by an allylic coagent, triallyl trimesate (TAM). Results showed vast improvement in linear viscoelastic (LVE)



properties, increased molar mass, and enhanced crystallization as a result of introduced branch architecture in modified PLA [42][57]–[59].

### **1.5.2 PHA Branching**

Similar approaches have been implemented to improve the properties of SCL-PHA, poly(3-hydroxybutyrate) (PHB). These include blending with co-polymers [60]–[62], addition of plasticizers [63]–[65], nucleating agents [66]–[68], or chain extenders [69]. The effect of peroxide on blends of poly [(3-hydroxybutyrate)-co-(3-hydroxyvalerate)] (PHBV) have also been studied [70][71]. These reports showed a decrease in melting point, crystallization temperature, and crystallinity, with the incorporation of peroxide. In the case of PHBV, there was also an increase in cross-link density and measurable gel content when 1 wt% of DCP was incorporated into the blend [70].

Wei et al. [23] examined peroxide induced cross-linking on PLA and PHB. According to this mechanism, free radicals are produced through thermal decomposition of DCP and can abstracted a hydrogen from the tertiary position of PBH or PLA, resulting in the formation of cross-linked structures. When low amounts of peroxide were used, degradation through chain scission was evident. As the peroxide content increased up to 1 wt% the production of these cross-linked structures was prominent with increases in complex viscosity, storage modulus, and broader molecular weight distributions.

Kolahchi and Kontopoulou [72] improved the rheological properties and thermal stability of chain extended PHB by reactive modification using DCP and the multifunctional coagent, TAM. A high degree of PHB branching and/or cross-linking was achieved. Improvements in thermal properties included: increase in the crystallization temperature and spherulitic structures, faster crystallization kinetics, and greater thermal stability of this material.

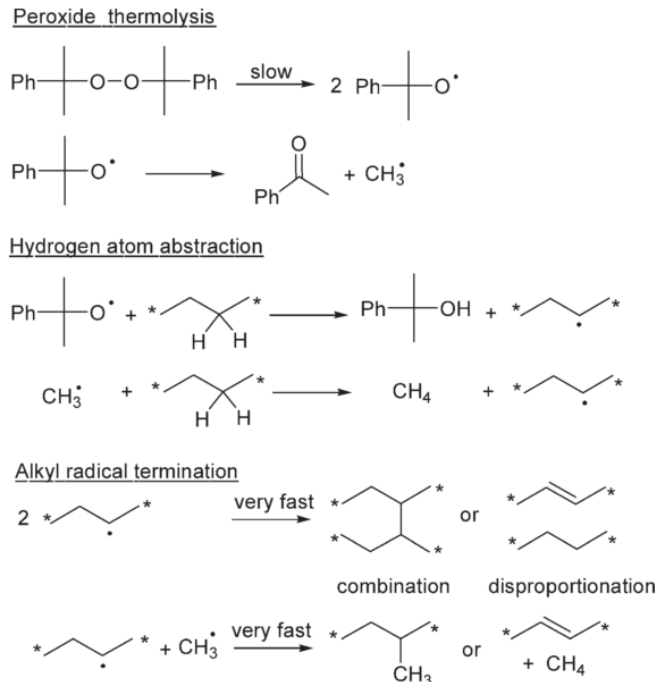
MCL-PHAs can also be modified by free radical mechanisms, but far less work has been done on this polymer. Gagnon et al. [73] and Fei et al. [70] proved that PHAs modified by peroxide are capable of producing cross-link structures, which enhance the materials elasticity. Nerkar et al. [57] claimed improvements in the melt properties of poly(3-hydroxyoctanoate) (PHO) when reactively modified with DCP and TAM.

## **1.6 Existing Polymer Free-radical Mechanisms**

Given the interest in free-radical modifications to accomplish branching and cross-linking in biopolyesters, the pertinent mechanisms for peroxide and coagent addition for polymer systems and common method of analysis of polymer reactivity are discussed in the following sections.

### **1.6.1 Peroxide Initiated Mechanism**

Peroxide-mediated reactions have been well known to introduce branches or cross-links in polymers, such as polyolefins. The pathway of this reaction for polyethelene is illustrated in Scheme 1.5. The thermolysis of the peroxide leads to the production of alkoxy radicals, which can participate in hydrogen abstraction to produce macroradicals. Termination of these macroradicals results in cross-links, formed either through recombination or fragmentation due to  $\beta$ -scission [74].



Scheme 1.5: Idealized mechanism for peroxide initiated curing of polyethylene, adapted from Molloy et al. 2014 [74].

Obtaining a balance between combination and disproportionation influences the dispersity and molecular weight of the system. This is exemplified in commodity polymers such as polyethylene, which is known to cross-link [75]–[78], as opposed to polypropylene which in the presence of peroxide, severely degrades because of disproportionation [79].

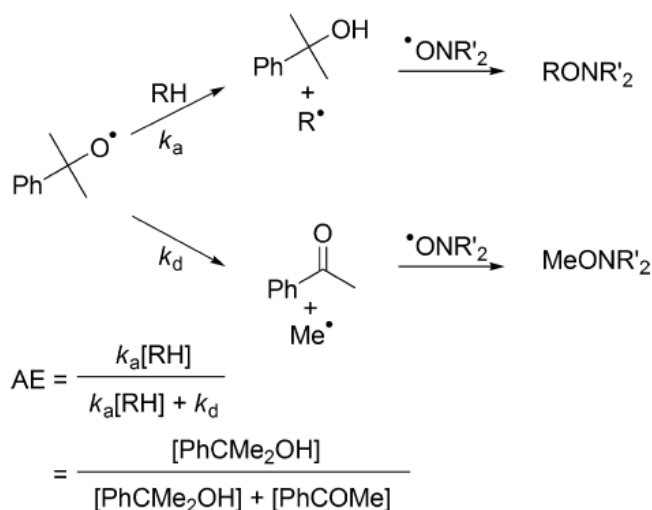
### 1.6.2 Coagent Grafting

Reactive modification by incorporating coagents is one way to overcome disproportionation and introduce LCB to a polymer. Coagents are multifunctional vinyl monomers which are highly reactive towards free radicals [80]. There are two main types of coagents; acrylate and allylic. Acrylate-based coagent, such as TMPTA, are more kinetically reactive and therefore require less peroxide to fully achieve full C=C conversion [79]. This results in a tendency to homopolymerize due to the readily accessible unsaturation, resulting in compromised cross-linking efficiency [80]. In contrast, allylic functionalities such as TAM or triallyl cyanurate (TAC), are less reactive with respect to radical addition [81][82], resulting in participation in intramolecular propagation

reactions [83]. The coagent can either participate in hydrogen atom transfer, resulting in grafting between polymer chains, or be subjected to an oligomerization reaction with itself prior to attaching to the polymer backbone, producing homopolymerized coagent [80]. A polymer which is a good hydrogen donor stands to benefit from improved kinetic chain length addition [84].

### 1.6.3 Abstraction Efficiency (AE)

The grafting of coagents is heavily dependent on the ability of the peroxide to abstract a hydrogen from the polymer backbone, creating a radical site. Garrett et al. [85] examined the thermolysis of DCP to measure the material's quality as a hydrogen donor known as the abstraction efficiency (AE). A poor hydrogen donor polymer produces lower macromolecule yields, resulting in proportionally lower cross-link density. DCP decomposes into two cumyloxy radicals, which can either abstract from the hydrocarbon to form cumyl alcohol and an alkoxy radical, or participate in a decomposition reaction and produce acetophenone and a methyl radical. The concentration of hydrogen atom donor in solution leads to the AE formula:  $AE = [\text{cumyl alcohol}] / ([\text{cumyl alcohol}] + [\text{acetophenone}])$ . This can also be represented as the ratio between the addition and fragmentation rate constants ( $k_a/k_d$ ), illustrated in Scheme 1.6 [85].



Scheme 1.6: Byproduct formed from the thermolysis of DCP accompanied by the AE formula adapted from Garret et al. 2014 [85].

#### **1.6.4 Graft Yields**

Examining the graft yields can assist in further understanding the ability of a coagent or antioxidant to modify a polymer. Graft yield is defined as the fraction of monomer that is grafted onto the polymer versus the amount that was unreacted or consumed in a side reaction. Graft yield is heavily influenced by multiple independent factors, including mixing efficiency, temperature, residence time, and polyolefins used (type, molecular weight, grade, etc.) [86]. Often, this analysis is accompanied by a model compound study, in an attempt to simplify the complex mechanisms that exist. Graft yield gives insight into the relationship between reaction conditions and graft yield and helps explain the improvements seen in rheological characterization, mechanical properties, as well as the molecular distributions of a sample [87]–[92].

#### **1.7 Thesis Objective**

Although significant literature exists on the reactive processing of thermoplastic biopolyesters to obtain branched or cross-linked structures, there is a lack of understanding of aspects such as the abstraction efficiency and coagent graft yields in these materials. Furthermore, the mechanisms of coagent grafting and the effects of different coagent structures are not understood adequately. This thesis aims to investigate the abstraction efficiency of two common types of biopolyesters, PLA and PHAs, and to compare the coagent graft yields of acrylate and allylic coagents.

#### **1.8 Thesis Organization**

This thesis is organized into four chapters. The present chapter has introduced the polymers under investigation and has presented a literature review on the pertinent reactive modification approaches. Chapter 2 examines the reactivity and efficiency of peroxide-initiated coagent modification on PLA. Chapter 3 examines the effectiveness of allylic and acrylate coagents in the

presence of peroxide on a group of PHAs. Chapter 4 serves as a summary of the conclusions made in this work and makes recommendations for future work.

## 1.9 References

- [1] K. Sudesh and T. Iwata, "Sustainability of Biobased and Biodegradable Plastics," *CLEAN - Soil, Air, Water*, vol. 36, no. 5–6, pp. 433–442, Jun. 2008.
- [2] C. R. Alvarez-Chevez, S. Edwards, R. Moure-Eraso, and K. Geiser, "Sustainability of bio-based plastics: General comparative analysis and recommendations for improvement," *J. Clean. Prod.*, vol. 23, no. 1, pp. 47–56, 2012.
- [3] M. Jamshidian, E. A. Tehrani, M. Imran, M. Jacquot, and S. Desobry, "Poly-Lactic Acid: Production, applications, nanocomposites, and release studies," *Compr. Rev. Food Sci. Food Saf.*, vol. 9, no. 5, pp. 552–571, 2010.
- [4] G. Kale, T. Kijchavengkul, R. Auras, M. Rubino, S. E. Selke, and S. P. Singh, "Compostability of bioplastic packaging materials: An overview," *Macromol. Biosci.*, vol. 7, no. 3, pp. 255–277, 2007.
- [5] W. J. Groot and T. Borén, "Life cycle assessment of the manufacture of lactide and PLA biopolymers from sugarcane in Thailand," *Int. J. Life Cycle Assess.*, vol. 15, no. 9, pp. 970–984, Nov. 2010.
- [6] R. M. Rasal, A. V. Janorkar, and D. E. Hirt, "Poly(lactic acid) modifications," *Prog. Polym. Sci.*, vol. 35, no. 3, pp. 338–356, Mar. 2010.
- [7] E. T. H. Vink, K. R. Rábago, D. A. Glassner, B. Springs, R. P. O'Connor, J. Kolstad, and P. R. Gruber, "The sustainability of nature works™ polylactide polymers and ingeo™ polylactide fibers: An update of the future. Initiated by the 1st International Conference on Bio-based Polymers (ICBP 2003), November 12-14 2003, Saitama, Japan," *Macromol. Biosci.*, vol. 4, no. 6, pp. 551–564, 2004.
- [8] S. Y. Lee, "Bacterial polyhydroxyalkanoates," *Biotechnol. Bioeng.*, vol. 49, no. 1, pp. 1–14, Mar. 1996.
- [9] J. Lu, R. C. Tappel, and C. T. Nomura, "Mini-Review: Biosynthesis of Poly(hydroxyalkanoates)," *Polym. Rev.*, vol. 49, no. 3, pp. 226–248, Aug. 2009.

- [10] M. Nerkar, J. A. Ramsay, B. A. Ramsay, M. Kontopoulou, and R. A. Hutchinson, "Determination of Mark-Houwink Parameters and Absolute Molecular Weight of Medium-Chain-Length Poly(3-Hydroxyalkanoates)," *J. Polym. Environ.*, vol. 21, no. 1, pp. 24–29, Mar. 2013.
- [11] C. S. . Reddy, R. Ghai, Rashmi, and V. . Kalia, "Polyhydroxyalkanoates: an overview," *Bioresour. Technol.*, vol. 87, no. 2, pp. 137–146, Apr. 2003.
- [12] E. Bugnicourt, P. Cinelli, A. Lazzeri, and V. Alvarez, "Polyhydroxyalkanoate (PHA): Review of synthesis, characteristics, processing and potential applications in packaging," *Express Polym. Lett.*, vol. 8, no. 11, pp. 791–808, 2014.
- [13] T. Keshavarz and I. Roy, "Polyhydroxyalkanoates: bioplastics with a green agenda," *Curr. Opin. Microbiol.*, vol. 13, no. 3, pp. 321–326, Jun. 2010.
- [14] A. J. R. Lasprilla, G. A. R. Martinez, B. H. Lunelli, A. L. Jardini, and R. M. Filho, "Polylactic acid synthesis for application in biomedical devices — A review," *Biotechnol. Adv.*, vol. 30, no. 1, pp. 321–328, Jan. 2012.
- [15] C. Nawrath, Y. Poirier, and C. Somerville, "Plant polymers for biodegradable plastics: Cellulose, starch and polyhydroxyalkanoates," *Mol. Breed.*, vol. 1, no. 2, pp. 105–122, Jun. 1995.
- [16] H. Mitomo, P. J. Barham, and A. Keller, "Crystallization and Morphology of Poly( $\beta$ -hydroxybutyrate) and Its Copolymer," *Polym. J.*, vol. 19, no. 11, pp. 1241–1253, Nov. 1987.
- [17] H. Mitomo, Y. Watanabe, I. Ishigaki, and T. Saito, "Radiation-induced degradation of poly(3-hydroxybutyrate) and the copolymer poly(3-hydroxybutyrate-co-3-hydroxyvalerate)," *Polym. Degrad. Stab.*, vol. 45, no. 1, pp. 11–17, Jan. 1994.
- [18] A. Dufresne and M. Vincendon, "Poly(3-hydroxybutyrate) and poly(3-hydroxyoctanoate) blends: Morphology and mechanical behavior," *Macromolecules*, vol. 33, no. 8, pp. 2998–3008, 2000.



- [19] L. M. W. K. Gunaratne and R. A. Shanks, "Multiple melting behaviour of poly(3-hydroxybutyrate-co-hydroxyvalerate) using step-scan DSC," *Eur. Polym. J.*, vol. 41, no. 12, pp. 2980–2988, Dec. 2005.
- [20] B. Rupp, C. Ebner, E. Rossegger, C. Slugovc, F. Stelzer, and F. Wiesbrock, "UV-induced crosslinking of the biopolyester poly(3-hydroxybutyrate)-co-(3-hydroxyvalerate)," *Green Chem.*, vol. 12, no. 10, p. 1796, 2010.
- [21] A. Curvelo, "Thermoplastic starch–cellulosic fibers composites: preliminary results," *Carbohydr. Polym.*, vol. 45, no. 2, pp. 183–188, Jun. 2001.
- [22] J. You, L. Lou, W. Yu, and C. Zhou, "The preparation and crystallization of long chain branching polylactide made by melt radicals reaction," *J. Appl. Polym. Sci.*, vol. 129, no. 4, pp. 1959–1970, Aug. 2013.
- [23] L. Wei and A. G. McDonald, "Peroxide induced cross-linking by reactive melt processing of two biopolyesters: Poly(3-hydroxybutyrate) and poly(lactic acid) to improve their melting processability," *J. Appl. Polym. Sci.*, vol. 132, no. 13, Apr. 2015.
- [24] J. H. Song, R. J. Murphy, R. Narayan, and G. B. H. Davies, "Biodegradable and compostable alternatives to conventional plastics," *Philos. Trans. R. Soc. B Biol. Sci.*, vol. 364, no. 1526, pp. 2127–2139, Jul. 2009.
- [25] S. Brockhaus, M. Petersen, and W. Kersten, "A crossroads for bioplastics: exploring product developers' challenges to move beyond petroleum-based plastics," *J. Clean. Prod.*, vol. 127, pp. 84–95, Jul. 2016.
- [26] P. M. Wood-Adams and J. M. Dealy, "Using Rheological Data To Determine the Branching Level in Metallocene Polyethylenes," *Macromolecules*, vol. 33, no. 20, pp. 7481–7488, Oct. 2000.
- [27] S. Costeux, P. Wood-Adams, and D. Beigzadeh, "Molecular Structure of Metallocene-Catalyzed Polyethylene: Rheologically Relevant Representation of Branching Architecture in Single Catalyst and Blended Systems," *Macromolecules*, vol. 35, no. 7, pp. 2514–2528, Mar. 2002.

- [28] G. J. Nam, J. H. Yoo, and J. W. Lee, "Effect of long-chain branches of polypropylene on rheological properties and foam-extrusion performances," *J. Appl. Polym. Sci.*, vol. 96, no. 5, pp. 1793–1800, Jun. 2005.
- [29] J. S. Parent, S. S. Sengupta, M. Kaufman, and B. I. Chaudhary, "Coagent-induced transformations of polypropylene microstructure: Evolution of bimodal architectures and cross-linked nano-particles," *Polymer*, vol. 49, no. 18, pp. 3884–3891, 2008.
- [30] F. J. Stadler, J. Kaschta, and H. Münstedt, "Thermorheological Behavior of Various Long-Chain Branched Polyethylenes," *Macromolecules*, vol. 41, no. 4, pp. 1328–1333, Feb. 2008.
- [31] K. El Mabrouk, J. S. Parent, B. I. Chaudhary, and R. Cong, "Chemical modification of PP architecture: Strategies for introducing long-chain branching," *Polymer*, vol. 50, no. 23, pp. 5390–5397, Nov. 2009.
- [32] D. Carlson, P. Dubois, L. Nie, and R. Narayan, "Free radical branching of polylactide by reactive extrusion," *Polym. Eng. Sci.*, vol. 38, no. 2, pp. 311–321, 1998.
- [33] M. Kapnistos, D. Vlassopoulos, J. Roovers, and L. G. Leal, "Linear Rheology of Architecturally Complex Macromolecules: Comb Polymers with Linear Backbones," *Macromolecules*, vol. 38, no. 18, pp. 7852–7862, Sep. 2005.
- [34] M. Kapnistos, G. Koutalas, N. Hadjichristidis, J. Roovers, D. J. Lohse, and D. Vlassopoulos, "Linear rheology of comb polymers with star-like backbones: melts and solutions," *Rheol. Acta*, vol. 46, no. 2, pp. 273–286, Nov. 2006.
- [35] K. M. Dean, E. Petinakis, S. Meure, L. Yu, and A. Chryss, "Melt Strength and Rheological Properties of Biodegradable Poly(Lactic Acid) Modified via Alkyl Radical-Based Reactive Extrusion Processes," *J. Polym. Environ.*, vol. 20, no. 3, pp. 741–747, Sep. 2012.
- [36] L. Gu, Y. Xu, G. W. Fahnhorst, and C. W. Macosko, "Star vs long chain branching of poly(lactic acid) with multifunctional aziridine," *J. Rheol. (N. Y. N. Y.)*, vol. 61, no. 4, pp. 785–796, Jul. 2017.

- [37] S. Nouri, C. Dubois, and P. G. Lafleur, "Synthesis and characterization of polylactides with different branched architectures," *J. Polym. Sci. Part B Polym. Phys.*, vol. 53, no. 7, pp. 522–531, Apr. 2015.
- [38] Y. Wang, L. Yang, Y. Niu, Z. Wang, J. Zhang, F. Yu, and W. E. T. Al, "Rheological and Topological Characterizations of Electron Beam Irradiation Prepared Long-Chain Branched Polylactic Acid," *J. Appl. Polym. Sci.*, vol. 122, no. 3, pp. 1857–1865, 2011.
- [39] D. N. Bikiaris and G. P. Karayannidis, "Chain extension of polyesters PET and PBT with two new diimidodiepoxides. II," *J. Polym. Sci. Part A Polym. Chem.*, vol. 34, no. 7, pp. 1337–1342, May 1996.
- [40] N. Najafi, M. C. Heuzey, P. J. Carreau, and P. M. Wood-Adams, "Control of thermal degradation of polylactide (PLA)-clay nanocomposites using chain extenders," *Polym. Degrad. Stab.*, vol. 97, no. 4, pp. 554–565, 2012.
- [41] P. Ma, X. Cai, Y. Zhang, S. Wang, W. Dong, M. Chen, and P. J. Lemstra, "In-situ compatibilization of poly(lactic acid) and poly(butylene adipate-co-terephthalate) blends by using dicumyl peroxide as a free-radical initiator," *Polym. Degrad. Stab.*, vol. 102, no. 1, pp. 145–151, Apr. 2014.
- [42] M. Nerkar, J. A. Ramsay, B. A. Ramsay, and M. Kontopoulou, "Dramatic Improvements in Strain Hardening and Crystallization Kinetics of PLA by Simple Reactive Modification in the Melt State," *Macromol. Mater. Eng.*, vol. 299, no. 12, pp. 1419–1424, Dec. 2014.
- [43] Y. Baimark and P. Srihanam, "Influence of chain extender on thermal properties and melt flow index of stereocomplex PLA," *Polym. Test.*, vol. 45, pp. 52–57, Aug. 2015.
- [44] M. Villalobos, A. Awojulu, T. Greeley, G. Turco, and G. Deeter, "Oligomeric chain extenders for economic reprocessing and recycling of condensation plastics," *Energy*, vol. 31, no. 15, pp. 3227–3234, 2006.
- [45] R. Al-Itry, K. Lamnawar, and A. Maazouz, "Improvement of thermal stability, rheological and mechanical properties of PLA, PBAT and their blends by reactive extrusion with functionalized epoxy," *Polym. Degrad. Stab.*, vol. 97, no. 10, pp. 1898–1914, 2012.

- [46] M. Takamura, T. Nakamura, T. Takahashi, and K. Koyama, "Effect of type of peroxide on cross-linking of poly(l-lactide)," *Polym. Degrad. Stab.*, vol. 93, no. 10, pp. 1909–1916, 2008.
- [47] M. Takamura, T. Nakamura, S. Kawaguchi, T. Takahashi, and K. Koyama, "Molecular characterization and crystallization behavior of peroxide-induced slightly crosslinked poly(L-lactide) during extrusion," *Polym. J.*, vol. 42, no. 7, pp. 600–608, 2010.
- [48] F. Signori, A. Boggioni, M. C. Righetti, C. E. Rondán, S. Bronco, and F. Ciardelli, "Evidences of transesterification, chain branching and cross-linking in a biopolyester commercial blend upon reaction with dicumyl peroxide in the melt," *Macromol. Mater. Eng.*, vol. 300, no. 2, pp. 153–160, 2015.
- [49] P. Nugroho, H. Mitomo, F. Yoshii, and T. Kume, "Degradation of poly(l-lactic acid) by  $\gamma$ -irradiation," *Polym. Degrad. Stab.*, vol. 72, no. 2, pp. 337–343, May 2001.
- [50] S. Loo, H. Tan, C. Ooi, and Y. Boey, "Hydrolytic degradation of electron beam irradiated high molecular weight and non-irradiated moderate molecular weight PLLA," *Acta Biomater.*, vol. 2, no. 3, pp. 287–296, May 2006.
- [51] M.-L. Cairns, G. R. Dickson, J. F. Orr, D. Farrar, K. Hawkins, and F. J. Buchanan, "Electron-beam treatment of poly(lactic acid) to control degradation profiles," *Polym. Degrad. Stab.*, vol. 96, no. 1, pp. 76–83, Jan. 2011.
- [52] H. Fang, Y. Zhang, J. Bai, Z. Wang, and Z. Wang, "Bimodal architecture and rheological and foaming properties for gamma-irradiated long-chain branched polylactides," *RSC Adv.*, vol. 3, no. 23, p. 8783, 2013.
- [53] H. Xu, H. Fang, J. Bai, Y. Zhang, and Z. Wang, "Preparation and Characterization of High-Melt-Strength Polylactide with Long-Chain Branched Structure through  $\gamma$ -Radiation-Induced Chemical Reactions," *Ind. Eng. Chem. Res.*, vol. 53, no. 3, pp. 1150–1159, Jan. 2014.
- [54] C.-Q. Chen, D.-M. Ke, T.-T. Zheng, G.-J. He, X.-W. Cao, and X. Liao, "An Ultraviolet-Induced Reactive Extrusion To Control Chain Scission and Long-Chain Branching Reactions of Polylactide," *Ind. Eng. Chem. Res.*, vol. 55, no. 3, pp. 597–605, Jan. 2016.

- [55] A. Babanalbandi, D. J. T. Hill, J. H. O'Donnell, P. J. Pomery, and A. Whittaker, "An electron spin resonance study on  $\gamma$ -irradiated poly(l-lactic acid) and poly(d,l-lactic acid)," *Polym. Degrad. Stab.*, vol. 50, no. 3, pp. 297–304, Jan. 1995.
- [56] A. Babanalbandi, D. J. T. Hill, and A. K. Whittaker, "Volatile products and new polymer structures formed on  $^{60}\text{Co}$   $\gamma$ -radiolysis of poly(lactic acid) and poly(glycolic acid)," *Polym. Degrad. Stab.*, vol. 58, no. 1–2, pp. 203–214, Jan. 1997.
- [57] M. Nerkar, J. A. Ramsay, B. A. Ramsay, A. A. Vasileiou, and M. Kontopoulou, "Improvements in the melt and solid-state properties of poly(lactic acid), poly-3-hydroxyoctanoate and their blends through reactive modification," *Polym. (United Kingdom)*, vol. 64, pp. 51–61, 2015.
- [58] M. Tiwary, P; Saraf, C; Kontopoulou, "2016, Tiwary, Saraf - Antec - Modification of the rheological and thermal properties of PLA by reactive extrusion." SPE ANTEC, Indianapolis, pp. 265–268, 2016.
- [59] P. Tiwary and M. Kontopoulou, "Tuning the rheological, thermal and solid-state properties of branched PLA by free-radical-mediated reactive extrusion," *ACS Sustain. Chem. Eng.*, vol. 51, no. 5–6, Dec. 2017.
- [60] M. Avella, E. Martuscelli, and M. Raimo, "Review Properties of blends and composites based on poly(3-hydroxy)butyrate (PHB) and poly(3-hydroxybutyrate-hydroxyvalerate) (PHBV) copolymers," *J. Mater. Sci.*, vol. 35, no. 3, pp. 523–545, 2000.
- [61] Y. Kumagai and Y. Doi, "Synthesis of a block copolymer of poly(3-hydroxybutyrate) and poly(ethylene glycol) and its application to biodegradable polymer blends," *J. Environ. Polym. Degrad.*, vol. 1, no. 2, pp. 81–87, Apr. 1993.
- [62] F. P. de Carvalho, A. C. Quental, and M. I. Felisberti, "Polyhydroxybutyrate/acrylonitrile-g-(ethylene-co-propylene-co-diene)-g-styrene blends: Their morphology and thermal and mechanical behavior," *J. Appl. Polym. Sci.*, vol. 110, no. 2, pp. 880–889, Oct. 2008.
- [63] G. Ceccorulli, M. Pizzoli, and M. Scandola, "Plasticization of Bacterial Poly(3-hydroxybutyrate)," *Macromolecules*, vol. 25, no. 12, pp. 3304–3306, 1992.

- [64] J. S. Choi and W. H. Park, "Effect of biodegradable plasticizers on thermal and mechanical properties of poly(3-hydroxybutyrate)," *Polym. Test.*, vol. 23, no. 4, pp. 455–460, Jun. 2004.
- [65] I. Armentano, E. Fortunati, N. Burgos, F. Dominici, F. Luzi, S. Fiori, A. Jiménez, K. Yoon, J. Ahn, S. Kang, and J. M. Kenny, "Processing and characterization of plasticized PLA/PHB blends for biodegradable multiphase systems," *Express Polym. Lett.*, vol. 9, no. 7, pp. 583–596, 2015.
- [66] R. E. Withey and J. N. Hay, "The effect of seeding on the crystallisation of poly(hydroxybutyrate), and co-poly(hydroxybutyrate-co-valerate)," *Polymer.*, vol. 40, no. 18, pp. 5147–5152, Aug. 1999.
- [67] H. Alata, B. Hexig, and Y. Inoue, "Effect of poly(vinyl alcohol) fine particles as a novel biodegradable nucleating agent on the crystallization of poly(3-hydroxybutyrate)," *J. Polym. Sci. Part B Polym. Phys.*, vol. 44, no. 13, pp. 1813–1820, Jul. 2006.
- [68] P. Maiti, C. A. Batt, and E. P. Giannelis, "New biodegradable polyhydroxybutyrate/layered silicate nanocomposites," *Biomacromolecules*, vol. 8, no. 11, pp. 3393–3400, 2007.
- [69] J. Lee and S. McCarthy, "Biodegradable poly(lactic acid) blends with chemically modified polyhydroxyoctanoate through chain extension," *J. Polym. Environ.*, vol. 17, no. 4, pp. 240–247, 2009.
- [70] B. Fei, C. Chen, S. Chen, S. Peng, Y. Zhuang, Y. An, and L. Dong, "Crosslinking of poly[(3-hydroxybutyrate)-co-(3-hydroxyvalerate)] using dicumyl peroxide as initiator," *Polym. Int.*, vol. 53, no. 7, pp. 937–943, Jul. 2004.
- [71] P. Ma, D. G. Hristova-Bogaerds, P. J. Lemstra, Y. Zhang, and S. Wang, "Toughening of PHBV/PBS and PHB/PBS Blends via In situ Compatibilization Using Dicumyl Peroxide as a Free-Radical Grafting Initiator," *Macromol. Mater. Eng.*, vol. 297, no. 5, pp. 402–410, May 2012.

- [72] A. R. Kolahchi and M. Kontopoulou, "Chain extended poly(3-hydroxybutyrate) with improved rheological properties and thermal stability, through reactive modification in the melt state," *Polym. Degrad. Stab.*, vol. 121, pp. 222–229, Nov. 2015.
- [73] K. . Gagnon, R. . Lenz, R. . Farris, and R. . Fuller, "Chemical modification of bacterial elastomers: 1. Peroxide crosslinking," *Polymer.*, vol. 35, no. 20, pp. 4358–4367, Sep. 1994.
- [74] B. M. Molloy, D. K. Hyslop, and J. Scott Parent, "Comparative analysis of delayed-onset peroxide crosslinking formulations," *Polym. Eng. Sci.*, vol. 54, no. 11, pp. 2645–2653, Nov. 2014.
- [75] G. Hulse, R. Kerstring, and D. Warfel, "Chemistry of dicumyl peroxide induced crosslinking of linear polyethylene," *J. Polym. Sci. Polym. Chem. Ed.*, vol. 19, pp. 655–667, 1981.
- [76] E. M. Kampouris and A. G. Andreopoulos, "Benzoyl peroxide as a crosslinking agent for polyethylene," *J. Appl. Polym. Sci.*, vol. 34, no. 3, pp. 1209–1216, Aug. 1987.
- [77] T. Bremner and A. Rudin, "Peroxide modification of linear low-density polyethylene: A comparison of dialkyl peroxides," *J. Appl. Polym. Sci.*, vol. 49, no. 5, pp. 785–798, Aug. 1993.
- [78] H. A. Khonakdar, J. Morshedian, U. Wagenknecht, and S. H. Jafari, "An investigation of chemical crosslinking effect on properties of high-density polyethylene," *Polymer.*, vol. 44, no. 15, pp. 4301–4309, Jul. 2003.
- [79] J. S. Parent, A. Bodsworth, S. S. Sengupta, M. Kontopoulou, B. I. Chaudhary, D. Poche, and S. Cousteaux, "Structure–rheology relationships of long-chain branched polypropylene: Comparative analysis of acrylic and allylic coagent chemistry," *Polymer.*, vol. 50, no. 1, pp. 85–94, Jan. 2009.
- [80] P. R. Dluzneski, "Peroxide Vulcanization of Elastomers," *Rubber Chem. Technol.*, vol. 74, no. 3, pp. 451–492, Jul. 2001.

- [81] J. Muenger, K. Fischer, "Separation of Polar and Steric Effects on Absolute Rate Constants and Arrhenius Parameters for the Reaction of tert-Butyl Radicals with Alkenes," *Int. J. Chem. Kinet.*, vol. 17, pp. 809–829, 1985.
- [82] T. Zytowski and H. Fischer, "Absolute Rate Constants for the Addition of Methyl Radicals to Alkenes in Solution: New Evidence for Polar Interactions," *J. Am. Chem. Soc.*, vol. 118, no. 2, pp. 437–439, Jan. 1996.
- [83] S. S. Sengupta, J. S. Parent, and J. K. Mclean, "Radical-mediated modification of polypropylene: Selective grafting via polyallyl coagents," *J. Polym. Sci. Part A Polym. Chem.*, vol. 43, no. 20, pp. 4882–4893, 2005.
- [84] K. V. S. Shanmugam, J. S. Parent, and R. A. Whitney, "C–H bond addition and copolymerization reactions of N-arylmaleimides: Fundamentals of coagent-assisted polymer cross-linking," *Eur. Polym. J.*, vol. 48, no. 4, pp. 841–849, Apr. 2012.
- [85] G. E. Garrett, E. Mueller, D. a Pratt, and J. S. Parent, "Reactivity of Polyolefins toward Cumyloxy Radical: Yields and Regioselectivity of Hydrogen Atom Transfer," *Macromolecules*, vol. 47, pp. 544–551, 2014.
- [86] G. Moad, "The synthesis of polyolefin graft copolymers by reactive extrusion," *Prog. Polym. Sci.*, vol. 24, no. 1, pp. 81–142, Apr. 1999.
- [87] I. Goñi, M. Gurruchaga, M. Valero, and G. M. Guzman, "Graft polymerization of acrylic monomers onto starch fractions. I. Effect of reaction time on grafting methyl methacrylate onto amylose," *J. Polym. Sci. A1.*, vol. 21, no. 8, pp. 2573–2580, 1983.
- [88] S. Al-Malaika and N. Suharty, "Reactive processing of polymers: mechanisms of grafting reactions of functional antioxidants on polyolefins in the presence of a coagent," *Polym. Degrad. Stab.*, vol. 49, no. 1, pp. 77–89, 1995.
- [89] D. Graebing, "Synthesis of Branched Polypropylene by a Reactive Extrusion Process," *Macromolecules*, vol. 35, no. 12, pp. 4602–4610, Jun. 2002.
- [90] M. Spencer, J. S. Parent, and R. A. Whitney, "Composition distribution in poly(ethylene-graft-vinyltrimethoxysilane)," *Polymer.*, vol. 44, no. 7, pp. 2015–2023, Mar. 2003.



- [91] W. Wu, J. S. Parent, S. S. Sengupta, and B. I. Chaudhary, "Preparation of crosslinked microspheres and porous solids from hydrocarbon solutions: A new variation of precipitation polymerization chemistry," *J. Polym. Sci. Part A Polym. Chem.*, vol. 47, no. 23, pp. 6561–6570, 2009.
- [92] J. Petruš, F. Kučera, and J. Petrůj, "Post-polymerization modification of poly(lactic acid) via radical grafting with itaconic anhydride," *Eur. Polym. J.*, vol. 77, pp. 16–30, 2016.

## **Chapter 2: Peroxide-initiated Graft Modification of Polylactic acid (PLA): Introduction of Long-Chain Branching**

### **2.1 Introduction**

Polylactic acid (PLA) is a biodegradable thermoplastic that can be synthesized from starch-based feedstocks, making it an attractive alternative to petroleum based plastics [1][2]. However, the material has notable deficiencies, such as poor melt-strength, pronounced brittleness, [3][4] and slow crystallization rates [5][6]. This has limited application development efforts to products where biocompatibility and biodegradability are paramount [7].

Several strategies for improving PLA properties have been attempted, including the addition of modifiers, blending with other polymers, and copolymerization of lactic acid with alternate monomers, [6]–[12] as well as chemical modifications initiated with UV, gamma ray, and electron beam irradiation [13]–[19]. Of principal interest to this work is the graft modification of PLA with organic peroxide formulations in a solvent-free, reactive melt compounding approach [20]–[23].

Takamura et al. [24][25] examined the effect of various peroxides on PLA, demonstrating the tendency of this polymer to cross-link in the presence of a radical initiator. Long chain branching (LCB) produced by this chemistry was shown to affect the nucleation of PLA crystallites, thereby enhancing crystallization rates. Wang et al. [16] and Fang et al. [17] examined the graft modification of PLA with a trifunctional monomer, trimethylolpropane triacrylate (TMPTA), using radiation-induced macroradical generation. In both cases, evidence of LCB was confirmed by melt-state rheology, as the chemically-modified derivatives showed more intense shear thinning and further deviation from a linear reference material in a van Gurp-Palmen plot. Similar results have been reported by You et al. [20], who used dicumyl peroxide (DCP) to initiate the addition

of pentaerythritol triacrylate (PETA) to PLA. This combination lead to the production of comb-like branch architecture, resulting in a lower crystallization temperature, and improved nucleation density during crystallization.

Recent research has revealed unexpectedly large changes in molecular weight distribution, melt-state rheological properties, and crystallization rates for coagent-modified derivatives of PLA [22][26]. Of particular interest has been the remarkable efficiency of the allylic coagent triallyl trimesate (TAM) when compared to the acrylate-based coagents in common use [21][23].

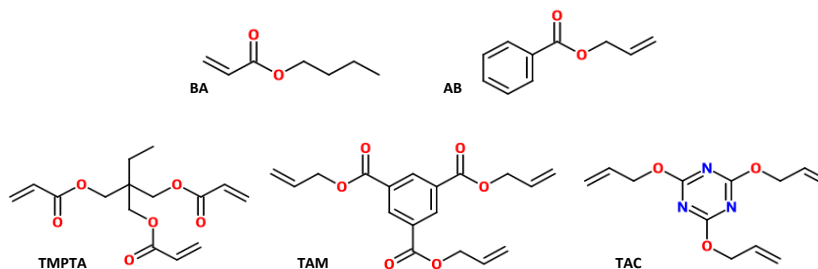
The objective of this work was to determine the underlying cause of the remarkable efficiency of allylic coagents in PLA graft modifications. Following a brief comparison of PLA derivatizations relative to better-understood polyolefin modifications, the study shifts to systematic examinations of potential ionic and radical reaction pathways. Measurements of monomer graft yield, H-atom transfer yields, melt-state rheology, and molecular weight distribution are discussed in the context of the efficiency of LCB generation in the PLA system.

## **2.2 Materials and Methods**

### **2.2.1 Materials**

An extrusion / thermoforming grade of polylactic acid (PLA, grade 2500 HP, MFI  $8.0\text{g} \cdot 10\text{min}^{-1}$  at  $190^\circ\text{C}$ ) was obtained from NatureWorks®, and purified by dissolution / precipitation (chloroform/methanol) and dried under vacuum at  $60^\circ\text{C}$  for 24 hr. Ethylene octene copolymer (EOC, grade 8200, 10 mol% octene [27], MFI  $5.0\text{g} \cdot 10\text{min}^{-1}$  at  $190^\circ\text{C}$ ) was used as received from Dow Chemical. Butyl acrylate (BA, 99%), dicumyl peroxide (DCP, 98%), triallyl cyanurate (TAC, 97%), and trimethylolpropane triacrylate (TMPTA, 70%) were used as received from

Sigma Aldrich. Allyl benzoate (AB, 98%) and triallyl trimesate (TAM, 98%) were used as received from TCI America and Monomer-Polymer Labs, respectively.



Scheme 2.1: Monomers for PLA and EOC graft modification.

## 2.2.2 Compounding

Samples for graft modification with monofunctional monomers AB and BA were prepared by coating the desired polymer (0.5 g) with an acetone solution to create a masterbatch containing DCP (0.001 g,  $18.5 \mu\text{mol}\cdot\text{g}^{-1}$ ), and monomer (0.05g,  $308.6 \mu\text{mol}\cdot\text{g}^{-1}$ ). After evaporation of acetone, masterbatches were charged to an Atlas Mixer at  $180^\circ\text{C}$  for 6 min. The products were purified by dissolution/precipitation and dried prior to further analysis.

Samples for trifunctional coagent graft modification were prepared by coating polymer (10g) with a mixture of DCP (0.01 g,  $3.7 \mu\text{mol}\cdot\text{g}^{-1}$ ) and coagent (0.04 g,  $12.1 \mu\text{mol}\cdot\text{g}^{-1}$ ) in an acetone solution, and dried under vacuum at  $60^\circ\text{C}$  before processing with a twin-screw DSM micro-compounder at  $180^\circ\text{C}$  for 6 min at a screw speed of 100 RPM.

Formulations are identified by the starting material, the amount of peroxide/coagent, and coagent type. For example, PLA 3.7/12.1 TAM denotes PLA reacted with  $[\text{DCP}] = 3.7 \mu\text{mol}\cdot\text{g}^{-1}$  and  $[\text{TAM}] = 12.1 \mu\text{mol}\cdot\text{g}^{-1}$ .

### **2.2.3 Rheology**

Compression molded discs were prepared on a Carver press at 180°C, yielding a diameter of 25 mm and thickness of 2 mm. The rheological properties were measured using an MCR-301 Anton Paar rheometer. Linear viscoelastic (LVE) properties were measured using the shear oscillatory mode by means of a 25 mm parallel plate at 180°C. The frequency used for these studies was 0.05 – 100 rad·s<sup>-1</sup>; lower frequencies were avoided to limit the extent of PLA degradation. All samples were dried under vacuum prior to analysis. Three replicates were conducted on all measurements.

### **2.2.4 Gel Permeation Chromatography (GPC)**

GPC analysis was conducted in tetrahydrofuran (THF) solutions using a Viscotek 270 max separation module equipped with differential refractive index (DRI), viscosity (IV), and light scattering (low angle and right angle) detectors. The separation module was maintained at 40°C and contained two porous PolyAnalytik columns in series with an exclusion molecular weight limit of 209,106 Da. The data was processed with Viscotek Omniseq software using dn/dc values of 0.0482 for PLA in THF [28] and 0.0788 for EOC in THF, the latter determined by analysis of EOC+THF solutions (0.2-1.0 mg·mL<sup>-1</sup>) with an Wyatt Opilab DSP refractometer operating at 690 nm. Three replicates were conducted on all measurements.

### **2.2.5 Gel Content**

Gel contents were measured according to ASTM D2765 by extracting polymer samples from stainless-steel wire mesh (120 sieve) for 8 hr using boiling THF. The samples were dried overnight in a vacuum oven at 60°C, with gel contents reported as weight percent of unextracted material.

### **2.2.6 Nuclear Magnetic Resonance (NMR) Spectroscopy**

$^1\text{H}$  NMR spectra were acquired with a Bruker AC-400 MHz spectrometer in d-chloroform ( $\text{d-CHCl}_3$ ) using polymer concentrations of  $10 \text{ mg}\cdot\text{mL}^{-1}$ , with chemical shifts referenced to the resonance of residual  $\text{CHCl}_3$  within the solvent.

### **2.2.7 Abstraction Efficiency (AE)**

Finely ground polymer (0.5 g) was coated with a solution of DCP in acetone ( $\sim 0.2 \text{ mL}$ ) to produce a peroxide concentration of 2 wt% ( $74.0 \text{ }\mu\text{mol}\cdot\text{g}^{-1}$ ). The acetone was allowed to evaporate before charging the mixture to an Atlas Laboratory Mixer at  $180^\circ\text{C}$  for 7 initiator half-lives (6min). The resulting material was dissolved in acetone and a small aliquot of the solution was injected into a Hewlett-Packard 5890 series II chromatograph equipped with a Superlco SPB-1 microbore column using  $2 \text{ mL}\cdot\text{min}^{-1}$  of helium as carrier gas. Injector and detector temperatures were held at  $275^\circ\text{C}$ , with the oven temperature starting at  $100^\circ\text{C}$  for 2 min, ramping to  $250^\circ\text{C}$  at  $22^\circ\text{C}\cdot\text{min}^{-1}$ , and holding for 6 min. Abstraction efficiencies are reported as  $[\text{cumyl alcohol}] / ([\text{cumyl alcohol}] + [\text{acetophenone}])$ .

## **2.3 Results and Discussion**

### **2.3.1 Long Chain Branching Efficiency of Coagent-based PLA Modifications**

Earlier reports of peroxide-initiated PLA modification have described the susceptibility of this thermoplastic to cross-link when it is subjected to radical chemistry, likely through H-atom abstraction from the polymer by initiator-derived radicals, followed by combination of the resulting macroradicals. This conventional peroxide cross-linking sequence is well-documented for ethylene-octene copolymer (EOC) [29]–[34] and, as such, EOC served as a benchmark for assessing the efficacy of different coagents on polymer branching. The EOC material used for this purpose was selected because its rheological properties were comparable to the PLA starting

material. Figure 2.1a-c provide the complex viscosity, storage modulus, and phase angle data for EOC and its derivatives, while Figure 2.1d-f illustrate the same measurements for the PLA system.

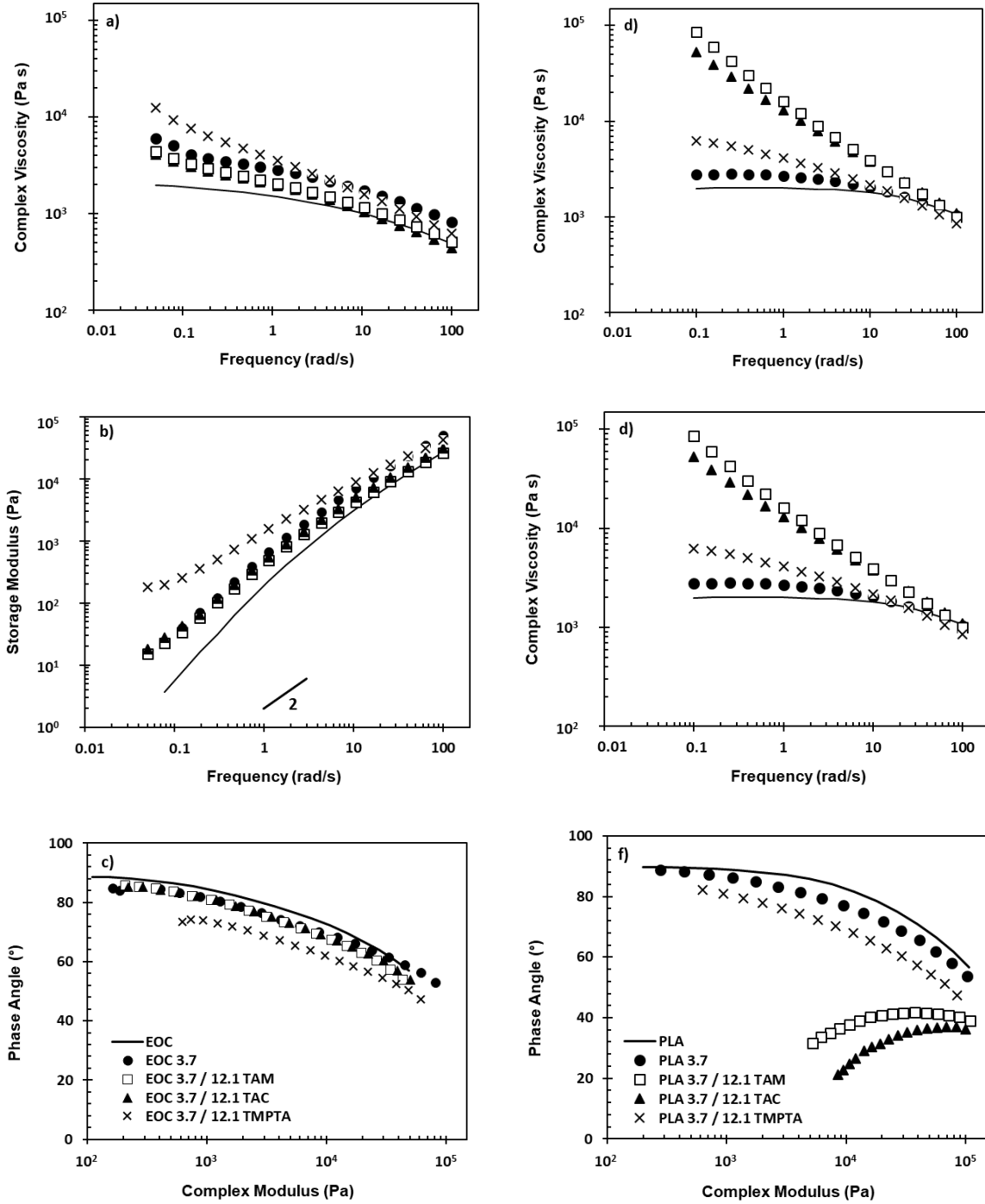


Figure 2.1: (a,d) complex viscosity and (b,e) storage modulus as a function of frequency, (c,f) van Gorp-Palmen plot for PLA and EOC formulations, respectively.

Although graft modification affected the zero-shear viscosity and the degree of shear thinning of both polymers, there were notable differences in terms of extent of the changes. Treatment of EOC with a peroxide loading of  $3.7 \mu\text{mol}\cdot\text{g}^{-1}$  eliminated the Newtonian plateau observed for the starting material (Figure 2.1a) and shifted the low frequency storage modulus away from a terminal slope of 2 that is characteristic of complete stress relaxation (Figure 2.1b). By comparison, treatment of PLA with peroxide alone produced a slight increase in the zero-shear viscosity without eliminating a Newtonian plateau (Figure 2.1d), and produced a marginal effect on the terminal flow relationship between its storage modulus and frequency (Figure 2.1e). The observed insensitivity of PLA to a peroxide-only formulation could result from lower H-atom donation yields for the polyester and/or differences in the extent of macroradical termination by combination as opposed to disproportionation. The reactivity of PLA in H-atom transfer reactions is examined further in Section 2.3.3.

Although PLA proved to be relatively unresponsive to peroxide-only formulations, its sensitivity to multifunctional monomers far exceeded that of EOC, particularly for the allylic coagents triallyl trimesate (TAM) and triallyl cyanurate (TAC). Consider the complex viscosity data plotted in Figure 2.1a and d, which reveal dramatic increases in PLA melt viscosity for DCP+TAM and DCP+TAC formulations, with the Newtonian plateau lost in favour of a power-law relationship. These changes, along with the shifts in low frequency storage modulus data plotted in Figure 2.1b and e, provide unambiguous evidence of the heightened reactivity of PLA to radical-mediated coagent modification.

Further insight into the architecture of modified PLA samples is provided by the van Gorp-Palmen plots of phase angle versus complex modulus provided in Figure 2.1c and f. The EOC and PLA starting materials demonstrated phase angles of  $90^\circ$  in the low modulus region, as is expected for



linear polymers whose terminal stress relaxation arises from limited chain entanglement. Long chain branching (LCB) created by coagent grafting changes the relaxation behaviour of chains when subjected to an oscillatory deformation, enhancing polymer elasticity at low frequency / complex modulus [35][36]. This is demonstrated by reduced phase angles, particularly for PLA that was reacted with both peroxide + allylic coagent formulations.

Table 2.1: Gel content and molecular weight data for unmodified polymers and their derivatives.

Sample				Properties			
Polymer	DCP Loading ( $\mu\text{mol/g}$ )	Coagent Loading ( $\mu\text{mol/g}$ )	Coagent	Gel Content (wt %)	<sup>a</sup> M <sub>n</sub> ( $\text{kg}\cdot\text{mol}^{-1}$ )	<sup>b</sup> M <sub>w</sub> ( $\text{kg}\cdot\text{mol}^{-1}$ )	<sup>c</sup> M <sub>z</sub> ( $\text{kg}\cdot\text{mol}^{-1}$ )
EOC	-	-	-	0	36	165	2888
EOC	3.7	-	-	0	44	181	1620
EOC	3.7	12.1	TAM	0	49	178	1627
EOC	3.7	12.1	TAC	0	47	174	7299
EOC	3.7	12.1	TMPTA	0	54	230	8178
PLA	-	-	-	0	44	86	162
PLA	3.7	-	-	0	42	86	173
PLA	3.7	12.1	TAM	18	-	-	-
PLA	3.7	12.1	TAC	21	-	-	-
PLA	3.7	12.1	TMPTA	0	34	165	5032
PLA	-	12.1	TAM	0	49	86	143
PLA	-	12.1	TAC	0	53	91	158

<sup>a</sup> M<sub>n</sub> – number average molecular weight, <sup>b</sup> M<sub>w</sub> – weight average molecular weight, <sup>c</sup> M<sub>z</sub> – the third moment of the distribution, - gelled sample not amenable to GPC analysis.

Table 2.1 provides a summary of the gel content and molecular weight distribution of the samples generated in this study. Under the conditions employed, none of the EOC materials contained a measurable gel content. However, the materials did have higher molecular weight averages than the starting material, consistent with the rheology data described above. The GPC profiles plotted in Figure 2.2a show these molecular weight increases to be the result of a high molecular weight tail that produces a strong response from the light scattering detector (Figure 2.2b). This observation is attributed to non-uniform branching distribution, which is a well-established consequence of a radical-mediated coagent grafting process [5][26][37].

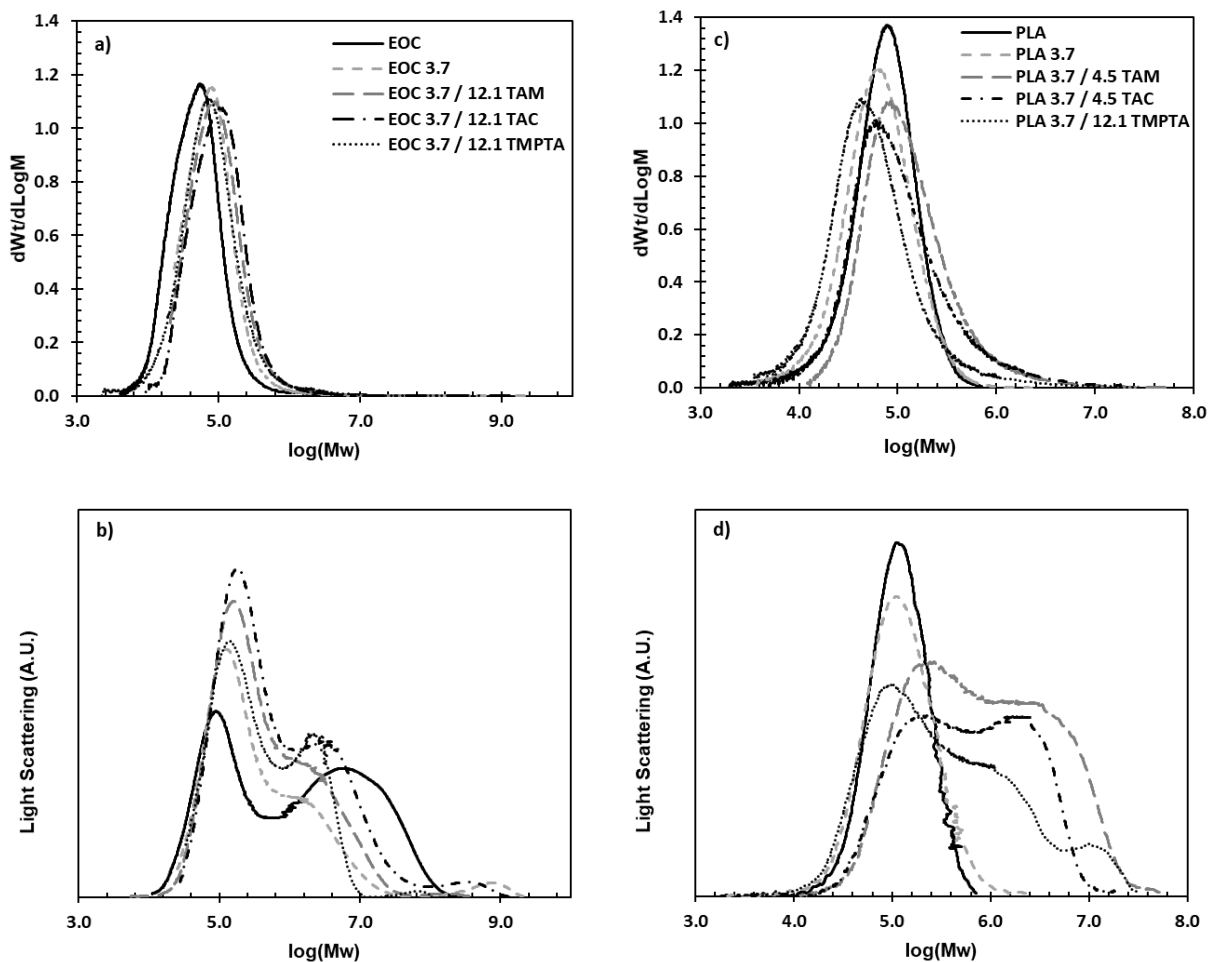


Figure 2.2: (a,c) molecular weight distribution and (b,d) GPC light scattering detector response for EOC and PLA samples respectively.

Gel content and GPC analyses of modified PLA samples were also consistent with melt-state rheology data. Whereas peroxide alone produced no measurable gel in PLA, the combination of an allylic coagent and peroxide produced substantial gel fractions. This precluded the molecular weight characterization of these samples. However, GPC analysis of PLA that was modified with just  $4.5 \mu\text{mol}\cdot\text{g}^{-1}$  allylic coagent was consistent with the EOC results (Figure 2.2b and d), with clear evidence of bimodal molecular weight and branching distributions.

### 2.3.2 Contribution of Ionic Reactions to PLA Modification

The susceptibility of PLA to hydrolysis is well documented [38]–[40], as is the potential for the material to engage in transesterification [11][41]–[44]. The latter is of particular interest to this work, given the observed efficiency of TAM in peroxide-initiated PLA branching chemistry. Note that these polymer modifications are conducted above the melting temperature of the thermoplastic for relatively short periods. If transesterification between PLA and coagent occurred under these conditions, it would produce a macromonomer derivative with a dramatically increased reactivity toward radical cross-linking. However, if transesterification is insignificant, then peroxide + TAM formulations operating on PLA would be limited to conventional radical grafting chemistry.

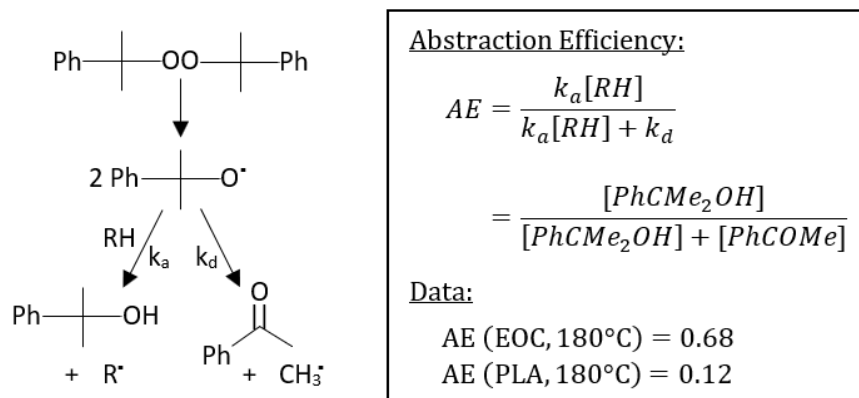
Rheology and GPC data acquired for the TAC system is noteworthy, as it indicates that the allyl cyanurate monomer, which is incapable of transesterification, is as effective as TAM in terms of PLA branching. More direct information regarding the intrinsic reactivity of PLA and TAM in the absence of peroxide was assessed by heating a sample containing  $12.1 \mu\text{mol}\cdot\text{g}^{-1}$  of the coagent to  $180^\circ\text{C}$  for 6 min, and measuring the molecular weight distribution and the polymer-bound allylic ester content of the product. GPC analysis showed the molecular weight of the TAM-treated material ( $M_n=48\text{K}$ ,  $M_w=86\text{K}$ ) to be nearly unchanged from the PLA starting material ( $M_n=46\text{K}$ ,  $M_w=86\text{K}$ ) (Table 2.1). Moreover, NMR analysis of purified product showed no evidence of allylic or aromatic functionality. Therefore, it can be concluded that the remarkable performance of allylic coagents with respect to PLA is not due to ionic reactions such as transesterification or allyl group transfer, but to radical grafting chemistry.

### 2.3.3 Abstraction Efficiency and Monofunctional Coagent Graft Modification

Although the H-atom transfer and monomer addition reactions that underlie the chemical modification of polyolefins have received considerable attention, very little is known about the

analogous PLA chemistry. A comprehensive understanding of coagent-based LCB processes requires knowledge of the rates and regioselectivity of macroradical creation by H-atom transfer to initiator-derived radicals, as well as the graft modification sequence involving C=C addition and H-atom abstraction by monomer-derived radicals. To date, this level of detail has not been acquired for any polymer modification process. However, simple measurements of peroxide abstraction efficiency and monomer graft yields have provided considerable insight. Through comparison of PLA performance relative to a conventional polyolefin system such as EOC, the unique response of the polyester to allylic coagents can be better understood.

Abstraction efficiency (AE) is a direct measure of the fraction of cumyloxy radicals that abstract an H-atom from the polymer as opposed to undergoing fragmentation to a methyl radical (Scheme 2.2) [45]. It is determined by the yield of cumyl alcohol, the byproduct of H-atom transfer, and the yield of acetophenone, the byproduct of cumyloxy radical fragmentation, with  $AE = [\text{cumyl alcohol}] / ([\text{cumyl alcohol}] + [\text{acetophenone}])$ . Since the rate of cumyloxy radical fragmentation is relatively insensitive to the reaction medium, it is solely a function of temperature [46][47], making AE a quantitative measure of H-atom donation reactivity [48].



Scheme 2.2: Byproducts of the thermolysis of DCP accompanied by abstraction efficiency (AE) formula and results for EOC and PLA, respectively.

Measurements of AE for DCP acting on the two polymers at 180°C were 0.68 for EOC and 0.12 for PLA. The PLA result is somewhat surprising, given that the lowest value previously reported was for polyisobutylene at 0.13 [45]. Note that H-atom transfer rates from a polymer depend upon the concentration and reactivity of each H-atom-bearing functional group in a material. The EOC used in this work was comprised of 90 mol% ethylene and 10 mol% octene, amounting to functional group contents of  $[-\text{CH}_2-] = 65 \text{ mmol}\cdot\text{g}^{-1}$ ,  $[-\text{CH}_3] = 2.7 \text{ mmol}\cdot\text{g}^{-1}$ , and  $[-\text{CH-}] = 2.7 \text{ mmol}\cdot\text{g}^{-1}$ . In contrast, a PLA homopolymer provides  $[-\text{CH}_3] = 13.9 \text{ mmol}\cdot\text{g}^{-1}$  and  $[-\text{CH-}] = 13.9 \text{ mmol}\cdot\text{g}^{-1}$ . Therefore, if AE is solely a function of the number of available sites for H-atom abstraction, PLA is expected to be the less reactive polymer.

Fundamental studies of H-atom transfer rates have established the importance of both enthalpic and entropic effects for different H-atom donors. Where steric inhibition is not operative, such as in H-atom abstraction from methyl groups, homolytic bond dissociation energy (BDE) can dominate patterns of reactivity. The relatively high BDE of methyl groups reduces H-atom abstraction from this site, as evidenced by the low AE of polyisobutylene, and can be expected to contribute relatively little to the reactivity of PLA. In contrast, the tertiary C-H position presents a relatively low BDE, owing to hyperconjugation with the adjacent methyl substituent, the potential lone-pair resonance effect of adjacent oxygen, and the potential inductive effect of the adjacent carbonyl – all acting to provide thermodynamic stability to a tertiary macroradical [49]. However, steric inhibition may act in opposition to these BDE effects, as recent experimental work, supported by quantum chemical calculations, have identified some H-atom transfers as entropy-controlled. Indeed, steric effects can outweigh enthalpic effects in tertiary H-atom donation, resulting in lower reactivity than is expected based on BDE arguments alone [50]. In

the case of PLA, steric inhibition of the tertiary position, coupled with the relatively low abundance of tertiary groups, can account for its observed AE.

The rheology data presented above demonstrated the relatively low reactivity of PLA toward peroxide-initiated cross-linking. This can be attributed to a low AE, since cross-linking yields are linked to the yield of macroradicals generated by H-atom donation from the polymer to peroxide-initiator fragments. However, the exceptional response to allylic coagents is more difficult to explain, given the close relationship previously reported between AE values and the yield of monomer grafting processes. Studies of vinyltrialkoxysilane addition to various polymers showed that graft yields correlated strongly with AE, and this relationship was justified on the basis that the monomer grafting sequence involves a H-atom transfer process [33][51][52].

To evaluate the reactivity of PLA toward monomer addition, the yields of peroxide-initiated allyl benzoate (AB) and butyl acrylate (BA) were measured as monofunctional analogues to TAM and TMPTA, respectively. The data listed in Table 2.2 show that PLA is relatively unreactive with respect to monomer grafting, producing reaction yields that are a fraction of those generated by EOC. This runs contrary to expectations based on the rheology data, which showed PLA to be much more responsive than EOC to LCB generation by an allylic coagent.

Table 2.2: Grafted amounts of allyl benzoate (AB) and butyl acrylate (BA) to EOC and PLA.

Polymer	Sample			Graft Yield	
	DCP Loading ( $\mu\text{mol}\cdot\text{g}^{-1}$ )	Monomer Loading ( $\mu\text{mol}\cdot\text{g}^{-1}$ )	Monomer	Graft Yield (%AB)	Graft Yield (%BA)
EOC	18.5	308.3	AB	35	-
EOC	18.5	308.3	BA	-	65
PLA	18.5	308.3	AB	5	-
PLA	18.5	308.3	BA	-	5

### 2.3.4 Solubility Considerations for PLA Branching

The data presented above have shown that the efficacy of allylic coagents toward PLA is not due to ionic reactions such as transesterification, nor is it attributable to an efficient radical grafting sequence. A third potential factor is the solubility of branched intermediates within the polymer matrix. Careful studies of polypropylene modification with TMPTA and TAM have shown that a precipitation polymerization mechanism operates concurrently with polymer branching during a peroxide-initiated process [53]. Furthermore, small molecule studies have confirmed that an initially homogeneous condition produces highly cross-linked particles, which are comprised principally of coagent when alkane solutions of TAM are heated with DCP. This cross-linked phase results from the precipitation of coagent oligomers from solution to generate a monomer-rich phase whose continued cross-linking produces insoluble particles. The result is a diversion of coagent from polyolefin cross-linking toward the generation of particles.

An examination of the Hansen solubility parameters used to assess the miscibility of polymers and solvent is revealing. The reported dispersion, polar, and hydrogen-bonding parameters for polyethylene ( $\delta_D = 16.9$ ,  $\delta_P = 0.8$ ,  $\delta_H = 2.8$ ) are consistent with its saturated hydrocarbon composition, while those of PLA ( $\delta_D = 18.6$ ,  $\delta_P = 9.9$ ,  $\delta_H = 6.0$ ) are indicative of the polarity of the polyester and its capacity for hydrogen bonding. Although Hansen parameters for TAM and TMPTA are unavailable, values for the difunctional analogues, diallyl phthalate ( $\delta_D = 22.2$ ,  $\delta_P = 12.2$ ,  $\delta_H = 8.6$ ) and 1,4-butanediyl diacrylate ( $\delta_D = 16.8$ ,  $\delta_P = 9.1$ ,  $\delta_H = 4.2$ ), provide insight into the phase equilibrium behaviour of allylic aromatic esters and acrylate monomers.

Based on these values, it is clear that PLA has a much greater thermodynamic affinity for coagents than does EOC, likely supporting solubility of the monomers and their oligomers. The latter are

particularly important, since initiation of coagent oligomerization by methyl radical addition, followed by precipitation of oligomer from the polymer matrix, renders the coagent ineffective with respect to polymer branching. However, retention of oligomerized coagent provides a multifunctional monomer bearing as many as five C=C groups, whose conversion to polymer grafts could produce a more extensive cross-link network than the trifunctional starting monomer. Based on the information available, it is this solubility difference that leads to the observed efficiency for TAM and TAC for the polyester, and the superior performance of the allylic monomers over TMPTA.

## **2.4 Conclusion**

Comparisons between PLA and EOC have shown the unique sensitivity of the polyester to allylic coagents is not a result of ionic chemistry or efficient radical grafting. In contrast, PLA is relatively unreactive toward radical graft modification, with low AE and graft yields attributable to a dearth of reactive H-atom donors. Consideration of Hansen solubility parameters confirm that PLA has a greater thermodynamic affinity for the polar coagents of interest than polyolefin systems, suggesting that improved solubility of coagent oligomers underlies the heightened reactivity of PLA toward the multifunctional allylic monomers.



## 2.5 References

- [1] A. K. Mohanty, M. Misra, and G. Hinrichsen, "Biofibres , biodegradable polymers and biocomposites : An overview," *Macromol. Mater. Eng.*, vol. 24, pp. 1–24, 2000.
- [2] C. R. Alvarez-Chevez, S. Edwards, R. Moure-Eraso, and K. Geiser, "Sustainability of bio-based plastics: General comparative analysis and recommendations for improvement," *J. Clean. Prod.*, vol. 23, no. 1, pp. 47–56, 2012.
- [3] L. Palade, H. J. Lehermeier, and J. R. Dorgan, "Melt Rheology of High l-Content Poly(lactic acid)," *Macromolecules*, vol. 34, no. 5, pp. 1384–1390, Feb. 2001.
- [4] J. R. Dorgan, J. Janzen, M. P. Clayton, S. B. Hait, and D. M. Knauss, "Melt rheology of variable L -content poly(lactic acid)," *J. Rheol. (N. Y. N. Y.)*, vol. 49, no. 3, pp. 607–619, May 2005.
- [5] J. R. Dorgan, J. S. Williams, and D. N. Lewis, "Melt rheology of poly(lactic acid): Entanglement and chain architecture effects," *J. Rheol. (N. Y. N. Y.)*, vol. 43, no. 5, pp. 1141–1155, Sep. 1999.
- [6] R. M. Rasal, A. V Janorkar, and D. E. Hirt, "Poly(lactic acid) modifications," *Prog. Polym. Sci.*, vol. 35, no. 3, pp. 338–356, Mar. 2010.
- [7] M. Jamshidian, E. A. Tehrany, M. Imran, M. Jacquot, and S. Desobry, "Poly-Lactic Acid: Production, applications, nanocomposites, and release studies," *Compr. Rev. Food Sci. Food Saf.*, vol. 9, no. 5, pp. 552–571, 2010.
- [8] J. H. Song, R. J. Murphy, R. Narayan, and G. B. H. Davies, "Biodegradable and compostable alternatives to conventional plastics," *Philos. Trans. R. Soc. B Biol. Sci.*, vol. 364, no. 1526, pp. 2127–2139, Jul. 2009.
- [9] H. Kaczmarek, M. Nowicki, and I. Vukovi, "Crosslinked blends of poly ( lactic acid ) and polyacrylates : AFM , DSC and XRD studies," *J. Polym. Res.*, vol. 20, no. 3, p. 91, 2013.
- [10] S. Detyothin, S. E. M. Selke, R. Narayan, M. Rubino, and R. Auras, "Reactive functionalization of poly(lactic acid), PLA: Effects of the reactive modifier, initiator and processing conditions on the final grafted maleic anhydride content and molecular weight of PLA," *Polym. Degrad. Stab.*, vol. 98, no. 12, pp. 2697–2708, 2013.
- [11] F. Signori, A. Boggioni, M. C. Righetti, C. E. Rondán, S. Bronco, and F. Ciardelli, "Evidences of transesterification, chain branching and cross-linking in a biopolyester commercial blend upon reaction with dicumyl peroxide in the melt," *Macromol. Mater. Eng.*, vol. 300, no. 2, pp. 153–160, 2015.
- [12] L. Wei and A. G. McDonald, "Peroxide induced cross-linking by reactive melt processing of two biopolyesters: Poly(3-hydroxybutyrate) and poly(lactic acid) to improve their melting processability," *J. Appl. Polym. Sci.*, vol. 132, no. 13, p. n/a-n/a, Apr. 2015.
- [13] A. Babanalbandi, D. J. T. Hill, J. H. O'Donnell, P. J. Pomery, and A. Whittaker, "An electron spin resonance study on  $\gamma$ -irradiated poly(l-lactic acid) and poly(d,l-lactic acid)," *Polym. Degrad. Stab.*, vol. 50, no. 3, pp. 297–304, Jan. 1995.

- [14] A. Babanalbandi, D. J. T. Hill, and A. K. Whittaker, "Volatile products and new polymer structures formed on  $^{60}\text{Co}$   $\gamma$ -radiolysis of poly(lactic acid) and poly(glycolic acid)," *Polym. Degrad. Stab.*, vol. 58, no. 1–2, pp. 203–214, Jan. 1997.
- [15] S. Loo, H. Tan, C. Ooi, and Y. Boey, "Hydrolytic degradation of electron beam irradiated high molecular weight and non-irradiated moderate molecular weight PLLA," *Acta Biomater.*, vol. 2, no. 3, pp. 287–296, May 2006.
- [16] Y. Wang, L. Yang, Y. Niu, Z. Wang, J. Zhang, F. Yu, and W. E. T. Al, "Rheological and Topological Characterizations of Electron Beam Irradiation Prepared Long-Chain Branched Polylactic Acid," *J. Appl. Polym. Sci.*, vol. 122, no. 3, pp. 1857–1865, 2011.
- [17] H. Fang, Y. Zhang, J. Bai, Z. Wang, and Z. Wang, "Bimodal architecture and rheological and foaming properties for gamma-irradiated long-chain branched polylactides," *RSC Adv.*, vol. 3, no. 23, p. 8783, 2013.
- [18] H. Xu, H. Fang, J. Bai, Y. Zhang, and Z. Wang, "Preparation and Characterization of High-Melt-Strength Polylactide with Long-Chain Branched Structure through  $\gamma$ -Radiation-Induced Chemical Reactions," *Ind. Eng. Chem. Res.*, vol. 53, no. 3, pp. 1150–1159, Jan. 2014.
- [19] C.-Q. Chen, D.-M. Ke, T.-T. Zheng, G.-J. He, X.-W. Cao, and X. Liao, "An Ultraviolet-Induced Reactive Extrusion To Control Chain Scission and Long-Chain Branching Reactions of Polylactide," *Ind. Eng. Chem. Res.*, vol. 55, no. 3, pp. 597–605, Jan. 2016.
- [20] J. You, L. Lou, W. Yu, and C. Zhou, "The preparation and crystallization of long chain branching polylactide made by melt radicals reaction," *J. Appl. Polym. Sci.*, vol. 129, no. 4, pp. 1959–1970, Aug. 2013.
- [21] M. Nerkar, J. A. Ramsay, B. A. Ramsay, and M. Kontopoulou, "Dramatic Improvements in Strain Hardening and Crystallization Kinetics of PLA by Simple Reactive Modification in the Melt State," *Macromol. Mater. Eng.*, vol. 299, no. 12, pp. 1419–1424, Dec. 2014.
- [22] M. Nerkar, J. A. Ramsay, B. A. Ramsay, A. A. Vasileiou, and M. Kontopoulou, "Improvements in the melt and solid-state properties of poly(lactic acid), poly-3-hydroxyoctanoate and their blends through reactive modification," *Polym. (United Kingdom)*, vol. 64, pp. 51–61, 2015.
- [23] P. Tiwary, C. Saraf, and M. Kontopoulou, "Modification of the rheological and thermal properties of PLA by reactive extrusion in the presence of a multifunctional coagent," *SPE ANTEC® 2016 - Proc. Tech. Conf. Exhib. Indianapolis, USA, May 23-25, 2016*, pp. 265–268, 2016.
- [24] M. Takamura, T. Nakamura, T. Takahashi, and K. Koyama, "Effect of type of peroxide on cross-linking of poly(l-lactide)," *Polym. Degrad. Stab.*, vol. 93, no. 10, pp. 1909–1916, 2008.
- [25] M. Takamura, T. Nakamura, S. Kawaguchi, T. Takahashi, and K. Koyama, "Molecular characterization and crystallization behavior of peroxide-induced slightly crosslinked poly(L-lactide) during extrusion," *Polym. J.*, vol. 42, no. 7, pp. 600–608, 2010.

- [26] P. Tiwary and M. Kontopoulou, "Tuning the rheological, thermal and solid-state properties of branched PLA by free-radical-mediated reactive extrusion," *ACS Sustain. Chem. Eng.*, vol. 51, no. 5–6, Dec. 2017.
- [27] DOW, "ENGAGE™ 8200," 2011. [Online]. Available: <http://dowglobal.ides.com/docselect.aspx?I=48244&E=30962&DOC=DOWTDS&DS=123&DK=STD&DC=en>.
- [28] P. Tiwary, C. B. Park, and M. Kontopoulou, "Transition from microcellular to nanocellular PLA foams by controlling viscosity, branching and crystallization," *Eur. Polym. J.*, vol. 91, no. April, pp. 283–296, Jun. 2017.
- [29] H.-J. Tai, "Molecular structure evolution in peroxide-initiated crosslinking of an ethylene vinyl acetate copolymer and a metallocene polyolefin elastomer," *Polym. Eng. Sci.*, vol. 39, no. 9, pp. 1577–1583, 1999.
- [30] J. Nicolás, N. Villarreal, I. Gobernado-Mitre, J. C. Merino, and J. M. Pastor, "Thermal Properties and SSA Fractionation of Metallocene Ethylene-Oct-1-ene Copolymers with High Comonomer Content Cross-linked by Dicumyl Peroxide or  $\beta$ -Radiation," *Macromol. Chem. Phys.*, vol. 204, no. 18, pp. 2212–2221, Dec. 2003.
- [31] H.-T. Liao and C.-S. Wu, "Study on Crosslinking of Polyethylene–Octene Elastomer with Dicumyl Peroxide," *Polym. Plast. Technol. Eng.*, vol. 42, no. 1, pp. 1–16, Jan. 2003.
- [32] K. Sirisinha and D. Meksawat, "Comparison in processability and mechanical and thermal properties of ethylene-octene copolymer crosslinked by different techniques," *J. Appl. Polym. Sci.*, vol. 93, no. 3, pp. 1179–1185, Aug. 2004.
- [33] R. Sengupta, S. Chakraborty, S. Bandyopadhyay, S. Dasgupta, R. Mukhopadhyay, K. Auddy, and a S. Deuri, "A Short Review on Rubber / Clay Nanocomposites With Emphasis on Mechanical Properties," *Engineering*, vol. 47, pp. 21–25, 2007.
- [34] P. Svoboda, S. Poongavalappil, R. Theravalappil, D. Svobodova, and P. Mokrejs, "Effect of octene content on peroxide crosslinking of ethylene-octene copolymers," *Polym. Int.*, vol. 62, no. 2, pp. 184–189, Feb. 2013.
- [35] S. Trinkle and C. Freidrich, "Van Gulp-Palmen-plot: A way to characterize polydispersity of linear polymers," *Rheol. Acta*, vol. 40, no. 4, pp. 322–328, 2001.
- [36] S. Trinkle, P. Walter, and C. Friedrich, "Van Gulp-Palmen Plot II - classification of long chain branched polymers by their topology," *Rheol. Acta*, vol. 41, no. 1–2, pp. 103–113, 2002.
- [37] B. K. Kim and K. J. Kim, "Cross-Linking of polypropylene by peroxide and multifunctional monomer during reactive extrusion," *Adv. Polym. Technol.*, vol. 12, no. 3, pp. 263–269, 1993.
- [38] S. J. De Jong, E. R. Arias, D. T. S. Rijkers, C. F. Van Nostrum, J. J. Kettenes-Van Den Bosch, and W. E. Hennink, "New insights into the hydrolytic degradation of poly(lactic acid): Participation of the alcohol terminus," *Polymer*, vol. 42, no. 7, pp. 2795–2802, 2001.

- [39] F. Codari, S. Lazzari, M. Soos, G. Storti, M. Morbidelli, and D. Moscatelli, "Kinetics of the hydrolytic degradation of poly(lactic acid)," *Polym. Degrad. Stab.*, vol. 97, no. 11, pp. 2460–2466, 2012.
- [40] G. Gorrasi and R. Pantani, "Effect of PLA grades and morphologies on hydrolytic degradation at composting temperature: Assessment of structural modification and kinetic parameters," *Polym. Degrad. Stab.*, vol. 98, no. 5, pp. 1006–1014, 2013.
- [41] G. Coullerez, C. Lowe, P. Pechy, H. H. Kausch, and J. Hilborn, "Synthesis of acrylate functional telechelic poly(lactic acid) oligomer by transesterification," *J. Mater. Sci. Mater. Med.*, vol. 11, no. 8, pp. 505–510, 2000.
- [42] F. Signori, M.-B. Coltelli, and S. Bronco, "Thermal degradation of poly(lactic acid) (PLA) and poly(butylene adipate-co-terephthalate) (PBAT) and their blends upon melt processing," *Polym. Degrad. Stab.*, vol. 94, no. 1, pp. 74–82, Jan. 2009.
- [43] M. B. Coltelli, S. Bronco, and C. Chinae, "The effect of free radical reactions on structure and properties of poly(lactic acid) (PLA) based blends," *Polym. Degrad. Stab.*, vol. 95, no. 3, pp. 332–341, 2010.
- [44] P. Ma, X. Cai, Y. Zhang, S. Wang, W. Dong, M. Chen, and P. J. Lemstra, "In-situ compatibilization of poly(lactic acid) and poly(butylene adipate-co-terephthalate) blends by using dicumyl peroxide as a free-radical initiator," *Polym. Degrad. Stab.*, vol. 102, no. 1, pp. 145–151, Apr. 2014.
- [45] G. E. Garrett, E. Mueller, D. a Pratt, and J. S. Parent, "Reactivity of Polyolefins toward Cumyloxy Radical: Yields and Regioselectivity of Hydrogen Atom Transfer," *Macromolecules*, vol. 47, pp. 544–551, 2014.
- [46] D. V. Avila, C. E. Brown, K. U. Ingold, and J. Lusztyk, "Solvent effects on the competitive .beta.-scission and hydrogen atom abstraction reactions of the cumyloxy radical. Resolution of a long-standing problem," *J. Am. Chem. Soc.*, vol. 115, no. 2, pp. 466–470, Jan. 1993.
- [47] H. Sakurai and A. Hosomi, "Polar and Solvent Effects on Homolytic Abstraction of Benzylic Hydrogen of Substituted Toluenes by t -Butoxy Radical," *J. Am. Chem. Soc.*, vol. 89, no. 2, pp. 458–460, Jan. 1967.
- [48] J. Lal, J. E. McGrath, and R. D. Board, "Effect of polymer structure on ease of hydrogen abstraction by cumyloxy radicals," *J. Polym. Sci. Part A-1 Polym. Chem.*, vol. 6, no. 4, pp. 821–828, Apr. 1968.
- [49] S. J. Blanksby and G. B. Ellison, "Bond Dissociation Energies of Organic Molecules," *Acc. Chem. Res.*, vol. 36, no. 4, pp. 255–263, 2002.
- [50] H. Mayr, "CC Bond Formation by Addition of Carbenium Ions to Alkenes: Kinetics and Mechanism," *Angew. Chemie Int. Ed. English*, vol. 29, no. 12, pp. 1371–1384, Dec. 1990.
- [51] M. Spencer, J. S. Parent, and R. A. Whitney, "Composition distribution in poly(ethylene-graft-vinyltrimethoxysilane)," *Polymer.*, vol. 44, no. 7, pp. 2015–2023, Mar. 2003.
- [52] S. S. Sengupta, J. S. Parent, and J. K. Mclean, "Radical-mediated modification of

polypropylene: Selective grafting via polyallyl coagents,” *J. Polym. Sci. Part A Polym. Chem.*, vol. 43, no. 20, pp. 4882–4893, 2005.

- [53] J. S. Parent, A. Bodsworth, S. S. Sengupta, M. Kontopoulou, B. I. Chaudhary, D. Poche, and S. Cousteaux, “Structure–rheology relationships of long-chain branched polypropylene: Comparative analysis of acrylic and allylic coagent chemistry,” *Polymer.*, vol. 50, no. 1, pp. 85–94, Jan. 2009.

# Chapter 3: Peroxide-initiated Modification of Poly(3-hydroxyalkanoates) (PHAs) with Tri-functional Allylic and Acrylic Coagents

## 3.1 Introduction

Poly(3-hydroxyalkanoates) (PHAs) are a group of thermoplastic biopolyesters that are classified into two groups: short-chain-length PHAs (SCL-PHAs) with side chains ranging from 3-5 carbons, and medium-chain-length PHAs (MCL-PHAs) which have side chains between 6-14 carbons. PHAs are produced through bacterial fermentation of sugars or lipids. The resulting chain length is dependent on the family of bacteria used, with *alcaligenes eutrophus* and *pseudomonas oleovorans* being the most common for the production of SCL-PHAs and MCL-PHAs, respectively [1]. PHAs have garnered interest as replacements for petroleum-based plastics, since they are both microbial-produced and derived from renewable resources [2]. At the end of their service life, they can be degraded into carbon dioxide and water by microorganisms found in soils, such as molds [3].

Despite these attractive qualities, application development for PHAs have suffered from slow crystallization kinetics, low melt viscosity, poor melt-strength, and a susceptibility to thermal degradation [4]–[6]. Research efforts into improving the processability and mechanical properties of these materials have generally focused on blending with other polymers and/or producing random copolymers containing hydroxyalkanoate functionality [7]–[15].

Gagnon et al. [39] and Dufresne et al. [8] examined the effect of peroxide thermolysis and gamma-ray radiation on poly(3-hydroxyoctanoate-co-undecenoate) (PHOU). Furthermore, Fei et al. [9] and Rupp et al. [40] examined peroxide-initiated and UV-induced cross-linking of

poly(3-hydroxybutyrate)-co-(3-hydroxyvalerate) (PHBV). These groups report that the architecture of the linear starting material was transformed by cross-linking, giving rise to an enhanced elastic response. Rupp et al. [40] further examined cross-linking by 2,6-bis(4-azidobenzylidene) - 4-methylcyclohexanone (BAM), which proved capable of controlling the rates of polymer cross-linking and concurrent chain scission.

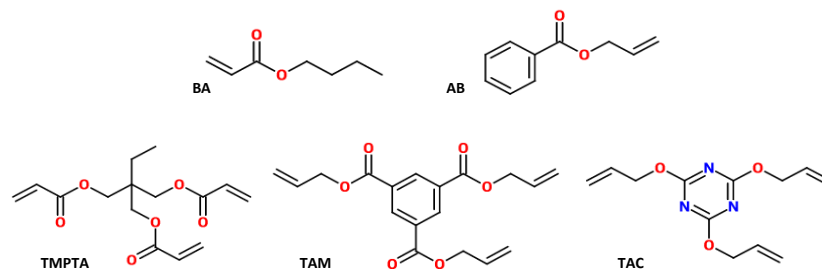
Radical-mediated solvent-free modification in the melt state is widely used to modify the properties of polyolefins [16]–[23] and biopolyesters, such as polylactic acid (PLA) [24]–[33]. These processes are generally considered suitable for large-scale production, and are more environmentally friendly compared to solution-borne reactions. An additional advantage of this approach is its amenability to conventional polymer processing equipment such as twin screw extruders [34]–[38]. Recent work on poly(3-hydroxybutyrate) (PHB) modification by reaction with peroxide and triallyl trimesate (TAM) has reportedly improved rheological properties and thermal stability [41]. A high degree of branching and/or cross-linking was attributed as the cause of a significant increase in crystallization temperature, finer spherulite formation, and faster crystallization kinetics.

The current study compares the effects of grafting allylic and acrylic tri-functional coagents on the linear viscoelastic (LVE) properties and molecular weight distribution of poly(3-hydroxyoctanoate) (PHO) and PHB, using dicumyl peroxide (DCP) as a radical initiator. These results are combined with studies of H-atom abstraction and monomer grafting reactions of various MCL-PHAs and SCL-PHAs to develop mechanistic insight into these modification processes.

## 3.2 Materials and Methods

### 3.2.1 Materials

Additive-free poly(3-hydroxybutyrate) (PHB) with a weight-average molecular weight of 1416 kg·mol<sup>-1</sup> and dispersity of 7 was supplied by Biomer, Germany. Poly(3-hydroxyoctanoate) (PHO) containing 98 mol% 3-hydroxyoctanoate and 2 mol% 3-hydroxyhexanoate, was produced in a chemostat culture with addition of acrylic acid to inhibit  $\beta$ -oxidation [42]. Poly(3-hydroxynonanoate) (PHN) and poly(3-hydroxydecanoate) (PHD) were produced in feed batch cultures with *pseudomonas putida*, by varying the feed rate and ratio of acetic acid, glucose, and nonanoic acid or decanoic acid for PHN and PHD, respectively.  $\beta$ -oxidation was used to knock out mutants of the same bacteria strain [43][44]. PHN contained 99 mol% 3-hydroxynonanoate and 1 mol% 3-hydroxypentanoate, whereas PHD contained 98 mol% 3-hydroxydecanoate and 2 mol% 3-hydroxyoctanoate. All polymers were purified by purified by dissolution / precipitation and dried under vacuum at 40°C for 24 hr. Butyl acrylate (BA, 99%), dicumyl peroxide (DCP, 98%), triallyl cyanurate (TAC, 97%), and trimethylolpropane triacrylate (TMPTA, 70%) were used as received from Sigma Aldrich. Allyl benzoate (AB, 98%), and triallyl trimesate (TAM, 98%) were used as received from TCI America and Monomer-Polymer Labs, respectively.



Scheme 3.1: Chemical structure of coagents used in the present work.



### 3.2.2 Compounding

Samples for graft modification with monofunctional monomers AB and BA were prepared by coating the desired polymer (0.5 g) with an acetone solution to create a masterbatch containing DCP (0.001 g,  $18.5 \mu\text{mol}\cdot\text{g}^{-1}$  or 0.1 wt-%), and monomer (0.05 g,  $308.6 \mu\text{mol}\cdot\text{g}^{-1}$  or approximately 5 wt-%). After evaporation of acetone, masterbatches were charged to an Atlas Mixer at  $180^\circ\text{C}$  for 6 min. The products were purified by dissolution /precipitation (chloroform/methanol) and dried prior to further analysis.

Samples for trifunctional coagent graft modification were prepared by coating polymer (10 g) with a mixture of DCP (0.01 g,  $3.7 \mu\text{mol}\cdot\text{g}^{-1}$  or 0.1 wt-%) and coagent (0.04 g – 0.08 g,  $12.1 - 24.2 \mu\text{mol}\cdot\text{g}^{-1}$  or approximately 0.4 – 0.8 wt-%) in acetone solution, and drying under vacuum at  $40^\circ\text{C}$  before processing with a twin-screw DSM micro-compounder at  $180^\circ\text{C}$  for 6 min at a screw speed of 100 RPM.

Formulations are identified by polymer type, followed by amount of peroxide/coagent and type of coagent used. For example, PHO 3.7/24.2 TAM denotes PHO reacted with  $3.7 \mu\text{mol}\cdot\text{g}^{-1}$  DCP and  $24.2 \mu\text{mol}\cdot\text{g}^{-1}$  TAM.

### 3.2.3 Rheology

The linear viscoelastic (LVE) properties were measured using an MCR-301 Anton Paar rheometer in the shear oscillatory mode by means of a 25 mm parallel plate at  $60^\circ\text{C}$  and  $180^\circ\text{C}$  for PHO and PHB, respectively. The frequency used for these studies was  $0.1 - 100 \text{ rad}\cdot\text{s}^{-1}$ ; lower frequencies were avoided to limit the degradation of the thermally sensitive bio-polymers. Due to PHB being extremely thermally unstable measurement at lower frequencies were not possible, thus limited to  $1 \text{ rad}\cdot\text{s}^{-1}$ . All samples were dried under vacuum prior to analysis. The measured data was fitted to the modified Cross-model. Three replicates were conducted on all measurements.

$$\eta(\omega) = \frac{\eta_o}{1 + |\lambda\omega|^{1-n}} \quad (3.1)$$

where  $\eta$  is the shear viscosity,  $\eta_o$  is the zero-shear viscosity,  $\lambda$  is the relaxation time,  $n$  is a constant related to the shear thinning behavior, and  $\omega$  is the frequency in  $\text{rad}\cdot\text{s}^{-1}$ .

### 3.2.4 Gas Permeation Chromatography (GPC)

GPC analysis was conducted in tetrahydrofuran (THF) solutions using a Viscotek 270max separation module equipped with differential refractive index (DRI), viscosity (IV), and light scattering (low angle, and right angle). The separation module was maintained at  $40^\circ\text{C}$  and contained two porous PolyAnalytik columns in series with an exclusion molecular weight limit of 209,106 Da. The data was processed with Viscotek Omniseq software using a  $dn/dc$  value of 0.0602 for PHO in THF [45]. Three replicates were conducted on all measurements.

### 3.2.5 Gel Content

The gel content was measured according to ASTM D2765 by extracting polymer samples from stainless-steel wire mesh (120 sieve) for 8 hr using boiling THF. The samples were dried overnight in a vacuum oven at  $40^\circ\text{C}$ , with gel content reported as weight percent of unextracted material. The characterizations revealed that all PHO samples were gel free.

### 3.2.6 Nuclear Magnetic Resonance (NMR) Spectroscopy

$^1\text{H}$  NMR spectra were acquired with a Bruker AC-400 MHz spectrometer in d-chloroform ( $d\text{-CHCl}_3$ ) using polymer concentrations of  $10 \text{ mg}\cdot\text{mL}^{-1}$ , with the chemical shift references to the resonance of residual  $\text{CHCl}_3$  within the solvent. Tetramethylsilane (TMS) was used as the internal standard for calculations.

### 3.2.7 Abstraction Efficiency (AE)

Chopped polymer (0.5 g) was coated with a solution of DCP (~0.2 mL) to produce a peroxide concentration of 2 wt.% (74.0  $\mu\text{mol}\cdot\text{g}^{-1}$ ). The acetone was allowed to evaporate before charging to an Atlas Laboratory Mixer at 150, 160, 170, and 180°C for seven initiator half-lives (105, 39, 14 and 6 min, respectively). The resulting material was dissolved in acetone and a small aliquot of the solution was injected into a Hewlett-Packard 5890 series II chromatograph equipped with a Superlco SPB-1 microbore column using 2 mL·min<sup>-1</sup> of helium as carrier gas. Injector and detector temperatures were held at 275°C, with the oven temperature starting at 100°C for 2 min, ramping to 250°C at 22°C·min<sup>-1</sup>, and holding for 6 min. Abstraction efficiencies are reported as [cumyl alcohol] / ([cumyl alcohol] + [acetophenone]) [23].

## 3.3 Results and Discussion

### 3.3.1 PHO Modification using Allylic and Acrylate Coagents

The molecular weight distributions and LVE properties of PHO samples modified with allylic and acrylic coagents are shown in Figure 3.1 and Figure 3.2, respectively. Table 3.1 summarizes the molecular weights of the various formulations and the corresponding Cross-model parameters, obtained from fitting the complex viscosity versus frequency curves using Equation 3.1.

Table 3.1: Molecular weight data, and Cross-model parameters for PHO formulations

Sample Designation				Properties				
Polymer	DCP Loading ( $\mu\text{mols}$ )	Coagent Loading ( $\mu\text{mols}$ )	Coagent Name	<sup>a</sup> $\mathcal{D}$	<sup>b</sup> $M_w$ ( $\text{kg}\cdot\text{mol}^{-1}$ )	<sup>c</sup> $M_z$ ( $\text{kg}\cdot\text{mol}^{-1}$ )	<sup>d</sup> $\eta_0$ ( $\text{Pa}\cdot\text{s}$ )	<sup>e</sup> $\lambda$ ( $\times 10^{-3}\cdot\text{s}$ )
PHO	-	-	-	1.8	107	170	152	2.0
PHO	3.7	-	-	2.8	98	828	116	3.0
PHO	3.7	24.2	TAM	5.5	660	10240	570	480
PHO	3.7	24.2	TAC	5.8	756	5495	719	480
PHO	3.7	24.2	TMPTA	6.9	561	7037	-	-

<sup>a</sup> $\mathcal{D}$  – dispersity ( $M_w/M_n$ ), <sup>b</sup> $M_w$  – weight average molecular weight, <sup>c</sup> $M_z$  – z-average molecular weight, <sup>d</sup> $\eta_0$  – zero-shear viscosity, and <sup>e</sup> $\lambda$  – relaxation time.

This data shows that PHO modification with peroxide alone had little effect on  $M_w$  and LVE properties. However, the GPC profiles plotted in Figure 3.1 reveal a high molecular weight chain population that produced a strong light scattering detector response. This high  $M_w$  tail produced a pronounced increase in  $M_z$  values and polydispersity (Table 3.1).

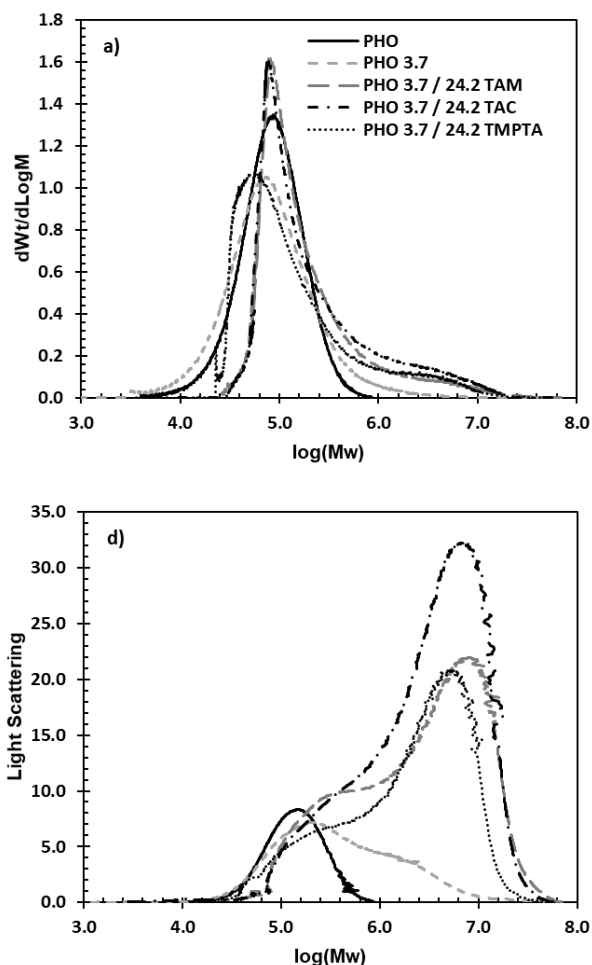


Figure 3.1: (a) Molecular weight distribution and (b) light scattering analysis of PHO modified with coagent loadings of 24.2  $\mu\text{mol}\cdot\text{g}^{-1}$  of coagent.

Formulations that included peroxide and coagent resulted in a dramatic increase in  $M_z$ , as well as pronounced bimodality in the light scattering data. This is a well-established consequence of radical-mediated coagent grafting, and is attributed to the a highly branched structure [46].

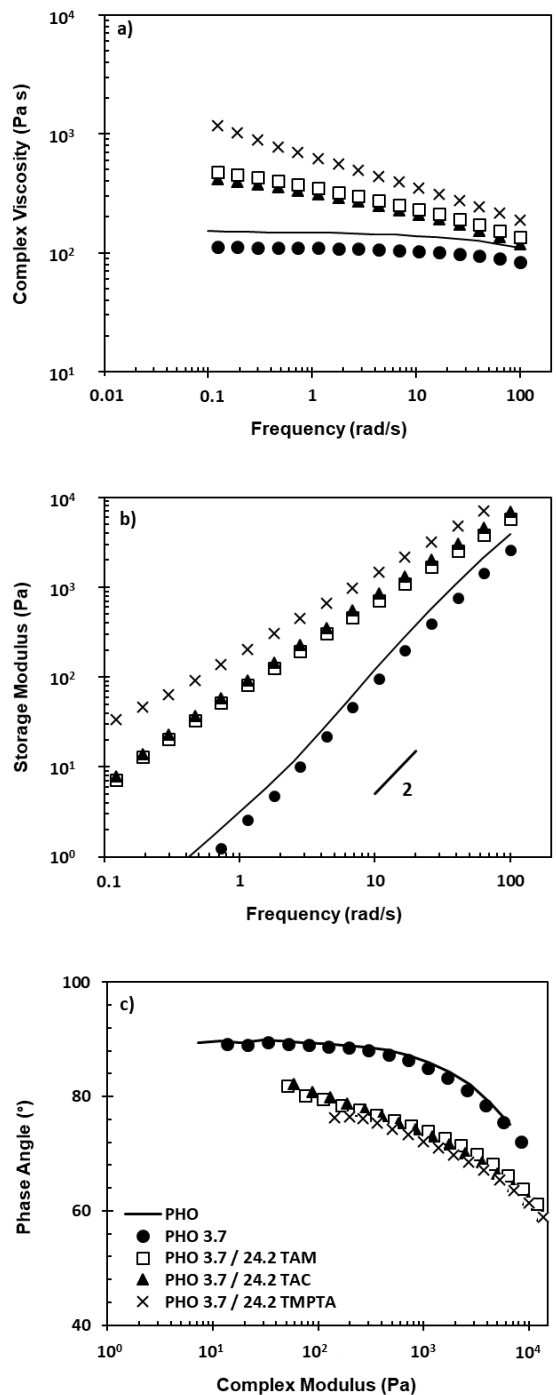


Figure 3.2: (a) Complex viscosity and (b) storage modulus versus frequency and (c) van Gurp-Palmen plot at 60°C with coagent loading of 24.2  $\mu\text{mol}\cdot\text{g}^{-1}$ .

Interestingly, in spite of similarities in the molecular weight, the acrylate coagent, TMPTA, produced a more pronounced increase in the low-shear viscosity, with a loss of the Newtonian plateau, as well as evidence of the onset of yielding. This prevented the fitting of the Cross-model

to this data set. Acrylate coagents are known to be more reactive and are prone to oligomerization side-reactions that compete with grafting to the polymer backbone [22]. These oligomerization reactions can lead to sub-micron size, coagent-rich particles, whose precipitation from the polymer matrix represents a loss of potential branching. These particles may further affect the low-frequency LVE response of the material.

### **3.3.2 PHB Modification using Allylic and Acrylate Coagents**

Radical modification of SCL-PHAs with coagent-based formulations is also of interest. Rheological data for PHB reacted with allylic and acrylic coagents are shown in Figure 3.3a-c. PHB is insoluble in THF, therefore it was not possible to measure molecular weight distributions by size exclusion chromatography.

Modification with a peroxide loading of  $3.7 \mu\text{mol}\cdot\text{g}^{-1}$  produced lower viscosity and storage modulus values at high frequencies (Figure 3.3a and b) compared to the starting material. It is known that PHB is thermally sensitive, and processing at high temperature can lead to degradation through random chain scission and pyrolysis mechanism [52]–[54]. This effect can be enhanced by  $\beta$ -scission of polymer radicals, leading to further degradation in the manner reported for polypropylene [22].

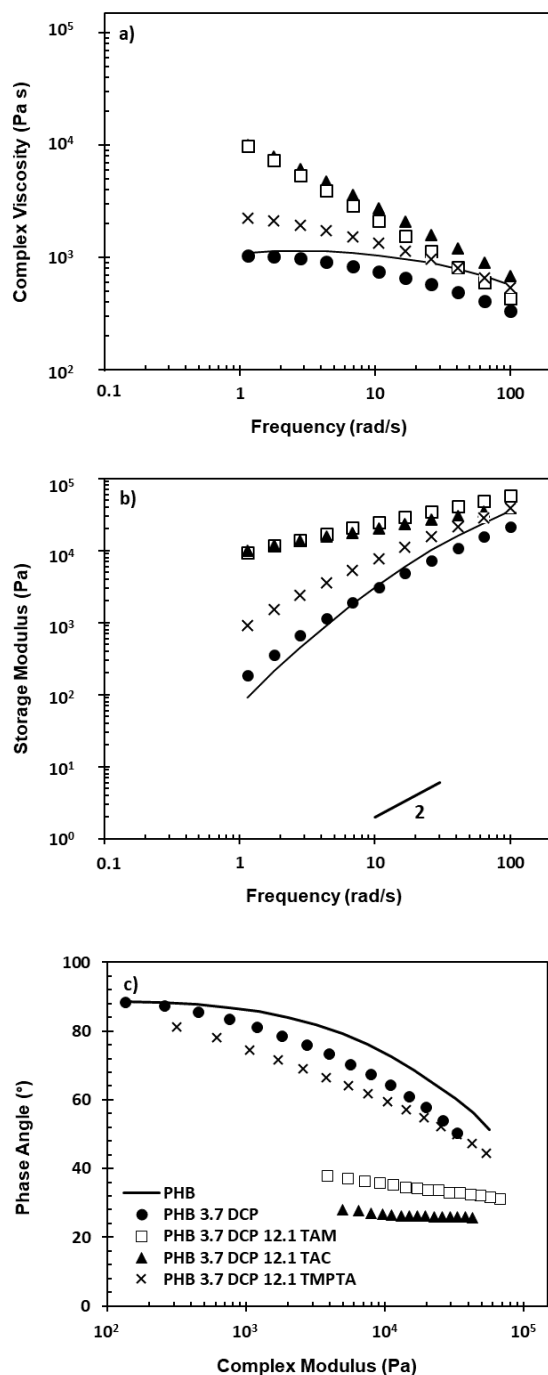


Figure 3.3: (a) Complex viscosity and (b) storage modulus versus frequency, and (c) van Gurp-Palmen plot at 180°C with coagent loadings of 12.1  $\mu\text{mol}\cdot\text{g}^{-1}$ .

Reaction with peroxide and coagents had pronounced effects on zero-shear viscosity and the degree of shear thinning. The formulation containing DCP and TMPTA produced an increase in zero-shear viscosity that is indicative of shear thinning, but the Newtonian plateau remained. A

slight deviation from the terminal slope of 2 in Figure 3.3b indicates slight architectural changes in the presence of acrylate coagent. On the other hand, the application of allylic coagents, TAM and TAC, produced dramatic changes to LVE properties. Consider the complex viscosity data plotted (Figure 3.3a), which reveal increased PHB melt viscosity, and pronounced shear thinning that is accompanied by the loss of the Newtonian plateau. Significant deviation in the storage modulus (Figure 3.3b) from a terminal flow condition indicates the presence of complex chain architecture and improved elasticity. These results are consistent with a previous report by Kolanchi and Kontopoulou in which PHB was modified by reaction with DCP and TAM [41].

Further comparison of the efficiency of the allylic versus acrylate coagents can be gained from the van Gorp-Palmen plot of phase angle versus complex modulus (Figure 3.3c). As expected, the linear starting material approaches the terminal phase angle of 90°. In the DCP and TMPTA formulation there is some deviation from the linear polymer response, however the material appears to approach terminal flow. In contrast, the allylic coagents generated a profound deviation, with phase angle values of approximately 40°. Such a decline of phase angle is often associated with extensive cross-linking up to and beyond the gel point. This was confirmed by gel content analysis, which revealed 10% gel in allylic modified samples, whereas the acrylate samples were found to be gel free. These results demonstrate that the allylic coagents are much more effective compared to the acrylate coagent in modifying PHB.

### **3.3.3 Abstraction Efficiency and Monofunctional Graft Modifications**

The results described above reveal that PHO and PHB engage in peroxide-mediated reactions. Insight into the intrinsic reactivity of each polymer with respect to DCP is gained by measurement of abstraction efficiency (AE). As discussed in Chapter 2, DCP thermolysis yields two cumyloxy radicals that either abstract an H-atom to form cumyl alcohol and a polymer macroradical, or



cleave to give acetophenone and a methyl radical. Therefore, a higher cumyl alcohol yield is reflective of a more efficient H-atom transfer reaction, and AE values calculated as  $[\text{cumyl alcohol}] / ([\text{cumyl alcohol}] + [\text{acetophenone}])$  can quantify the reactivity of a given polymer toward DCP [23]. AE measurements are illustrated in Figure 3.4 for a variety of MCL-PHAs (PHO, PHN, and PHB), as well as the SCL-PHA, PHB. These results show that MCL-PHAs are better H-atom donors than SCL-PHA, producing AE values closer to those of an ethylene octene copolymer (EOC) polyolefin than a polyester such as PLA (Table 3.2).

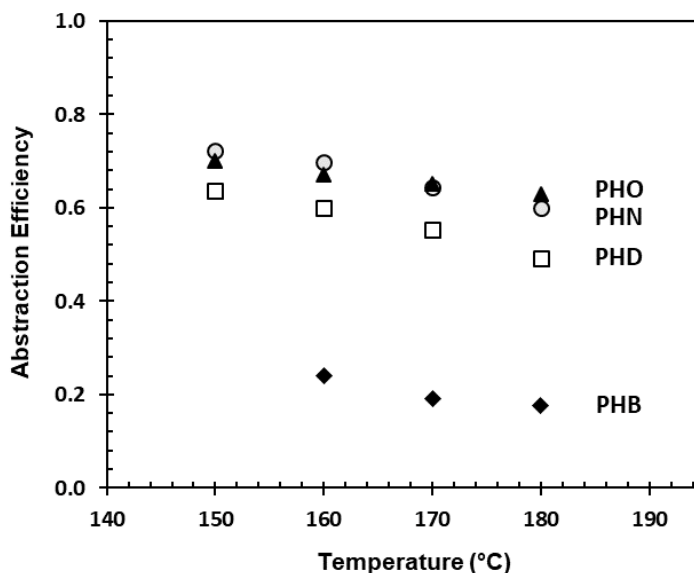


Figure 3.4: Abstraction efficiency as a function of reaction temperature. The 150°C melting point of PHB precluded an AE measurement at this temperature obtained.

Table 3.2: AE, functional group content, and graft yield of various polymers.

Polymer	AE (180°C)	[-CH-] (mmol·g <sup>-1</sup> )	[-CH <sub>2</sub> -] (mmol·g <sup>-1</sup> )	[-CH <sub>3</sub> ] (mmol·g <sup>-1</sup> )	Graft Yield AB (%)	Graft Yield BA (%)
PLA	0.12	13.9	0.0	13.9	5	5
EOC	0.68	2.7	65.0	2.7	35	65
PHB	0.18	11.6	11.6	11.6	-	-
PHO*	0.60	7.0	32.2	7.0	40	75
PHN*	0.63	6.4	38.5	6.4	-	-
PHD*	0.49	5.9	41.3	5.9	-	-

\* functional group content within MCL-PHAs was calculated for homopolymer, due to the low comonomer content.

Since H-atom transfer rates from a polymer depends upon the concentration and reactivity of each H-atom-bearing functional group in the material, an examination of the composition of each polymer is warranted (Table 3.2). PHB and PLA are structurally similar, as they both have an ester functionality and a methyl group, but PHB has an additional methylene group on the backbone. The presence of this secondary H-atom donor likely accounts for the slightly higher AE for PHB.

The MCL-PHAs have a considerably higher hydrocarbon content arising from their long alkane side chain, making them structurally more similar to EOC. Overall, as the length of alkane side chains increase, there is a rise in [-CH<sub>2</sub>-] content and a decrease in [-CH<sub>3</sub>] and [-CH-] content. Therefore, if AE is solely a function of the number of available sites, the longer the alkane chain; there is an increase in available hydrogen donation sites, thus increased H-atom transfer reactivity.

To improve understanding of the reactivity of MCL-PHAs toward monomer addition, PHO samples were graft-modified with allyl benzoate (AB) and butyl acrylate (BA) as monofunctional analogues to TAM and TMPTA respectively. Proton NMR spectra used to calculate graft content can be found in Appendix B, while the percent of monomer grafted is illustrated in Table 3.2. It is no surprise with these graft efficiencies and high AE that PHO has an affinity for graft propagation. The increased grafting ability of the acrylate over the allylic coagent is expected, as the former are more kinetically reactive. These results are in line with the findings for EOC and with literature reports on polyethylene functionalization [23].

The insolubility of PHB in chloroform precluded a measurement of its AB and BA graft yields. However, the rheology data showed that allylic coagents are highly effective on this polyester, just as they are with for PLA, as reported in Chapter 2. An examination of the Hansen solubility parameters used to assess the miscibility of polymers and solvent is revealing. The reported

dispersion, polar, and hydrogen bonding parameters for PHB ( $\delta_D = 15.5$ ,  $\delta_P = 9.1$ ,  $\delta_H = 4.2$ ) are similar to those documented for PLA ( $\delta_D = 18.6$ ,  $\delta_P = 9.9$ ,  $\delta_H = 6.0$ ) [55]. As such, this short chain branched polyester may be expected to share PLA's thermodynamic affinity for allylic coagents such as TAM.

### **3.4 Conclusions**

This work has compared the effect of the type (allylic versus acrylic) and amount of tri-functional coagent on the LVE properties of PHO and PHB in the presence of peroxide. Based on detailed rheological and molecular weight distribution characterizations, PHO showed an affinity for both acrylate and allylic coagents and resulted in increases in complex viscosity, evidence of shear thinning, and bimodal molecular weight distributions. Abstraction efficiency evaluations revealed that MCL-PHAs are significantly more reactive H-atom donors compared to SCL-PHAs, owing to their greater methylene group content. The unique efficiency of allylic coagents acting upon PHB is consistent with the previously described findings for PLA, and likely arises from the enhanced solubility of coagents within the thermoplastic polyester melt.

### 3.5 References

- [1] S. Y. Lee, "Bacterial polyhydroxyalkanoates," *Biotechnol. Bioeng.*, vol. 49, no. 1, pp. 1–14, Mar. 1996.
- [2] U. J. Hanggi, "Requirements on bacterial polyesters as future substitute for conventional plastics for consumer goods," *FEMS Microbiol. Rev.*, vol. 16, no. 2–3, pp. 213–220, Feb. 1995.
- [3] C. Nawrath, Y. Poirier, and C. Somerville, "Plant polymers for biodegradable plastics: Cellulose, starch and polyhydroxyalkanoates," *Mol. Breed.*, vol. 1, no. 2, pp. 105–122, Jun. 1995.
- [4] A. El-Hadi, R. Schnabel, E. Straube, G. Müller, and S. Henning, "Correlation between degree of crystallinity, morphology, glass temperature, mechanical properties and biodegradation of poly (3-hydroxyalkanoate) PHAs and their blends," *Polym. Test.*, vol. 21, no. 6, pp. 665–674, Jan. 2002.
- [5] S. Modi, K. Koelling, and Y. Vodovotz, "Assessment of PHB with varying hydroxyvalerate content for potential packaging applications," *Eur. Polym. J.*, vol. 47, no. 2, pp. 179–186, Feb. 2011.
- [6] P. Ma, D. G. Hristova-Bogaerds, P. J. Lemstra, Y. Zhang, and S. Wang, "Toughening of PHBV/PBS and PHB/PBS Blends via In situ Compatibilization Using Dicumyl Peroxide as a Free-Radical Grafting Initiator," *Macromol. Mater. Eng.*, vol. 297, no. 5, pp. 402–410, May 2012.
- [7] A. Dufresne and M. Vincendon, "Poly(3-hydroxybutyrate) and poly(3-hydroxyoctanoate) blends: Morphology and mechanical behavior," *Macromolecules*, vol. 33, no. 8, pp. 2998–3008, 2000.
- [8] A. Dufresne, L. Reche, R. H. Marchessault, and M. Lacroix, "Gamma-ray crosslinking of poly(3-hydroxyoctanoate-co-undecenoate)," *Int. J. Biol. Macromol.*, vol. 29, no. 2, pp. 73–82, Aug. 2001.
- [9] B. Fei, C. Chen, S. Chen, S. Peng, Y. Zhuang, Y. An, and L. Dong, "Crosslinking of poly[(3-hydroxybutyrate)-co-(3-hydroxyvalerate)] using dicumyl peroxide as initiator," *Polym. Int.*, vol. 53, no. 7, pp. 937–943, Jul. 2004.
- [10] M. Avella, E. Martuscelli, and M. Raimo, "Review Properties of blends and composites based on poly(3-hydroxy)butyrate (PHB) and poly(3-hydroxybutyrate-hydroxyvalerate) (PHBV) copolymers," *J. Mater. Sci.*, vol. 35, no. 3, pp. 523–545, 2000.
- [11] L. Savenkova, Z. Gerberg, V. Nikolaeva, A. Dzene, I. Bibers, and M. Kalnin, "Mechanical properties and biodegradation characteristics of PHB-based films," *Process Biochem.*, vol. 35, no. 6, pp. 573–579, Jan. 2000.
- [12] R. T. Chan, H. Marçal, T. Ahmed, R. A. Russell, P. J. Holden, and L. J. R. Foster, "Poly(ethylene glycol)-modulated cellular biocompatibility of polyhydroxyalkanoate films," *Polym. Int.*, vol. 62, no. 6, pp. 884–892, 2013.

- [13] M. Nerkar, J. A. Ramsay, B. A. Ramsay, and M. Kontopoulou, "Melt Compounded Blends of Short and Medium Chain-Length Poly-3-hydroxyalkanoates," *J. Polym. Environ.*, vol. 22, no. 2, pp. 236–243, Jun. 2014.
- [14] W. Chen, D. J. David, W. J. MacKnight, and F. E. Karasz, "Miscibility and morphology of blends of poly (3-hydroxybutyrate) and poly (vinyl butyral)," *Polymer.*, vol. 42, no. 20, pp. 8407–8414, 2001.
- [15] L. Yu, K. Dean, and L. Li, "Polymer blends and composites from renewable resources," *Prog. Polym. Sci.*, vol. 31, no. 6, pp. 576–602, Jun. 2006.
- [16] B. K. Kim and K. J. Kim, "Cross-Linking of polypropylene by peroxide and multifunctional monomer during reactive extrusion," *Adv. Polym. Technol.*, vol. 12, no. 3, pp. 263–269, 1993.
- [17] X. Wang, C. Tzoganakis, and G. L. Rempel, "Chemical modification of polypropylene with peroxide/pentaerythritol triacrylate by reactive extrusion," *J. Appl. Polym. Sci.*, vol. 61, no. 8, pp. 1395–1404, Aug. 1996.
- [18] G. Moad, "The synthesis of polyolefin graft copolymers by reactive extrusion," *Prog. Polym. Sci.*, vol. 24, no. 1, pp. 81–142, Apr. 1999.
- [19] A. D. Gotsis, B. L. F. Zeevenhoven, and A. H. Hogt, "The effect of long chain branching on the processability of polypropylene in thermoforming," *Polym. Eng. Sci.*, vol. 44, no. 5, pp. 973–982, May 2004.
- [20] G. J. Nam, J. H. Yoo, and J. W. Lee, "Effect of long-chain branches of polypropylene on rheological properties and foam-extrusion performances," *J. Appl. Polym. Sci.*, vol. 96, no. 5, pp. 1793–1800, Jun. 2005.
- [21] K. El Mabrouk, J. S. Parent, B. I. Chaudhary, and R. Cong, "Chemical modification of PP architecture: Strategies for introducing long-chain branching," *Polymer.*, vol. 50, no. 23, pp. 5390–5397, Nov. 2009.
- [22] J. S. Parent, A. Bodsworth, S. S. Sengupta, M. Kontopoulou, B. I. Chaudhary, D. Poche, and S. Cousteaux, "Structure–rheology relationships of long-chain branched polypropylene: Comparative analysis of acrylic and allylic coagent chemistry," *Polymer.*, vol. 50, no. 1, pp. 85–94, Jan. 2009.
- [23] G. E. Garrett, E. Mueller, D. a Pratt, and J. S. Parent, "Reactivity of Polyolefins toward Cumyloxy Radical: Yields and Regioselectivity of Hydrogen Atom Transfer," *Macromolecules*, vol. 47, pp. 544–551, 2014.
- [24] Y. Di, S. Iannace, E. Di Maio, and L. Nicolais, "Reactively Modified Poly(lactic acid): Properties and Foam Processing," *Macromol. Mater. Eng.*, vol. 290, no. 11, pp. 1083–1090, Nov. 2005.
- [25] S. lin Yang, Z. H. Wu, W. Yang, and M. B. Yang, "Thermal and mechanical properties of chemical crosslinked polylactide (PLA)," *Polym. Test.*, vol. 27, no. 8, pp. 957–963, 2008.

- [26] M. B. Coltelli, S. Bronco, and C. China, "The effect of free radical reactions on structure and properties of poly(lactic acid) (PLA) based blends," *Polym. Degrad. Stab.*, vol. 95, no. 3, pp. 332–341, 2010.
- [27] D. N. Bikiaris and G. P. Karayannidis, "Chain extension of polyesters PET and PBT with two new diimidodiepoxides. II," *J. Polym. Sci. Part A Polym. Chem.*, vol. 34, no. 7, pp. 1337–1342, May 1996.
- [28] J. You, L. Lou, W. Yu, and C. Zhou, "The preparation and crystallization of long chain branching polylactide made by melt radicals reaction," *J. Appl. Polym. Sci.*, vol. 129, no. 4, pp. 1959–1970, Aug. 2013.
- [29] R. M. Rasal, A. V. Janorkar, and D. E. Hirt, "Poly(lactic acid) modifications," *Prog. Polym. Sci.*, vol. 35, no. 3, pp. 338–356, Mar. 2010.
- [30] M. Nerkar, J. A. Ramsay, B. A. Ramsay, and M. Kontopoulou, "Dramatic Improvements in Strain Hardening and Crystallization Kinetics of PLA by Simple Reactive Modification in the Melt State," *Macromol. Mater. Eng.*, vol. 299, no. 12, pp. 1419–1424, Dec. 2014.
- [31] Y. Baimark and P. Srihanam, "Influence of chain extender on thermal properties and melt flow index of stereocomplex PLA," *Polym. Test.*, vol. 45, pp. 52–57, Aug. 2015.
- [32] H. Chen and J. Kong, "Hyperbranched polymers from A<sub>2</sub> + B<sub>3</sub> strategy: recent advances in description and control of fine topology," *Polym. Chem.*, vol. 7, no. 22, pp. 3643–3663, 2016.
- [33] P. Tiwary, C. B. Park, and M. Kontopoulou, "Transition from microcellular to nanocellular PLA foams by controlling viscosity, branching and crystallization," *Eur. Polym. J.*, vol. 91, no. April, pp. 283–296, Jun. 2017.
- [34] D. Graebing, "Synthesis of Branched Polypropylene by a Reactive Extrusion Process," *Macromolecules*, vol. 35, no. 12, pp. 4602–4610, Jun. 2002.
- [35] T. F. Otero, "Reactive conducting polymers as actuating sensors and tactile muscles," *Bioinspir. Biomim.*, vol. 3, no. 3, p. 35004, Sep. 2008.
- [36] T. F. Otero, J. Arias-Pardilla, and E. Chermak, "Reactive polymer films. Polypyrrole oxidation kinetics in aqueous solution," *Synth. Met.*, vol. 160, no. 5–6, pp. 425–431, 2010.
- [37] G. Moad, "Chemical modification of starch by reactive extrusion," *Prog. Polym. Sci.*, vol. 36, no. 2, pp. 218–237, 2011.
- [38] S. Detyothin, S. E. M. Selke, R. Narayan, M. Rubino, and R. Auras, "Reactive functionalization of poly(lactic acid), PLA: Effects of the reactive modifier, initiator and processing conditions on the final grafted maleic anhydride content and molecular weight of PLA," *Polym. Degrad. Stab.*, vol. 98, no. 12, pp. 2697–2708, 2013.
- [39] K. . Gagnon, R. . Lenz, R. . Farris, and R. . Fuller, "Chemical modification of bacterial elastomers: 1. Peroxide crosslinking," *Polymer.*, vol. 35, no. 20, pp. 4358–4367, Sep. 1994.

- [40] B. Rupp, C. Ebner, E. Rossegger, C. Slugovc, F. Stelzer, and F. Wiesbrock, "UV-induced crosslinking of the biopolyester poly(3-hydroxybutyrate)-co-(3-hydroxyvalerate)," *Green Chem.*, vol. 12, no. 10, p. 1796, 2010.
- [41] A. R. Kolahchi and M. Kontopoulou, "Chain extended poly(3-hydroxybutyrate) with improved rheological properties and thermal stability, through reactive modification in the melt state," *Polym. Degrad. Stab.*, vol. 121, pp. 222–229, Nov. 2015.
- [42] X. Jiang, Z. Sun, R. H. Marchessault, J. A. Ramsay, and B. A. Ramsay, "Biosynthesis and Properties of Medium-Chain-Length Polyhydroxyalkanoates with Enriched Content of the Dominant Monomer," *Biomacromolecules*, vol. 13, no. 9, pp. 2926–2932, Sep. 2012.
- [43] X. Jiang, Z. Sun, J. A. Ramsay, and B. A. Ramsay, "Fed-batch production of MCL-PHA with elevated 3-hydroxynonanoate content," *AMB Express*, vol. 3, no. 1, p. 50, 2013.
- [44] J. Gao, J. A. Ramsay, and B. A. Ramsay, "Fed-batch production of poly-3-hydroxydecanoate from decanoic acid," *J. Biotechnol.*, vol. 218, pp. 102–107, 2016.
- [45] M. Nerkar, J. A. Ramsay, B. A. Ramsay, M. Kontopoulou, and R. A. Hutchinson, "Determination of Mark-Houwink Parameters and Absolute Molecular Weight of Medium-Chain-Length Poly(3-Hydroxyalkanoates)," *J. Polym. Environ.*, vol. 21, no. 1, pp. 24–29, Mar. 2013.
- [46] J. S. Parent, S. S. Sengupta, M. Kaufman, and B. I. Chaudhary, "Coagent-induced transformations of polypropylene microstructure: Evolution of bimodal architectures and cross-linked nano-particles," *Polymer.*, vol. 49, no. 18, pp. 3884–3891, 2008.
- [47] S. Trinkle and C. Friedrich, "Van Gorp-Palmen-plot: A way to characterize polydispersity of linear polymers," *Rheol. Acta*, vol. 40, no. 4, pp. 322–328, 2001.
- [48] S. Trinkle, P. Walter, and C. Friedrich, "Van Gorp-Palmen Plot II - classification of long chain branched polymers by their topology," *Rheol. Acta*, vol. 41, no. 1–2, pp. 103–113, 2002.
- [49] F. J. Stadler, J. Kaschta, and H. Münstedt, "Thermorheological Behavior of Various Long-Chain Branched Polyethylenes," *Macromolecules*, vol. 41, no. 4, pp. 1328–1333, Feb. 2008.
- [50] Y. Wang, L. Yang, Y. Niu, Z. Wang, J. Zhang, F. Yu, and W. E. T. Al, "Rheological and Topological Characterizations of Electron Beam Irradiation Prepared Long-Chain Branched Polylactic Acid," *J. Appl. Polym. Sci.*, vol. 122, no. 3, pp. 1857–1865, 2011.
- [51] P. Tiwary and M. Kontopoulou, "Tuning the rheological, thermal and solid-state properties of branched PLA by free-radical-mediated reactive extrusion," *ACS Sustain. Chem. Eng.*, vol. 51, no. 5–6, Dec. 2017.
- [52] F.-D. Kopinke and K. Mackenzie, "Mechanistic aspects of the thermal degradation of poly(lactic acid) and poly( $\beta$ -hydroxybutyric acid)," *J. Anal. Appl. Pyrolysis*, vol. 40–41, no. 14, pp. 43–53, May 1997.

- [53] Y. Aoyagi, K. Yamashita, and Y. Doi, "Thermal degradation of poly[(R)-3-hydroxybutyrate], poly[ $\epsilon$ -caprolactone], and poly[(S)-lactide]," *Polym. Degrad. Stab.*, vol. 76, no. 1, pp. 53–59, 2002.
- [54] S. Nguyen, G. E. Yu, and R. H. Marchessault, "Thermal degradation of poly(3-hydroxyalkanoates): Preparation of well-defined oligomers," *Biomacromolecules*, vol. 3, no. 1, pp. 219–224, 2002.
- [55] M. Terada and R. H. Marchessault, "Determination of solubility parameters for poly(3-hydroxyalkanoates)," *Int. J. Biol. Macromol.*, vol. 25, no. 1–3, pp. 207–215, Jun. 1999.



## **Chapter 4: Thesis Overview**

### **4.1 Thesis Conclusions**

This work was able to significantly improve the understanding of the reactivity of polylactic acid (PLA) and poly(3-hydroxyalkanoates) (PHAs) in the presence of peroxide-initiated radicals and multifunctional coagents. In Chapter 2, PLA's enhanced VLE properties in the presence of allylic coagents was attributed to a radical mechanism, eliminating the potential of ionic chemistry. Furthermore, the surprisingly low AE and graft content of this polyester concluded that the enhancement with allylic coagents can be attributed to enhanced solubility of coagents within the thermoplastic polyester melt.

The knowledge gained In Chapter 2 was applied to a group of PHAs in Chapter 3. The AEs of medium-chain length PHAs (MCL-PHAs) are similar to polyolefins with long side chains and can be explained by the increased methylene content which promotes hydrogen abstraction. Poly(3-hydroxooctanoates) PHO showed an affinity for both allylic and acrylate coagents with increases in viscosity, presence of shear thinning, and bimodality in the molecular weight distributions. On the other hand, poly(3-hydroxybutyrate) PHB had a heightened affinity for allylic coagents as seen with PLA. These biopolyesters have similar structures, therefore these enhancements can again be linked to solubility within the polymer melt during processing.

### **4.2 Future Work**

This work was able to answer many fundamental questions about the reactivity of the biopolyesters. There are many opportunities for further work in this field, a few of which are listed below.

- I. This work showed EOC to be efficient in H-atom abstraction and monomer grafting, whereas these effects were not as prominent with PLA. It was predicted that solubility

was the reason for the enhancements seen in PLA in the presence of allylic coagents. To confirm these predictions, the use of hot stage microscopy to examine the optical transparency of the polymer in the absence and presence of peroxide and coagent could be revealing. Further insight into the formations of these particles could enhance the solubility arguments made in Chapter 2.

- II. It would be interesting to examine what effect various grades of PLA (different molecular weights, D versus L content, etc.) have on the peroxide and coagent modification process. Investigating the trends in improvements in physical and mechanical properties would help better understand how to achieve certain properties for a variety of applications. Furthermore, a study should be conducted on the mechanism of degradation of these modified formulations, to ensure biodegradability can still be achieved.
- III. Further study into the graft modification of PHAs would be beneficial. Significant research has been conducted in PHB, but less work has been done with MCL-PHAs. The effect of peroxide and coagent amount on the VLE properties and molecular distribution of various chain length would help detect if a trend exists on the physical and mechanical properties. Also examining the changes in crystallization and mechanical properties, such as tensile strength, would be of interest. Furthermore, conducting model compound work combined with advanced NMR techniques can be used to determine the graft location of coagents on the polymer backbone.

# Appendix A: Effect of amount of TAM and TAC coagents on PLA

## (Rheology)

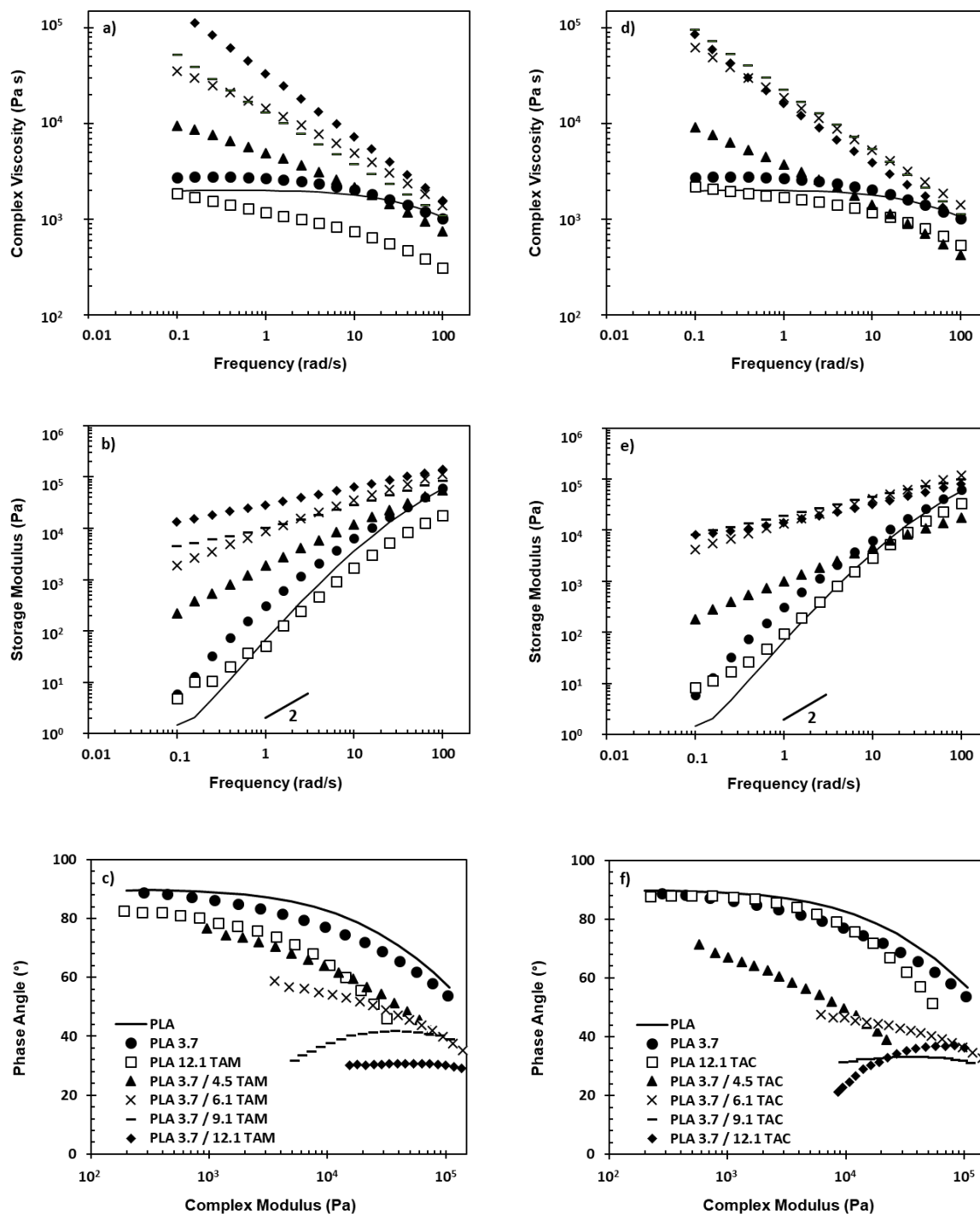


Figure A.1: (a,d) Complex viscosity and (b,e) storage modulus versus frequency, and (c,f) van Gurp-Palmen plot at 180°C for PLA with various loadings of allylic coagents, TAM and TAC respectively.

## Appendix B: PHO <sup>1</sup>H NMR

To determine the amount of mono-functional coagent that was grafted, peaks for AB grafting were analyzed by the two protons on the aromatic at 8.1 ppm (a) and the methylene group at 4.3 ppm (b). Both groups showed identical results.

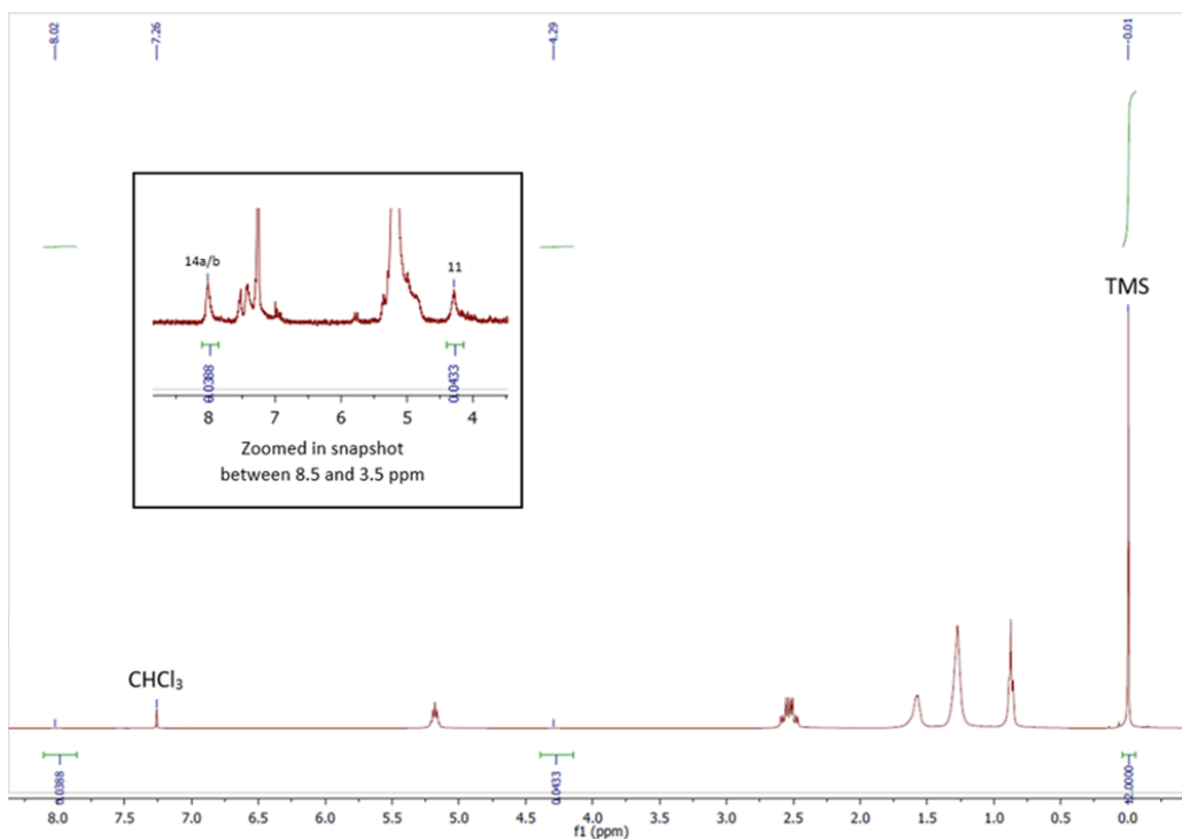
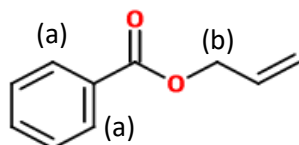


Figure B.1: <sup>1</sup>H NMR of PHO with grafted AB. Since there are more un-grafted PHO chains in the polymer, this results in small peaks from the coagent. The internal standard used for calculations was TMS, the solvent was chloroform and are represented by the peaks at 0.00 ppm and 7.26 ppm respectively.

To determine the amount of mono-functional coagent that was grafted, peaks for BA grafting were analyzed by the methylene group at 4.1 ppm (a).

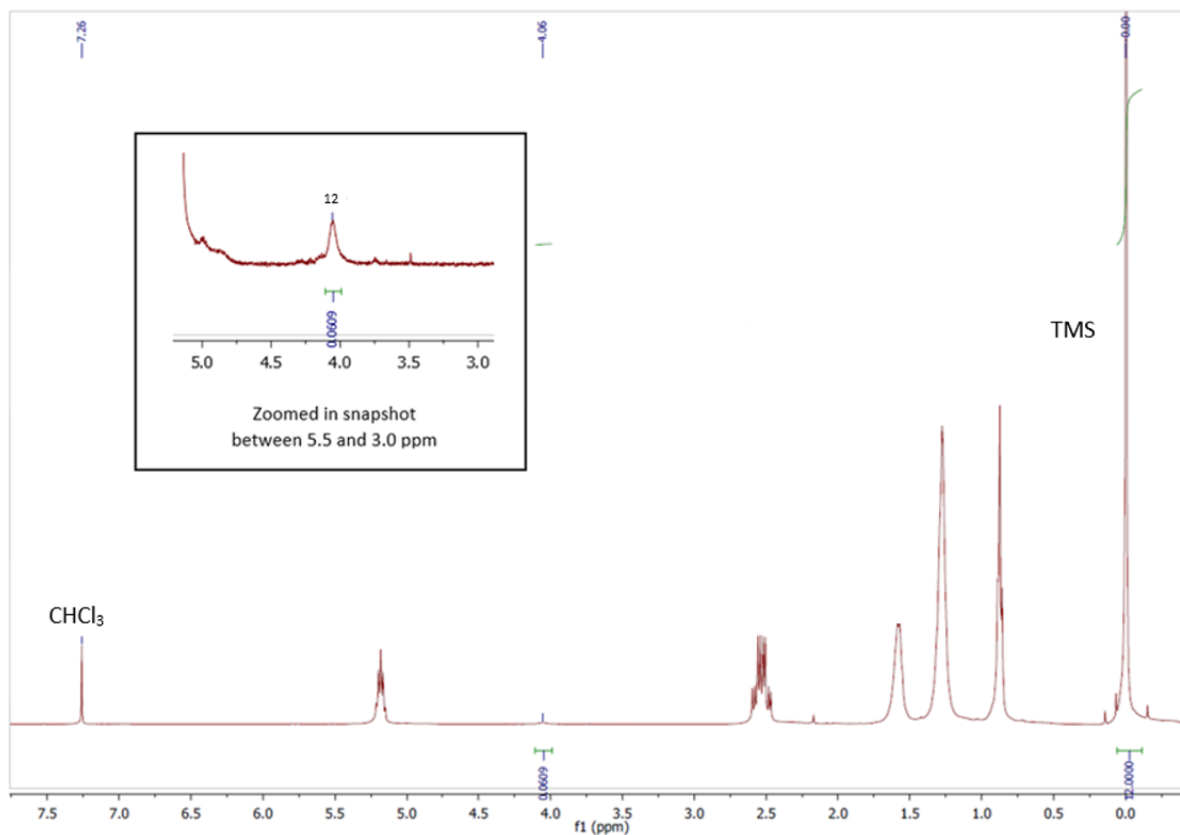
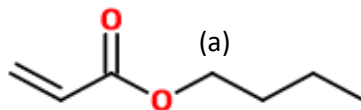


Figure B.2: <sup>1</sup>H NMR of PHO with grafted BA. Since there are more un-grafted PHO chains in the polymer, this results in small peaks from the coagent. The internal standard used for calculations was TMS, the solvent was chloroform and are represented by the peaks at 0.00 ppm and 7.26 ppm respectively.

Sample  $^1\text{H}$  NMR calculation for AB grafted onto PHO using the integral from the aromatic protons.

*Sample: 0.0148 g*

*Standard: 0.0048g*

$$0.0048\text{g STD} * \frac{\text{mol}}{88.22\text{g}} = 5.44 \times 10^{-5} \text{ mols}$$

$$\frac{0.0256 \text{ Integral Sample}}{2 \text{ Protons}} * \frac{12 \text{ Protons}}{12 \text{ Integral STD}} = 1.27 \times 10^{-2}$$

$$5.44 \times 10^{-5} \text{ mols} * 1.27 \times 10^{-2} = 6.91 \times 10^{-7} \text{ mols AB}$$

$$\frac{\text{monomer mols grafted}}{\text{g polymer}} = 6.91 \times 10^{-7} \text{ mols AB} * \frac{162.19\text{g}}{\text{mol}} * \frac{1}{0.0148 \text{ g Sample}} = 0.75 * 100\% \\ = 75\%$$

## Appendix C: Cross-model Fit

Viscosity versus frequency data collect from the oscillatory measurements were used to fit the Cross-model. A sample of the fit applied to neat PHO is illustrated below.

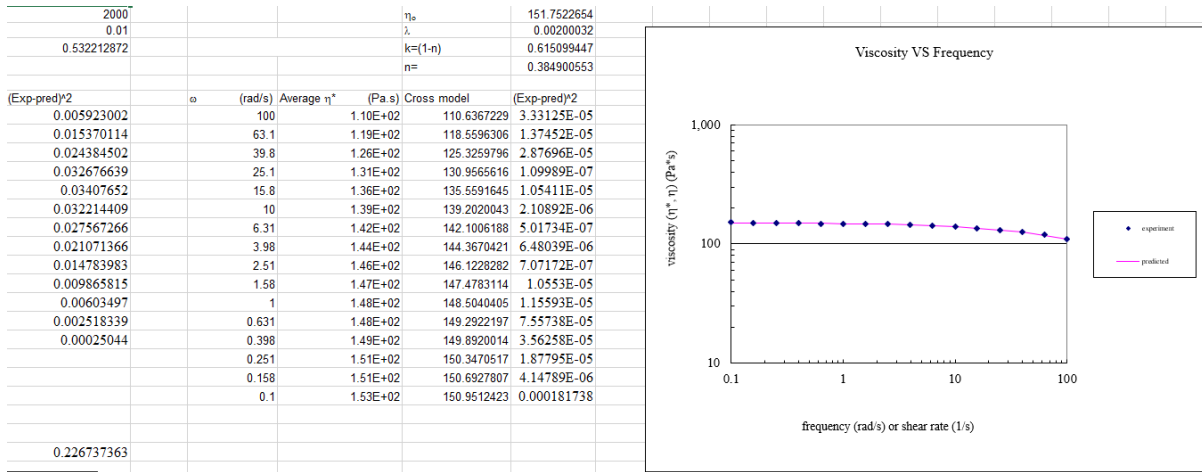


Figure C.1: Output of the Cross-model fit for neat PHO applying equations 3.1.