Copolymerization of Limonene

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Thesis submitted to the
Faculty of Graduate and Postdoctoral Studies
In partial fulfillment of the requirements
For the degree of
Master of Applied Science

Department of Chemical Engineering

Faculty of Engineering

University of Ottawa

Abstract

In this thesis, we explored the use of a renewable resource to produce more sustainable polymeric materials. Limonene, a monocyclic terpene existing in many essential oils extracted from citrus rinds, was the renewable monomer investigated. The d-limonene ((+)-limonene) isomer is a major component (~90%) of orange oils from orange juicing and peel processing. Having been used as a flavour and fragrance additive in cosmetics, foods and beverages, as well as a green solvent, limonene is of particular interest in polymerization, because it contains double bonds, which provide the bifunctionality necessary for polymerization. Limonene is also an allylic monomer (CH_2=CH-CH_2Y), which presents challenges in free-radical homopolymerization and thus, copolymerization was investigated herein to overcome this difficulty.

2-Ethylhexyl acrylate (EHA) and n-butyl methacrylate (BMA) were used in two separate projects, as comonomers with limonene. Using bulk free-radical copolymerization at 80℃, with benzoyl peroxide (BPO) as the initiator, high molecular weight (>100,000) EHA/limonene and BMA/limonene copolymers were produced. Reactivity ratios, important parameters used in the prediction of copolymer composition, were estimated and shown to accurately predict the copolymer composition of subsequent experiments. These can now be used for the application of appropriate semi-batch policies to further enhance limonene incorporation into the copolymers.

Résumé

Dans cette thèse, nous avons exploré l'utilisation d'une ressource renouvelable pour produire des matériaux polymériques plus durables. Le limonène, un terpène monocyclique existant dans de nombreuses huiles essentielles extraites des pelures d'agrumes, était le monomère renouvelable en enquête. L'isomère d-limonène ((+)-limonène) est un composant majeur (~90%) provenant des huiles d'orange et du jus et pelure d'oranges. Utilisé déjà comme un additif d'arôme et de parfum dans les produits cosmétiques, les produits alimentaires et les boissons, ainsi comme solvant "vert", le limonène est d'un intérêt particulier à la polymérisation, car il contient des liens doubles, qui fournissent une fonctionnalité nécessaire pour la polymérisation. Le limonène est également un monomère allylique (CH_2=CH-CH_2Y), qui présente des défis dans la homopolymérisation à radicaux libres et donc, la copolymérisation a fait l'objet de l'enquête dans ce projet pour surmonter cette difficulté.

L'acrylate 2-éthylehexyle (EHA) et le méthacrylate de n-butyle (BMA) ont été utilisées dans deux projets distincts, comme comonomères avec le limonène. Utilisant la copolymérisation à radicaux libres en vrac à 80°C, avec le peroxyde de benzoyle (BPO) en tant qu'initiateur, des copolymères EHA/limonène et BMA/limonène à poids moléculaire élevé (>100 000) ont été produites. Les ratios de réactivité, qui sont d'importants paramètres utilisés dans la prédiction de composition de copolymères, ont été estimés et illustré à prédire avec exactitude la composition de copolymères

provenant d'expériences ultérieures. Ces ratios peuvent maintenant être utilisés pour l'application appropriée d’une politique “semi-batch” pour incorporer d’avantage le limonène dans les copolymères.

Statement of Contributions

I hereby declare that I am the sole author of this thesis. I performed the polymerization experiments, polymer characterization including thermal and chromatographic analysis, and all the associated data analysis.

The scientific guidance throughout the project and editorial comments of the written work were provided by my thesis supervisor Dr. Marc A. Dubé of the Department of Chemical and Biological Engineering at the University of Ottawa.

Yujie Zhang Date: 5/28/2014

Acknowledgement

I would like express my deep gratitude to my supervisor Dr. Marc A. Dubé for his patient guidance, considerable encouragement and support throughout this project. I wish to thank all the members in our research group: Esther, Shanshan, Stéphane, Sara, Shidan, and Samaneh. I am grateful to Dr. Glenn Facey, from the Department of Chemistry, for his help with the NMR spectrum identification. I also extend my thanks to Mr. Louis Tremblay of the Department of Chemical and Biological Engineering, for his help in glass blowing our ampoules.

Financial support for this work through the Natural Sciences and Engineering Research Council (NSERC) of Canada, the Canada Foundation for Innovation (CFI) and Intellectual Ventures is gratefully acknowledged.

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Nomenclature

Symbols

$[M_i]$	Concentration of monomer i in the feed (mol L^{-1})
f_i	Feed composition of monomer I (mol fraction)
F_i	Overall instantaneous mole fraction of monomer i (mol fraction)
k_{pij}	Propagation rate parameter for the addition of monomer j to a growing radical chain ending in monomer I (L mol^{-1} min^{-1})
r_i	Reactivity ratio for monomer I (dimensionless)

Abbreviations

AIBN	Azobisisobutyronitrile
BMA	n-Butyl Methacrylate
BPO	Benzoyl Peroxide
DMA	Dodecyl Methacrylate
DSC	Differential Scanning Calorimetry
EHA	2-Ethylhexyl Acrylate
GPC	Gel Permeation Chromatography
^{1}H-NMR	Proton Nuclear Magnetic Resonance Spectroscopy
IBA	Isobutyl Acrylate

LIM	Limonene
MAnh	Maleic Anhydride
MEHQ	Monomethyl Ether Hydroquinone
MMA	Methyl Methacrylate
M_n	Number-Average Molecular Weight
M_w	Weight-Average Molecular Weight
NMP	Nitroxide Mediated Radical Polymerization
PFS	2,3,4,5,6-Pentafluorostyrene
PIN	β-Pinene
PSAs	Pressure-Sensitive Adhesives
STY	Styrene
T_g	Glass Transition Temperature
THF	Tetrahydrofuran

1. Introduction

Polymers are large molecules, or macromolecules, consisting of many smaller chemically-linked molecules, termed monomer[1]. Polymers play an essential role in our lives owing to the variety of their properties. Up to now, fossil fuels have been the major source for the production of synthetic polymers. Of course, for a very long period, fossil fuels have provided an extraordinary variety of monomers at a relatively low price; however, things have changed. The depletion of fossil fuel reserves has led to a significant increase in the price of fossil fuel-based resources. In addition, growing environmental concerns have driven us to pursue a more sustainable way to produce polymer products.

Sustainable polymer reaction engineering is a field of application which seeks an effective and sustainable path towards the production of polymers, for instance, using renewable resources and developing solvent-free polymerization processes.[2] Actually, the rich diversity of renewable resources and their chemical structure indicate their strong potential for the production of more sustainable polymers in place of traditional fossil-based polymer products.

In this project, we explored the use of limonene as a candidate to make more sustainable polymers. Limonene is a monocyclic terpene, and is the major component of many citrus fruit oils, at a concentration of ~90%. Until now, limonene has been widely used in various applications, such as cosmetics, foods, medicines, and solvents. Of particular interest in polymerization, limonene contains two double bonds, which provides the bifunctionality necessary for polymerization.

Copolymerization is a technique that has been used to achieve desired polymer properties. Often, monomers forming low glass transition temperature (T_g) polymers (e.g., 2-ethylhexyl acrylate, T_g = -70°C) are incorporated with high polymer T_g producing monomers (e.g., styrene, T_g = 100°C). Poly(limonene) has a relatively high T_g of 116°C[3], so a lower T_g comonomer is required to obtain desired product properties (e.g., for adhesives). In this project, our goal was to produce limonene-containing copolymers via a free-radical mechanism. A screening study was conducted at the beginning of the project to identify proper comonomers to copolymerize with limonene. The decision was made based on the requirements of target products, copolymer composition and degree of limonene incorporation into the copolymers.

1.1. Thesis Objectives

The primary objective of this thesis was to incorporate significant quantities of limonene into a free-radical copolymerization. In order to achieve this, a proper comonomer should be chosen. This choice should be made based on the conversion, the amount of limonene incorporation in the copolymer, copolymer molecular weight and the copolymer T_g according to the desired product specifications (e.g., pressure-sensitive adhesives or PSAs). One challenge in copolymer production lies in the phenomenon of compositional drift due to unequal comonomer reactivity. Thus, a second objective was to estimate the monomer reactivity ratios, important parameters used to predict copolymer composition, and ultimately, molecular weight and other properties.

1.2. Thesis Outline

This thesis contains six chapters. After the introductory chapter, Chapter 2 presents a literature review, including the polymerization of common terpene monomers via both cationic free-radical mechanisms. Chapters 3 and 4 consist of manuscripts submitted for publication in refereed scientific journals. Chapter 3 reports on, the copolymerization of n-butyl methacrylate and limonene while in Chapter 4, the free-radical copolymerization of 2-ethyhexyl acrylate and limonene is presented. In Chapter 5, a summative discussion of the thesis is presented and this includes a report on the comonomer selection process. The thesis concludes with thoughts on the potential impact of the work and some ideas on how to improve the incorporation of limonene into polymers.

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2. Literature Review

2.1. Terpenes

Terpenes are one of the vastest families of organic compounds, produced by various plants, particularly conifers, but also by some insects, marine micro-organisms and fungi. Most terpenes are derived from isoprene (2-methyl-1, 4-butadiene, see Figure 2-1), which can be linked together “head to tail” to form linear chains and rings. Many terpenes have been used as components in natural agricultural pesticides, as green solvent[1], and in flavours and fragrances[2]. Based on the number of isoprene units, terpenes are classified into groups shown in Table 2-1. Among those groups, monoterpenes have captured the greatest attention because of the diversity in their molecular backbone structures. This diversity is a result of the isomerization between various molecular structural forms and a large group of derivatives (e.g., monoterpene alcohols). Monoterpenes have two isoprene units (see Figure 2-2) with the molecular formula $C_{10}H_{16}$. Other than the applications mentioned earlier, the bifunctionality of the monoterpenes, owing to the presence of double bonds, makes them potential candidates for polymerization feedstock. Limonene, α-pinene, and β-pinene are the best known monoterpenes and have been investigated to some extent for that purpose.

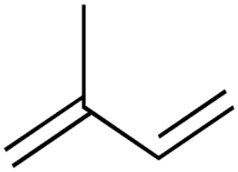

Figure 2-1 Chemical structure of isoprene

Table 2-1 Classification of terpenes [3]

Classification	Isoprene units
Hemiterpenes	1
Monoterpenes	2
Sesquiterpenes	3
Diterpenes	4
Sesterpenes	5
Triterpenes	6
Tetraterpenes	8
Polyterpenes	n

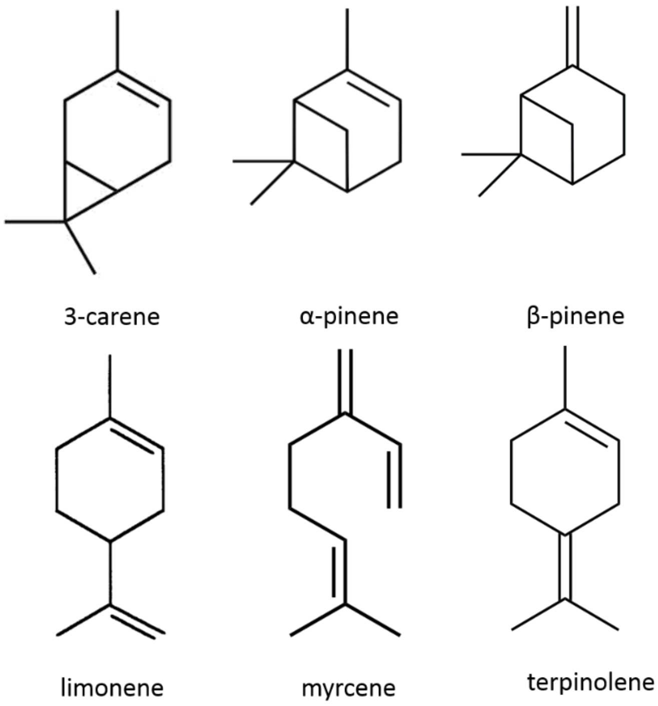
3-carene
α-pinene
β-pinene
limonene
myrcene
terpinolene

Figure 2-2 Chemical structures of common monoterpenes

2.1.1. **Limonene**

Limonene is a monocyclic terpene. D-Limonene ((+)-limonene, see Figure 2-3) isomer is a major component of citrus fruit oils (e.g., lemons, oranges, grapefruits) and has an evident orange odour; l-limonene ((-)-limonene, see Figure 2-3) isomer can be found in many essential oils (e.g., conifers) and has a smell of pine. In this thesis, we henceforth refer to d-limonene as “limonene”. In Figure 2-4, the production process of limonene from oranges is shown. Orange oils are the main source of limonene, as both the cold press oil from the juice/oil mixture and the technical grade oil from the orange peels (see Figure 2-4) contain ~90-95% limonene. Furthermore, limonene has a low freezing point (-96°C)[4], which makes it easier to separate from other components.

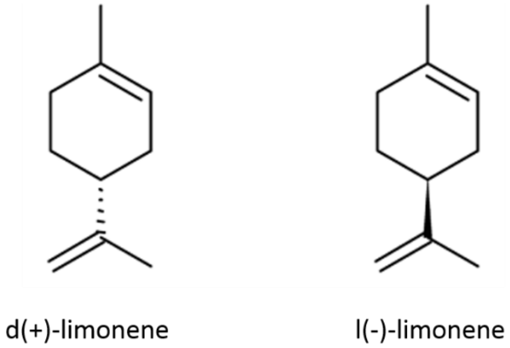

Figure 2-3 Chemical structure of limonene enantiomers

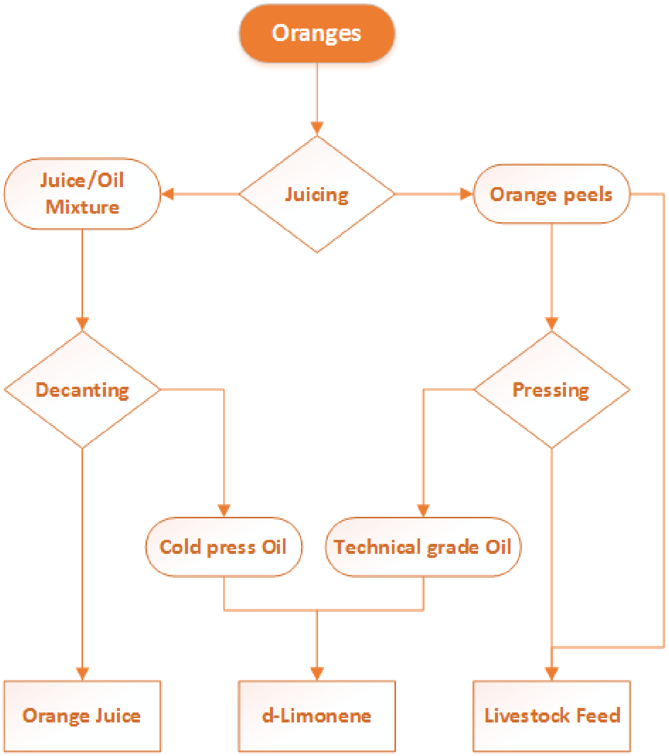

Figure 2-4 d-Limonene extraction process

Up to now, limonene has been widely used in different applications. Most commonly, limonene has been added to cosmetics, medicines and foods because of its orange odour.[2] It has also been used as a green solvent for cleaning purposes.[1] As mentioned earlier, monoterpenes contain double bonds, which present an element of bifunctionality and this makes it a good candidate for the production of more sustainable polymers.

2.2. Cationic Polymerization of Monoterpenes

The first reported polymerization of terpenes was in 1798, when Bishop Watson added a drop of sulphuric acid to terpene and produced a sticky resin.[5] However, at that time, researchers were not able to recognize the interesting properties of this material, which delayed its further study for another half century. In 1950, William Roberts studied the cationic polymerization of limonene, α-pinene and β-pinene with Friedel-Crafts type catalysts (such as $AlBr_3$, $SnCl_4$ and $ZnCl_2$), using toluene as a solvent.[6] By adding less than 1% of aluminum chloride ($AlCl_3$), a solid polymer of β-pinene was produced with an average molecular weight of ~1500. The degree of polymerization of β-pinene, though admittedly quite low, was higher than that of the other two monomers. The β-pinene reaction provided maximum polymer yields at -30 ℃, while for α-pinene the maximum was at 40℃. Additionally, the β-pinene polymers contained a great deal of recurring monocyclic units with one double bond, and the α-pinene polymers had about one double bond for every two recurring units. No further details about the structure of poly(limonene) was provided. It was suggested that part of the α-pinene was isomerized to limonene and subsequently polymerized, and the properties of limonene polymers are known to be quite similar to that of α-pinene.[6]

In 1965, Modena's group discovered Ziegler-Type catalysts to make poly(limonene) and other terpene polymers.[7] The maximum conversion they were able to reach was 67.5 % at 0℃, using $Al(i\text{-}Bu)_2Cl$ and $TiCl_4$ as catalysts, but the reaction took 5 days. Despite obtaining only low molecular weight polymers, the structure of poly(limonene) was clarified. They claimed that the limonene polymer had only 0.36-0.44 double bond per recurring unit. Based on that, the main conclusion was that this limonene polymer was different from α-pinene polymer.[7] A considerable amount of research has since contributed enormously to our understanding of cationic polymerization of terpenes, but most were focused on α-pinene and β-pinene. [8-10]

In a recent master's thesis from Sweden, the cationic polymerization of limonene was performed with $AlCl_3$ as the catalyst. The polymerization was conducted at various temperatures and it was shown to be most efficient at 40℃. The average molecular weight of the poly(limonene) was 400-600 g mol^{-1}, which indicates that only small oligomers were produced. Copolymerization of limonene with other monomers (e.g., styrene, butyl vinyl ether) was attempted but only the cationic copolymerization of styrene and limonene proved successful.[11]

2.3. Free-Radical Polymerization of Monoterpenes

It is difficult to homopolymerize monoterpenes via free-radical mechanisms due to the presence of allylic C-H bonds (See Figure 2-5). As a result, a degradative chain transfer mechanism would compete with propagation, which effectively results in the termination of the growing polymer chains and the production of low molecular weight oligomers.[12] Various reported attempts to homopolymerize limonene, α-pinene and β-pinene via free-radical mechanisms have resulted in homopolymers with unacceptably low chain lengths if they polymerized at all.[13-15] Nevertheless, there are reports of the copolymerization of monoterpenes with other monomers, which has led researchers on a new path to sustainable polymer synthesis.

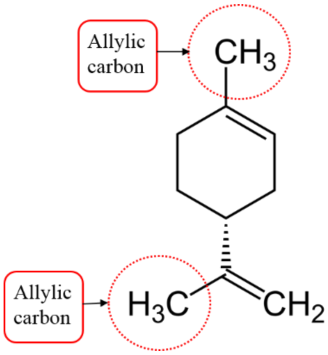

Figure 2-5 Examples of allylic carbon in limonene structure

The first radical copolymerizations of β-pinene and α-pinene were reported in 1998. Both β-pinene and α-pinene were copolymerized with methyl methacrylate and styrene and relatively high molecular weight copolymers were produced (M_n ranges from 11,500 to 53,000).[15] Since then, β-pinene has been copolymerized with 2,3,4,5,6-pentafluorostyrene (PFS)[16], methyl acrylate[17], acrylonitrile[18], n-butyl acrylate[19] and N-substituted maleimides[20, 21].

Limonene was first copolymerized with maleic anhydride (MAnh) via free-radical polymerization in 1994.[22] Both azobisisobutyronitrile (AIBN) and benzoyl peroxide (BPO) were used as initiators at a temperature range of 20-70℃ in various solvents. The copolymers produced consisted of 38~50 mol% limonene, and relatively high conversions (88.2 wt.%) were achieved.

Later on, Srivastava's group reported the solution free-radical copolymerization of limonene with methyl methacrylate[23], styrene[24], acrylonitrile[25], as well as the terpolymerization of limonene, styrene and methyl methacrylate[26]. They studied the copolymerization kinetics but the conversions were limited to a maximum of 20wt.%. It is worth mentioning that in the Swedish master's thesis mentioned earlier[11], that the work of Srivastava was not reproducible (at least for styrene and methyl methacrylate).

2.4. Free-Radical Polymerization Kinetics

Free-radical polymerization is a radical chain polymerization, which normally contains the following steps: initiation, propagation, termination, and often, chain transfer reactions. Polymerization begins with the initiation reaction which involves two steps. First, an initiator (I) decomposes to free radicals (R·) by thermal, redox, or photochemical means:

$$\boldsymbol{I \xrightarrow{k_d} 2R\cdot} \qquad \textbf{Equation 2-1}$$

where k_d is the initiator decomposition rate constant. The next step is the addition of a monomer molecule (M) to the initiator free radical (R·) to produce chain initiating radicals (M·)

$$\boldsymbol{R\cdot + M \xrightarrow{k_i} M\cdot} \qquad \textbf{Equation 2-2}$$

where M represents the monomer molecule, and k_i is the initiation rate constant.

Propagation involves the rapid addition of large numbers of monomers, which is shown as:

$$\boldsymbol{M_n \cdot + M \xrightarrow{k_p} M_{n+1} \cdot} \qquad \textbf{Equation 2-3}$$

where k_p is the propagation rate constant.

The polymerization ends with a termination reaction. Typically, there are two types of termination reactions; one by way of combination:

$$\boldsymbol{M_n \cdot + M_m \cdot \xrightarrow{k_{tc}} M_{n+m}} \qquad \textbf{Equation 2-4}$$

where k_{tc} is the termination by combination rate constant; the other is by disproportionation:

$$\boldsymbol{M_n \cdot + M_m \cdot \xrightarrow{k_{td}} M_n + M_m} \qquad \textbf{Equation 2-5}$$

where k_{td} is the termination by disproportionation rate constant.

Chain transfer events are observed in some free-radical polymerization reactions. One can express these as

$$\boldsymbol{M_n \cdot + XA \xrightarrow{k_{tr}} M_n - X + A \cdot} \qquad \textbf{Equation 2-6}$$

where XA can be monomer, initiator, solvent or other components, and X is the atom or groups transferred. Chain transfer reactions result in the premature termination of propagating polymer chains, but without the reduction in number of free radicals. The end result is a reduction in polymer molecular weight.

In free-radical polymerization, the kinetic expression for the rate of polymerization is

$$\boldsymbol{R_p = k_p[M]\left(\frac{R_i}{2k_t}\right)^{1/2}}$$ **Equation 2-7**

where R_p is the rate of polymerization, [M] is the monomer concentration, and R_i is the rate of initiation.

2.5. Reactivity Ratios Estimation

In order to predict copolymer composition, the so-called "terminal model" proposed by Mayo and Lewis was used.[27] The terminal model assumes that the chemical reactivity of a growing polymer chain only depends on the monomer radical at the end, with this assumption, the following differential equation is derived:

$$\boldsymbol{\frac{d[M_1]}{d[M_2]} = \frac{k_{p11}[P_1][M_1]+k_{p21}[P_2][M_1]}{k_{p12}[P_1][M_2]+k_{p22}[P_2][M_2]}}$$ **Equation 2-8**

where $[M_i]$ is the concentration of monomer *i*, $[P_i]$ is the concentration of growing chain P with monomer *i* radical at the end, and k_{pij} is the propagation rate parameter for the addition of monomer *j* to a growing radical chain ending in monomer *i*. To eliminate the concentration of growing polymer chain $[P_i]$ in Equation2-8, it is assumed that the conversion rate of a growing polymer chain P_i to monomer *j* is the same with the conversion rate of a growing polymer chain P_j to monomer *I.* This is known as the quasi-steady-state assumption:

$$\boldsymbol{k_{p21}[P_2][M_1] = k_{p12}[P_1][M_2]} \qquad \textbf{Equation 2-9}$$

Monomer reactivity ratios (r_i) are defined as

$$\boldsymbol{r_i = \frac{k_{pii}}{k_{pij}}} \qquad \textbf{Equation 2-10}$$

By substitute Equations 2-9 and 2-10 into Equation 2-8, we obtain the Mayo-Lewis equation:

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1](r_1[M_1]+[M_2])}{[M_2](r_2[M_2]+[M_1])} \qquad \textbf{Equation 2-11}$$

In this project, Mayo-Lewis equation was used to predict instantaneous copolymer composition and was further integrated to predict cumulative copolymer composition (i.e., the composition actually measured).

2.6. Challenges

As mentioned earlier, limonene is an allylic monomer ($CH_2=CH-CH_2Y$), which means that limonene radicals tend to undergo degradative chain transfer. As a result, this degradative chain transfer mechanism competes with propagation. Unlike the regular chain transfer mechanism, this degradative chain transfer not only dramatically decreases the size of the growing polymer chain, but also results in a considerable drop in propagation rate.[12] When another monomer is involved, as in copolymerization, this situation may be noticeably improved.

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3. Copolymerization of n-Butyl Methacrylate and d-Limonene

Chapter 3 contains a manuscript submitted for publication in the journal Macromolecular Reaction Engineering. It was submitted in May 2014.

Copolymerization of n-Butyl Methacrylate and d-Limonene

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Abstract

The bulk free-radical copolymerization of n-butyl methacrylate (BMA) and d-limonene was carried out at 80℃ using benzoyl peroxide (BPO) as initiator. Low conversion experiments were conducted to estimate the copolymer reactivity ratios while full conversion runs were performed to verify the estimates and to achieve high monomer conversions. Reactivity ratios of r_1 = 6.0957 and r_2 = 0.0459 (1 = BMA, 2 = d-limonene) were obtained using a non-linear, error-in-variables method with the RREVM computer program. Full conversions and reasonably high molecular weights were achieved at high BMA feed concentrations. Achieving high conversion was limited by a degradative chain transfer mechanism due to the d-limonene.

Introduction

The large majority of polymer products are produced from fossil-based resources. Given that fossil resources are dwindling, and the environmental concerns associated with these resources, it is necessary to explore alternative renewable resources to produce sustainable polymer materials.[1]

Limonene is a monocyclic terpene existing in many essential oils extracted from citrus rind. The d-limonene ((+)-limonene) isomer is a major by-product of the orange juice production process, as over 90% of orange oil from juicing and peel processing is d-limonene.[2] In this paper, we henceforth refer to d-limonene as “limonene”. To date, limonene has been widely used in a broad range of products such as cosmetics, as food additives, in medicines and even as a green solvent.[3, 4] Of some interest to the current work, limonene has also been used as a renewable chain transfer agent for metallocene polymerizations.[5]

Limonene has one internal double bond and one external double bond, which indicates potential to be polymerized due to its bifunctionality (see Figure 3-1). However, the presence of allylic C-H bonds, poses challenges to the free-radical homopolymerization of limonene. This results in a degradative chain transfer mechanism which competes with propagation.[6, 7] The growing polymer chains are thus terminated at unacceptably low chain lengths. On the other hand, limonene can be homopolymerized using cationic polymerization, with Friedel-Crafts type catalysts[8] and with Ziegler-Natta catalysts[9]. There are however, reports of limonene copolymers produced via free-radical mechanisms. The first reports were of copolymerization with maleic anhydride[10] followed by the work of Srivastava describing the solution free-radical copolymerization of limonene with methyl methacrylate (MMA)[11], styrene[12], acrylonitrile (AN)[13], as well as the solution terpolymerization of limonene, styrene and MMA[14]. Very recently, periodically functionalized and grafted copolymers of limonene and maleimide derivatives via free-radical mechanisms were produced.[15]

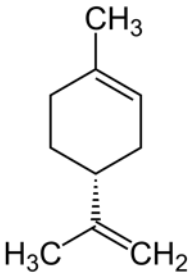

Figure 3-1 Chemical structure of limonene.

In many polymer products (e.g., adhesives), it is desired to tune the polymer composition to achieve a glass transition temperature (T_g) in a desired range. Commonly, a low T_g component (e.g., butyl acrylate) may be copolymerized with a higher T_g component to achieve desired properties. Poly(limonene) has a T_g of 116°C[7] while poly(n-butyl methacrylate) (pBMA) has a T_g of 20°C[16]. To achieve the desired properties, one should first of all, control the copolymer composition followed by manipulation of operating conditions to modify the polymer molecular weight and other properties. Copolymer composition is normally predicted using the Mayo-Lewis equation which requires estimation of the reactivity ratios, parameters in that equation[17].

In this work, we present an investigation of the bulk free-radical copolymerization of limonene (LIM) with BMA. We report on the estimation of reactivity ratios and on the results of higher conversion reactions at selected conditions.

Experimental Section

Materials

BMA (99%, stabilized with methyl ethyl hydroquinone (MEHQ)) and d-limonene (96%, stabilized with tocopherol), henceforth referred to as monomers 1 and 2, respectively, were purchased from Acros Organics, distilled under reduced pressure, and stored at 4°C. The initiator, benzoyl peroxide (BPO, 75% in water, Acros Organics), was recrystallized twice using methanol and chloroform. The solvents methanol and chloroform, purchased from Fisher Scientific, and tetrahydrofuran (THF, HPLC grade) purchased from Sigma Aldrich, were used without further purification.

Polymerization and Characterization

Monomers and initiator were weighed to prepare desired reaction mixture concentrations; ~5 g each of the reaction mixtures was pipetted into glass ampoules (20 cm length, 14 mm outer diameter). The ampoules were degassed using three freeze-pump-thaw cycles and were subsequently flame-sealed.

Polymerizations were carried out in a silicone oil bath at 80 ±1°C. After the desired reaction time, each ampoule was removed and cooled in an ice water-filled beaker (~10 min) to quench the reaction. The ampoules were then weighed, scored, broken and their contents poured into a 10-fold excess of methanol to precipitate the polymer. Samples were then allowed to dry in a fume hood for at least 24 h, followed by drying in a vacuum oven at room temperature until constant weight was achieved. The conversion was calculated gravimetrically and based on dried copolymer.

Samples were characterized for composition using proton nuclear magnetic resonance (^{1}H NMR) spectroscopy with a Bruker Avance 400 MHz NMR spectrometer, using $CDCl_3$ as solvent and 32 scans per readout. Approximately 0.02 g dry polymer sample and 1.5 g $CDCl_3$ were used to prepare each sample.

Molecular weight averages and distribution of selected samples were measured using gel permeation chromatography (GPC). The GPC system (Agilent) was run at 25℃, with THF as the eluting solvent delivered at a flow rate of 1 $mL \cdot min^{-1}$ through two MZGel SD Plus columns (10^5 and 10^4 Å pore size). Detectors included a multi-angle light scattering (MALS) instrument (DAWN HELEOS II), a differential index detector (Optilab T-rEX) and a differential viscometer (ViscoStar II) all from Wyatt Technologies. The polymer sample solution was prepared at a concentration ~0.05 g polymer/10 mL THF. The dn/dc value for poly n-butyl methacrylate (pBMA), 0.067 mL/g[18], was used for all copolymers as all samples tested had a pBMA concentration >92 mol%.

Differential scanning calorimetry (DSC) was used on selected samples to measure the glass transition temperature (T_g) of the dry polymer. The measurement was carried out on a QA series TA1000 DSC analyzer (TA Instruments) under nitrogen atmosphere. Calibration with indium and sapphire standards from -90 to 300℃ was performed. About 5 to 10 mg dry polymer was sealed in aluminum pans and an empty pan served as a reference. The samples were scanned from -20 to 160℃ at a constant heat rate of 10°C/min, held isothermally for 3 min, and then scanned from 160 to -20℃ at the same heat rate. This heating and cooling cycle was repeated three times and the second scan was used to determine T_g at the heat curve inflection point.

Design of Experiments

Table 3-1 shows the experimental conditions (i.e., monomer feed compositions) of a series of equidistant points for reactivity ratio estimation. A minimum of two experiments at each condition was performed. For these experiments, conversions were deliberately kept below 8 wt. %. These data were used to provide an initial estimate of the reactivity ratios, r_1 (BMA) and r_2 (LIM), using the RREVM computer program[19, 20]. The preliminary estimates were then used in Equations 3-1 and 3-2, the Tidwell-Mortimer criterion[21], and four replicate runs were carried out at each of two different monomer feed compositions (see Table 3-1):

$$\boldsymbol{f'_{10} = 2/(2 + r_1)} \qquad \text{Equation 3-1}$$

and

$$\boldsymbol{f''_{10} = r_2/(2 + r_2)} \qquad \text{Equation 3-2}$$

Final reactivity ratios were then calculated using both the preliminary and Tidwell-Mortimer criterion data.

Table 3-1 Reactivity ratio experimental design

Run condition	BMA [mol fraction]	LIM [mol fraction]	BPO [mol %]
1	0.10	0.90	0.14
2	0.20	0.80	0.14
3	0.30	0.70	0.13
4	0.40	0.60	0.13
5	0.50	0.50	0.12
6	0.60	0.40	0.14
7	0.70	0.30	0.32
8	0.80	0.20	0.29
9	0.90	0.10	0.29
TM1	0.31	0.69	0.13
TM2	0.05	0.95	0.16

Full conversion range experiments were conducted at the same feed compositions as reactivity ratio runs 7, 8 and 9 (see Table 3-1). These were chosen on the basis of target T_g values for future desired applications (e.g., adhesives). At each feed composition, seven or more samples were run at 80 ±0.1℃ with the goal of achieving the highest conversion possible.

Results and Discussion

Of primary concern in this work was the assignment of peaks to the ^{1}H NMR spectrum of the copolymer samples. A sample spectrum is shown in Figure 3-2 with corresponding peak identifications. These peak identifications were confirmed by 2D-

COSY NMR and ^{13}C-NMR. In Figure 3-2, peak *a* at ~3.9 δ, was assigned to the ester group protons of BMA, while the three peaks between 4.6-5.5 δ were due to the protons related to the limonene double bonds, peaks *g* and *g'* relate to the internal double bond, while peak *m* is due to the external double bond. Copolymer compositions were calculated based on the above peak assignments.

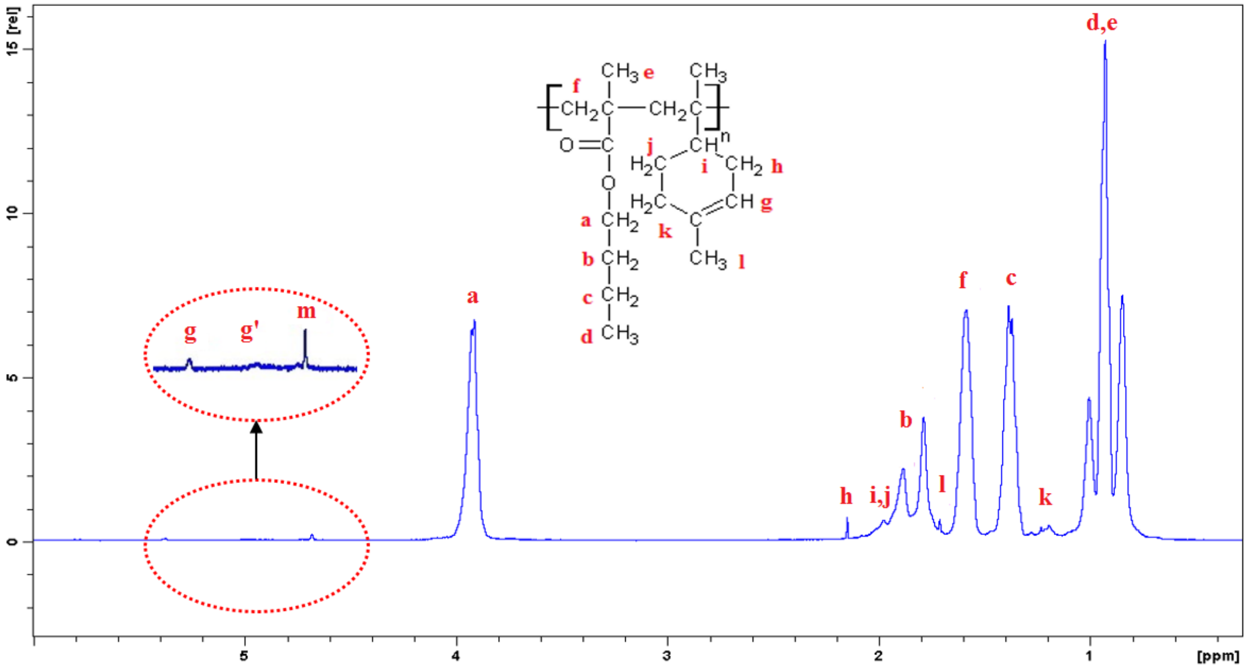

Figure 3-2 ^{1}H NMR spectrum of the copolymer LIM/BMA, [BMA] = 5.0129 mol·L^{-1}, [LIM] = 1.2510 mol·L^{-1}, [BPO] = 0.0179 mol·L^{-1}.

The three limonene peaks between 4.6-5.5 δ provide interesting insight into the polymerization. Peak *m*, related to the external double bond of limonene, would be expected to disappear with conversion, assuming that the locus of polymerization would be at the external double bond. Owing to steric hindrance, polymerization through the internal double bond would be very limited if at all possible. Particular care was taken to fully extract any unreacted limonene monomer, which was confirmed by the lack of sharp peaks representing the monomer as opposed to the broader polymer-related peaks. In addition, confirmation by comparing results using decantation as opposed to simple evaporation during gravimetric analysis was made. Furthermore, the ratio of the internal double bond peaks to that of the external double bonds in the monomer is 1:2 whereas the polymer spectra revealed ratios where the amount of internal double bonds exceeded that of the external double bonds. Thus, it can be concluded that a significant amount of polymerization did in fact occur at the external double bonds. However, if polymerization was assumed not to occur at the internal double bonds, another mechanism for incorporation of limonene into the copolymers must have been active. This would suggest that significant chain transfer reactions were occurring with limonene monomer. As noted earlier, limonene is known to undergo degradative chain transfer because of its allylic carbons (see Figure 3-3)[6]. When a growing polymer chain ending with a limonene radical encounters limonene monomer, it has a significant tendency towards chain transfer. This will terminate the polymer chain growth and transfer the radical to the limonene monomer, which due to electronic resonance, will stabilize between two structures (see Figure 3-3). These limonene radicals are highly stable, resulting essentially in the loss of reactivity of those radicals. This is the principle of degradative chain transfer. Because degradative chain transfer is such a significant event for limonene polymerization, this explains the presence of unreacted limonene external double bonds in the copolymer chains.

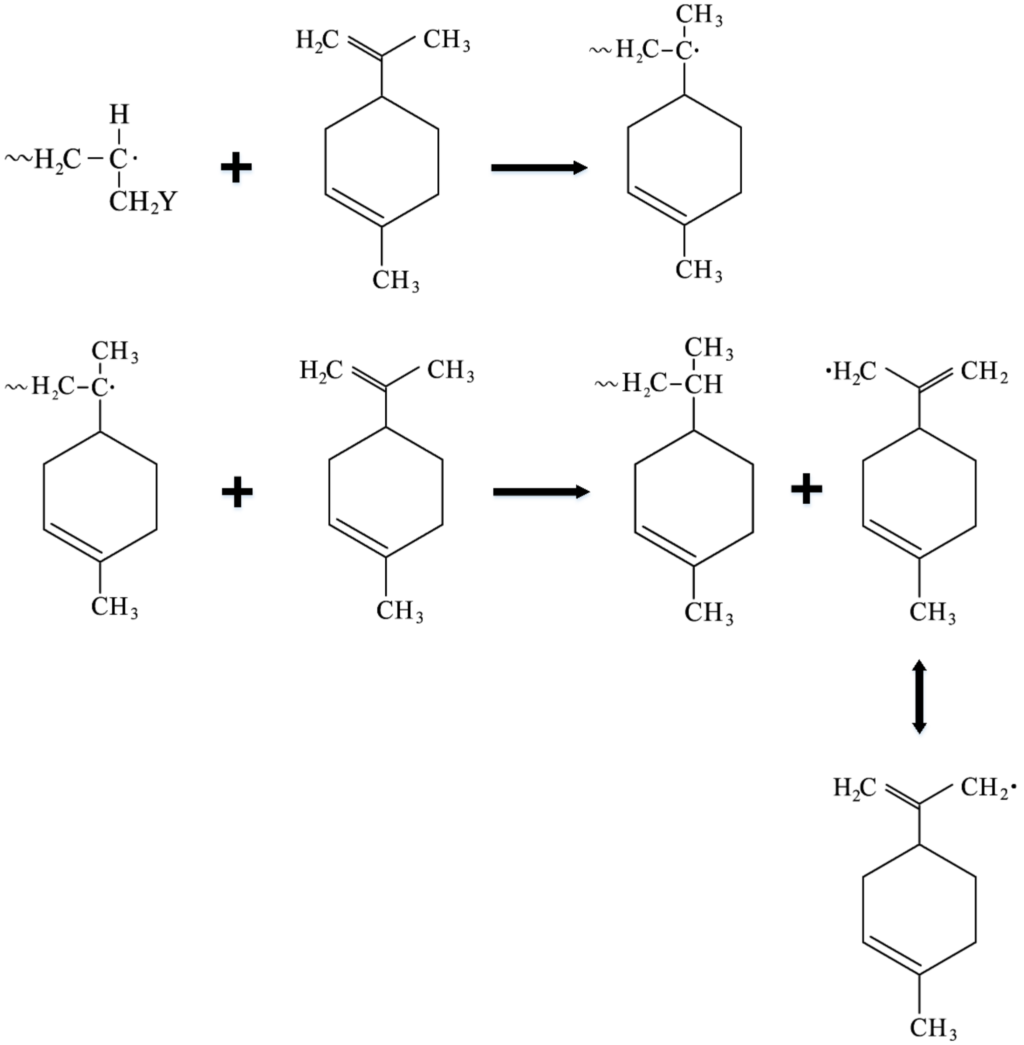

Figure 3-3 Mechanism of degradative chain transfer in limonene polymerization.

Reactivity Ratio Estimation

The reactivity ratios were estimated using the non-linear error-in-variables method with the RREVM computer program[19, 20], which employs the Mayo-Lewis equation:

$$\frac{F_1}{F_2} = \frac{[M_1](r_1[M_1]+[M_2])}{[M_2](r_2[M_2]+[M_1])}$$ **Equation 3-3**

where F_i represents the overall instantaneous mole fraction of monomer *i* in the copolymer, $[M_i]$ is the concentration of the monomer *i* in the feed, and r_i is the reactivity ratio of monomer *i*, defined as:

$$r_i = \frac{k_{pii}}{k_{pij}}$$ **Equation 3-4**

where k_{pij} is the propagation rate parameter for the addition of monomer *j* to a growing radical chain ending in monomer *i*.

Results for the reactivity ratio estimation runs are shown in Table 3-2. These include repeat runs for the preliminary round of equidistant points as well as the replicate runs for the final round of experiments performed according to the Tidwell-Mortimer criterion (see Equations 3-1 and 3-2).[21]

Table 3-2 Reactivity ratio experimental data

Run	f_{BMA} [mol fraction]	F_{BMA} [mol fraction]	Conversion [wt.%]
1-1	0.099	0.535	0.51
1-2	0.099	0.564	0.50
2-1	0.202	0.668	0.43
2-2	0.202	0.697	0.62
3-1	0.302	0.754	0.77
3-2	0.302	0.754	0.93
4-1	0.401	0.814	0.48
4-2	0.401	0.841	1.40
5-1	0.504	0.877	1.33
5-2	0.504	0.895	1.96
6-1	0.605	0.934	0.89
6-2	0.605	0.933	2.17
7-1	0.700	0.932	3.84
7-2	0.700	0.961	7.28
8-1	0.800	0.979	1.56
8-2	0.800	0.974	5.21
9-1	0.900	0.990	1.69
9-2	0.900	0.992	8.11
TM 1-1	0.311	0.769	1.17
TM 1-2	0.311	0.760	1.16
TM 1-3	0.311	0.752	1.24
TM 1-4	0.311	0.754	1.24
TM 2-1	0.047	0.403	0.51
TM 2-2	0.047	0.406	0.50
TM 2-3	0.047	0.405	0.54
TM 2-4	0.047	0.395	0.56

At the conclusion of the preliminary round of equidistant experimental points, reactivity ratios of r_1 = 6.4336 and r_2 = 0.0463 were calculated. These were input to Equations 3-1 and 3-2 to yield the feed mole fractions according to the Tidwell-Mortimer criterion of f_{1o}' = 0.3107 and f_{1o}'' = 0.047. After completing a set of 4 replicate runs at each of these feed compositions (see Table 2), final reactivity ratios were calculated using all of the data from Table 3-2. Values of r_1 = 6.0957 and r_2 = 0.0459 were estimated. A joint confidence region for these values is shown in Figure 3-4. These reactivity ratios clearly indicate that the polymerization of BMA is favored in the copolymerization with limonene. The Mayo-Lewis model using the predicted reactivity ratios along with the experimental data are shown in Figure 3-5; excellent fit to the data is evident.

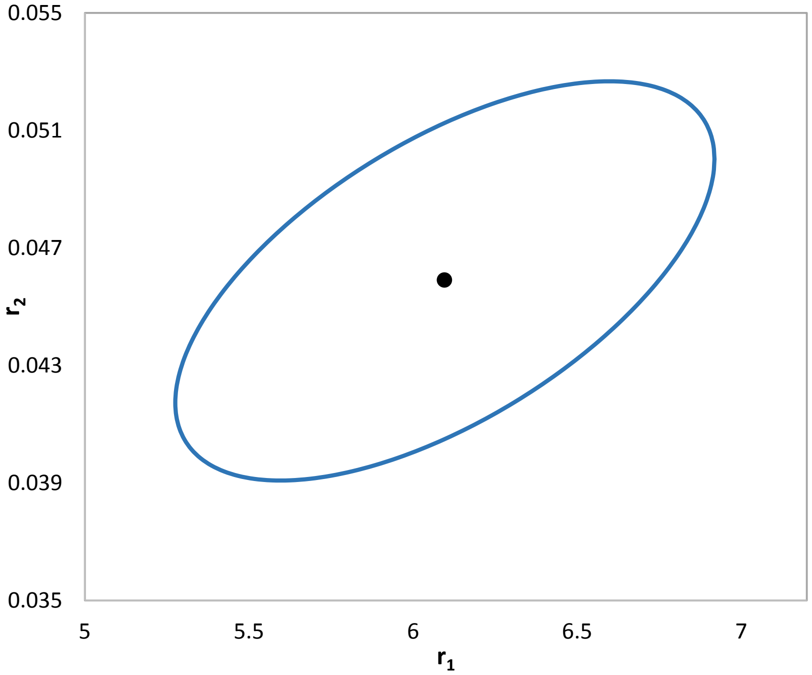

Figure 3-4 BMA/LIM reactivity ratios, 95% posterior probability contour.

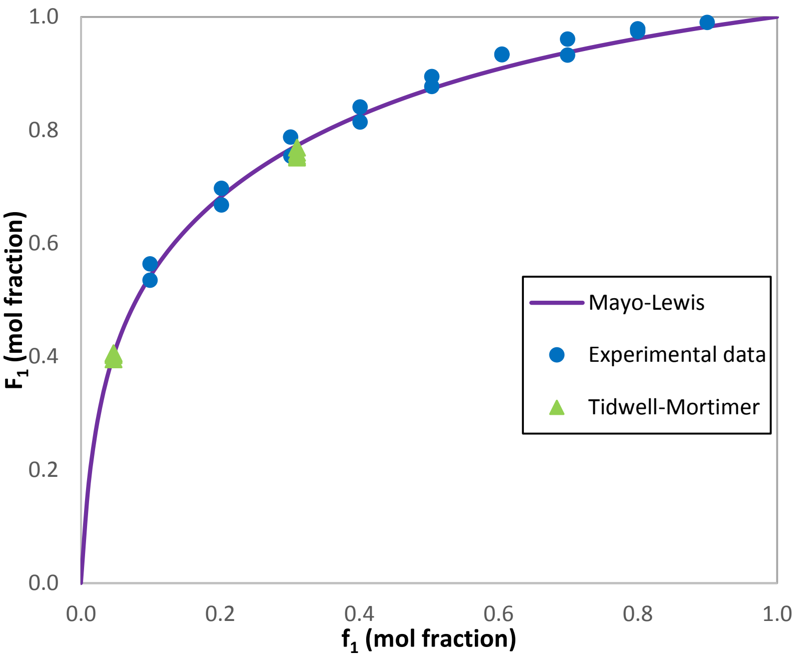

Figure 3-5 Dependence of copolymer composition, F_1, on monomer feed composition, f_1.

Full Conversion Experiments

Full conversion experiments were run at three monomer feed compositions (see conditions 7, 8 and 9 in Table 3-1) at 80°C. Conversion vs. time data for these runs are shown in Figure 3-6. All three polymerizations exhibited a ~10 min induction period. Nearly complete monomer conversion was achieved at the highest BMA content (f_1 = 90 mol%) whereas the runs using increasing amounts of limonene, f_1 = 0.8 and 0.7, exhibited limiting conversions of 87 and 75 wt.%, respectively. This corresponded (with composition data) to a maximum limonene incorporation of less than 10 mol%.

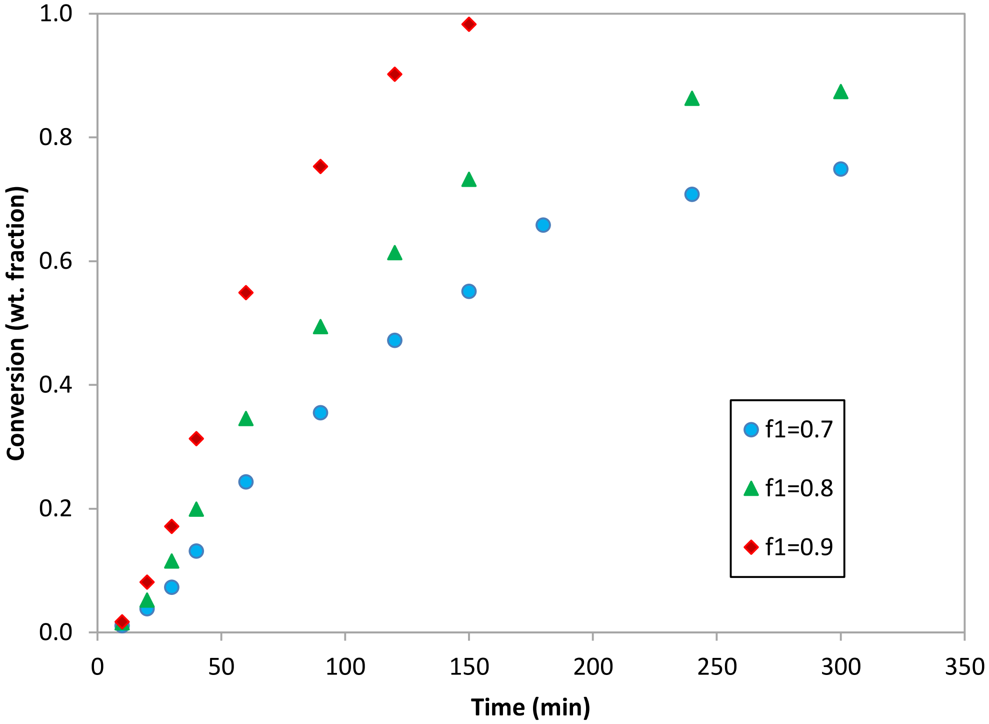

Figure 3-6 Conversion vs. time.

The cumulative copolymer compositions for the three full conversion runs are plotted in Figure 3-7. Clearly, the copolymerization was dominated by BMA with only small amounts of limonene being incorporated into the copolymer. Model predictions using the integration of the Mayo-Lewis equation along with the estimated reactivity ratios reveal good predictions of the composition. In Figure 3-8, a comparison of the cumulative composition and the prediction of instantaneous composition is shown. The steep decline in BMA composition at high conversions implies more frequent reactions between limonene-ended growing radical chains with limonene monomers. Given limonene's difficulty to homopolymerize, it is therefore not surprising that limiting conversions were achieved when the amount of BMA neared depletion. Of course, one could implement starved-fed semi-batch policies to encourage greater limonene incorporation.[22]

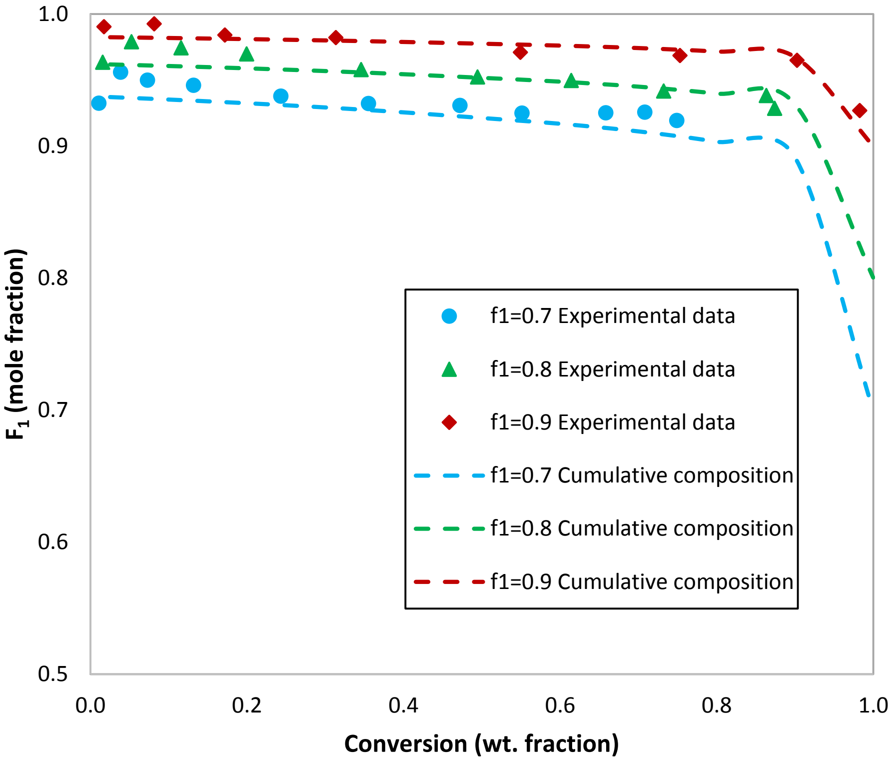

Figure 3-7 Copolymer composition vs. conversion.

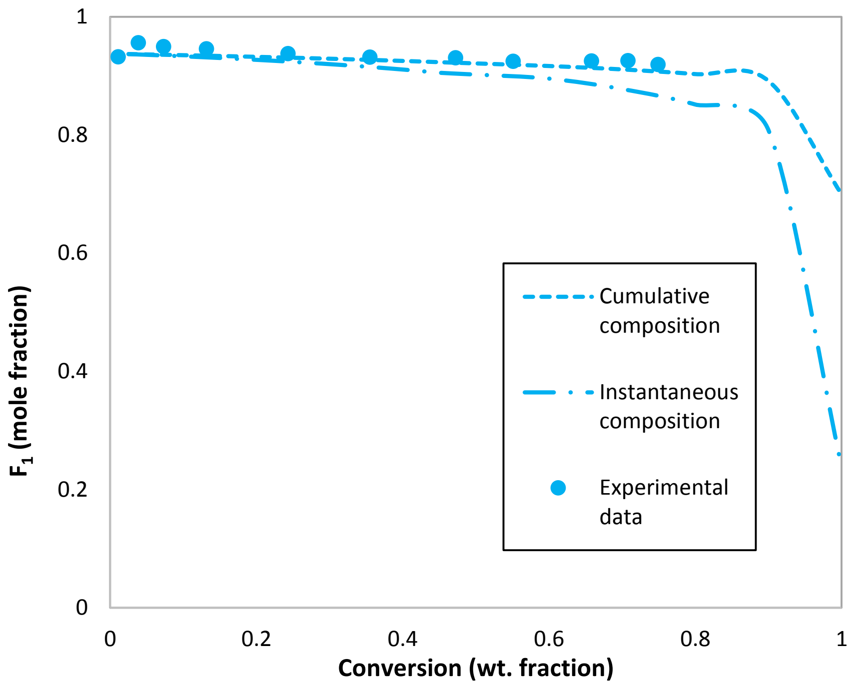

Figure 3-8 Cumulative and instantaneous copolymer composition vs. conversion, f_1=0.7.

The above observations were further confirmed with DSC analysis. In the selective analysis of several samples, each copolymer displayed only a single glass transition temperature (T_g) at ~24℃ (see Table 3-3). This is consistent with the production of a homogeneous copolymer. Recalling the T_g values of poly(limonene) and pBMA cited earlier as 116 and 20°C, respectively, one can recognize that the T_g is not that of pure pBMA but has been modified by the incorporation of albeit small amounts of limonene.

Table 3-3 Glass transition temperature of selected samples

f_1 [mol fraction]	F_1 [mol fraction]	Conversion [wt. fraction]	T_g [℃]
0.70	0.932	0.36	23.97
0.80	0.958	0.35	23.63
0.90	0.971	0.55	23.61

The weight-average molecular weights for the full conversion experiments are plotted in Figure 3-9. The relatively flat molecular weight profiles are indicative of polymerizations with significant chain transfer events. This becomes particularly apparent near higher conversion levels when the limonene concentrations are higher and when a moderate dip in molecular weight averages is observed. One should recall that these are cumulative molecular weight results and thus, similar to the case for composition, a minor decrease in cumulative molecular weight is indicative of a significant decrease in instantaneous molecular weight. Again, this is consistent with the effect of degradative chain transfer due to the presence of limonene, as discussed earlier.

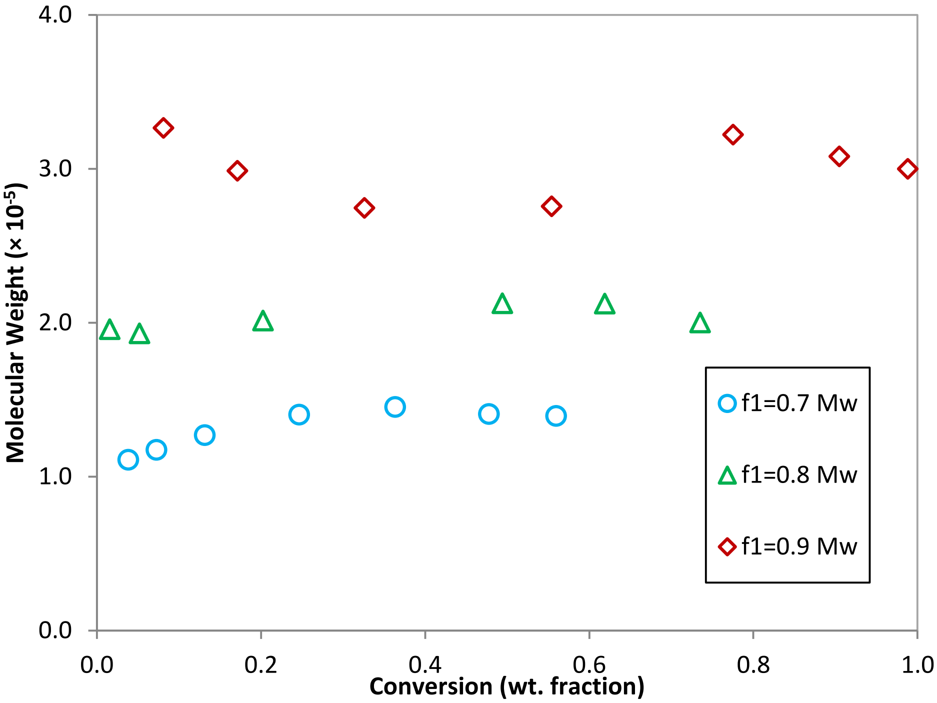

Figure 3-9 Weight-average molecular weights

Conclusions

In this study, the bulk free-radical copolymerization of d-limonene with n-butyl methacrylate was performed at 80°C. The use of low conversion experiments in an iterative procedure was demonstrated. A set of equidistant experiments along the feed composition axis provided an initial estimate of the reactivity ratios which were then used to identify d-optimal conditions, as suggested by Tidwell and Mortimer[21] , to provide a complete set of experiments. The combined data were used along with a statistically valid, non-linear, error-in variables method (RREVM computer program) to estimate reactivity ratios, r_1 = 6.0957 and r_2 = 0.0459. These values reveal that BMA is favored in the copolymerization. High conversion experiments at high BMA concentrations confirmed the accuracy of the reactivity ratios for prediction of copolymer composition. DSC results also confirmed the homogeneity of the copolymer composition. That is, the polymers produced were indeed copolymers as opposed to homopolymers. The conversion, composition and molecular weight data all confirmed the presence of a degradative chain transfer effect due to limonene. This effect served to limit monomer conversion and also control molecular weight development. Nonetheless, limonene can be incorporated into the copolymer and the reactivity ratios can now be used to identify appropriate conditions for a starved-fed, semi-batch policy to achieve greater limonene incorporation and control of the copolymer composition.

Acknowledgement

Financial support for this work through the Natural Sciences and Engineering Research Council (NSERC) of Canada, Canada Foundation for Innovation (CFI) and Intellectual Ventures is gratefully acknowledged.

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4. Copolymerization of 2-Ethyhexyl Acrylate and d-Limonene

Chapter 4 contains a manuscript submitted for publication in the journal Polymer Plastics Technology & Engineering. It was submitted in May 2014.

Copolymerization of 2-Ethyhexyl Acrylate and d-Limonene

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Abstract

The bulk free-radical copolymerization of d-limonene and 2-ethylhexyl acrylate (EHA) was conducted at 80°C using benzoyl peroxide (BPO) as initiator. Low conversion experiments were conducted to estimate the copolymer reactivity ratios. The reactivity ratios r_1 = 6.896 and r_2 = 0.032 (1 = EHA, 2 = d-limonene) were obtained using a non-linear, error-in-variables method with the RREVM computer program. High conversion experiments were performed and revealed that a degradative chain transfer mechanism for d-limonene dominated the polymerization.

Keywords: d-limonene, 2-ethyhexyl acrylate, reactivity ratios, copolymerization, degradative chain transfer

Introduction

During the last century, the massive exploitation of fossil fuels led to the creation of a broad range of inexpensive monomers to produce synthetic polymers. As a result, the polymer industry has been dominated by fossil-based resources. With the depletion of fossil fuels and the environmental concerns raised because of their use, renewable resources have come to the forefront as an alternative feedstock for polymer production. Indeed, a tremendous variety of renewable monomers are available to drive us toward a more sustainable polymer production.[1]

Limonene is a monocyclic terpene found in many essential oils. The d-limonene ((+)-limonene) isomer occurs in citrus peel oils, especially in orange peels, at a concentration of ~90%.[2] We henceforth refer to d-limonene as “limonene”. Up to now, limonene has been used as a flavor and fragrance additive in cosmetics, foods and beverages, owing to its pleasant odor.[3] Recently, it has been used as a green solvent to replace traditional cleaning solvents.[4]

Limonene presents itself as an interesting candidate as a renewable monomer due to the presence of internal and external double bonds in its molecular structure (see Figure 4-1). It is important to note that limonene contains allylic C-H bonds, which can present challenges in free-radical homopolymerization due to competing mechanisms for propagation and degradative chain transfer.[5,6] However, it is possible to obtain low molecular weight poly(limonene) via cationic polymerization.[7,8] On the other hand, the incorporation of limonene in copolymers has been possible using a free-radical mechanism. Limonene/maleic anhydride copolymer was produced in 1994[9]. Afterwards, Srivastava’s group reported on a series of solution free-radical copolymerizations of limonene with styrene[10], acrylonitrile[11], and methyl methacrylate[12]. More recently, we have reported on the production of high concentration, high molecular weight limonene/butyl methacrylate (BMA) copolymers.[13] Therein, reactivity ratios were reported.

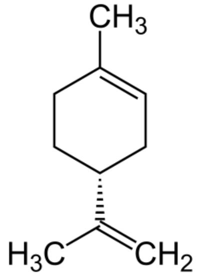

Figure 4-1 Chemical structure of d-limonene.

Pressure sensitive adhesives (PSAs) are designed to stick to almost any surface with light pressure, and in order to meet that requirement, one of the most important parameters is the glass transition temperature (T_g). Typical PSA formulations consist of a low T_g component (e.g., 2-ethylhexyl acrylate (EHA), n-butyl acrylate) and a relatively high T_g component (e.g., methyl methacrylate) to adjust the T_g to an appropriate range.[14] EHA is a long, side chain acrylic monomer commonly used to produce PSAs; poly(2-ethylhexyl acrylate) has a T_g of -70℃.[15] Poly(limonene) has a T_g of 116℃[5], due to its hard carbon ring backbone structure. In PSA production, one normally manipulates the copolymer composition to obtain the desired T_g. For that purpose, the reactivity ratios, parameters in the well-known copolymer composition (Mayo-Lewis) equation are required.[16]

Herein, we report on the bulk free-radical copolymerization of limonene (LIM) with EHA to produce polymers with greater amounts of renewable components. The reactivity ratios were estimated using low conversion experiments and were validated at selected conditions with high conversion runs.

Experimental Section

Materials

EHA (98%, stabilized with monomethyl ether hydroquinone (MEHQ), Sigma Aldrich), referred to as monomer 1, was purified by passing the monomer through inhibitor removal columns (Sigma Aldrich). LIM (96%, stabilized with tocopherol, Acros Organics), referred to as monomer 2, was distilled under reduced pressure and stored at 4°C. The initiator, benzoyl peroxide (BPO, 75% in water, Acros Organics), was recrystallized twice using methanol and chloroform. The solvents methanol and chloroform (Fisher Scientific), and tetrahydrofuran (THF, HPLC grade, Sigma Aldrich), were used without further distillation.

Polymerization

Desired monomer mixture concentrations were prepared using ~5 g each of the reaction mixtures pipetted into glass ampoules (200 mm length, 14 mm outer diameter). Three freeze-pump-thaw cycles were performed to remove any dissolved oxygen from the reaction mixtures; the ampoules were subsequently flame-sealed.

Polymerizations were conducted in a silicone oil bath at 80°C. The ampoules were immersed in the oil bath for a recorded time period, then removed and cooled in ice water (~10 min) to quench the reaction. The ampoules were then weighed, scored, broken, and the polymer-monomer mixtures were precipitated using a 10-fold excess of methanol. Samples were then dried in a fume hood for at least 24 h, followed by drying in a vacuum oven at room temperature until constant weight was achieved. The conversion was calculated gravimetrically and was based on dried copolymer. Dried polymer were also characterized for composition, molecular weight and T_g.

Characterization

Proton nuclear magnetic resonance (^{1}H-NMR) spectroscopy was used to characterize the copolymer composition with a Bruker Avance 400 MHz NMR spectrometer, using $CDCl_3$ as solvent and 32 scans per readout. Samples of 0.02 g dry polymer sample and 1.5 g $CDCl_3$ were prepared.

Molecular weight averages and distributions of selected samples were measured using gel permeation chromatography (GPC). The GPC system (Agilent) was run at 25°C, with THF as the eluting solvent delivered at a flow rate of 1 $mL \cdot min^{-1}$ through two MZGel SD Plus columns (10^5 and 10^4 Å pore size). Detectors included a multi-angle light scatterer (MALS) (DAWN HELEOS Ⅱ), a differential index detector (Optilab T-rEX) and a differential viscometer (ViscoStar Ⅱ). The polymer sample solution was prepared at a concentration ~0.05 g polymer/10 mL THF. The dn/dc value for poly 2-ethylhexyl acrylate (pEHA), 0.058 mL/g[17], was used for all copolymers as all samples characterized for molecular weight had a pEHA concentration >91wt.%.

The T_g of selected samples (~10 mg dry copolymer) was measured using differential scanning calorimetry (DSC). A QA series TA1000 DSC analyzer (TA Instruments) was calibrated and used under nitrogen atmosphere. Samples were scanned from -90 to 160℃ at a constant heat rate of 10°C/min, held isothermally for 3 min, and then scanned from 160 to -90℃ at the same heat rate. This heating and cooling cycle was repeated three times and the second scan was used to determine T_g at the inflection point of the heating curve.

Experimental Design

Reactivity ratio estimations were carried out over a series of equidistant monomer feed compositions (see Table 4-1). At each monomer feed composition, the conversion was intentionally limited to <10 wt.%. From those results, preliminary estimates of the reactivity ratios, r_1 (EHA) and r_2 (LIM), were obtained using the RREVM computer program.[18,19] These estimates were used to generate two comonomer feed compositions using the Tidwell-Mortimer criterion[20]:

$$\boldsymbol{f'_{10} = 2/(2 + r_1)} \qquad \textbf{Equation 4-4-1}$$

and

$$\boldsymbol{f''_{10} = r_2/(2 + r_2)} \qquad \textbf{Equation 4-4-2}$$

Five replicate experiments at each of the two comonomer feed compositions were then performed (see Table 4-1). Final reactivity ratios were calculated using the combined data set consisting of the preliminary and Tidwell-Mortimer runs.

Table 4-1 Experimental design

Run condition	EHA [mol fraction]	LIM [mol fraction]
1	0.10	0.90
2	0.20	0.80
3	0.30	0.70
4	0.40	0.60
5	0.50	0.50
6	0.60	0.40
7	0.70	0.30
8	0.80	0.20
9	0.90	0.10
TM1	0.30	0.70
TM2	0.05	0.95

Following the reactivity ratio experiments, high conversion experiments were performed at run conditions 4, 5, 7, 9 (see Table 4-1), chosen based on the T_g of the desired products. Five samples were run at each condition.

Results and Discussions

As a first important step, the copolymer peak identification of the ^{1}H-NMR spectra was performed. In Figure 4-2, a sample spectrum with corresponding peak assignments is presented. These peak assignments were confirmed by 2D-COSY NMR and ^{13}C-NMR. The peak *a* at ~3.9 δ is due to protons attached to the ester group of EHA, whereas the peaks *g*, *g′*, *m* between 4.6-5.5 δ are assigned to the protons associated with the double bonds in limonene; the peaks *g* and *g′* are due to the internal double bonds, while peak *m* is related to the external double bonds.

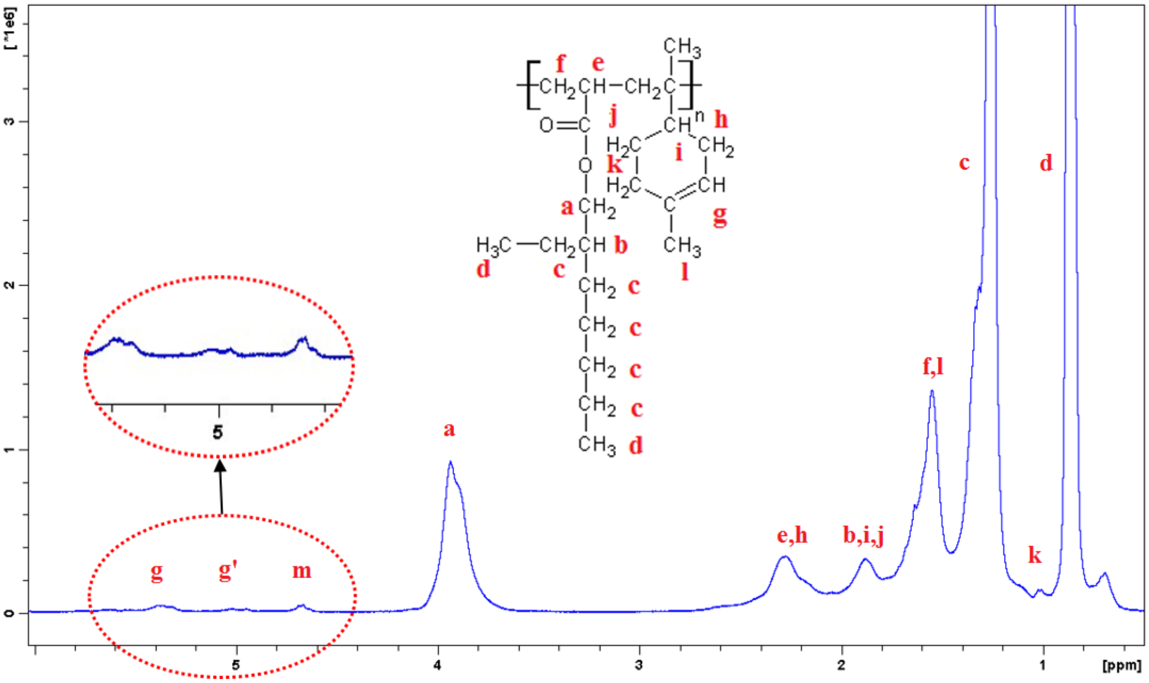

Figure 4-2 ^{1}H NMR spectrum of the copolymer LIM/EHA, f_1 =60.09 mol %, [BPO] = 1.73 mol %.

As noted in our previous study of BMA/LIM copolymers[13], the peak *m* at ~4.7 δ provides an indication that the external double bond is not necessarily consumed during the polymerization. Some of the external double bonds were consumed as noted by the increasing ratio of internal to external double bonds. However, the presence of the external double bonds indicates an alternative mechanism for the incorporation of limonene in the copolymer; that is, a degradative chain transfer mechanism. The possibility of polymerization through the internal double bond is extremely low due to steric hindrance and experimental verification of the extraction of unreacted limonene monomer from the reaction mixture further supports this explanation. As mentioned earlier, the allylic C-H bonds in limonene are the root cause of the degradative chain transfer reaction (see Figure 4-3). When a growing polymer chain ending with a limonene radical reacts with a limonene monomer, the chain transfer mechanism is favored over propagation at the external double bond. Polymer chain growth will then terminate and the radical transferred to the limonene monomer to form a limonene radical. Owing to electronic resonance, the limonene radical will stabilize between two structures (see Figure 4-3), and eventually lose the ability to continue propagating.

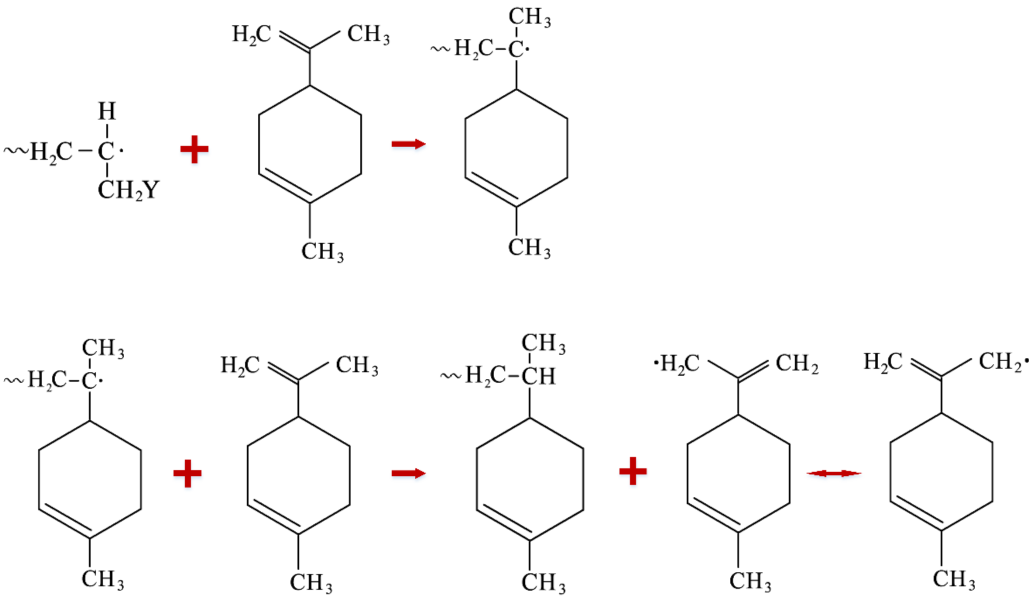

Figure 4-3 Degradative chain transfer mechanism for limonene free-radical polymerization.

Reactivity Ratios Estimation

The reactivity ratio estimation was carried out using the RREVM computer program, based on a non-linear, error-in-variables method[18,19], which employs the Mayo-Lewis equation[16]:

$$\frac{F_1}{F_2} = \frac{[M_1](r_1[M_1]+[M_2])}{[M_2](r_2[M_2]+[M_1])} \qquad \text{Equation 4-3}$$

where F_i is the overall instantaneous mole fraction of monomer *i* in the copolymer, $[M_i]$ represents the concentration of the monomer *i* in the feed, and r_i is the reactivity ratio of monomer *i*, defined as:

$$r_i = \frac{k_{pii}}{k_{pij}} \qquad \text{Equation 4-4}$$

where k_{pij} is the propagation rate parameter for the addition of monomer j to a growing radical chain ending in monomer i.

Using the results from run conditions 1 through 9 (see Table 4-2), reactivity ratios of r_1 = 6.755 and r_2 = 0.031 were obtained. These were then used in Equations 4-1 and 4-2 to generate the Tidwell-Mortimer feed conditions (i.e., TM1 and TM2 in Table 4-2). Five replicates were performed at each feed composition f_{1o}' = 0.30 and f_{1o}'' = 0.05. Final reactivity ratio estimates of r_1 = 6.896 and r_2 = 0.032 were calculated using the entire data set. A joint confidence contour for the reactivity ratio estimates using a 95% posterior probability is shown in Figure 4-4. In Figure 4-5, the experimental data and the Mayo-Lewis model predictions are shown. The reactivity ratio values and Figure 4-5 illustrate the preference for EHA incorporation into the copolymer.

Table 4-2 Reactivity ratios experimental data

Run	f_{EHA} [mol fraction]	F_{EHA} [mol fraction]	BPO [mol%]	Conversion [wt.%]
1	0.10	0.58	0.29	1.08
2	0.20	0.72	0.31	5.14
3	0.30	0.79	1.50	7.79
4	0.40	0.85	0.33	8.06
5	0.50	0.88	0.34	7.80
6	0.60	0.89	1.73	2.25
7	0.70	0.94	0.71	3.63
8	0.80	0.94	0.78	3.25
9	0.90	0.98	1.18	9.91
TM 1-1	0.30	0.77	0.25	2.78
TM 1-2	0.30	0.80	0.25	3.00
TM 1-3	0.30	0.79	0.25	2.80
TM 1-4	0.30	0.80	0.25	2.91
TM 1-5	0.30	0.78	0.25	2.90
TM 2-1	0.05	0.46	0.30	1.41
TM 2-2	0.05	0.46	0.30	1.53
TM 2-3	0.05	0.46	0.30	1.33
TM 2-4	0.05	0.46	0.30	1.35
TM 2-5	0.05	0.45	0.30	1.38

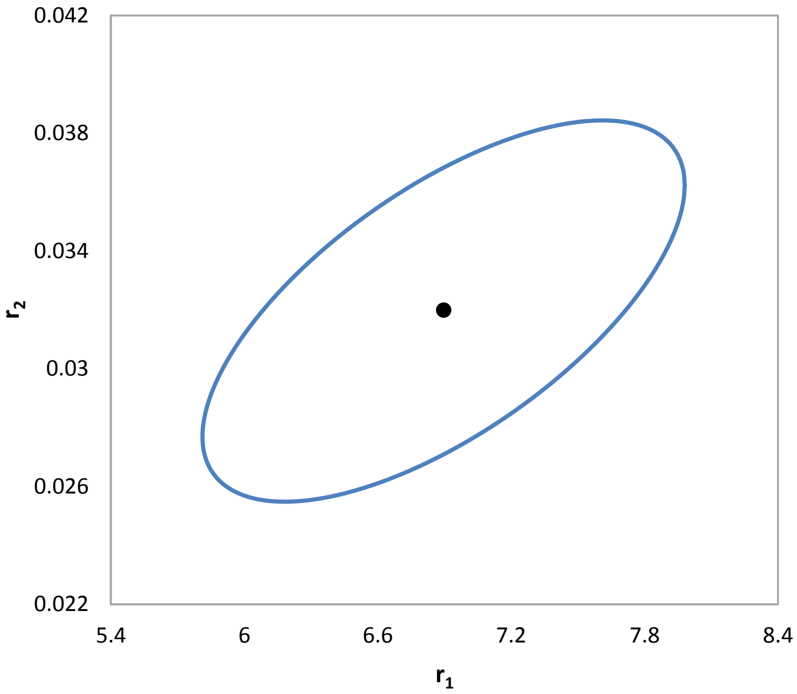

Figure 4-4 EHA/LIM reactivity ratios, 95% posterior probability contour.

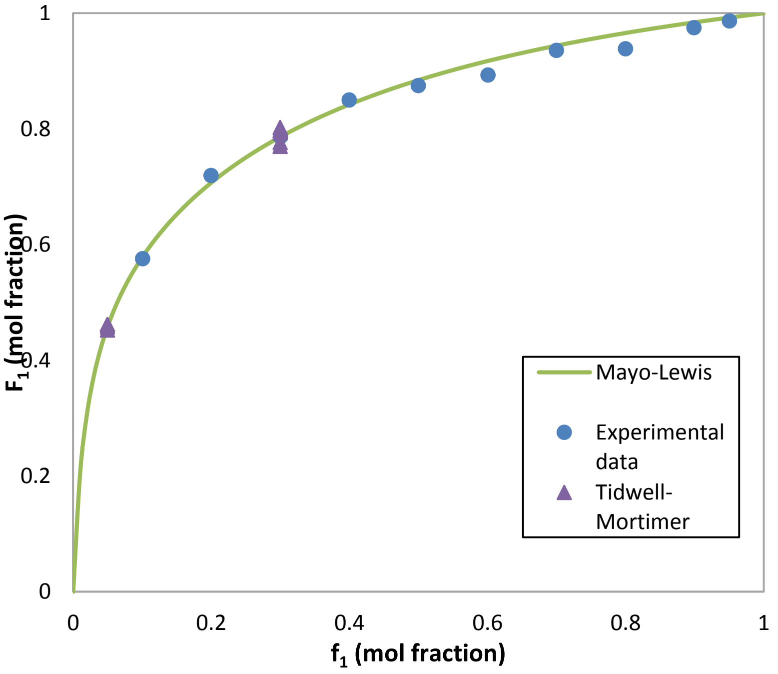

Figure 4-5 Dependence of copolymer composition, F_1, on monomer feed composition, f_1.

High Conversion Experiments

Four monomer feed compositions (runs 4, 5, 7 and 9 in Table 4-1) were chosen to carried out high conversion experiments. In Figure 4-6**Error! Reference source not found.**, the monomer conversion results are shown. Excluded from Figure 4-6 are data for runs 4 and 5 up to 20 h; these conversions remained unchanged beyond 5.5 h. This is partly attributed to the depletion of BPO initiator because the initiator half-life at 80^{o}C is 4.3 h. The highest conversion achieved was 54 wt.% at $f_1 = 0.9$.

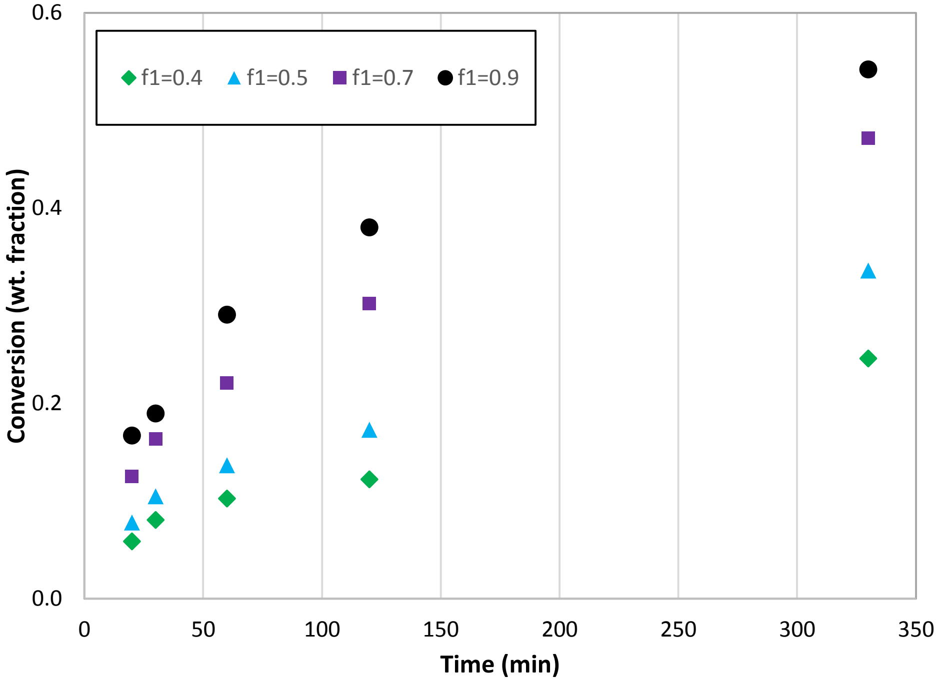

Figure 4-6 Conversion vs. time.

The experimental copolymer compositions along with the predicted cumulative copolymer compositions using the integration of the Mayo-Lewis equation (and the estimated reactivity ratios) are plotted in Figure 4-7. Among the four runs, the maximum limonene incorporation was 26 mol%. Significant deviation from Mayo-Lewis model predictions is evident. The Mayo-Lewis model does not account for the influence of chain transfer reactions and this implies that chain transfer in these reactions was significant. Deviation from model predictions intensified with increasing limonene content in the feed mixture. Limitations to the conversion levels also support this explanation. Nevertheless, it was possible to incorporate limonene into the copolymer and future investigations using semi-batch feed policies may provide a means towards greater limonene incorporation.[21]

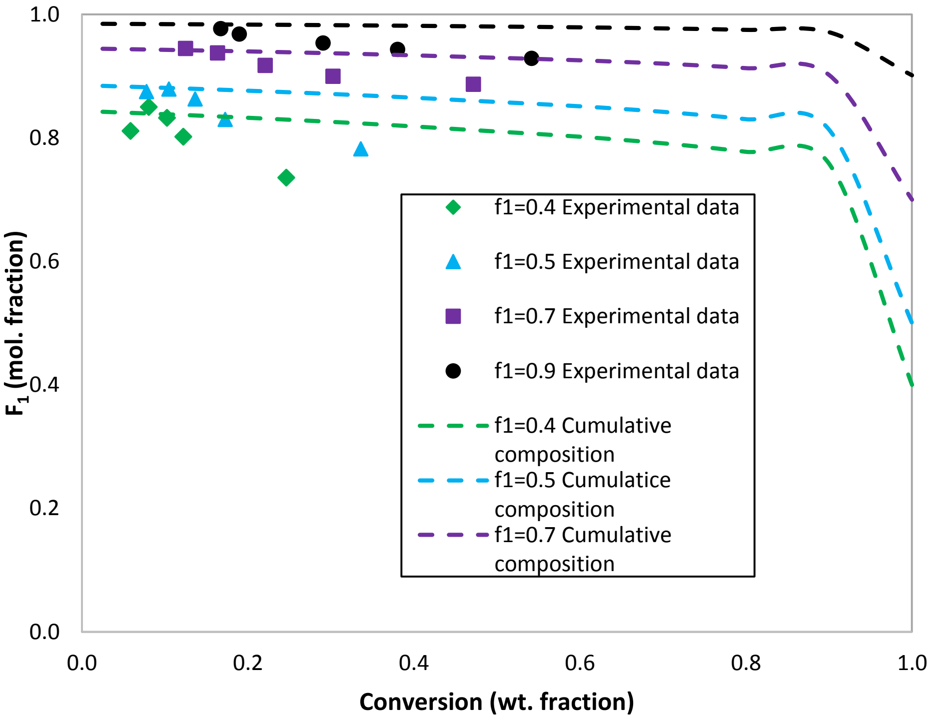

Figure 4-7 Copolymer composition vs. conversion.

Molecular weight results also support the existence of degradative chain transfer. The number- and weight-average molecular weights for runs 7 and 9 are presented in Figure 4-8. The pronounced decrease in molecular weight with conversion supports the notion of a chain transfer dominated molecular weight development. A trend towards lower molecular weights with increasing limonene content further supports this observation.

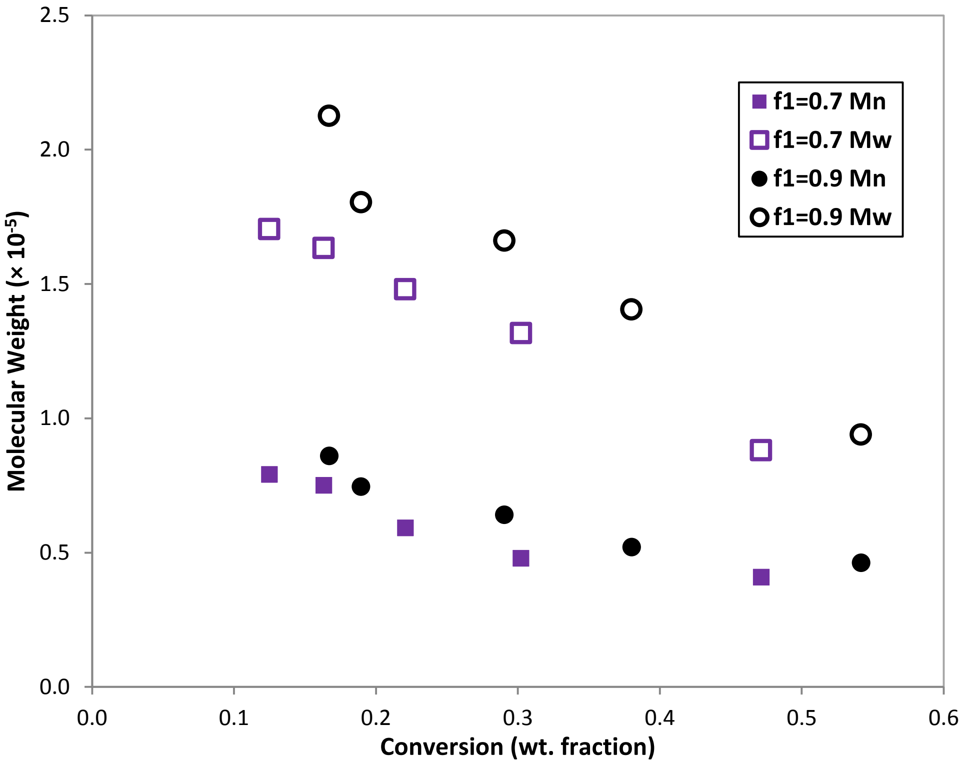

Figure 4-8 Average molecular weight vs. conversion.

DSC analysis was used to confirm that homogeneous copolymers were produced because a single glass transition was observed in each sample. The T_g of selected samples are shown in Table 4. As mentioned earlier, the T_g of poly(limonene) and pEHA are 116 and -70°C, respectively. The copolymer T_g differed significantly from that of pEHA and increased with limonene concentration, as expected.

Table 4-3 Glass transition temperature of selected samples

f_1 [mol fraction]	F_1 [mol fraction]	Conversion [wt. fraction]	T_g [°C]
0.40	0.80	0.12	-61.25
0.50	0.83	0.17	-63.64
0.70	0.90	0.30	-65.77
0.90	0.93	0.54	-67.21

Conclusions

The bulk free-radical copolymerization of d-limonene with 2-ethylhexyl acrylate was conducted at 80°C. Reactivity ratios were estimated using an iterative procedure beginning with equidistant experimental feed composition points followed by replicate runs as determined using the Tidwell-Mortimer criterion. Reactivity ratios of r_1 = 6.896 and r_2 = 0.032 were obtained which indicated the dominance of EHA in the copolymerization. Homogeneous copolymers were produced owing to the moderate drift in copolymer composition; of course, high conversions were not achieved. High conversion tests results point to significant degradative chain transfer of limonene in the polymerization. This degradative chain transfer in turn limited conversion, lowered molecular weight (and dominated the molecular weight development) and resulted in significant deviation of copolymer composition model predictions. Future modeling efforts invoking the degradative chain transfer mechanism should reveal better predictions for composition and would facilitate the use of semi-batch feed policies for greater incorporation of limonene into the copolymer.

Acknowledgements

Financial support for this work through the Natural Sciences and Engineering Research Council (NSERC) of Canada, Canada Foundation for Innovation (CFI) and Intellectual Ventures is gratefully acknowledged.

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5. General Discussion, Conclusion and Recommendations

In order to discover a good candidate for copolymerization with limonene, at the beginning of our project, a screening study was conducted. Six monomers (see Table 5-1) with different glass transition temperatures were chosen to carry out free-radical copolymerization with limonene at the same reaction temperature (80^{o}C), same reaction time (60 and 120 min), same initiator concentration (0.2 and 1 wt.% BPO) and same monomer feed composition (50:50 mol:mol).

Table 5-1 Glass transition temperature of polymers

Monomer	**Polymer T_g (℃)**
Limonene (LIM)	116
Isobutyl acrylate (IBA)	-24
2-Ethylhexyl acrylate (EHA)	-70
Dodecyl methacrylate (DMA)	-65
Methyl methacrylate (MMA)	105
n-Butyl methacrylate (BMA)	20
Styrene (STY)	100

In the screening study, our primary concerns were to achieve elevated monomer conversions and adequate limonene incorporation. As shown in Figure 5-1, methacrylate monomers yielded the highest conversions (note: an additional figure with a different initiator concentration is shown in the appendix A). Based on conversion results, dodecyl methacrylate (DMA) and n-butyl methacrylate (BMA) appeared to be the best candidates for copolymerization. On the other hand, based on copolymer T_g results and our target product (i.e., adhesives), copolymerization with 2-ethylhexy acrylate (EHA) would be a good choice. Furthermore, copolymerization using DMA with limonene, presented challenges in separating the DMA monomer from the monomer-polymer mixture. In the interest of time and having identified two reasonable candidate comonomers, BMA and EHA were chosen to continue the next stages of our project.

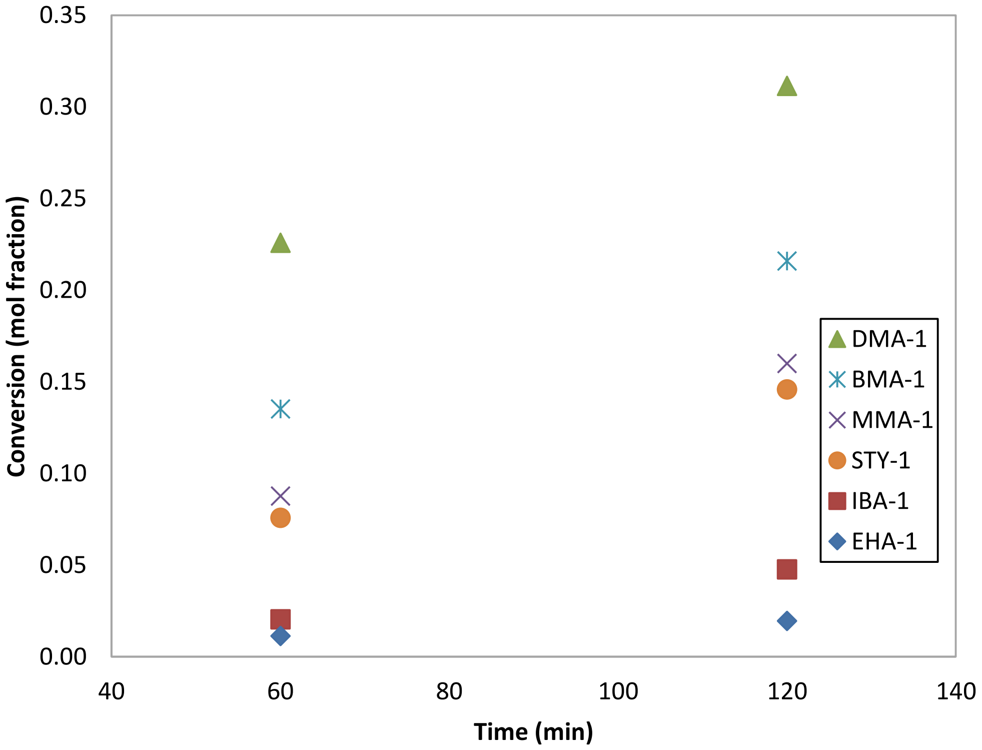

Figure 5-1 Conversion vs. time, with 0.2 wt.% BPO.

In this thesis, the study of copolymerization of limonene with BMA and EHA was shown. We were able to produce homogeneous copolymers containing limonene with relatively high molecular weights (>100,000) for both systems. Reactivity ratios were also estimated in both systems: for BMA and limonene, r_{BMA} = 6.096 and r_{LIM} = 0.046; and for EHA and limonene, r_{EHA} = 6.896 and r_{LIM} = 0.032. Based on the conversion results, BMA/LIM copolymers with high BMA contents resulted in almost complete monomer conversion, while conversion was limited to 54 wt.% for the EHA/LIM copolymers. There is no doubt that the degradative chain transfer due to limonene monomer manifests itself in both polymerizations. However, for BMA/LIM, the molecular weight of the copolymers was stable with increasing conversion, while for EHA/LIM, a significant molecule weight decrease was evident as conversion increased. The conversion, copolymer composition and molecular weight results all revealed that BMA performed better in the copolymerization with limonene. Nevertheless, the limonene incorporation in the copolymers was still limited. However, with the estimated reactivity ratios, it should be possible to employ a semi-batch monomer feed policy to encourage limonene incorporation.[1]

This project has laid the groundwork to enable us to proceed towards the production of limonene-containing copolymers; but, there are still many possibilities for future work:

1. Given the information obtained in this project, the emulsion polymerization of limonene and BMA can now be pursued to produce more sustainable polymer materials (e.g., pressure sensitive adhesives).

2. As mentioned in Chapter 4 (EHA/LIM), significant deviations between the experimental data and the Mayo-Lewis model predictions were evident. The Mayo-Lewis equation doesn’t account for the degradative chain transfer mechanism of limonene, which is dominant in the polymerization. Thus, new models incorporating this mechanism should be developed.
3. DMA may still be a good candidate for copolymerization with limonene as our screening study showed conversions beyond that of BMA/LIM. Appropriate monomer solvents/polymer non-solvents need to be identified to facilitate proper sample work-up. Alternatively, other characterization methods may be employed to decouple the monomer and polymer compositions.
4. As indicated in the literature review, the copolymerization of limonene via cationic initiation is another interesting option. However, at the laboratory scale, experimental conditions for cationic polymerization (i.e., strictly oxygen- and water-free) are difficult to achieve. Thus, the identification of a less moisture-sensitive catalyst would be helpful.
5. Nitroxide mediated radical polymerization (NMP) of limonene is another possibility. NMP is a “living” radical polymerization technique that makes it possible to control macromolecular architecture.[2] It is of great interest to see how “living” radicals might compete with degradative chain transfer reactions.
6. It is entirely possible that the activation energies of the propagation and degradative chain transfer reactions are different. To that end, polymerization at lower (or higher) temperatures may reveal interesting results.

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[1] S. Sharma and A. Srivastava, *Synthesis and Characterization of Copolymers of Limonene with Styrene Initiated by Azobisisobutyronitrile*, Eur. Polym. J. 40 (2004), pp. 2235-2240.

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Appendix A

Additional Figures and Tables

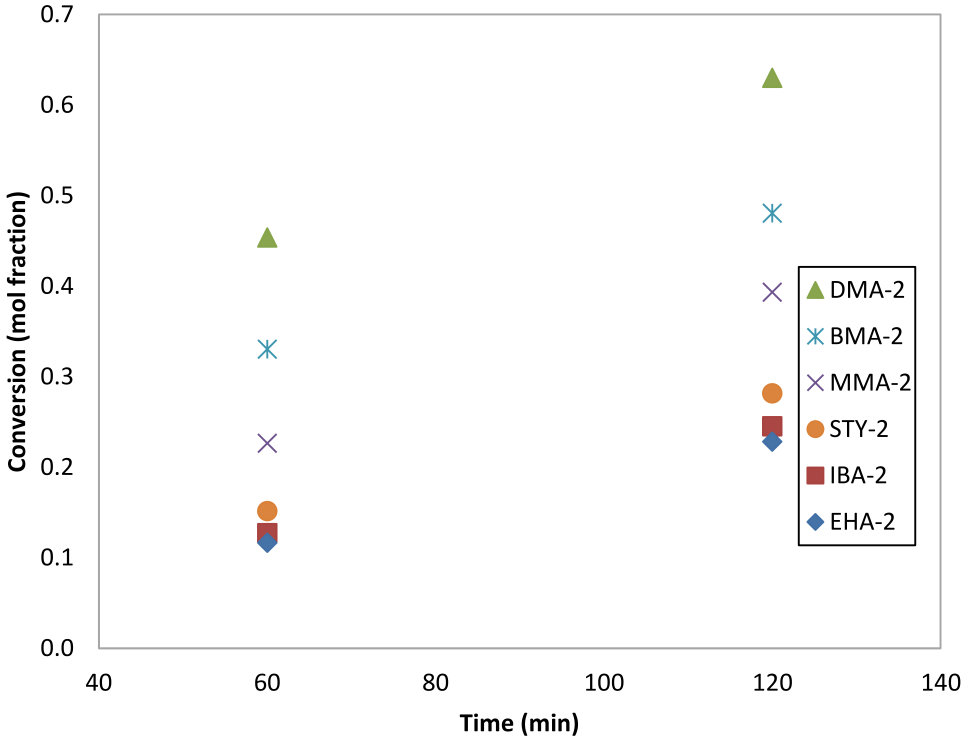

Figure A-1 Screening study, conversion vs. time, with 1 wt.% BPO.

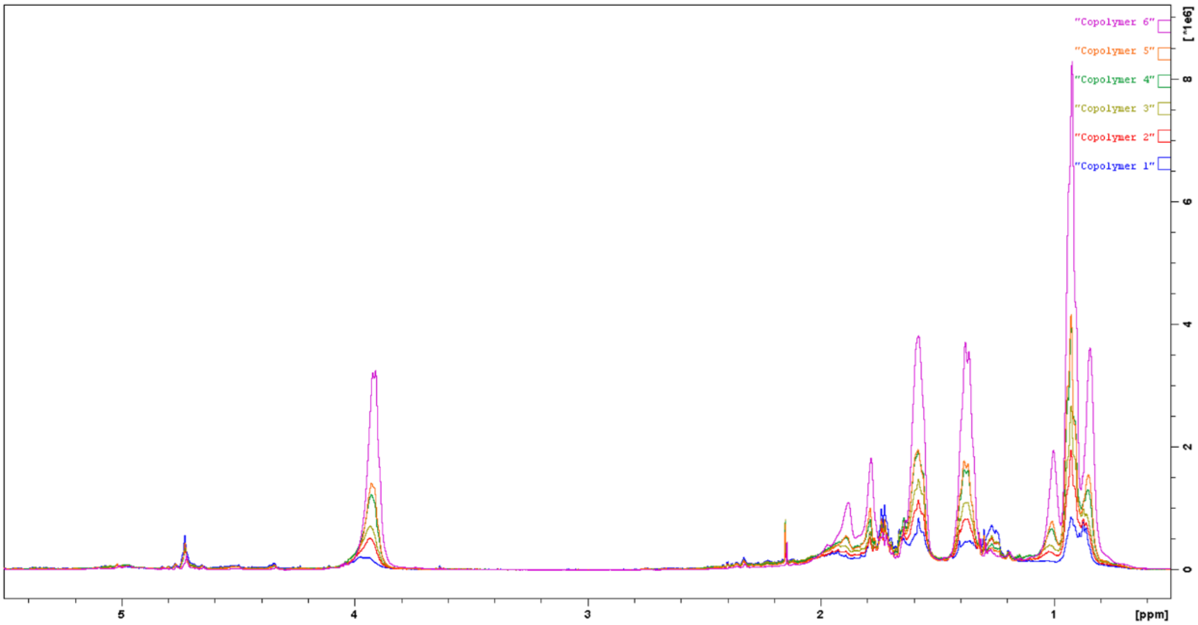

Figure A-2 BMA/LIM, ^{1}H-NMR spectrum with different feed compositions.

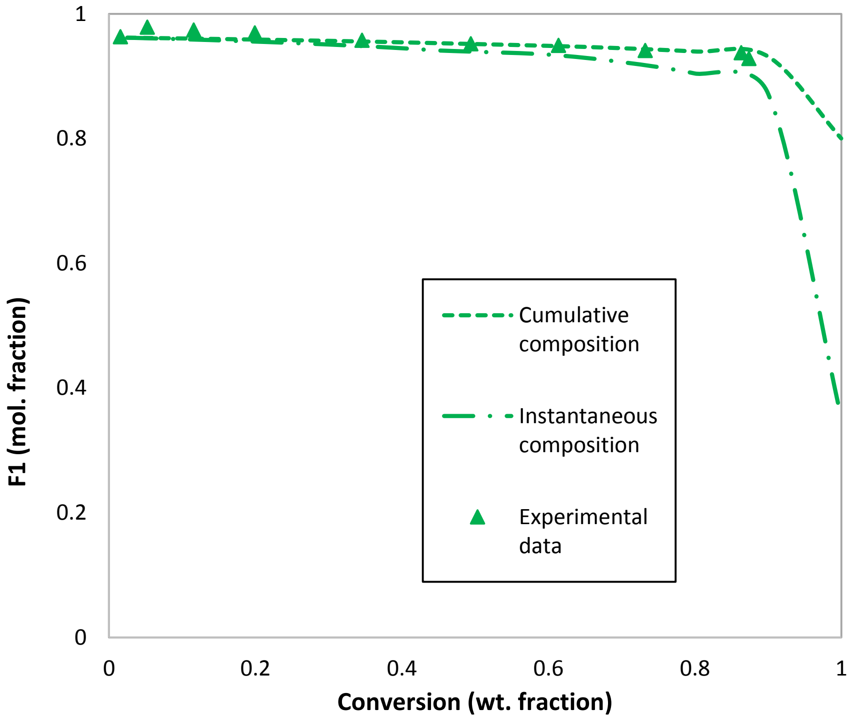

Figure A-3 BMA/LIM, cumulative and instantaneous copolymer composition vs. conversion, f_1=0.8.

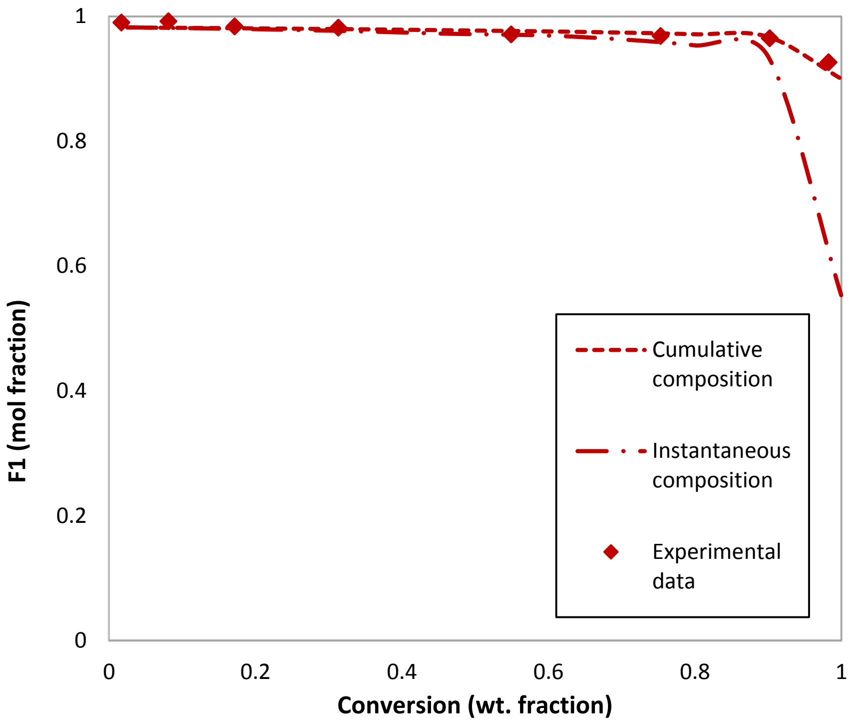

Figure A-4 BMA/LIM, cumulative and instantaneous copolymer composition vs. conversion, f_1=0.8.

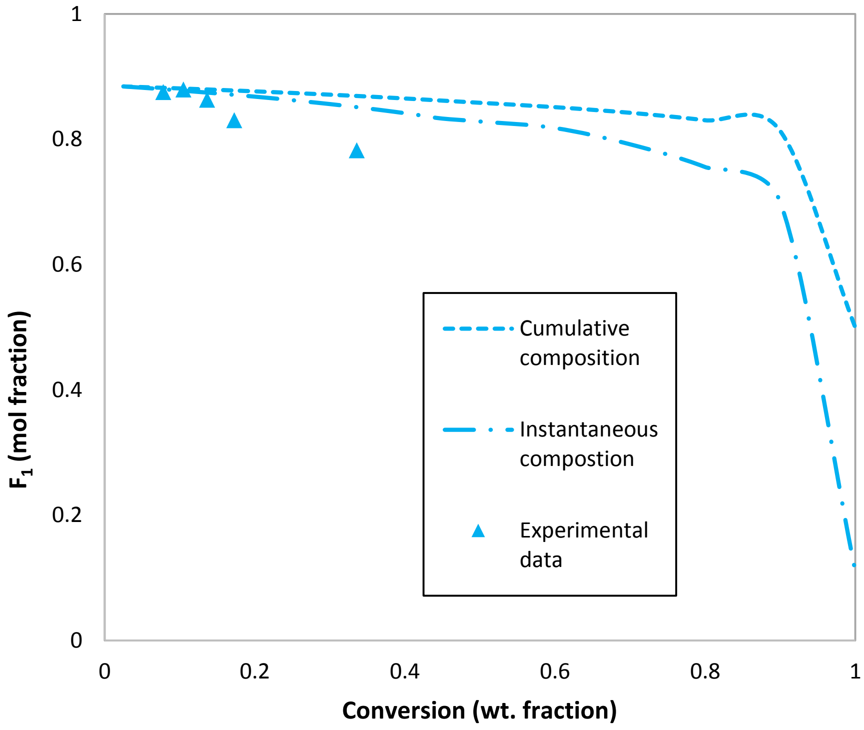

Figure A-5 EHA/LIM, cumulative and instantaneous copolymer composition vs. conversion, f_1=0.5.

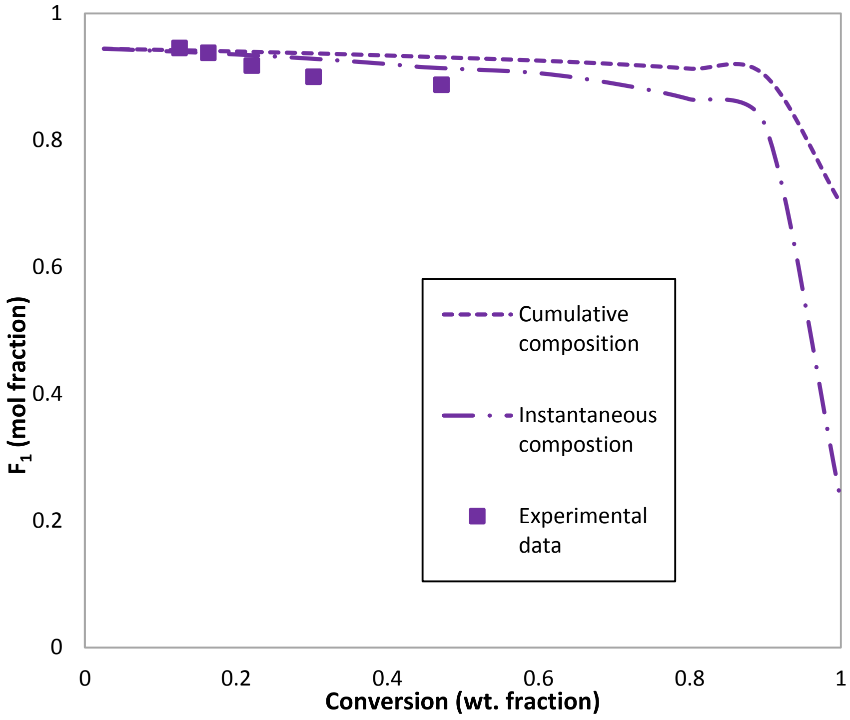

Figure A-6 EHA/LIM, cumulative and instantaneous copolymer composition vs. conversion, f_1=0.7.

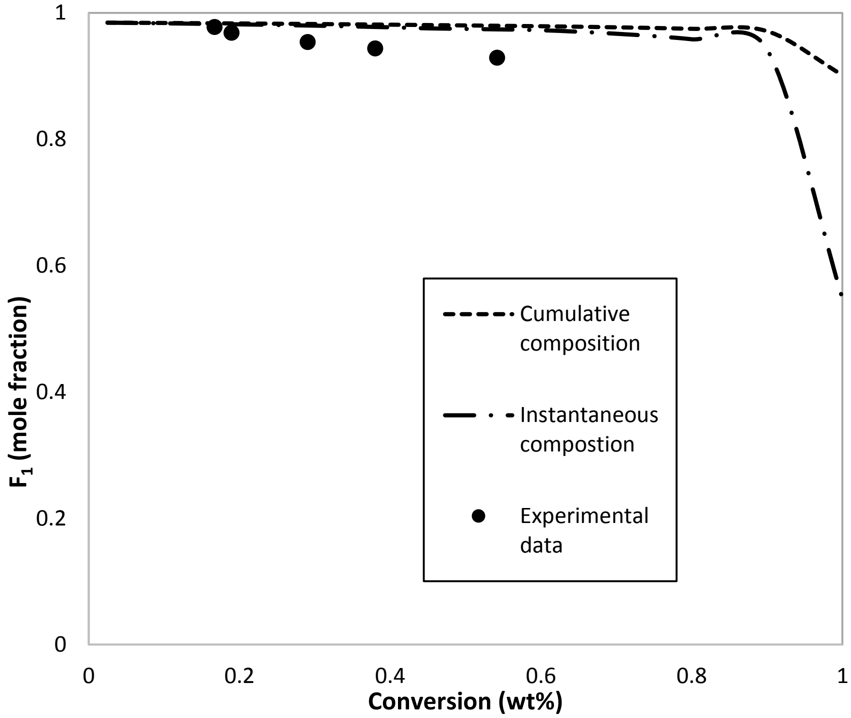

Figure A-7 EHA/LIM, cumulative and instantaneous copolymer composition vs. conversion, f_1=0.9.

Appendix B

Health and Safety Assessment

Safety precautions are necessary when handling monomers and solvents, and to conduct experiments safely. While working in the laboratory, safety glasses, nitrile gloves, lab coat and a respirator were used to protect from hazards.

Pressure extremes

Monomer purification and degassing were carried out under vacuum, therein the apparatus was set up in the fume hood. Coated glassware to protect from implosion was used.

Temperature extremes

In this project, the polymerization was conducted at 80^{o}C. When removing ampoules from the oil bath, heat-resistant gloves were used. The same protection was used when working with liquid nitrogen.

Chemical hazards

In Table B-1, all chemicals used in this project, as well as the corresponding hazards, storage methods and protective measures are shown. This information was obtained from the material safety data sheets.

All of the monomers and initiators were stored in a refrigerator (~5°C). Work (e.g., weighing, pipetting, freeze-pump-thaw) related to liquid monomers was conducted in the fume hood.

Table B-1 Hazards, protective measures and storage methods of chemicals

Type	Compound	Hazard	Storage method	Protective measures
Monomers	Limonene	low toxicity, mild irritant	Dry ventilated place	Use personal protective equipment (safety glasses, nitrile gloves, lab coat and respirator)
	2-Ethyhexyl acrylate	Toxic; irritant (skin/eye/inhalation/ingestion)	Dry ventilated place	
	n-Butyl methacrylate	Irritant (skin/eye/inhalation/ingestion); possible teratogen, possible reproductive effects	Dry ventilated place	
	Dodecyl methacrylate	Toxic; irritant (skin/eye/inhalation/ingestion)	Dry ventilated place	
	Methyl methacrylate	Toxic; irritant (skin/eye/inhalation/ingestion)	Dry ventilated place	
	Styrene	Carcinogenic effects; irritant (skin/eye/inhalation/ingestion)	Dry Ventilated place	
	Acetone	Toxic; irritant (skin/eye/inhalation/ingestion)	Flammables area	

Solvents	Methanol	Mutagenic effects; possible teratogenic effects; irritant (skin/eye/inhalation/ingestion)	Flammables area	Use personal protective equipment (safety glasses, nitrile gloves, lab coat and respirator)
	THF	Acute toxicity; irritant (skin/eye/inhalation/ingestion)	Flammables area	
	Chloroform-d	Toxic; carcinogen; moderate irritant (skin/eye/inhalation/ingestion)	dark place (light-sensitive)	
Initiator	BPO	Extremely hazardous (skin/eye/inhalation/ingestion)	in refrigerator	