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The challenge of degradative chain transfer in renewable monomer polymerization

Marc Dube
University of Ottawa

THE CHALLENGE OF DEGRADATIVE CHAIN TRANSFER IN RENEWABLE MONOMER POLYMERIZATION

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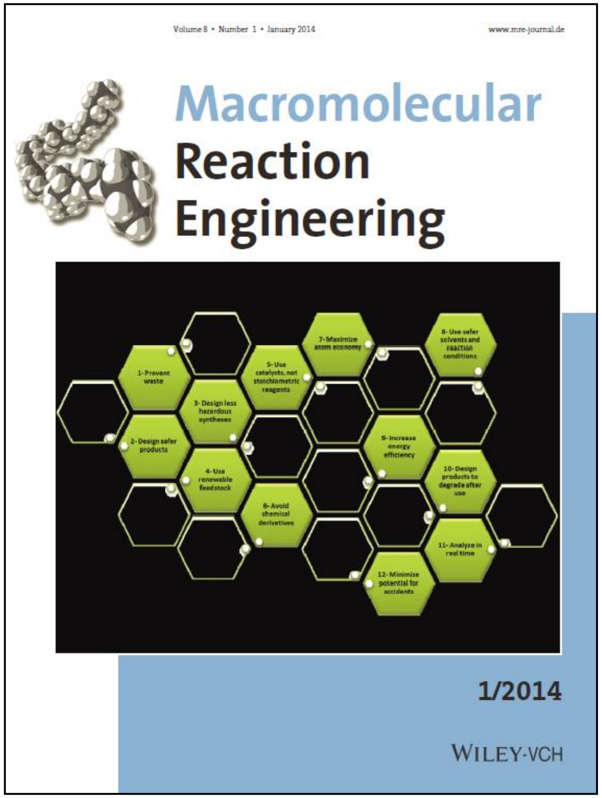
Department of Chemical and Biological Engineering
Centre for Catalysis Research and Innovation

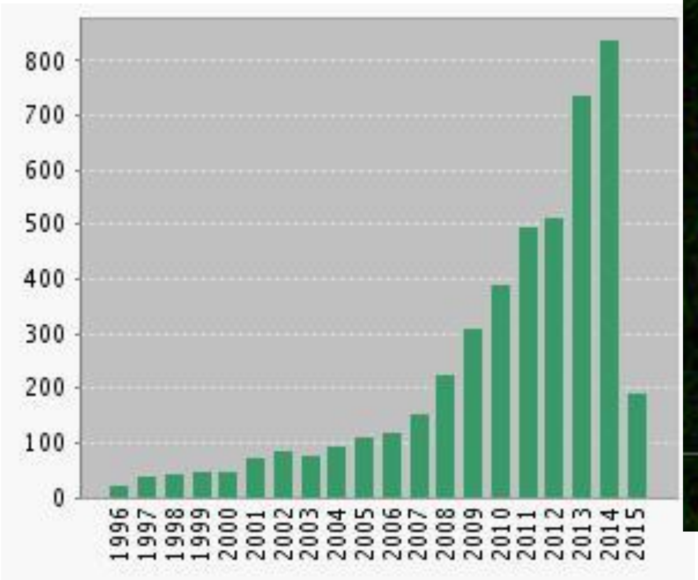
The 12 Principles of Green Chemistry:

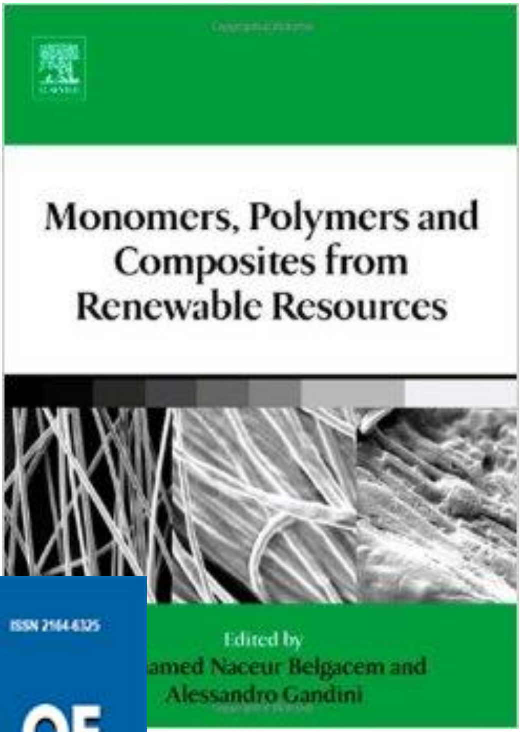
1. Prevent waste
2. Design safer chemicals and products
3. Design less hazardous chemical syntheses
4. Use renewable feedstock
5. Use catalysts
6. Avoid chemical derivatives
7. Maximize atom economy
8. Use safer solvents and reaction conditions
9. Increase energy efficiency
10. Design chemicals and products to degrade after use
11. Analyze in real time to prevent pollution
12. Minimize the potential for accidents



Dubé, M.A. and Salehpour, S. (2014), Applying the Principles of Green Chemistry to Polymer Production Technology. Macromolecular Reaction Engineering, 8:7–28.

Renewable Materials





Terpenes

- large and diverse class of organic compounds, produced by a variety of plants, particularly conifers, (some by insects, e.g., termites);
- often strong-smelling;
- insecticidal properties;
- terpenes are hydrocarbons; terpenoids contain additional functional groups.

Macromolecular Rapid Communications

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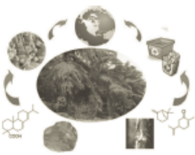
Review

Progress in Renewable Polymers from Natural Terpenes, Terpenoids, and Rosin

Perry A. Wilbon, Fuxiang Chu,* Chuanbing Tang*

The development of sustainable renewable polymers from natural resources has increasingly gained attention from scientists, engineers as well as the general public and government agencies. This review covers recent progress in the field of renewable bio-based monomers and polymers from natural resources: terpenes, terpenoids, and rosin, which are a class of hydrocarbon-rich biomass with abundance and low cost, holding much potential for utilization as organic feedstocks for green plastics and composites. This review details polymerization and copolymerization of terpenes such as pinene, limonene, and myrcene and their derivatives, terpenoids including carvone and menthol, and rosin-derived monomers. The future direction on the utilization of these natural resources is discussed.



1. Introduction

One of the most pressing issues for future generations is the development of a sustainable society. Fossil fuel used for both energy production and plastic manufacturing has finite availability. Within the next century, it will be nearly depleted. Approximately 7% of the global production of fossil fuel goes into the synthesis of plastic materials.[1–13]

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should not be neglected. In addition to the economic influence, the undesirable environmental impact by non-renewable resources has contributed to the rebirth of renewable resource alternatives. Burning fossil fuel has led to increased greenhouse gas emissions, reduced air quality, and global warming.[14] Most plastics derived from non-renewable resources have led to water and land pollution due to their inability to undergo biodegradation.

The environmental concerns, along with depleting oil reserves, have led to an increased interest in the development of green plastics derived from renewable natural resources.[3,6,7,10–12,15–29] The large-scale production of green plastics primarily depends on the integration of biorefineries.[8,9,30] A biorefinery, as defined by the National Renewable Energy Laboratory, is a facility that integrates biomass conversion processes and equipment to produce fuels, power, and chemicals from biomass and is analogous to today's petrochemical refineries.[31] The importance of these refineries to develop green plastics, without impacting the food and feed production in a negative manner, is essential for future growth.

Green plastics can be classified into three primary categories. The first class of natural resources is natural polymers including lignin, cellulose, hemicellulose, polysaccharide, and chitin.[22,32–43] Many of these biopolymers display excellent biocompatibility and biodegradability. These natural polymers have long been exploited without

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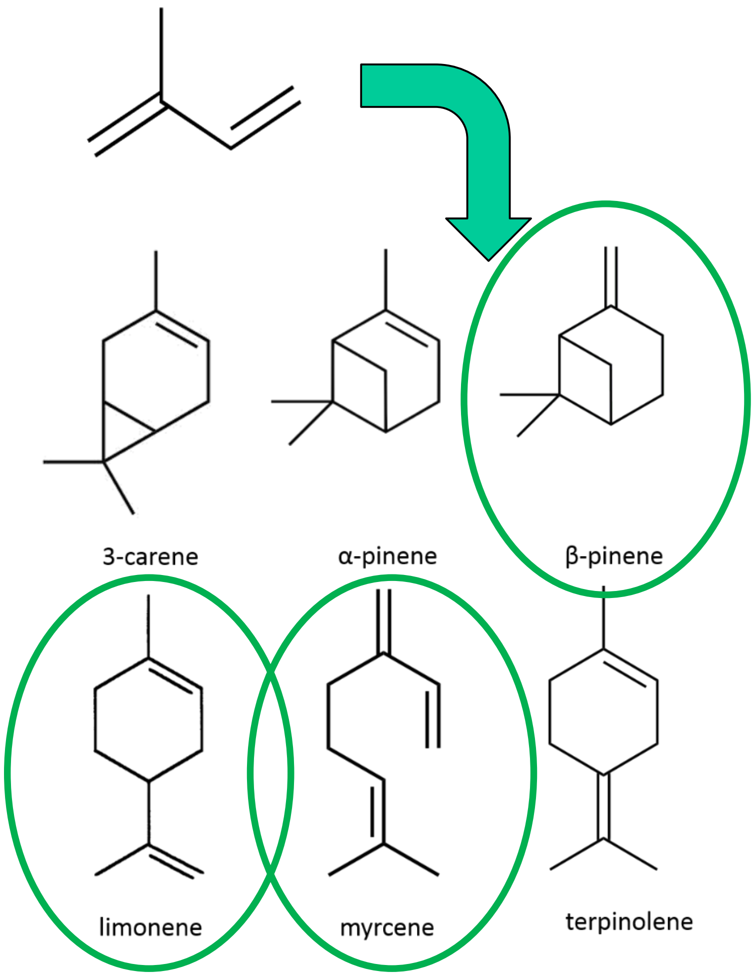
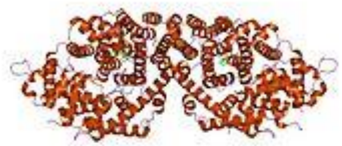
Terpenes

- Derived commercially from conifer resins, such as those made by pine;
- found in essential oils which are used widely as
  - natural flavor additives for food,
  - fragrances in perfumery, and
  - in medicine and alternative medicines such as aromatherapy;
- synthetic variations and derivatives of natural terpenes and terpenoids also greatly expand the variety of aromas used in perfumery and flavors used in food additives;
- Vitamin A is a terpene.

Terpenes



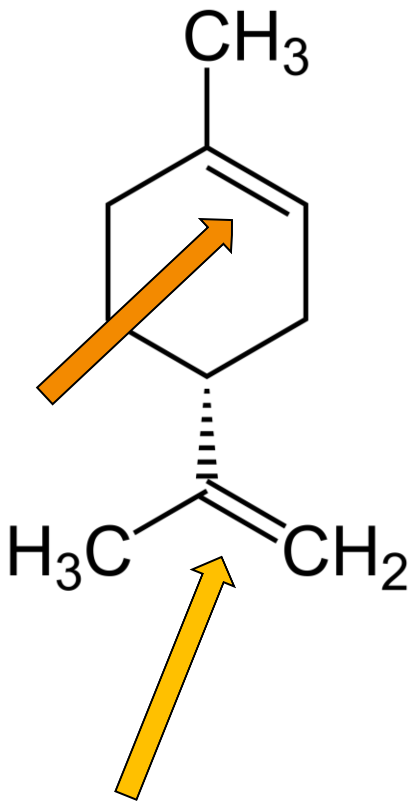
- Derived biosynthetically from units of isoprene by terpene synthase;



- multiples of isoprene, $(C_5H_8)_n$, linked "head to tail" to form linear chains or arranged to form rings;
- classified sequentially by size as hemiterpenes, monoterpenes, sesquiterpenes, diterpenes, sesterterpenes, etc.

Limonene

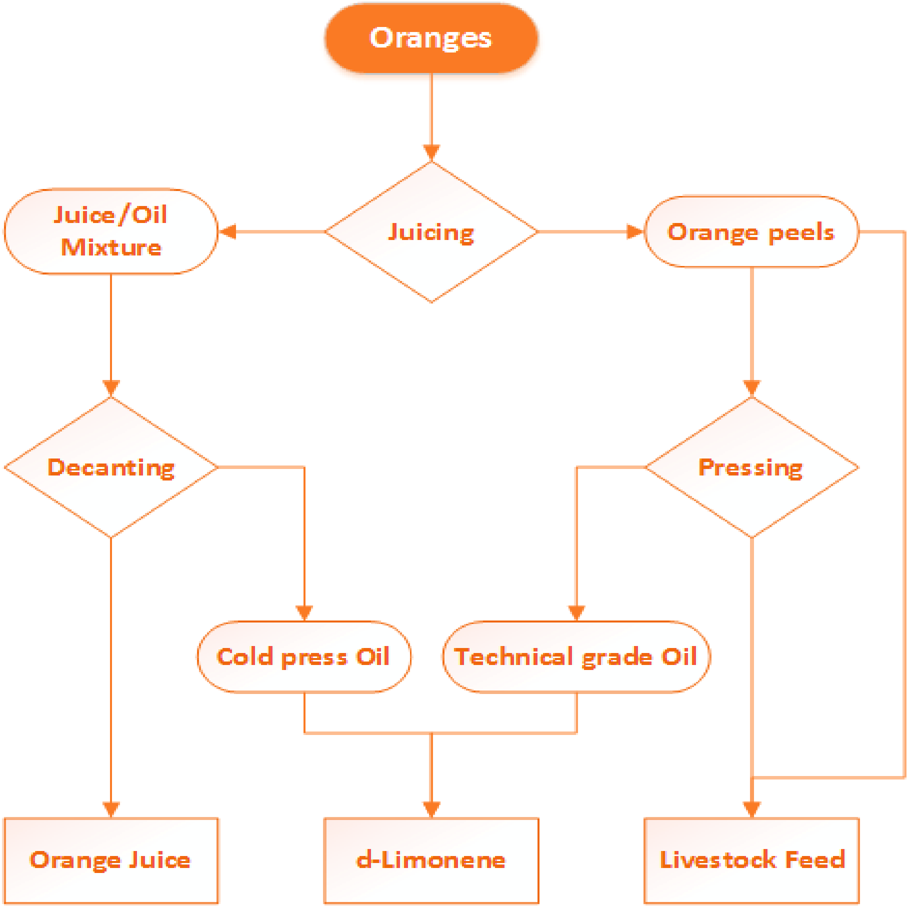
- Monocyclic terpene in many essential oils (e.g., lemons, oranges, grapefruits).
- Optically active
- Low toxicity (*D*-limonene smells of oranges)
- Can be purchased in pure state



D-Limonene production

- Oil from juicing and peel processing of oranges consists of ~90-95% limonene

Essential Oil	D-limonene content
Grapefruit	95%
Tangerine	94%
Orange	91%
Mandarin	72%
Lemon	65%
Lime	49%



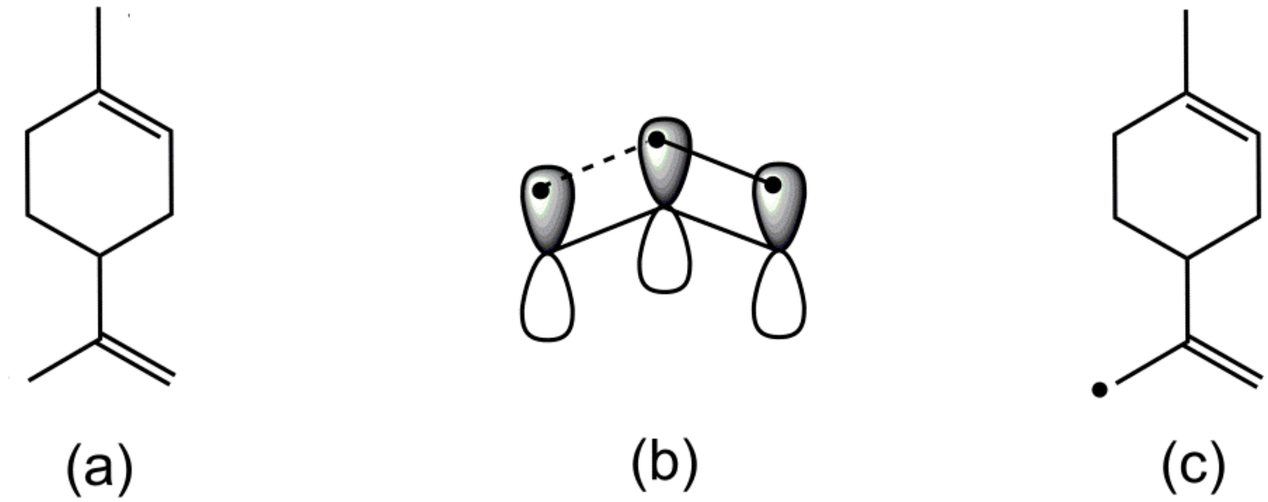
D-Limonene - Applications

Cosmetics

Medicine

Green solvent

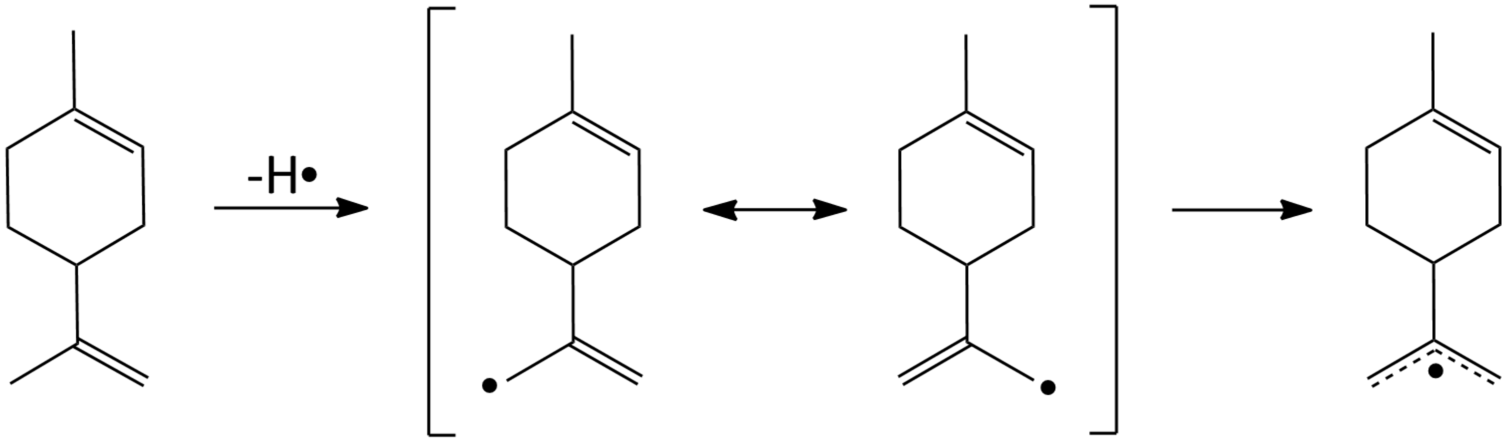
D-Limonene and allylic hydrogen…



Vinyl group = candidate for polymerization

Free-radical homopolymerization?

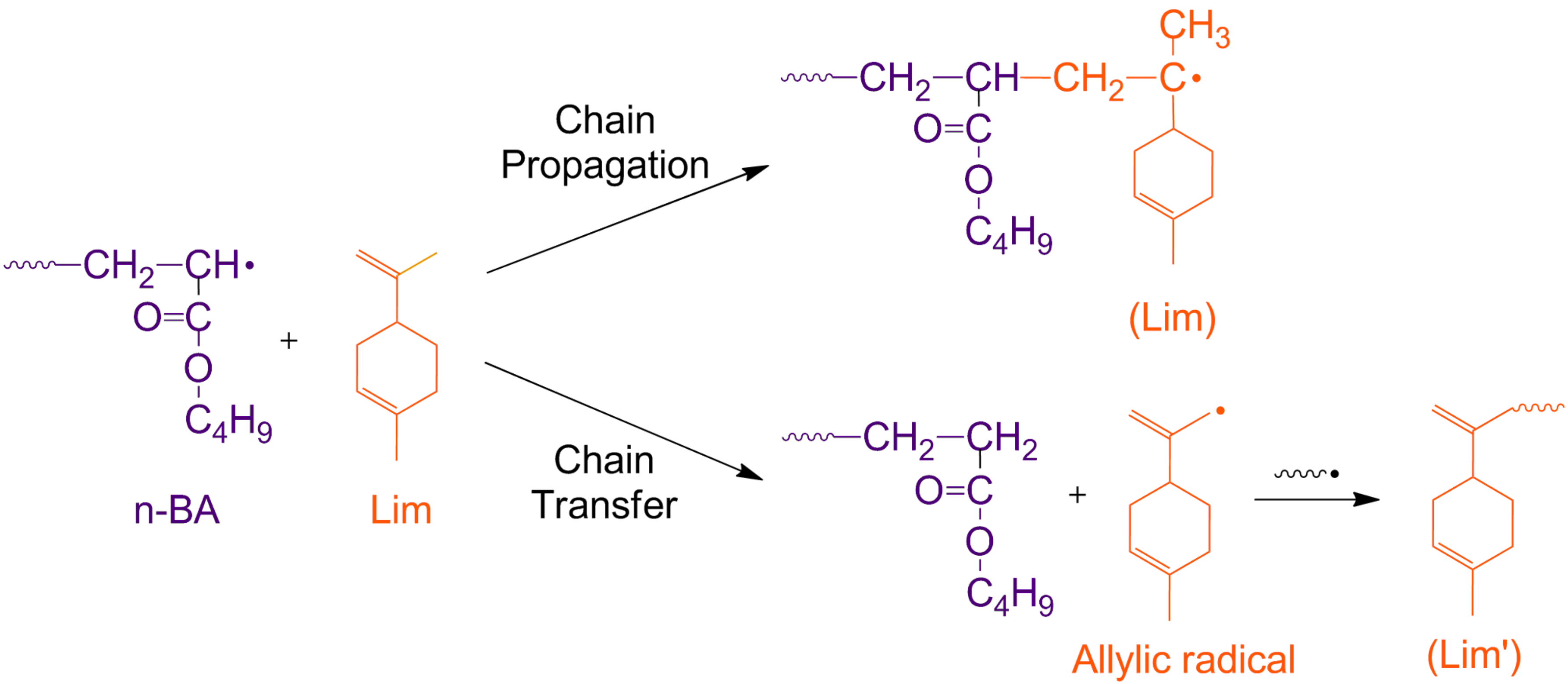
D-Limonene and allylic hydrogen…



Cationic homopolymerization?

Copolymerization (e.g., MA, AN, MMA, Sty)

Degradative chain transfer



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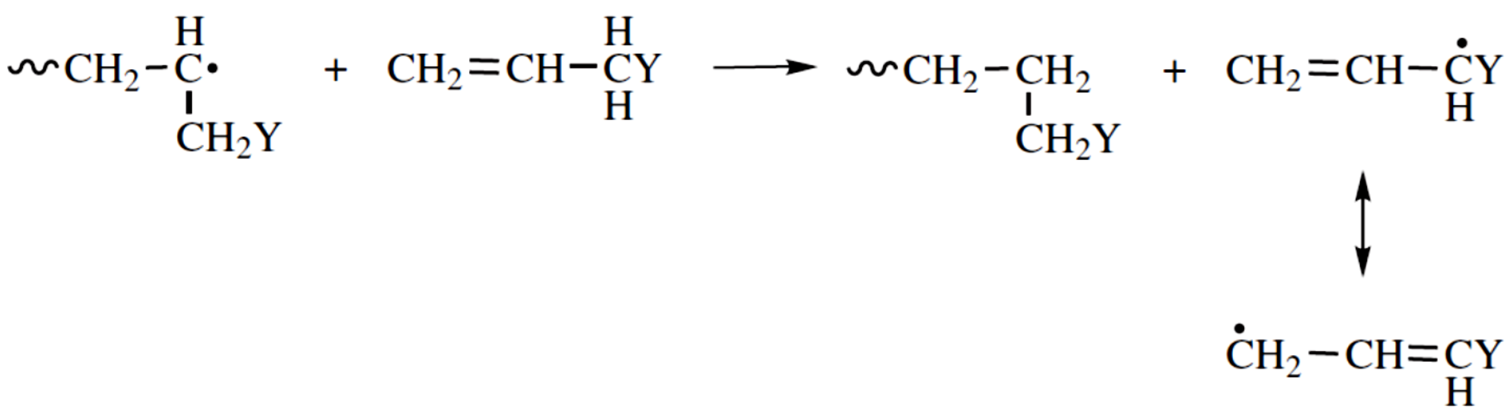
Degradative chain transfer

Normal chain transfer: $\overline{X_n}\downarrow$ $R_p\sim$constant

$$M_n\bullet + XA \xrightarrow{k_{tr}} M_n{-}X + A\bullet$$

Degradative chain transfer: $\overline{X_n}\downarrow$ $R_p\downarrow$



Objectives

- **Free-radical copolymerization of limonene**

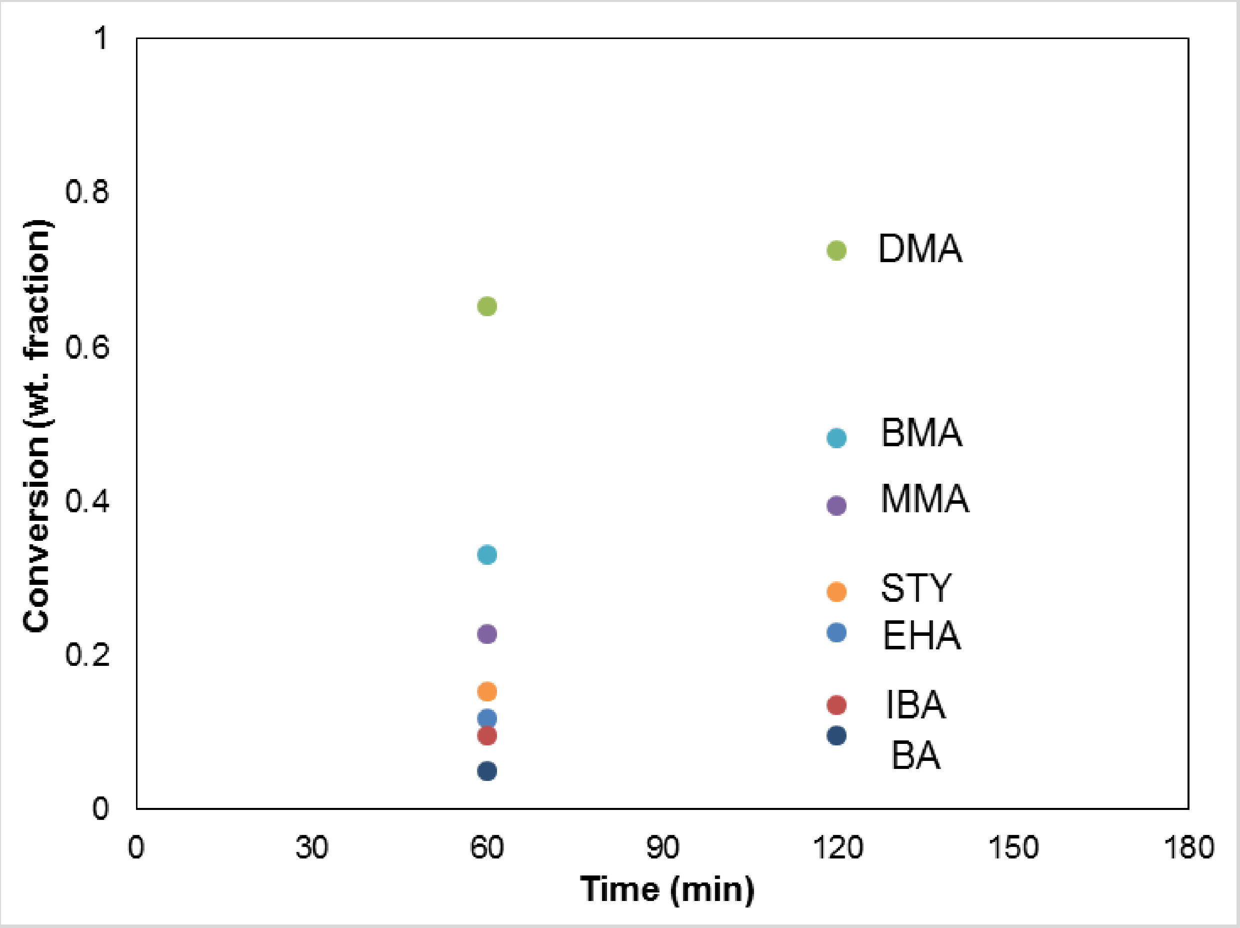
- **Target application: pressure-sensitive adhesives**

Experimental plan

- Screening study
- Low conversion experiments:
  - reactivity ratios
- Full conversion experiments:
  - copolymer composition
  - molecular weight
  - glass transition temperature
- Modelling
- Extension to terpolymerization

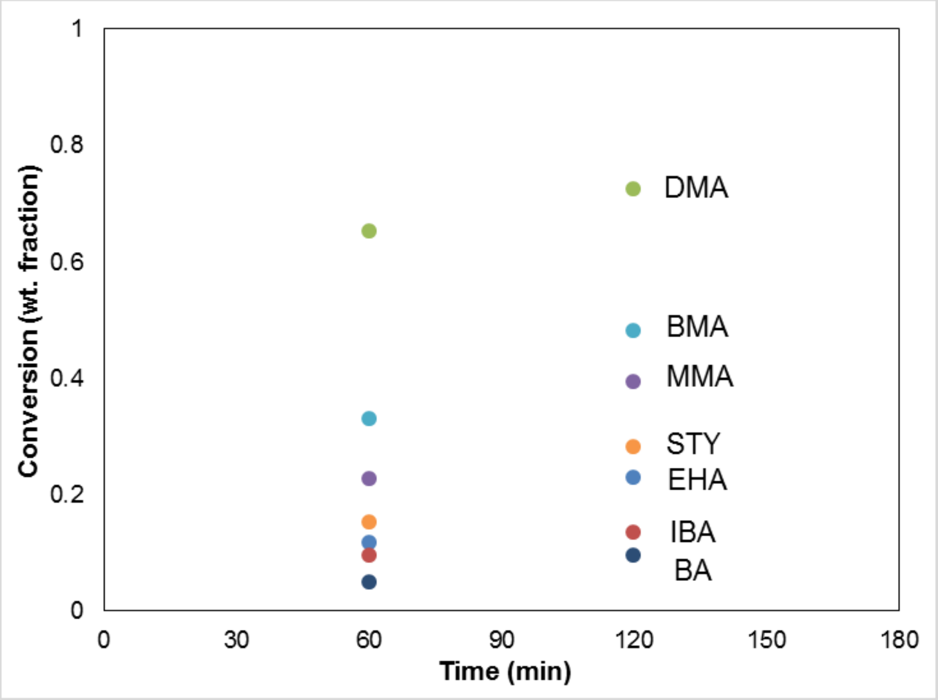
Screening study

- 50/50 mol/mol monomer feed composition
- 1 wt.% BPO
- <u>**60 ºC**</u>



Glass transition temperature - PSA

Monomer	Polymer T_g (°C)
Limonene (LIM)	116
Methyl methacrylate (MMA)	105
Styrene (STY)	100
Butyl methacrylate (BMA)	20
Isobutyl acrylate (IBA)	-24
n-Butyl acrylate (BA)	-54
Dodecyl methacrylate (DMA)	-65
2-Ethylhexyl acrylate (EHA)	-70



Reactivity ratio estimation

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

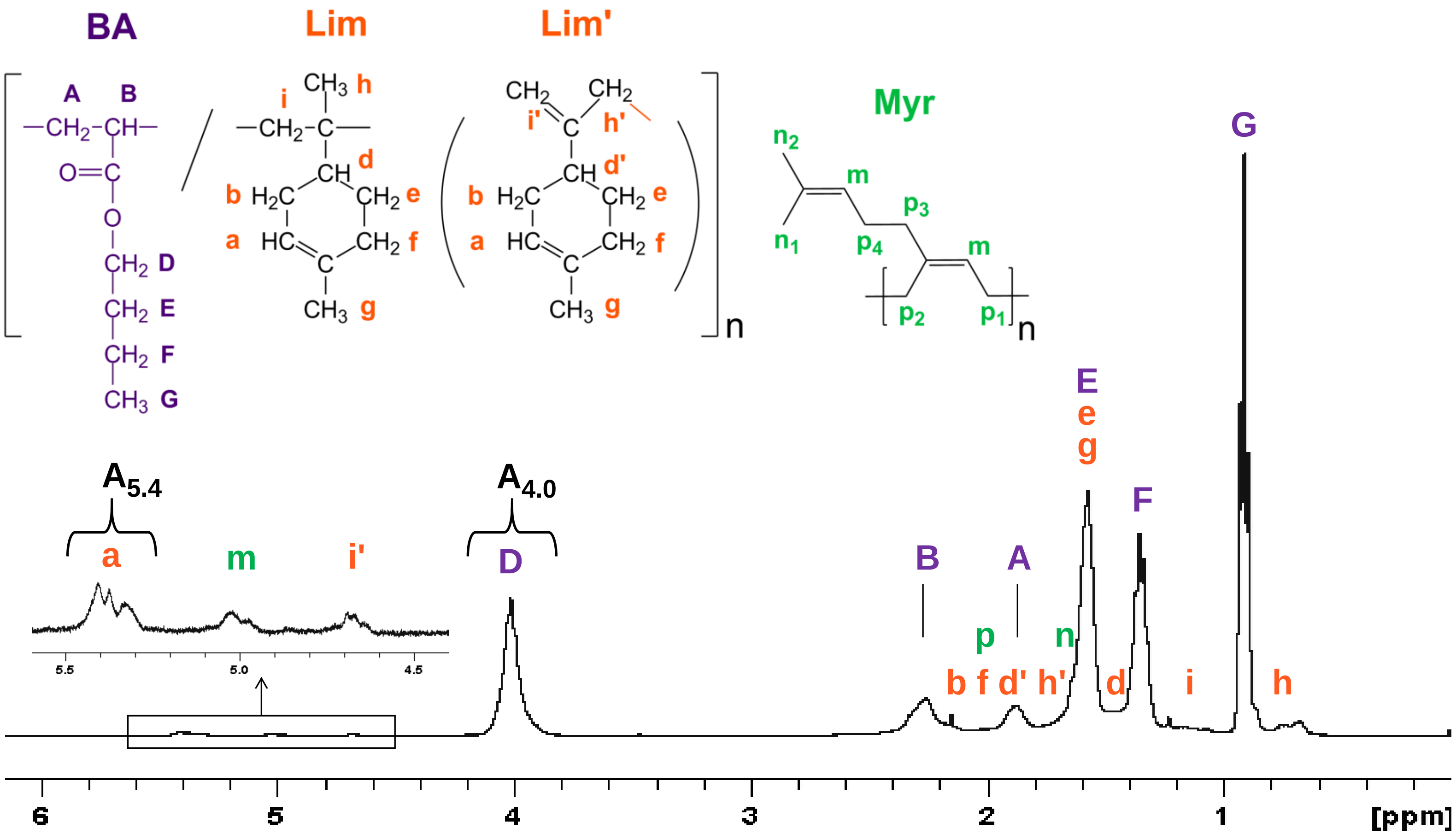
$$r_i = \frac{k_{pii}}{k_{pij}}$$

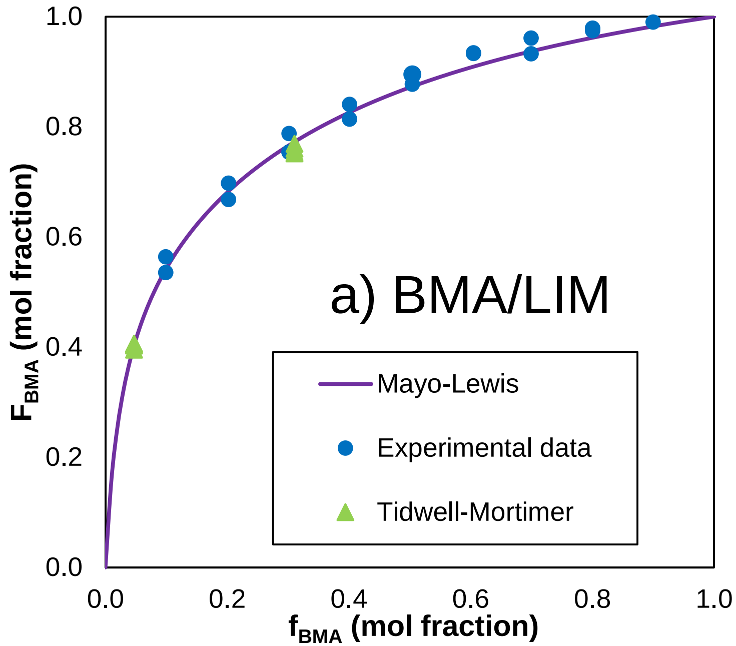
$$f'_{10} = \frac{2}{2+r_1}$$

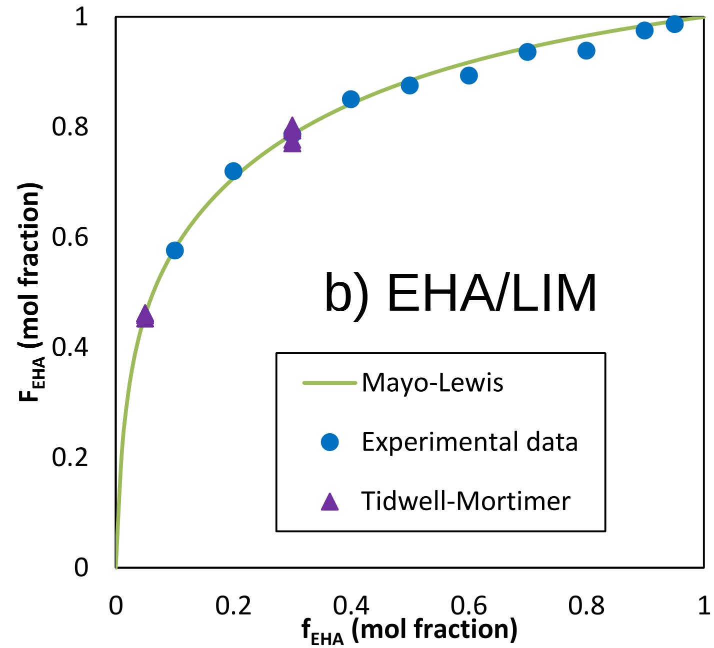
$$f''_{10} = \frac{r_2}{2 + r_2}$$

Recall assumptions!

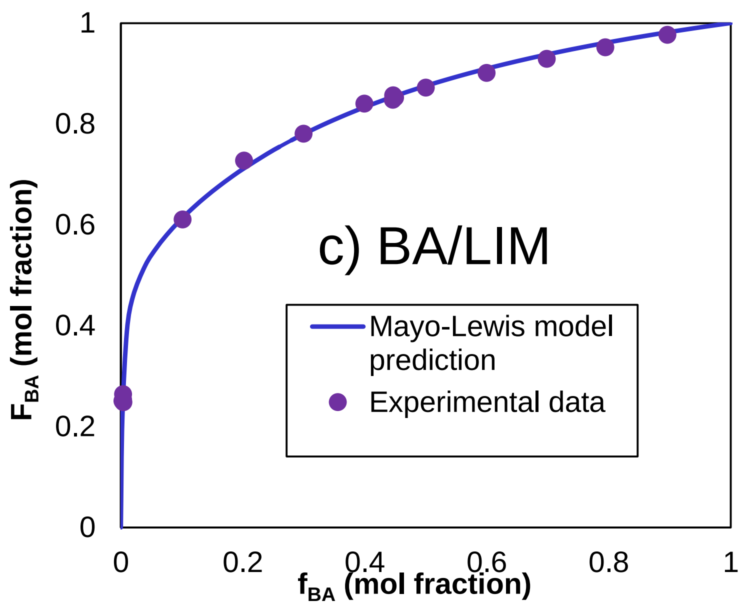
Copolymer composition – ^{1}H-NMR





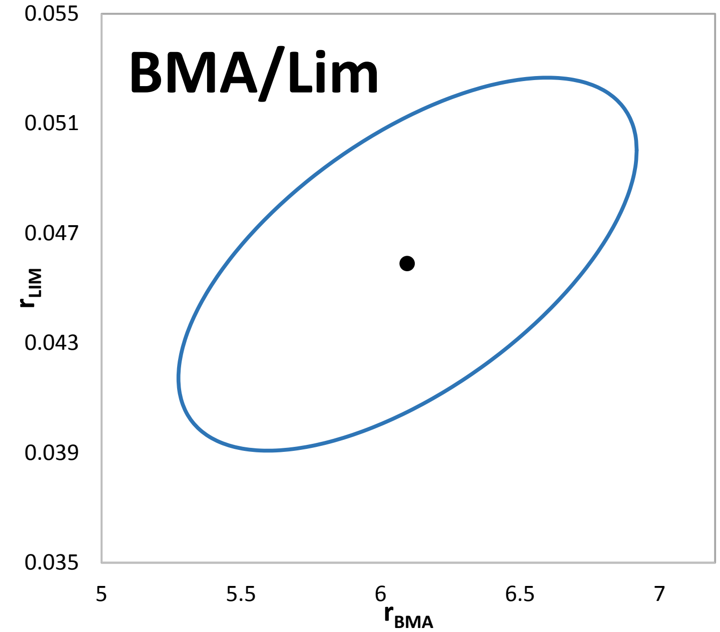


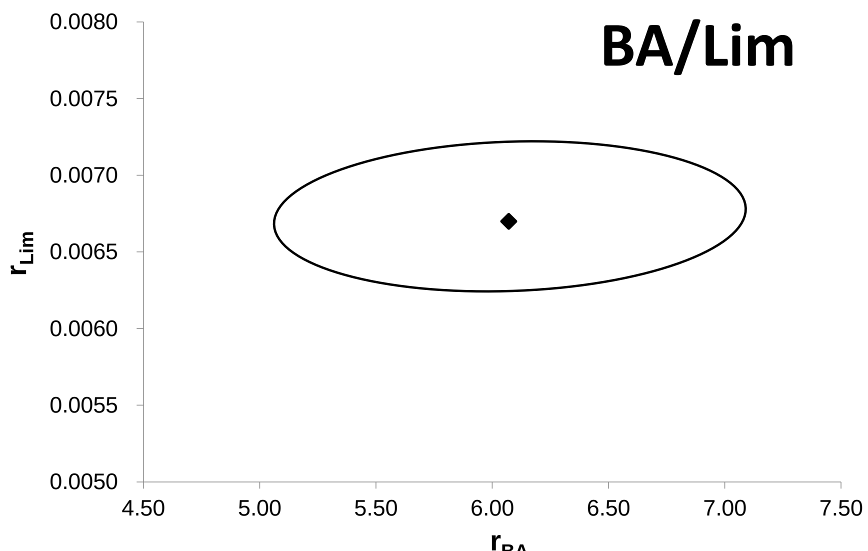
Low conversion, Mayo-Lewis plots (<u>80 °C</u>).

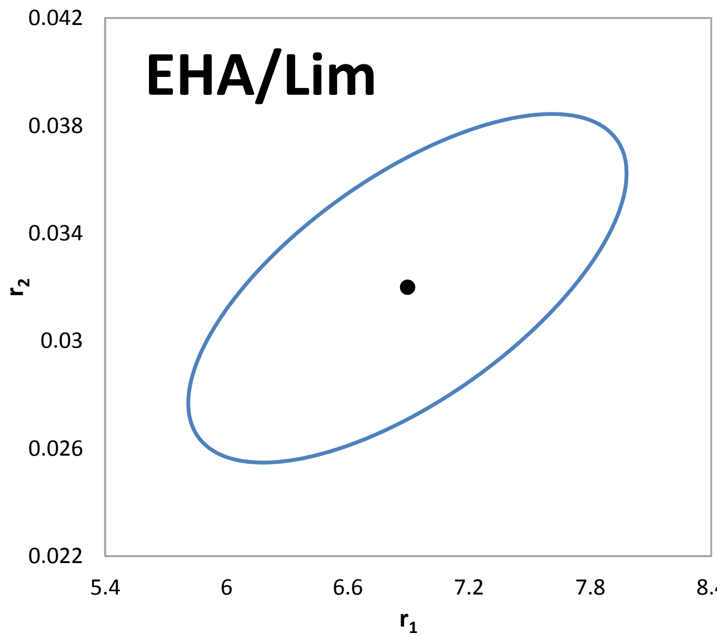


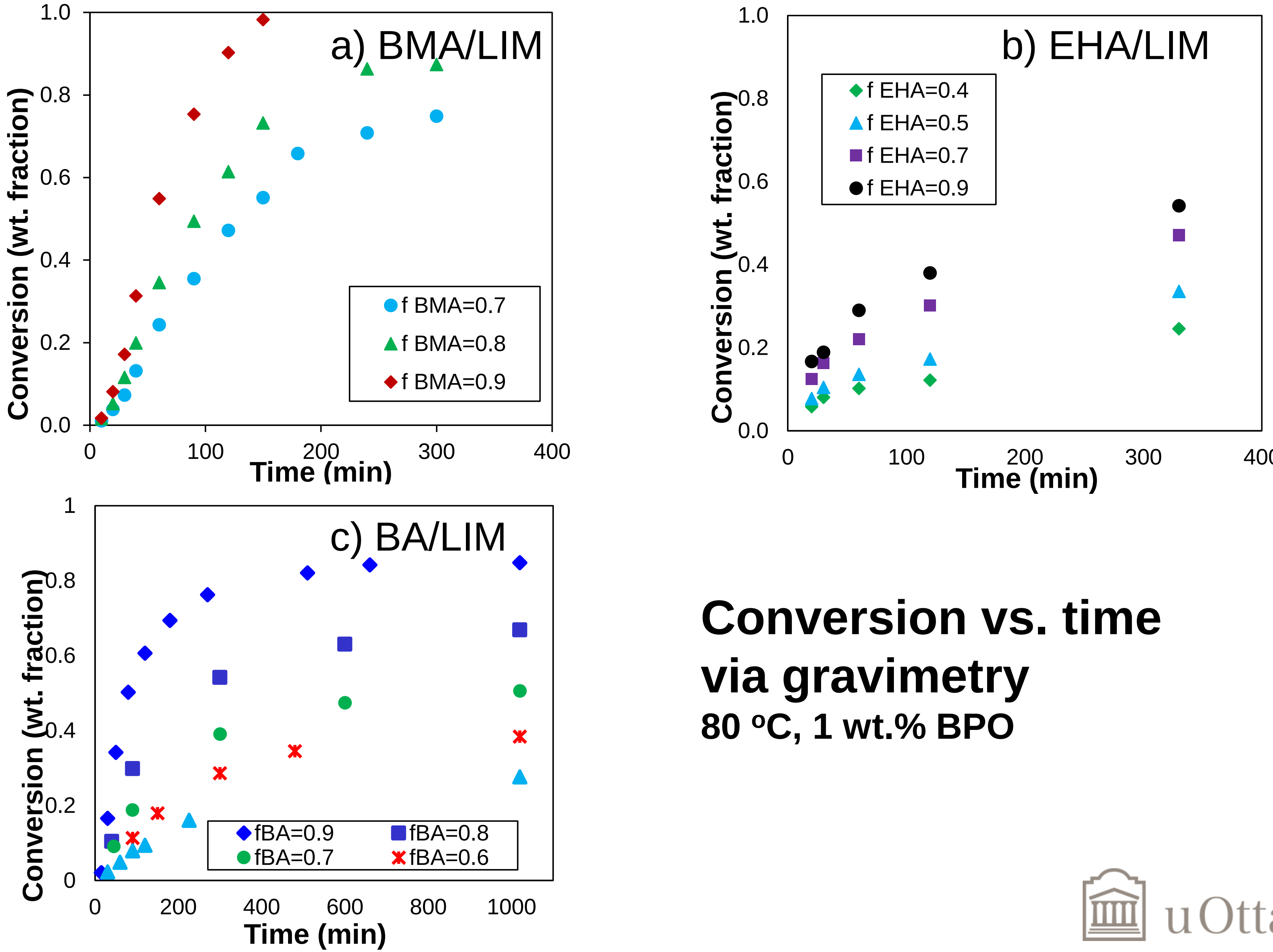
Reactivity ratios

Comonomers	Copolymer reactivity ratios (80 °C)	
	r_1	r_2
EHA/Lim	6.896	0.032
BMA/Lim	6.096	0.046
BA/Lim	6.008	0.007



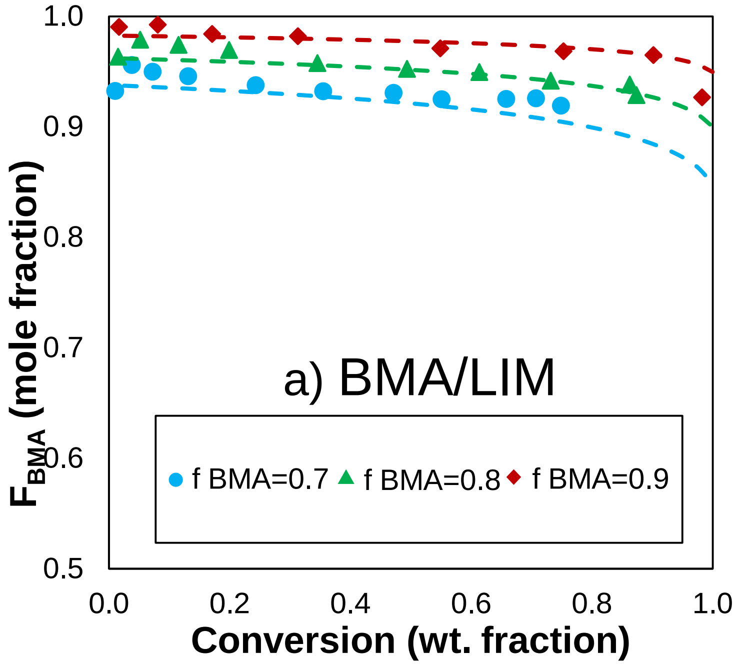


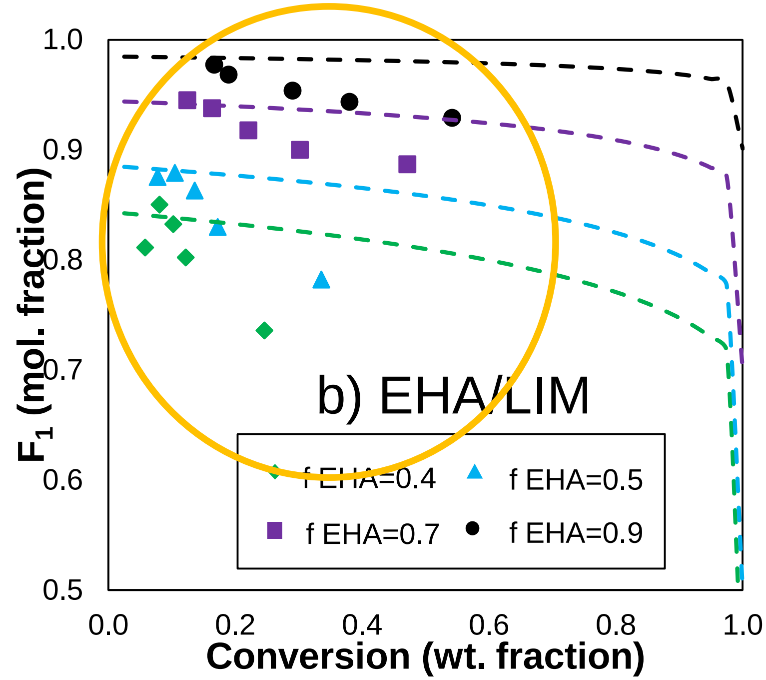


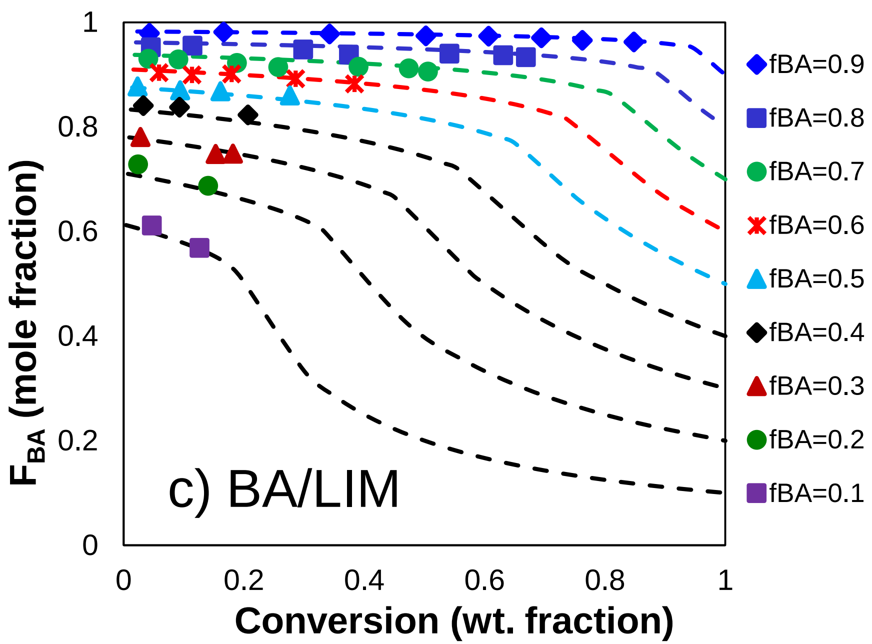


Conversion vs. time via gravimetry

80 °C, 1 wt.% BPO

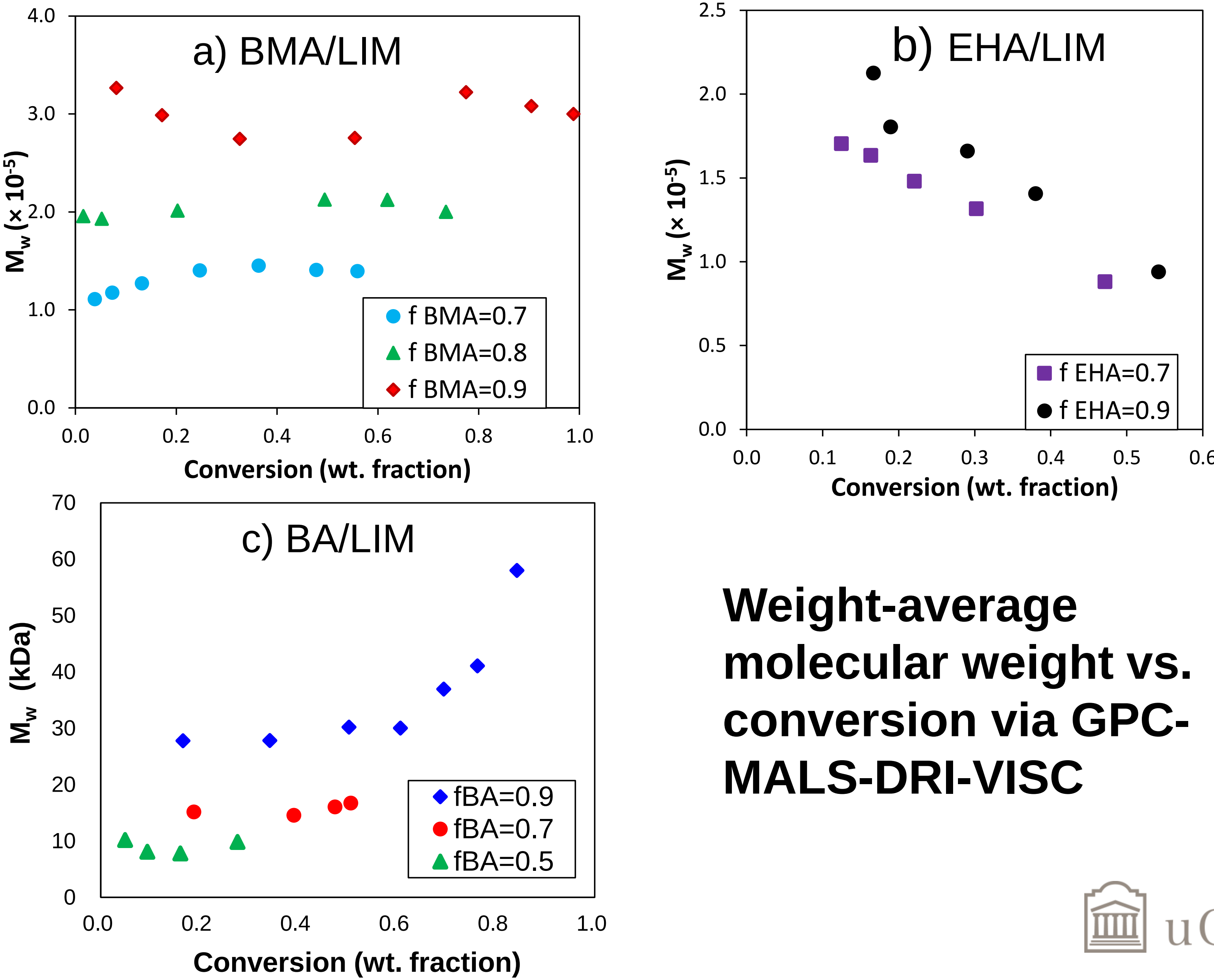






Copolymer composition vs. conversion via ^{1}H-NMR spectroscopy

80 °C, 1 wt.% BPO



Weight-average molecular weight vs. conversion via GPC-MALS-DRI-VISC

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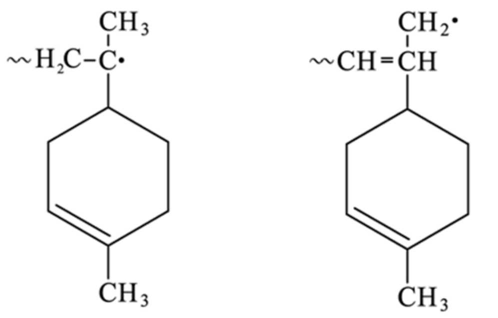
Model development
(with E. Vivaldo-Lima)

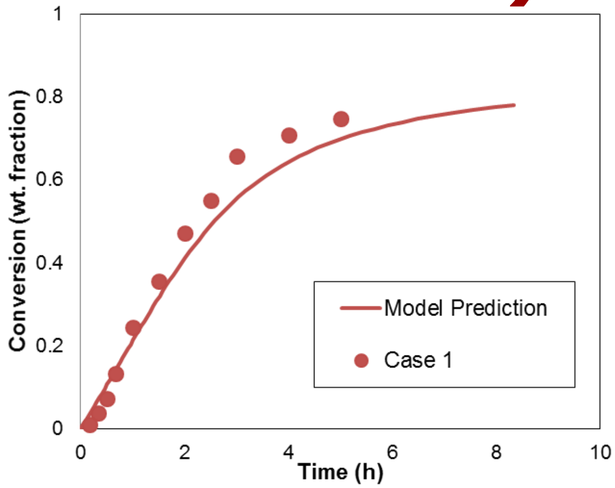


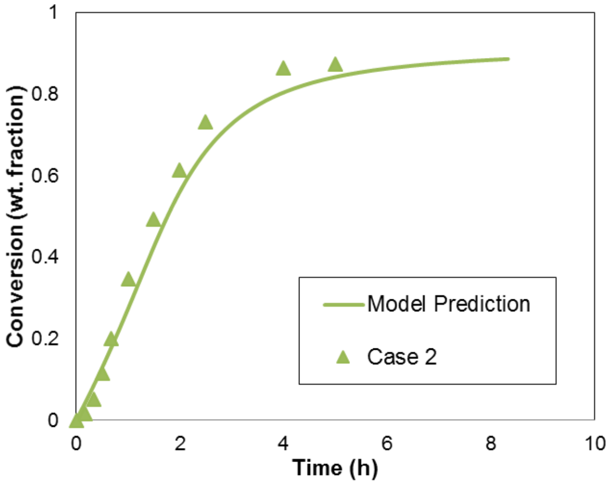
a) $RM_1^{\cdot}$ b) $RM_1^{\cdot\prime}$

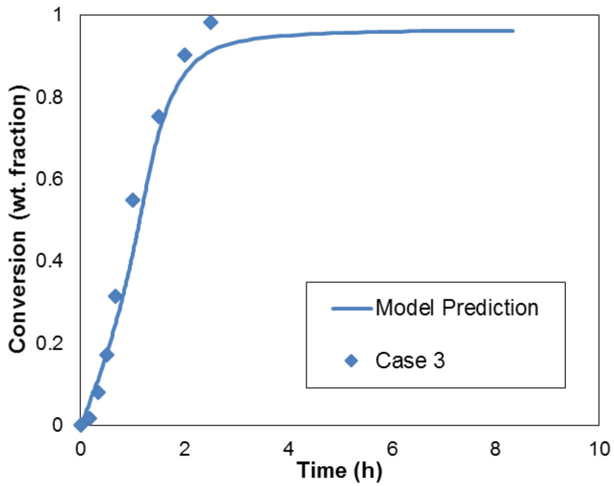
Reaction	Step
Chemical Initiation	$I \rightarrow 2f\ R^{\cdot}$
	$R^{\cdot}+M_1 \rightarrow RM_1^{\cdot}$
	$R^{\cdot}+M_1 \rightarrow RM_1^{\cdot\prime}$
	$R^{\cdot}+M_2 \rightarrow RM_2^{\cdot}$
Propagation	$RM_{1,r}^{\cdot}+M_1 \rightarrow RM_{1,(r+1)}^{\cdot}$
	$RM_{1,r}^{\cdot}+M_2 \rightarrow RM_{2,(r+1)}^{\cdot}$
	$RM_{2,r}^{\cdot}+M_1 \rightarrow RM_{1,(r+1)}^{\cdot}$
	$RM_{2,r}^{\cdot}+M_2 \rightarrow RM_{2,(r+1)}^{\cdot}$
	$RM_{1,r}^{\cdot\prime}+M_1 \rightarrow RM_{1,(r+1)}^{\cdot\prime}$
	$RM_{1,r}^{\cdot\prime}+M_2 \rightarrow RM_{2,(r+1)}^{\cdot\prime}$
Chain Transfer to Monomer	$RM_{1,r}^{\cdot}+M_2 \rightarrow P_r + RM_2^{\cdot}$
	$RM_{2,r}^{\cdot}+M_2 \rightarrow P_r + RM_2^{\cdot}$
	$RM_{1,r}^{\cdot}+M_1 \rightarrow P_r + RM_1^{\cdot\prime}$
	$RM_{2,r}^{\cdot}+M_1 \rightarrow P_r + RM_1^{\cdot\prime}$

Reaction	Step
Termination by Combination	$RM_{1,r}^{\cdot} + RM_{1,s}^{\cdot} \rightarrow P_{(r+s)}$
	$RM_{1,r}^{\cdot} + RM_{2,s}^{\cdot} \rightarrow P_{(r+s)}$
	$RM_{2,r}^{\cdot} + RM_{2,s}^{\cdot} \rightarrow P_{(r+s)}$
	$RM_{1,r}^{\cdot\prime} + RM_{1,s}^{\cdot\prime} \rightarrow P_{(r+s)}$
	$RM_{1,r}^{\cdot} + RM_{1,s}^{\cdot\prime} \rightarrow P_{(r+s)}$
	$RM_{2,r}^{\cdot} + RM_{1,s}^{\cdot\prime} \rightarrow P_{(r+s)}$
Termination by Disproportionation	$RM_{1,r}^{\cdot} + RM_{1,s}^{\cdot} \rightarrow P_r + P_s$
	$RM_{1,r}^{\cdot} + RM_{2,s}^{\cdot} \rightarrow P_r + P_s$
	$RM_{2,r}^{\cdot} + RM_{2,s}^{\cdot} \rightarrow P_r + P_s$

Model development
(with E. Vivaldo-Lima)



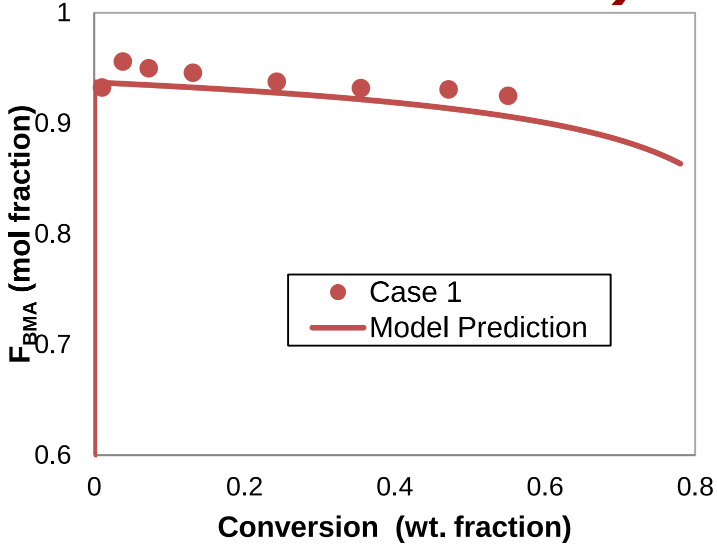


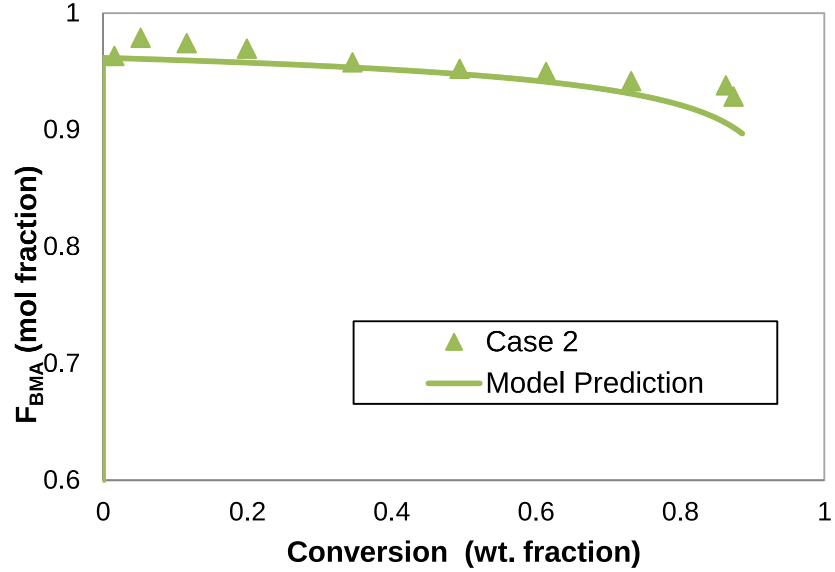


Case	BMA/LIM (mol/mol)	BPO (mol·L^{-1})	Reaction Temperature (^{o}C)
1	90/10	0.020	80
2	80/20	0.018	80
3	70/30	0.019	80

Model development

(with E. Vivaldo-Lima)





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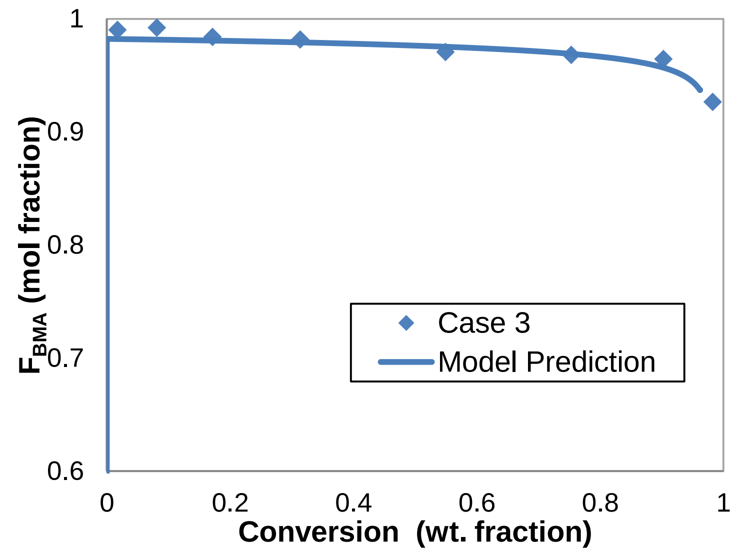

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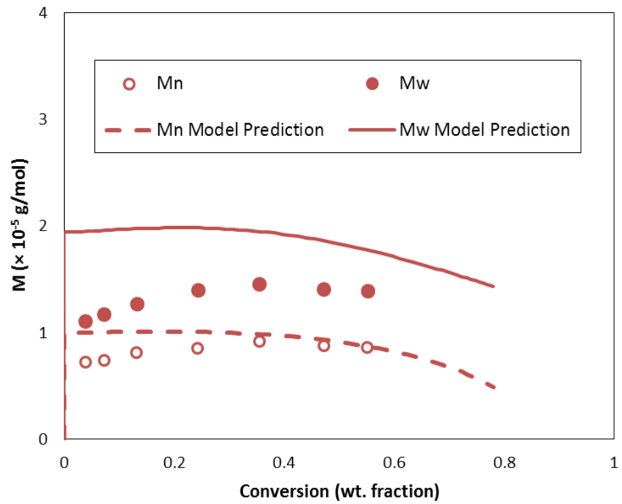
(with E. Vivaldo-Lima)



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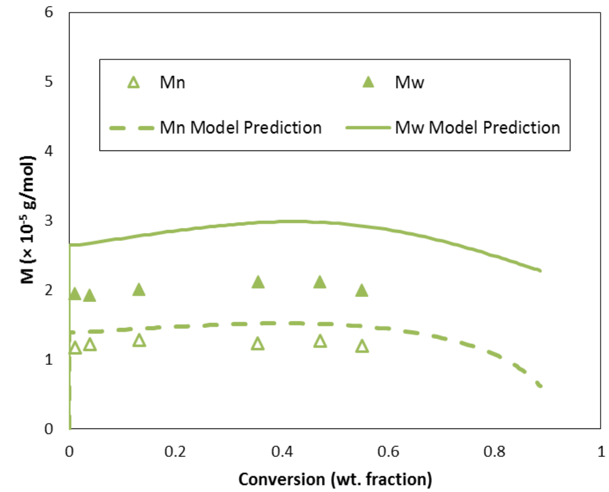

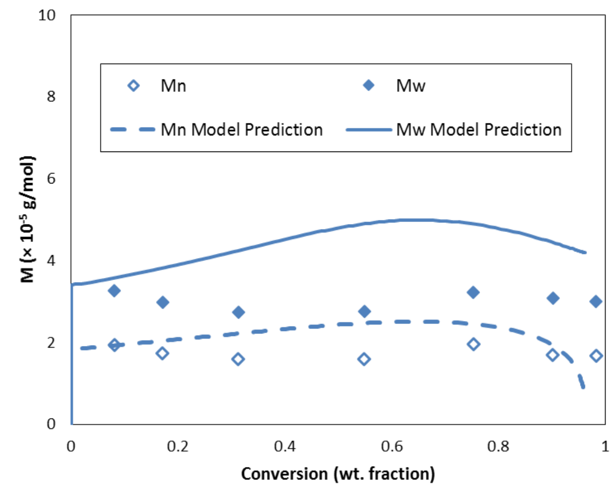

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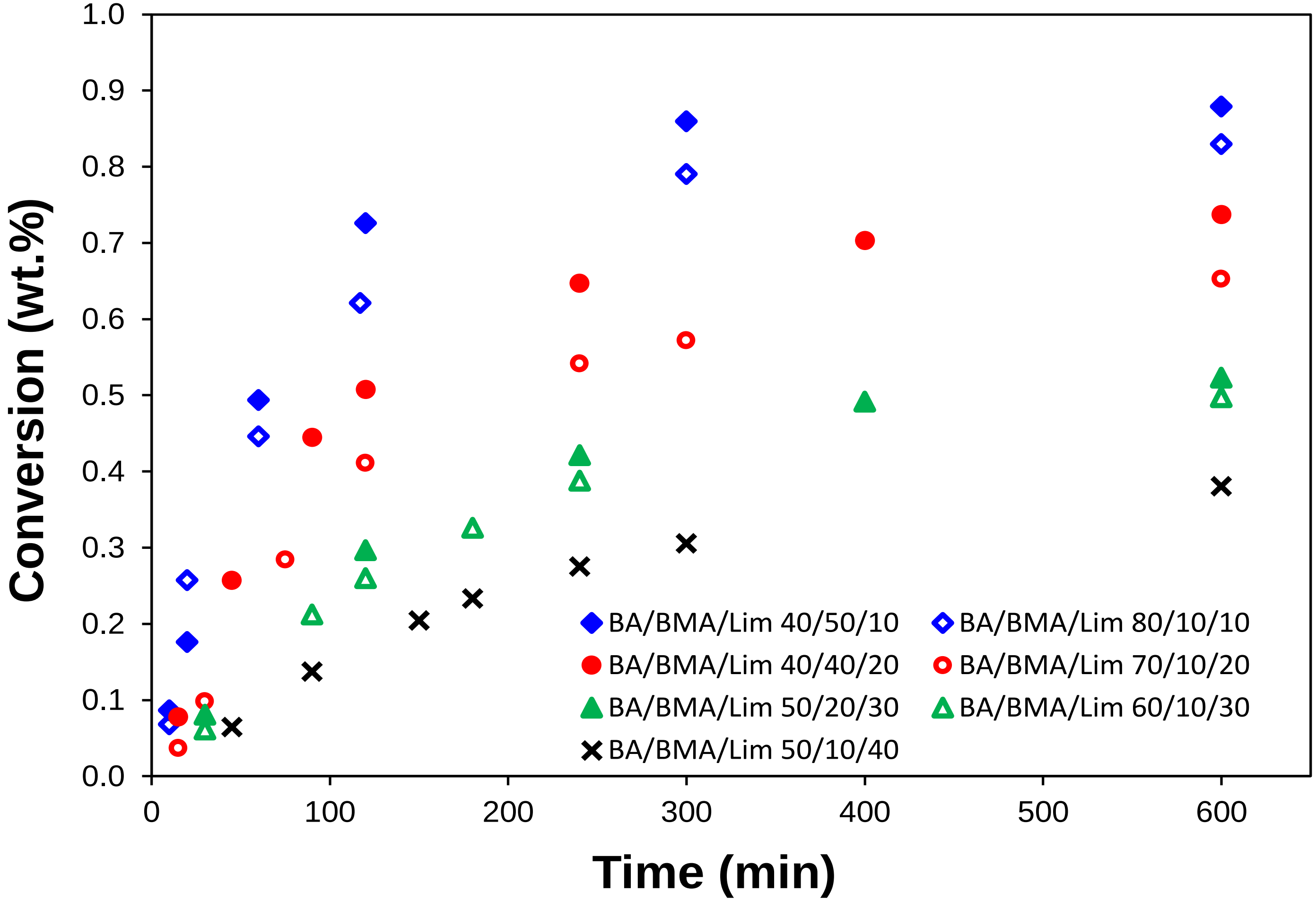
Terpolymerization

Reaction conditions
Glass ampoules
Monomers (~5 g)
BPO 1 wt.%
80 ^oC
Precipitate in MeOH
Dry to constant weight

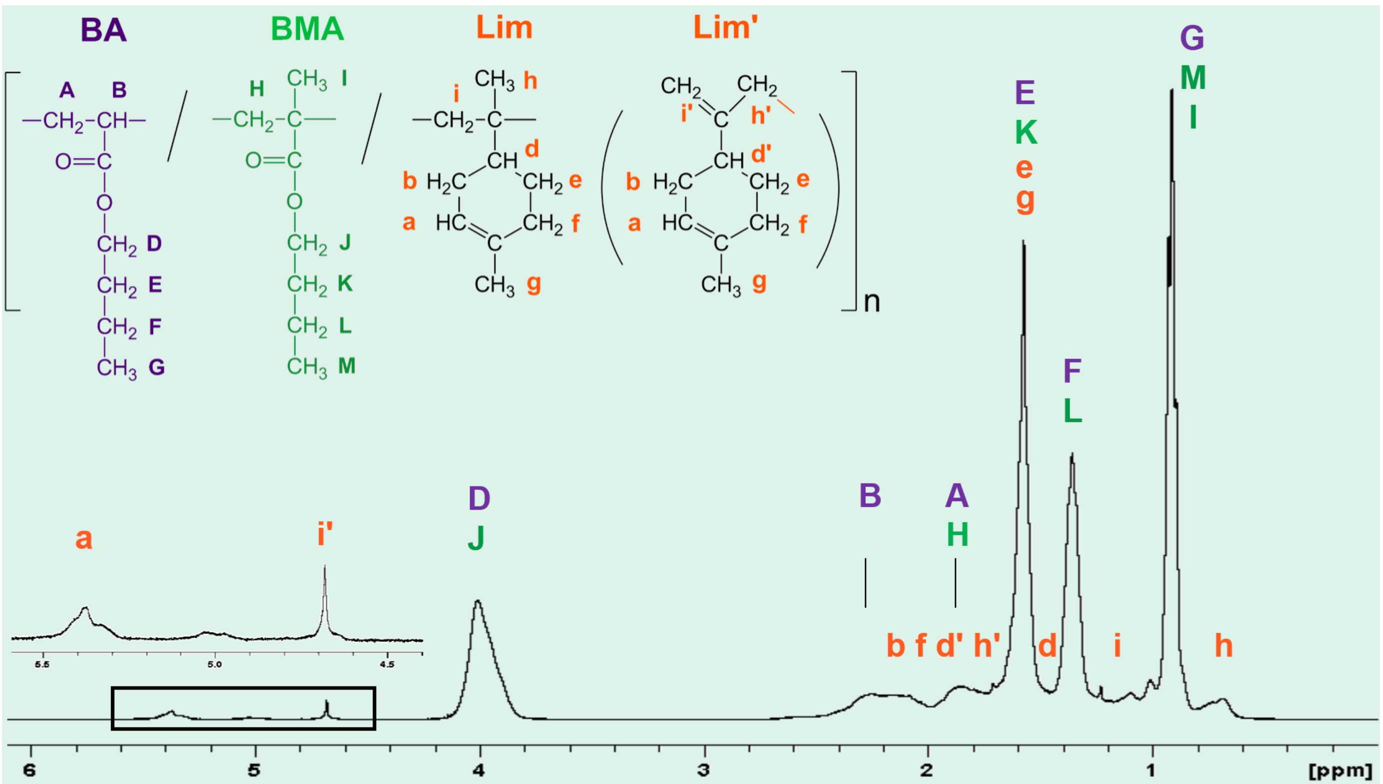
BA/BMA/Lim Feed (molar ratio)
80/10/10
40/50/10
70/10/20
40/40/20
60/10/30
50/20/30
50/10/40

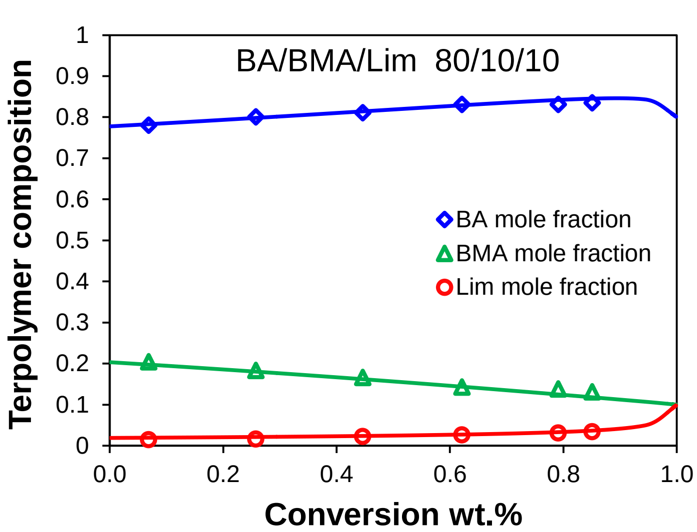
Terpolymer conversion

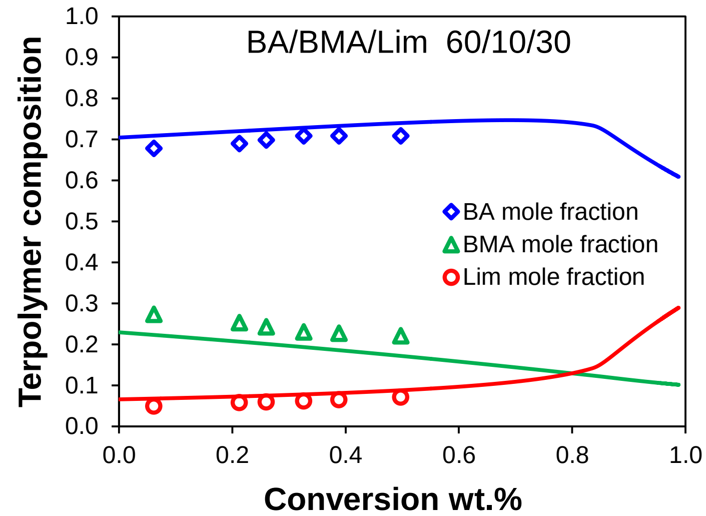


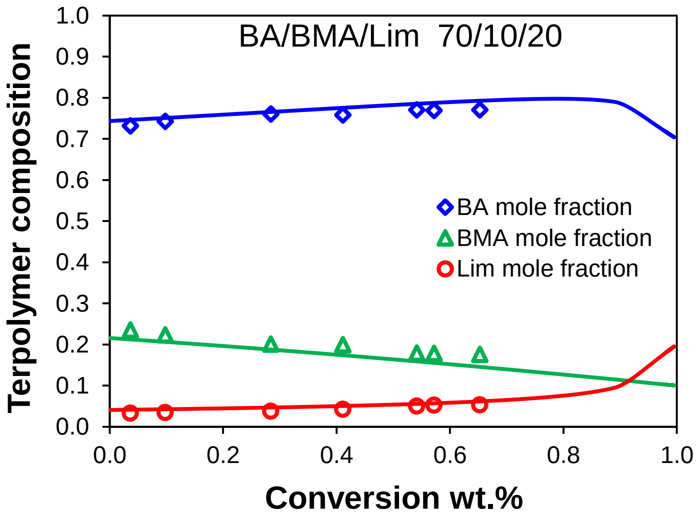
Terpolymer composition

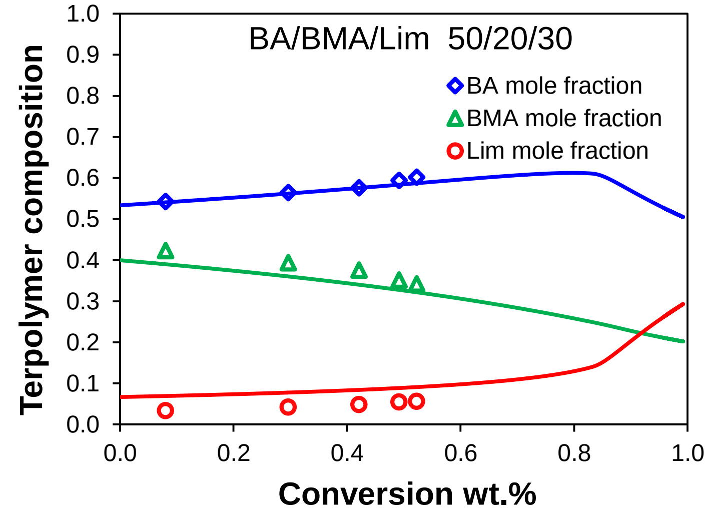
Monomers	Copolymer reactivity ratios	
	r_1	r_2
BMA/BA	2.008	0.460
BMA/Lim	6.096	0.046
BA/Lim	6.008	0.007



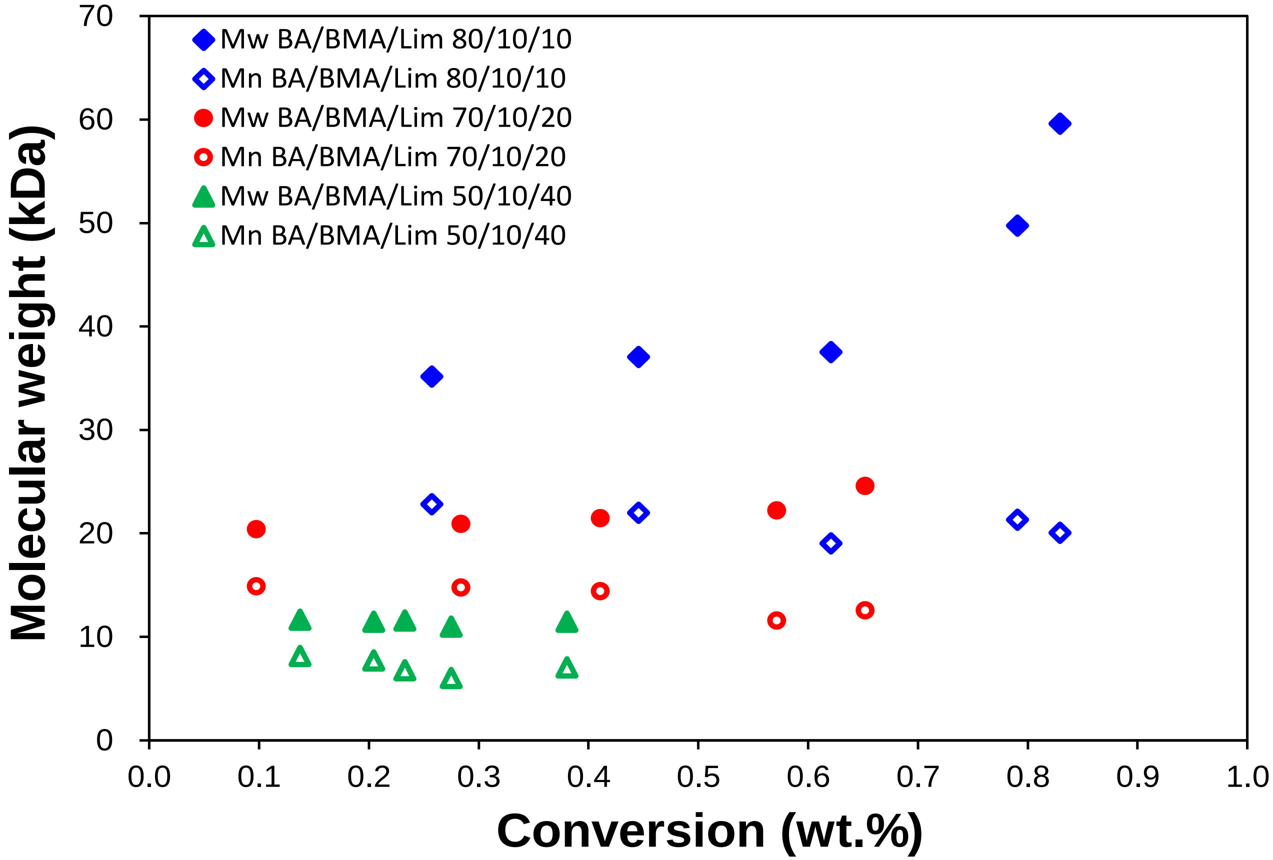

BA/BMA/Lim 80/10/10
BA mole fraction
BMA mole fraction
Lim mole fraction
Terpolymer composition
Conversion wt.%
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
0.0
0.2
0.4
0.6
0.8
1.0


BA/BMA/Lim 60/10/30
BA mole fraction
BMA mole fraction
Lim mole fraction
Terpolymer composition
Conversion wt.%
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
0.0
0.2
0.4
0.6
0.8
1.0


BA/BMA/Lim 70/10/20
BA mole fraction
BMA mole fraction
Lim mole fraction
Terpolymer composition
Conversion wt.%
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
0.0
0.2
0.4
0.6
0.8
1.0


BA/BMA/Lim 50/20/30
BA mole fraction
BMA mole fraction
Lim mole fraction
Terpolymer composition
Conversion wt.%
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
0.0
0.2
0.4
0.6
0.8
1.0

Terpolymer molecular weight



Terpolymer glass transition temperature

BA/BMA/Lim feed composition (mol/mol/mol)	F_{BA} (mol fraction)	F_{BMA} (mol fraction)	F_{Lim} (mol fraction)	T_g (ºC)
80/10/10	0.835	0.132	0.034	-39.6
40/50/10	0.434	0.550	0.016	-16.6
70/10/20	0.770	0.176	0.053	-35.9
40/40/20	0.441	0.527	0.032	-16.1
60/10/30	0.708	0.221	0.071	-31.8
50/20/30	0.602	0.342	0.056	-30.9
50/10/40	0.653	0.254	0.092	-30.2

Conclusion

- Challenge: further increase to the incorporation of limonene into co- and terpolymers
  - Crosslinkers?
  - NMP? (see poster by Ren)
  - Temperature effects?
  - Semibatch feed/emulsion?
- <u>Potential to unlock a treasure trove of allylic monomers</u>

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Sustainable Polymer Reaction Engineering

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