

# Characterization of Sustainably Degradable Polymers via Mass Spectrometry Techniques

Kayla Williams-Pavlantos<sup>1</sup>, Luis D. Garcia Espinosa<sup>1</sup>, Pierre Canisius Mbarushimana<sup>2</sup>, Savannah R. Snyder<sup>2</sup>, James M. Eagan<sup>1</sup>, Chrys Wesdemiotis<sup>1</sup>, Artem Filipenko<sup>2</sup>, <sup>1</sup>The University of Akron, Akron, Ohio 44325; <sup>2</sup>Bruker Daltonics Inc., 40 Manning Road, Manning Park, Billerica, MA 01821, USA

## Introduction

Most commonly used thermoplastic materials contain strong carbon-carbon polymer backbones which are desirable for their consumer applications; unfortunately, this feature restricts the ability to sustainably degrade the products after use, creating an environmental concern. Incorporating CO<sub>2</sub> into the polymer backbone generates an easily degradable and recyclable material, but synthesis of such macromolecules can be challenging. Ongoing efforts seek to combine thermoplastic properties and degradability to make both synthetically favorable and degradable polymers. This work requires sensitive and structurally specific analytical tools to gauge progress and make proper synthesis modifications. Here, we illustrate how this goal is achieved by multidimensional mass spectrometry (MS and MS/MS) using either matrix assisted laser desorption ionization (MALDI) or electrospray ionization (ESI).

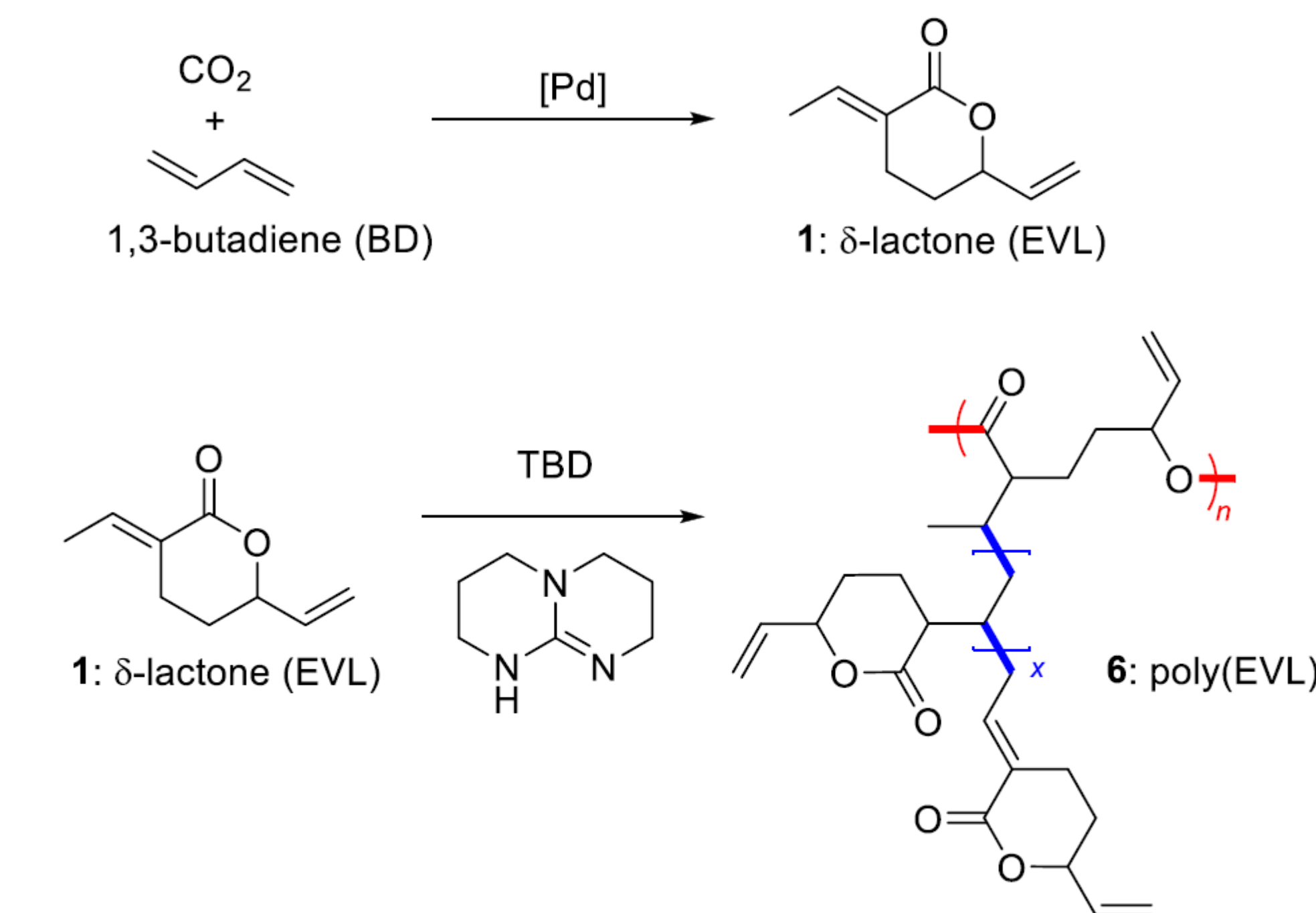


Fig. 1. Telomerization of 1,3-butadiene and CO<sub>2</sub> to form EVL. Ring-opening (1,4-conjugate) homopolymerization of EVL.

## Methods

The polymers investigated in this study were synthesized by new polymerization methods developed at The University of Akron, as described in the literature (Figure 1) [1]. Prior to analysis, all samples were dissolved in methanol and diluted to appropriate concentrations. MALDI experiments were performed on tandem time-of-flight (ToF/ToF) instrumentation using CHCA as matrix and sodium trifluoroacetate (NaTFA) as the cationizing salt. ESI experiments were run on quadrupole/time-of-flight (Q/ToF) equipment. MS/MS spectra were acquired with either the ToF/ToF or the Q/ToF instrument, using laser induced fragmentation and collisionally activated dissociation (CAD) with argon gas at a collision energy of 45 eV.

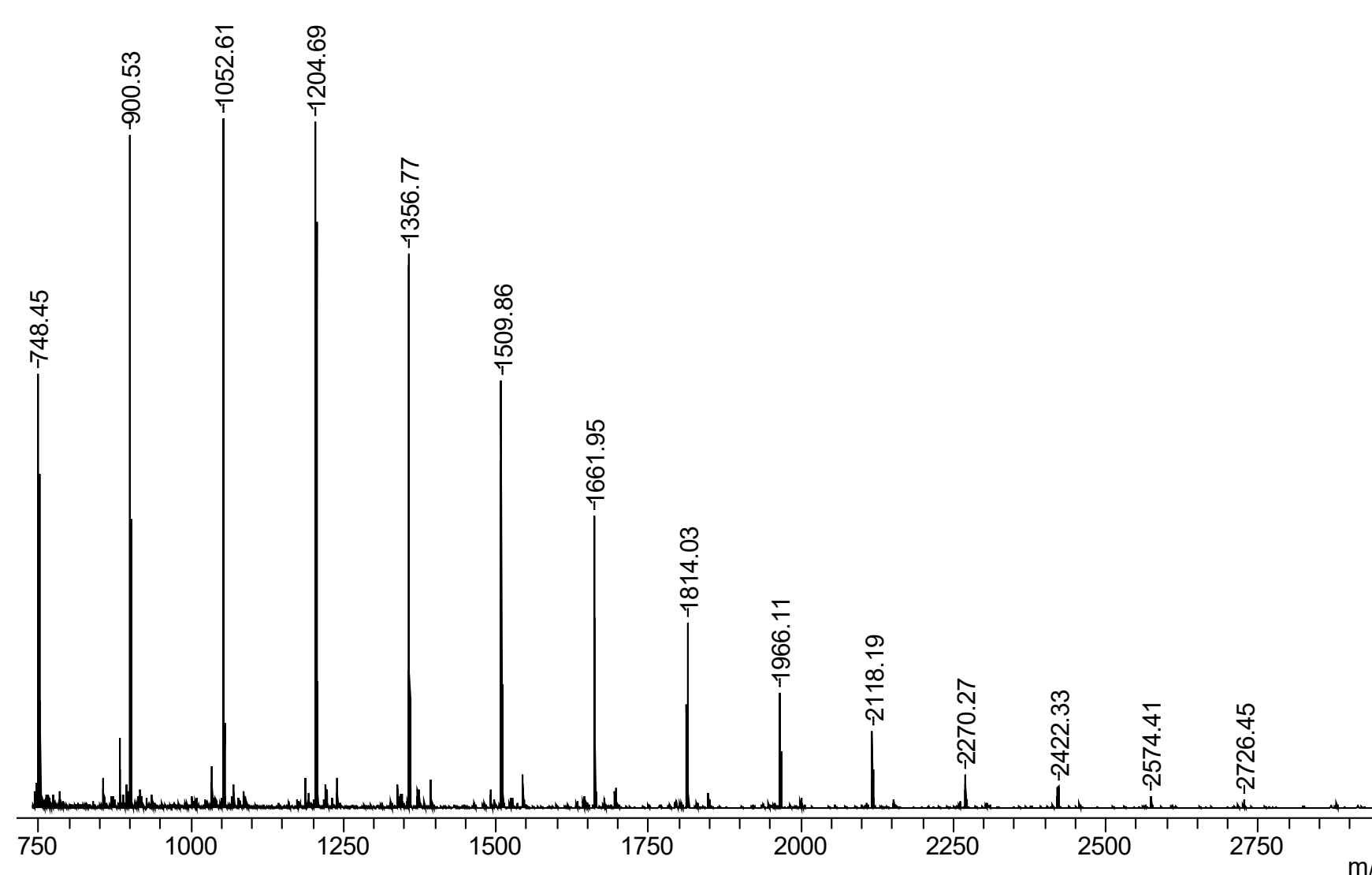


Fig. 2. MALDI-TOF-MS analysis of poly(EVL).

## Results

To develop a synthetically favorable and degradable polymer, CO<sub>2</sub> was reacted with butadiene to form a δ-lactone known commonly as EVL (1). Although EVL has been used as a monomer in polymer synthesis, previous efforts resulted in either materials that cannot be degraded or strained copolymers with undesirable properties. To resolve this issue, a new method was designed for the synthesis of poly(EVL) homopolymer, utilizing 1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD) as a ring opening catalyst.

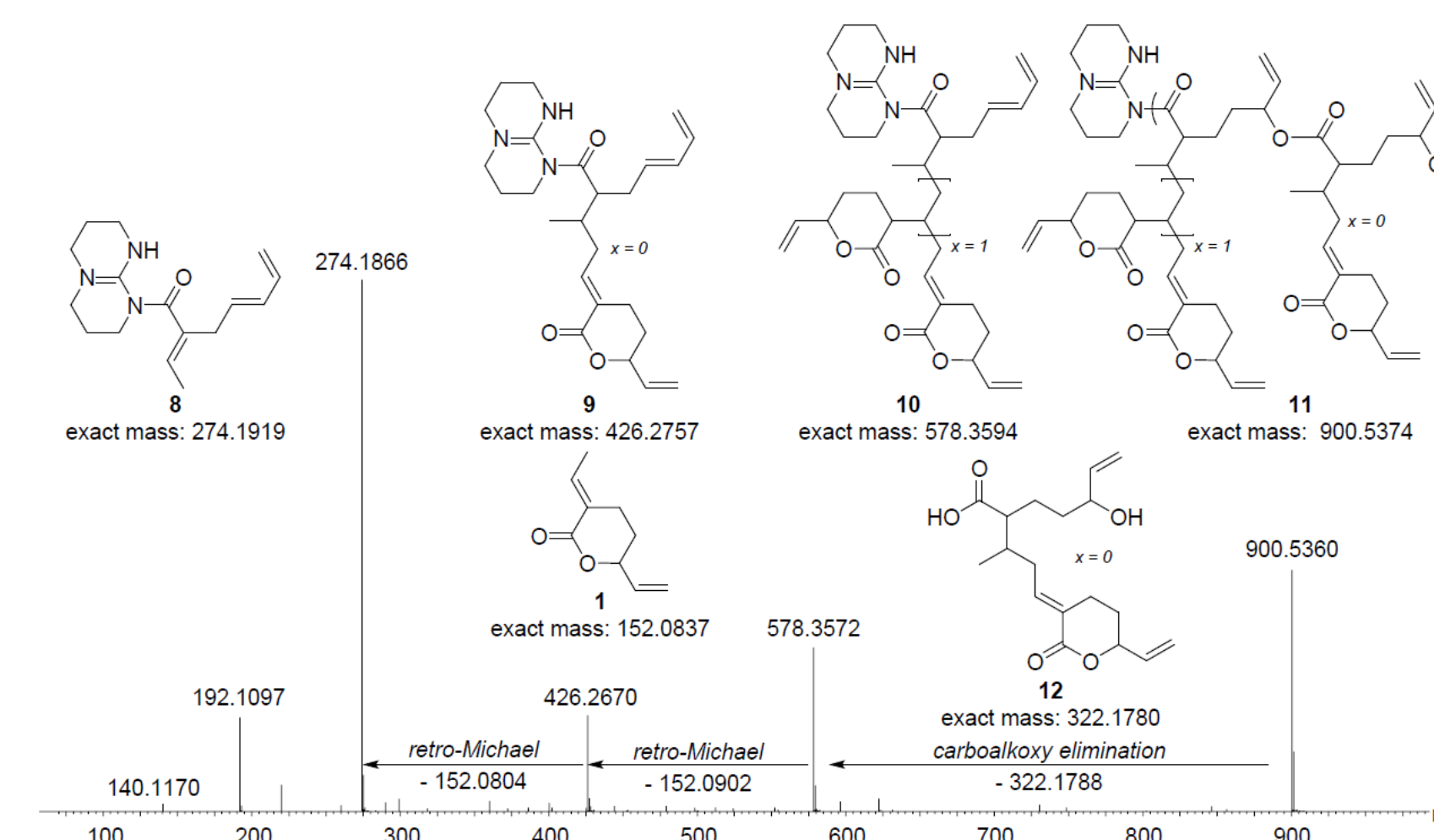


Fig. 3. ESI-MS/MS spectra of poly(EVL) from ion fragment 900.53 m/z (5-mer).

Initial MALDI-MS analysis led to one main distribution with a repeat unit of 152 Da (2x butadiene + CO<sub>2</sub>), confirming the formation of a homopolymer as opposed to a copolymer comprising monomeric units with or without the CO<sub>2</sub> moiety (Figure 2). More importantly, exact mass measurement and end group calculations suggested that the homopolymeric chain includes a TBD molecule from the catalyst also acting as a mediator in the ring opening polymerization. Substantiating evidence for this structure was obtained by ESI-MS/MS and MALDI-MS/MS, which was used to elucidate the connectivity of the synthesized material. The MS/MS fragmentation products conclusively indicated that the product contained EVL monomeric units plus a TBD molecule at the initiating (or α) chain end. The fragmentation pattern further showed the proclivity of poly(EVL) to decompose via retro-Michael reactions which release the repeating unit, strongly suggesting that the monomer is thermally recoverable (Figure 3). Hence, the multidimensional MS/MS analysis not only confirmed the successful outcome of the designed synthetic procedure, but also unveiled important information about the polymerization and depolymerization mechanisms; this information was difficult to obtain by other analytical techniques probing the bulk of the product.

## Future Work

Poly(EVL) has a backbone structure that can be controllably degraded under various hydrolytic conditions. Ongoing studies investigate the exact products arising in these processes in order to elucidate the corresponding degradation and recycling mechanisms.

Chemical degradation of poly(EVL) was performed under hydrolytic conditions using aqueous NaOH at high temperature (80 °C). The resulting crude products were absent of polymeric species by GPC analysis (Figure 4).

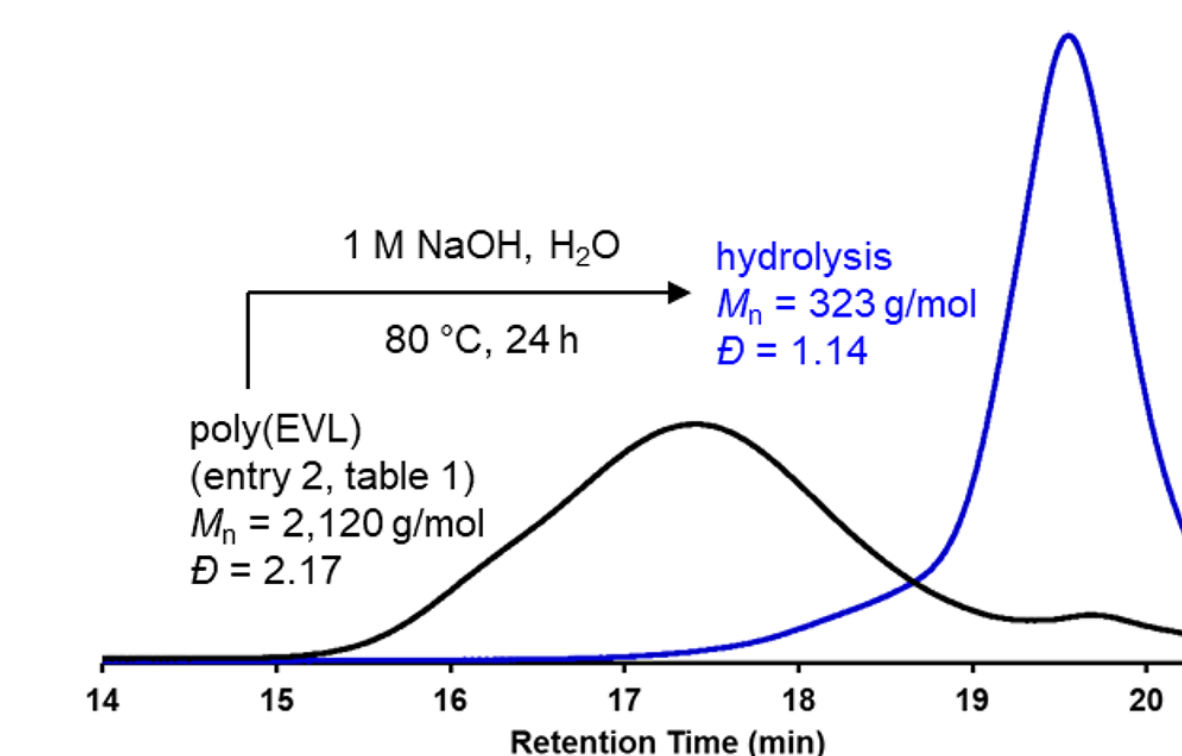


Fig. 4. GPC analysis of poly(EVL) and the crude degradation product after hydrolysis in 1M NaOH at 80 °C.

## References

[1] J.M. Eagan et al., ACS Macro Lett. 10 (2021) 1254

## Conclusion

- The catalytic telomerization of 1,3-butadiene with CO<sub>2</sub> produces a lactone (EVL).
- EVL undergoes polymerization to degradable poly(EVL) via a vinylogous 1,4-conjugate addition to form a di-EVL dimer.
- MALDI-MS was used to confirm the formation of the poly(EVL) homopolymer.
- MALDI-MS/MS and ESI-MS/MS were used to confirm the presence EVL monomeric units, determine end-groups, as well as confirm the decomposition of poly(EVL) via a retro-Michael reaction, suggesting that the monomer is thermally recoverable.