Photoinitiated RAFT Copolymerization of α-Lipoic Acid and Acrylates for Degradable Polymers

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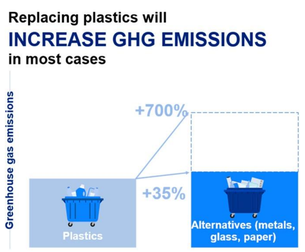
Introduction

Discarded plastic bottles and garbage on the Vacha River in Bulgaria.

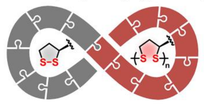


Paper bags weigh significantly more than HDPE bags, leading to higher GHG emissions for production and transportation.

Pure Polymer:

Degradable Polymer:

Closed-loop recyclable poly(disulfides)

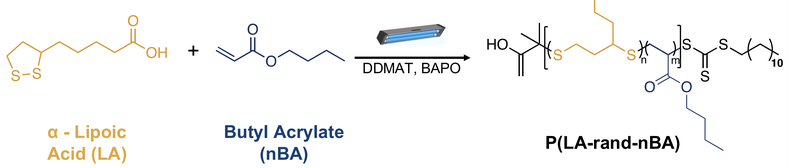


While C-C bonds are difficult to break, disulfide bonds (S-S) are much easier to cleave, making them ideal for forming the degradable backbone of polymers.

Objective: To develop sustainable polymer, we copolymerized α - Lipoic Acid with acrylate-based monomer through photoinitiated reversible addition fragmentation chain transfer.

Polymerization Mechanism

Synthesis of Degradable Polymer:

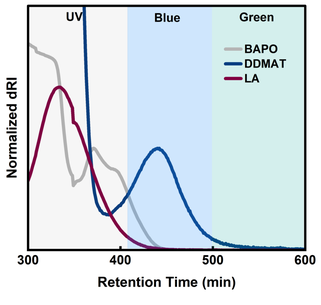


α - Lipoic Acid (LA)

Butyl Acrylate (nBA)

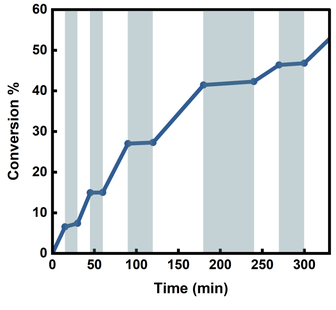
P(LA-rand-nBA)

Ultraviolet-Visible Spectroscopy



LA and DDMAT both absorb blue light and generate radicals.

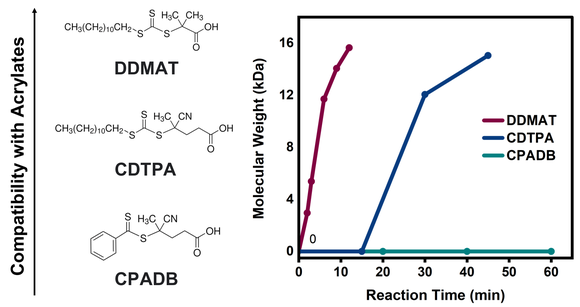
Light Temporal Control



The polymerization only proceed under blue light exposure.

Results and Discussion

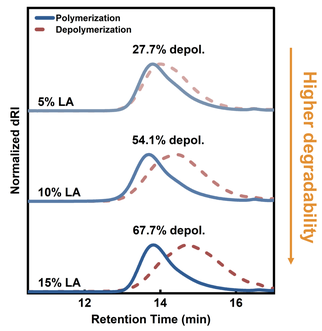
Effect of Chain Transfer Agent (CTA):



DDMAT outperforms CDTPA with higher compatibility of nBA and shorter induction time, while CPADB polymerizes none.

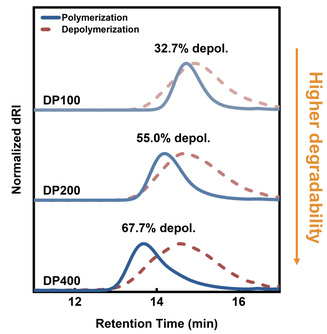
Effect of Reaction Conditions:

Effect of LA feed%:



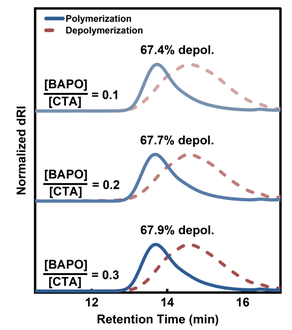
- As LA feed% increases, the depol.% increases due to more S-S linkage.

Effect of Degree of Polymerization:



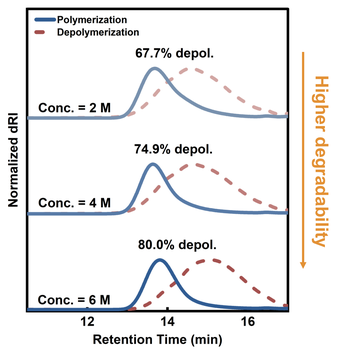
- As DP increases, the depol.% increases.

Effect of Photoinitiator Amount:

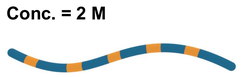


- As BAPO (photoinitiator) increases, the depol.% remains constant.

Effect of Concentration:



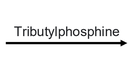
Conc. = 2 M



More disulfide S-S block in polymer.

Conc. = 6 M

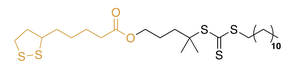
Tributylphosphine



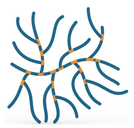
Higher degradability

Tributylphosphine

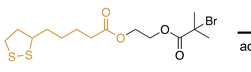
Synthesis of Complex Structures:



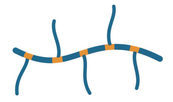
LA-CTA



Degradable hyperbranched polymer

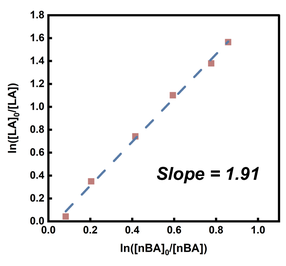


LA-ATRP

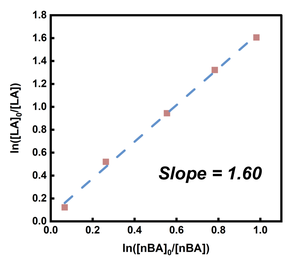


Comb polymer with a degradable backbone

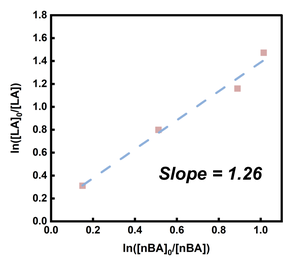
Concentration = 6 M



Concentration = 4 M

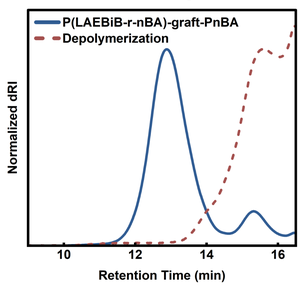


Concentration = 2 M

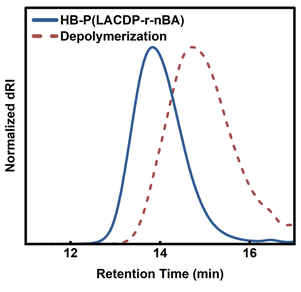


Increasing LA reactivity with reaction concentration

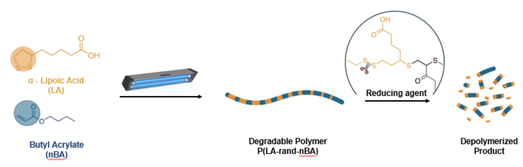
Comb Polymer



Hyperbranched Polymer



Conclusion



Highlights:

- ✓ Degradable Polymer
- ✓ Controlled MW
- ✓ Synthesis of Complex Architectures

References

- Environ. Sci. Technol. 2024, 58, 6, 2716–2727
- Matter 4, 1352–1364 April 7, 2021

Acknowledgement

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