Hydrogen Bonding in Polylactones to Improve Intermolecular Strength

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Abstract

Biodegradable plastics are a growing field in the realm of renewable resources. Non-biodegradable plastics use carbon chains and aryl rings as a main component of the polymer plastic backbone. Polyhydroxyalkonoates (PHA) integrate oxygen into the backbone, which makes the polymer biodegradable by certain bacteria and organisms. These molecules have small intermolecular forces that lead to reduced mechanical properties, such as brittleness, which make them unusable for everyday plastic uses. My research involves taking δ-valerolactone, alpha substituting with aryl rings of different functionality, and polymerizing with ring-opening polymerization. The product will have increased order and mechanical properties because of the aryl π-stacking. Aryl rings with hydrogen bond donors/acceptors will further increase the order by increasing the intermolecular forces between the aryl rings. The higher ordered systems will make a stronger polymer plastic that can potentially replace non-biodegradable plastics and still retain the biodegradable characteristics that are valued.

Research Plan

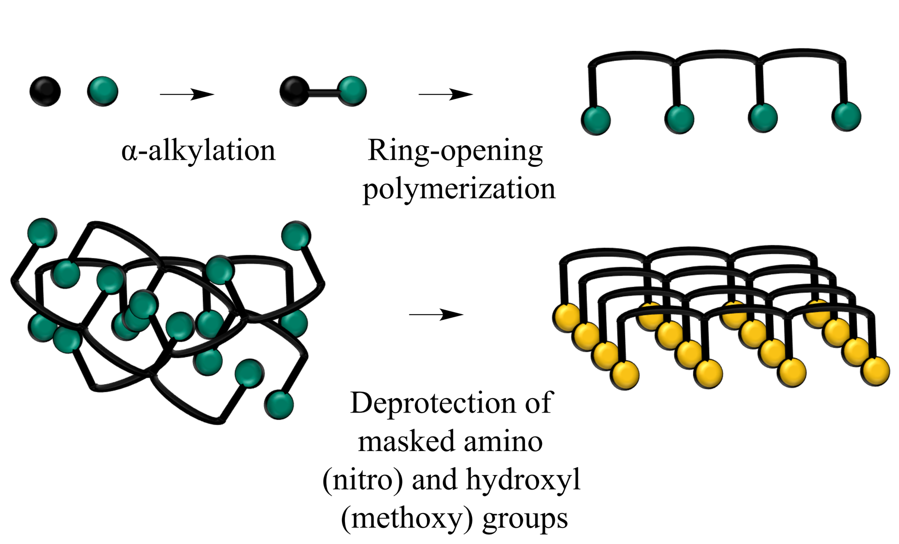
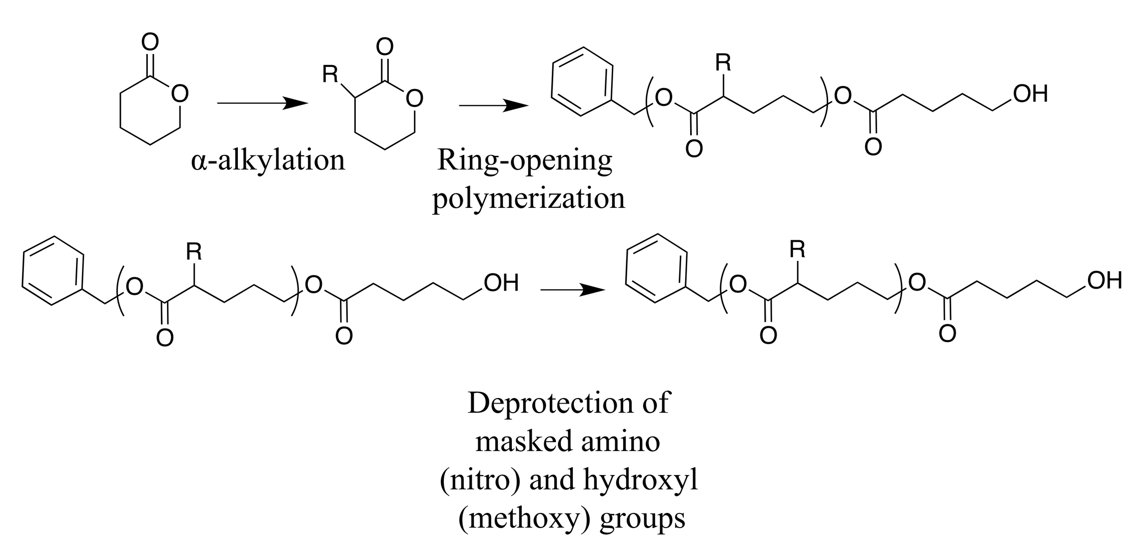
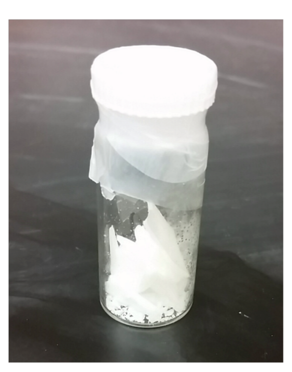


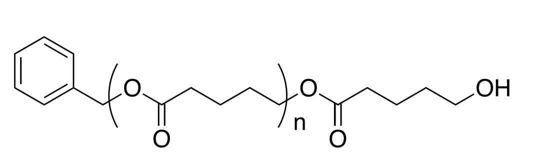
Figure 1. Cartoon illustrating monomer modification, polymerization, and deprotection that will result in a structurally more organized polymer, increasing crystallinity.



Scheme 1. Monomer modification, polymerization, and deprotection results in a structurally more organized polymer, increasing crystallinity.

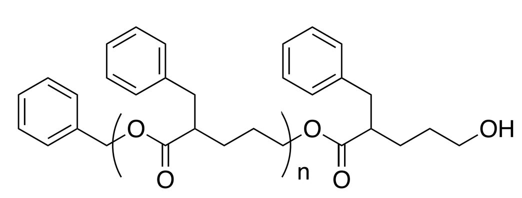
Target Polymers





1

Poly(δ-Valerolactone)
- Control Polymer
- Waxy white solid



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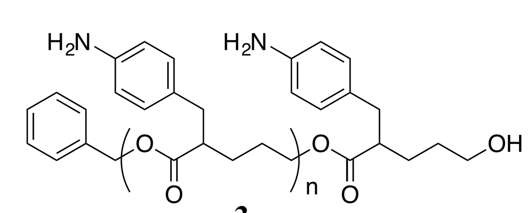
Polybenzyl(δ-Valerolactone)
- Second Control – aryl ring stacking



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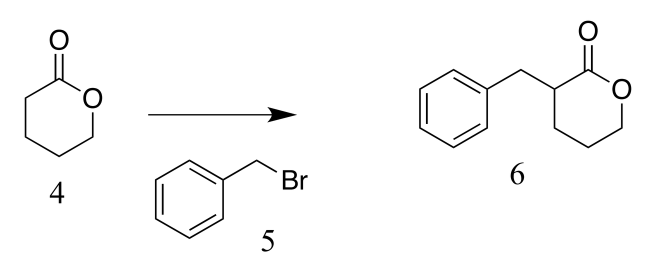
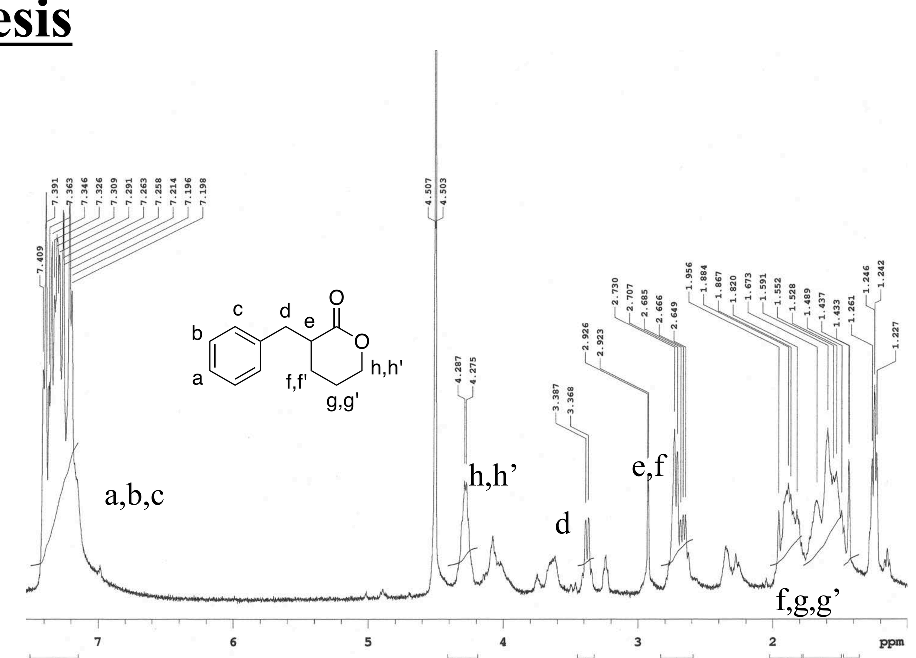
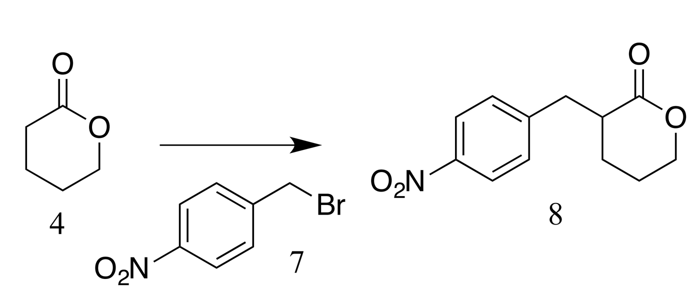
Poly(p-toluidinyl) (δ-Valerolactone)
- Hydrogen bond donors/ acceptors

Synthesis

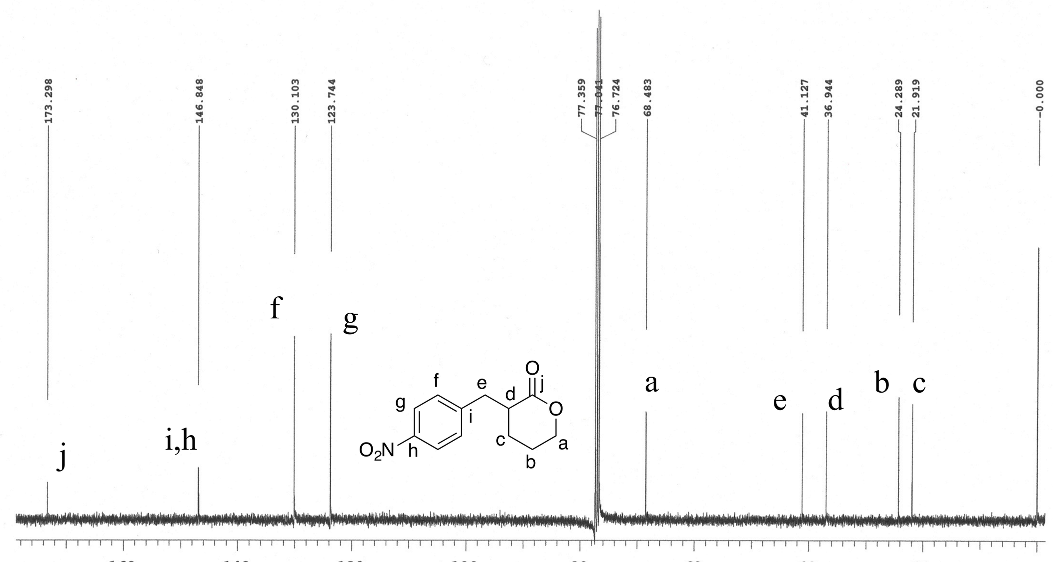


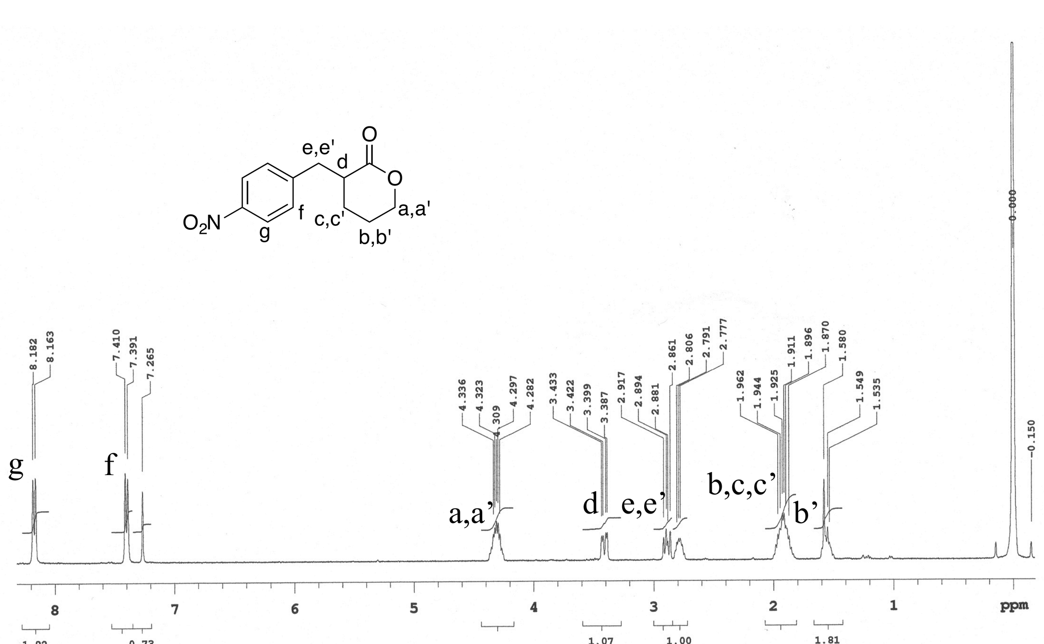
Scheme 2. α-alkylation of δ-valerolactone (**4**) with (**5**) DMPU, LDA, -78°C , 6hr

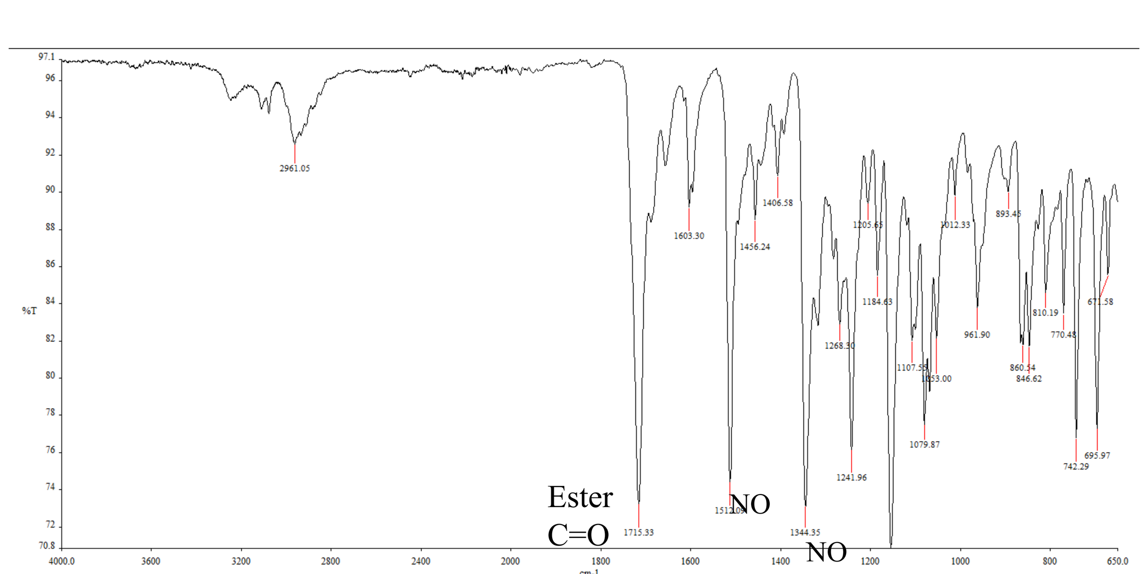


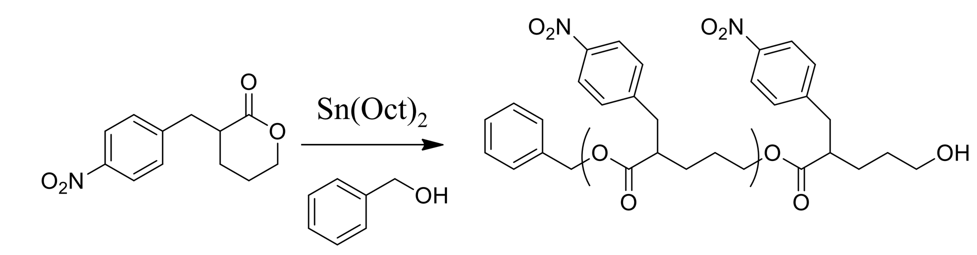


Scheme 3. α-alkylation of δ-valerolactone (**4**) with (**7**) DMPU, LDA, -78°C , 6hr



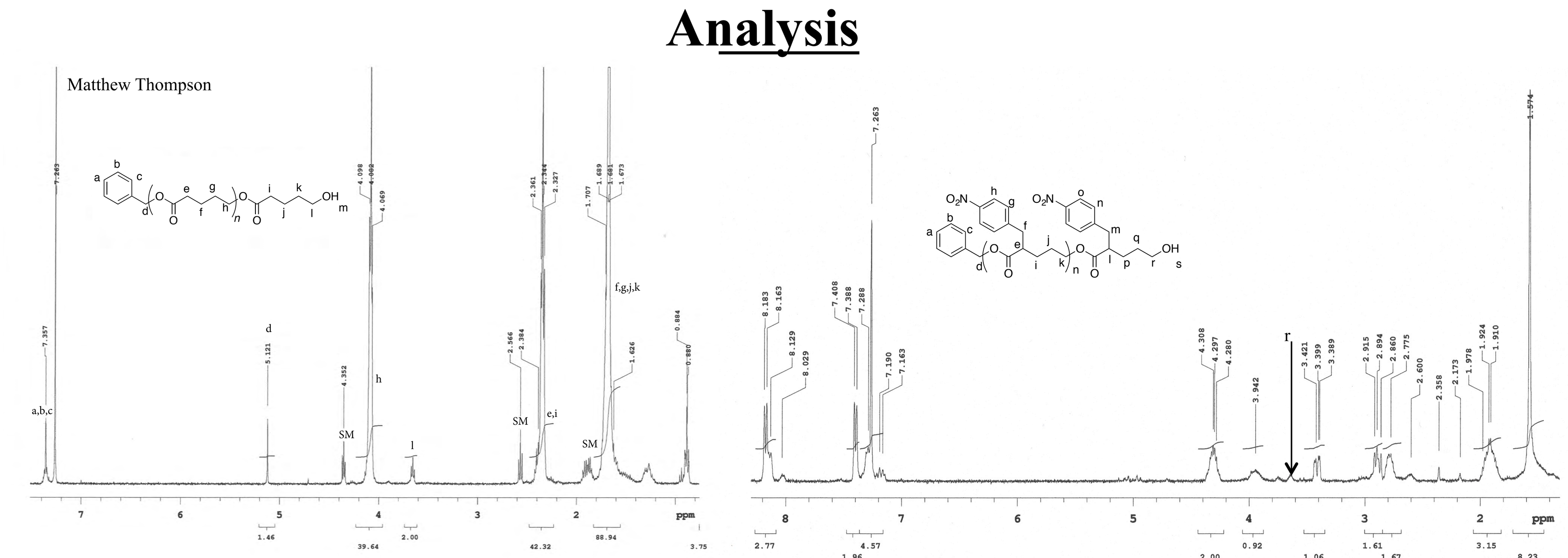




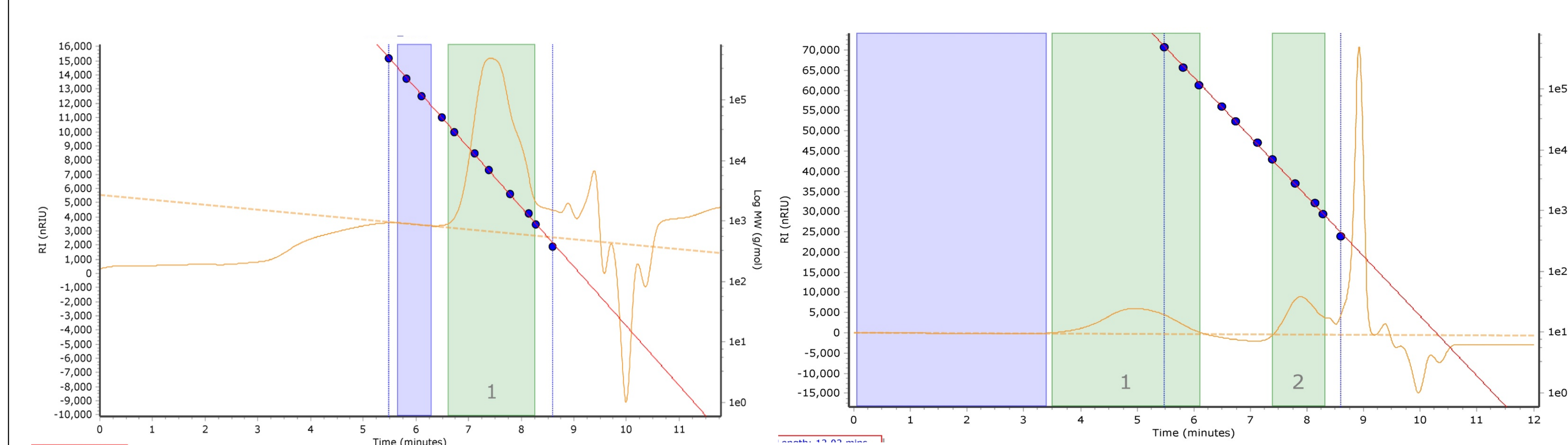


Scheme 4. Polymerization of monomer (**8**) with $Sn(Oct)_2$ catalyst, BnOH initiator, in toluene (100:0.5:10) to produce polymer (**9**).

Analysis

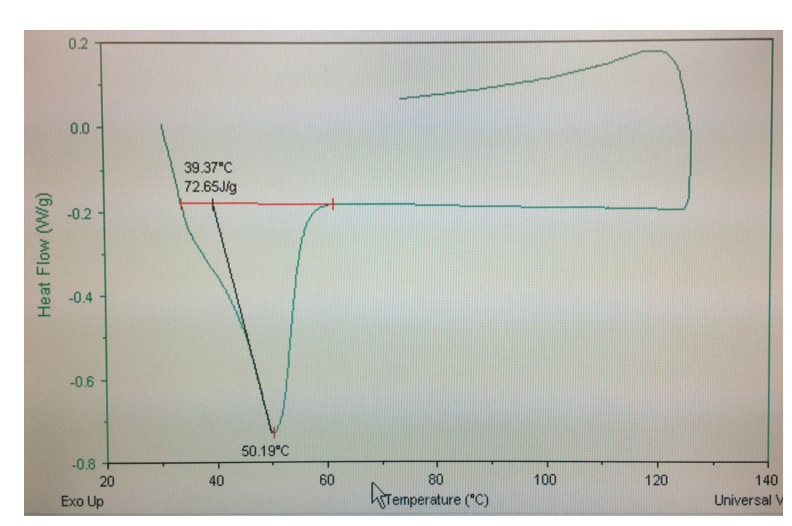


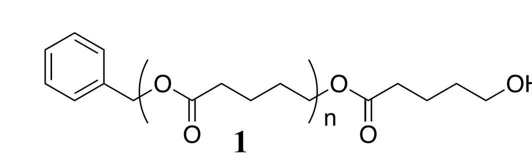
^{1}H Nuclear Magnetic Resonance Spectroscopy



Material	M_p (g/mol)	M_n (g/mol)	M_w (g/mol)	M_z (g/mol)	M_v (g/mol)	PD	Units
Poly(δ-Valerolactone)(**1**)	6067	3677	6565	10648	10024	1.785	36.8
Poly(*p*-nitrobenzyl)(δ-Valerolactone)(**9**)	2152	1789	2227	2731	2656	1.245	7.6

Gel Permeation Chromatography

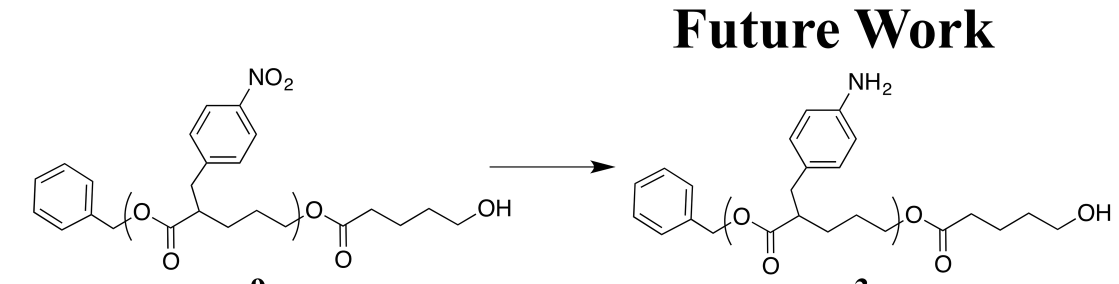




Material	MP
Poly(δ-Valerolactone) (**1**)	50 °C

Differential Scanning Calorimetry

Future Work



Scheme 5. Reduction of (**9**).

Trial	Conditions
1	3.5 eq. $HSiCl_3$, 5 eq. DIPEA in MeCN, 0ºC, 18hr
2	3 eq. Fe, 1 eq. $CaCl_2$ in 20:1 EtOH/H_2O for 30 min, 60ºC

- Purification of (**9**).
- Melting point and glass transition point of (**9**) by DSC.
- Refinement of polymerization conditions.

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References

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