Analyzing Thermodynamics for PAMAM Dendrimer Synthesis

RYUTARO EINAR JACOBSON

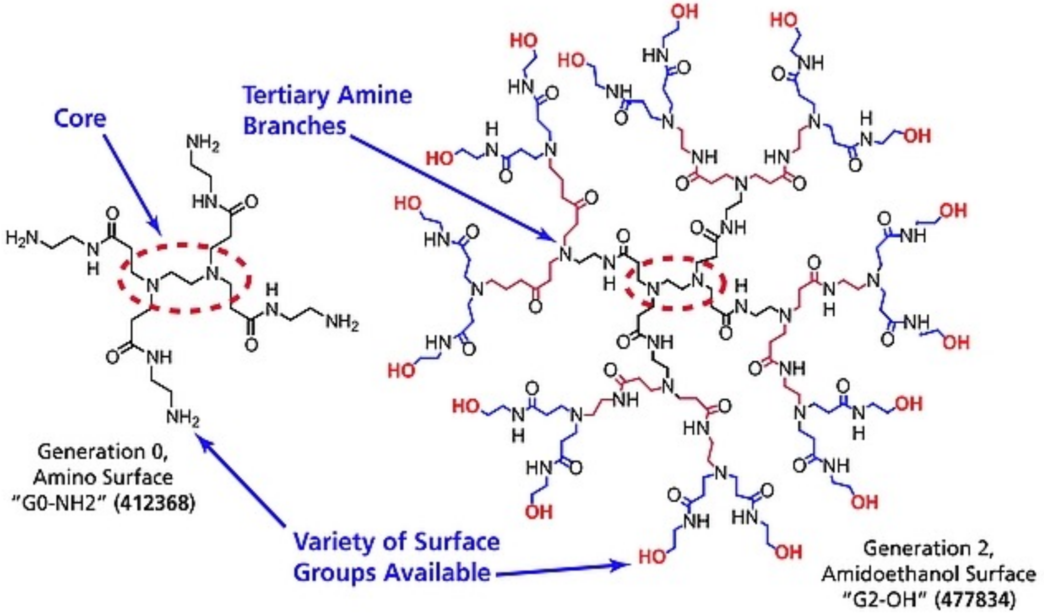
Background Information

Characteristics of Dendrimers:

- Synthesized through repeated Michael additions
- Highly branched
- Variable surface groups

Synthesis Process:

- Time consuming
- Expensive in materials
- It works, but hasn't been optimized



Objectives

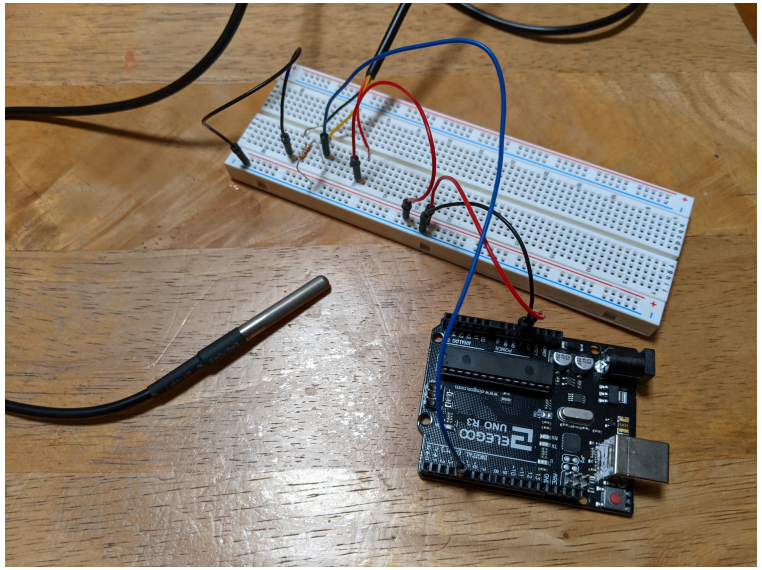
Three Objectives:

1. Determine rate law of reaction between ethylene diamine (EDA) and methyl acrylate (MA)
2. Calculate Arrhenius pre-exponential factor (A) and activation energy (E_a)
3. Begin testing reactant flow control

Tools

For temperature sensor:

- Arduino UNO microcontroller
- DS18B20 temperature sensor
- 4.7kΩ resistor



For cooling system:

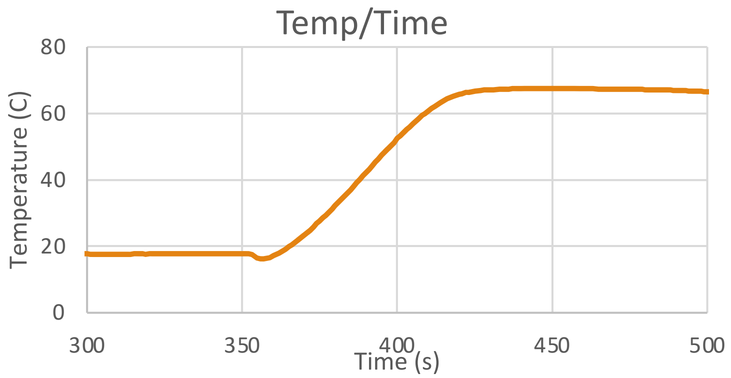
- Small pump (103 L/hr output)
- Stainless steel pipe

Methods 1: Rate Law

Used Method of Initial Rates

- Starting concentrations are varied
- Reaction rates are compared to starting concentrations with Equation 1.
- Use relative changes to determine α and β
- Calculate rate constant k at recorded temperature conditions

$$1.\ \frac{r_1}{r_2} = \frac{k[A]_1^{\alpha}[B]_1^{\beta}}{k[A]_2^{\alpha}[B]_2^{\beta}}$$



Methods 2: A and E_a

Needed rate law to calculate A and E_a

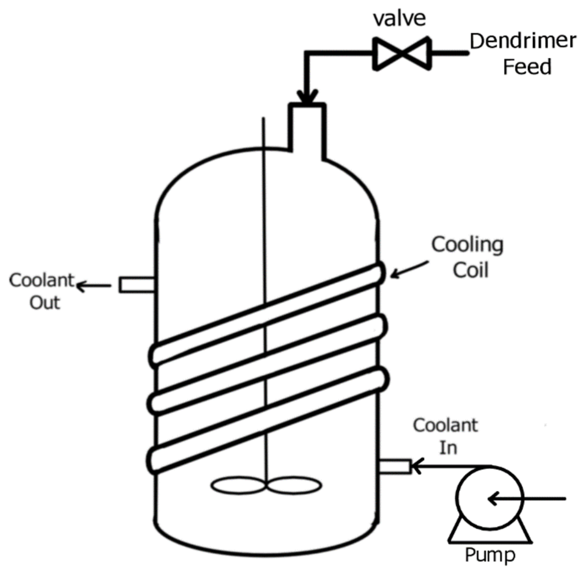
- Run same reaction with different temperatures
- Modify Equation 2 into Equation 3
- Use temperature and k values to solve for E_a
- Solve for A

$$2.\ k = Ae^{\frac{-E_a}{RT}} \qquad 3.\ E_a = \frac{R\ ln\frac{k_2}{k_1}}{\frac{1}{T_1}-\frac{1}{T_2}}$$

Methods 3: Feed Control

Controlled dripwise reactant feed

- Add EDA to MA drop by drop from addition funnel
- Establish constant drip rate per minute (dpm)
- Observe temperature for varying dpm
- Establish drip rate to keep temperature under 30°C



Dripwise Added Batch Reactor
With Semi-Indirect Cooling

Results: Rate Law

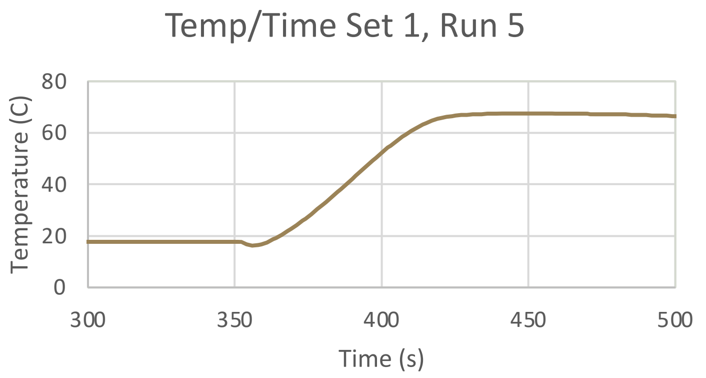
- Set 1 used concentrations from existing procedures
- Set 2 reduced MA concentration by 50%
- Set 3 reduced EDA concentration by 50%
- Rate law: $r = k[EDA]^{1/2}$
- Rate constant: 0.0083 s^{-1}
- Reactions run at 15-20°C

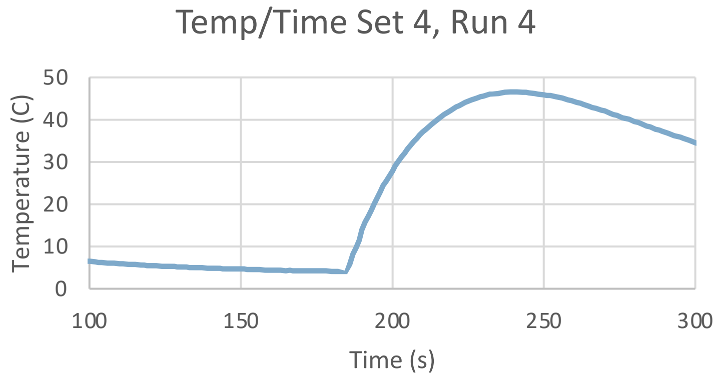
	[EDA] (M)	[MA] (M)	Time (s)
Set 1	1.61	6.76	99.3
Set 2	1.61	3.38	100.5
Set 3	0.80	6.76	130.4

Results: A and E_a

- Reactions were run at 4.5°C
- Coolant was too effective
- Temperature peaked lower and earlier
- Calculated E_a was negative, which is impossible
- Instrument limitations prevented calculation
- Example: 92.5s to peak in 1.5 (uncooled),

  55.5s to peak in 4.4 (cooled)





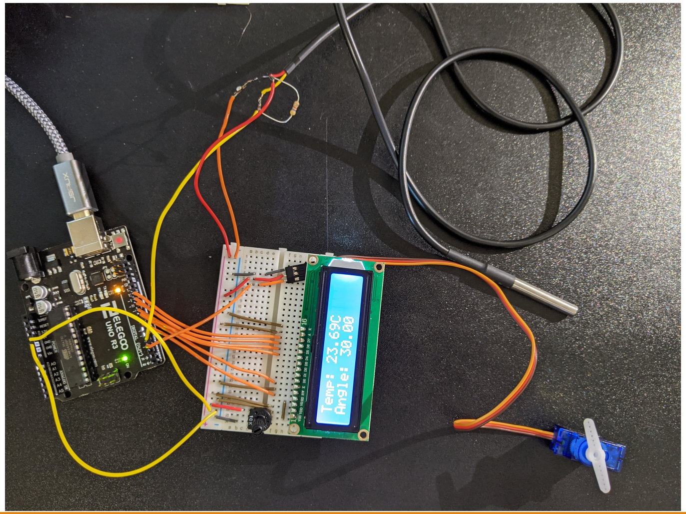
Results: Feed Control

- Reactions run with cooling at 4.5°C
- Feed control caused more gradual heating
- Around 20 dpm kept temperature below 30°C
- 20 dpm will still cross 30°C eventually

	Drip Rate (drops/minute)	High Temperature (°C)
Reaction 5.1	130	35.81
Reaction 5.2	35	34.63
Reaction 5.3	20	24.62
Reaction 5.4	22	22.50

Conclusions/Next Steps

- More efficient research/production
- Methods effective for finding rate law
- Unable to determine A and E_a
- Feed control works, needs feedback control



Prototype Feedback Control Circuit using servo and temperature sensor

- Measure concentration to find A and E_a
- PID feedback controller finished
- Controller needs tuning to reaction
- Effective feed control valve needed

Acknowledgements

Dr. Ryan Hayes