Vanishing Devices – From Sensors to Drones Enabled by Transient Polymers

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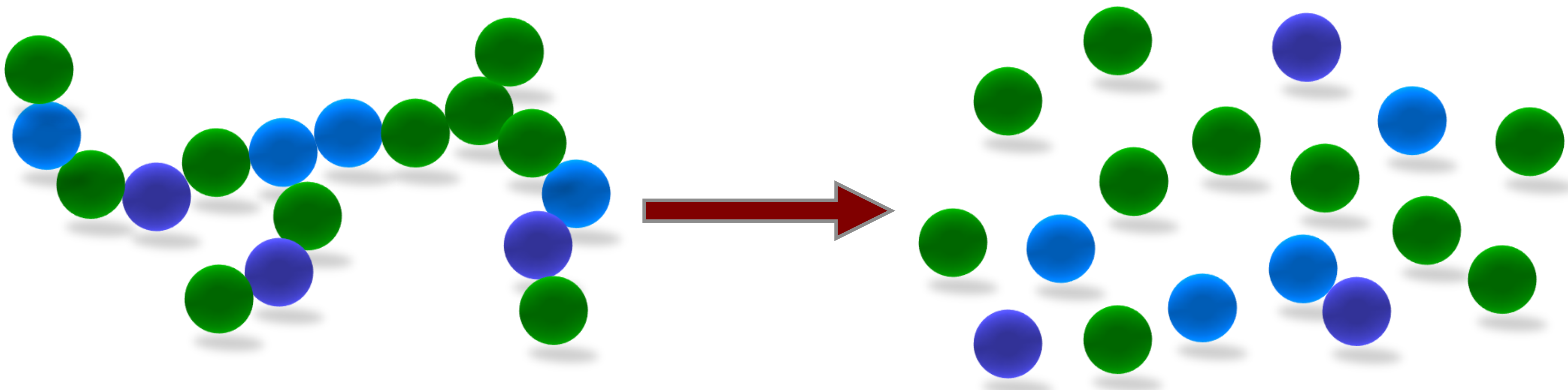
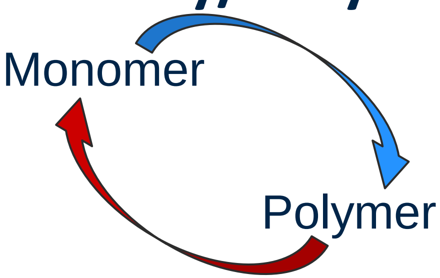
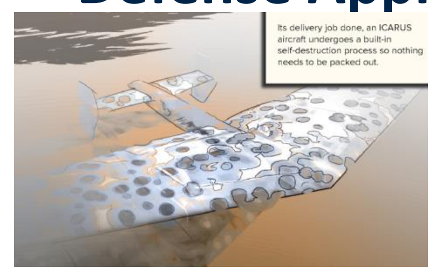
Degradable Polymers



Renewability/Recyclability



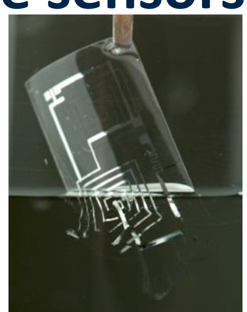
Defense Applications



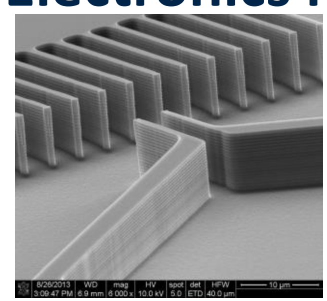
Vanishing UAVs

Eco/bio-resorbable sensors

Recovery of device is undesired



Electronics Manufacturing



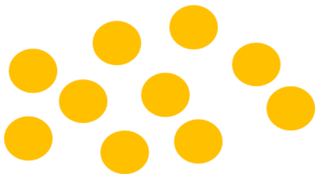
Patterning & MEMs devices

Classes of Decomposable Polymers

Ceiling temperature (T_c): temperature at which the rate of polymerization equals rate of depolymerization. Below T_c - polymer is favored.

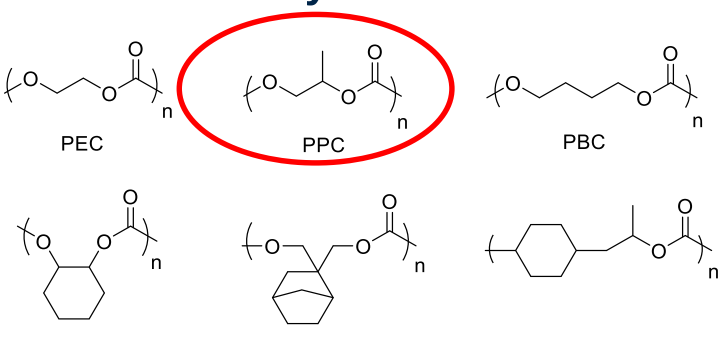
Polymer Formation

$< T_c <$



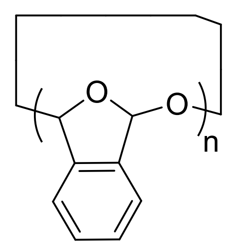
Monomer Formation

High Ceiling Temperature Polymers



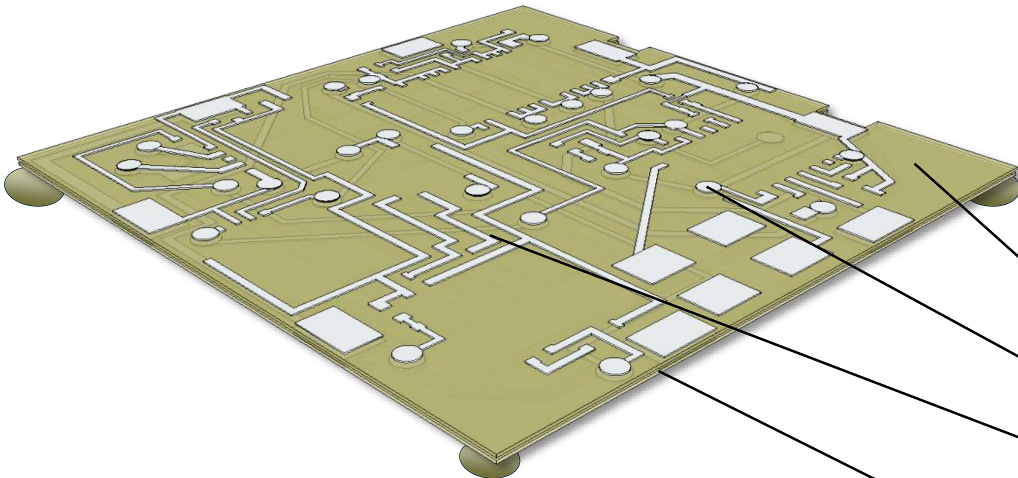
- Polycarbonates
  - T_d = 200 °C - 300 °C
  - T_d (acid) ~ 100 °C

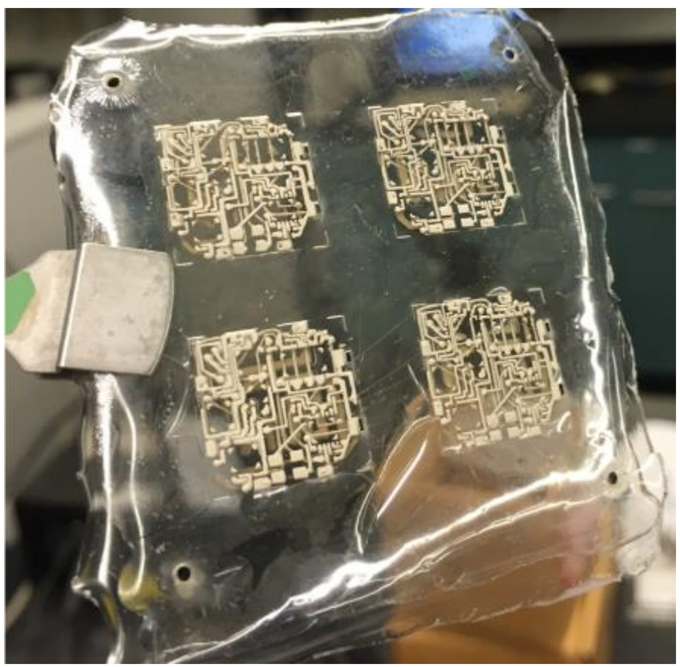
Low Ceiling Temperature Polymers



- Polyaldehyde
  - T_c = -40°C

Application – Degradable Sensors





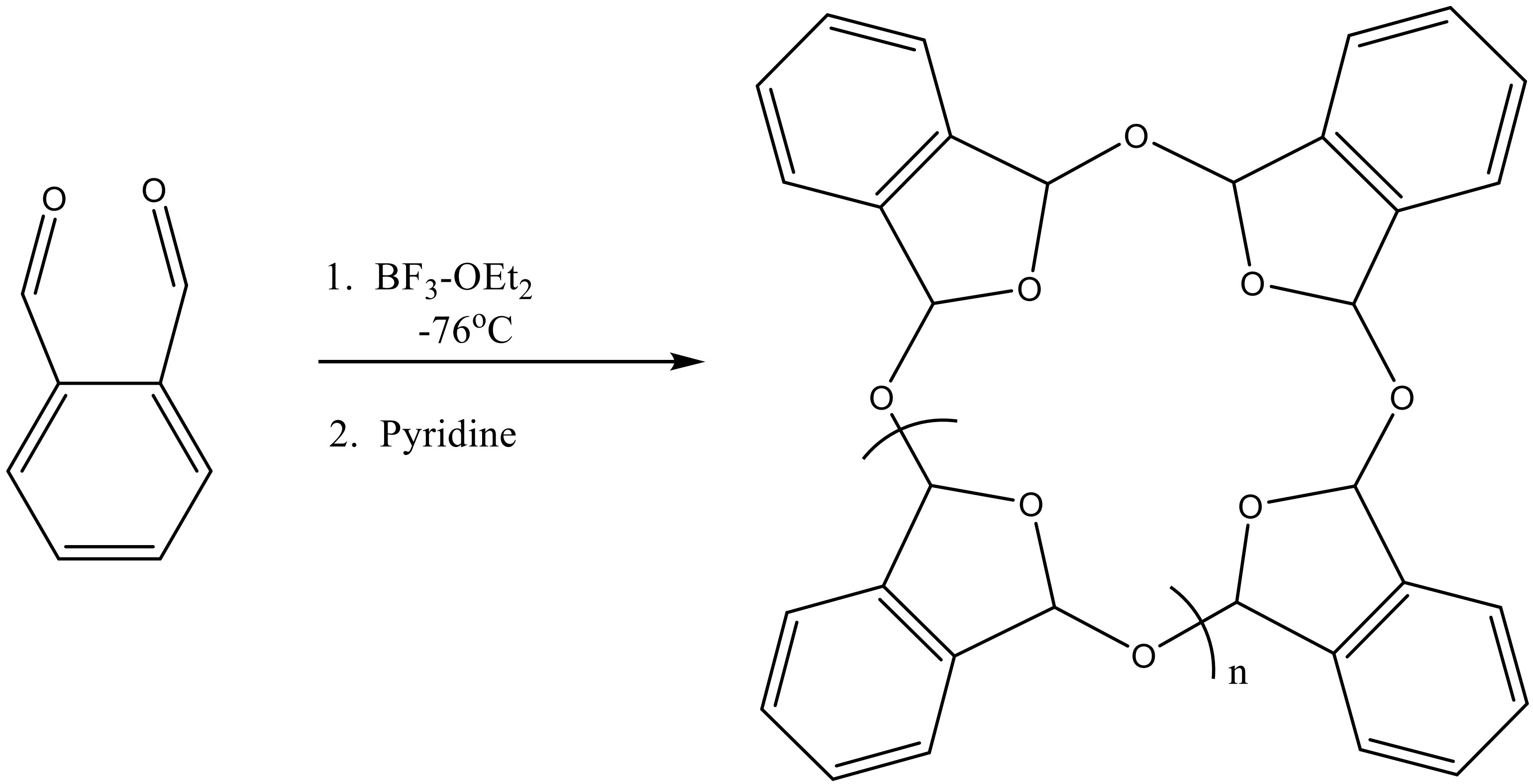
1. Stable polymer film
2. CO_2 laser-cut vias
3. Screen-printed silver/polymer wiring
4. Multilayered substrate (laminated films)
5. Final assembly: chip attachment
   - Conductive paste
   - Wire-bonding

Gourdin et al. *Proc. – Electron. Components Technol. Conf*. IEEE, 2017, 190

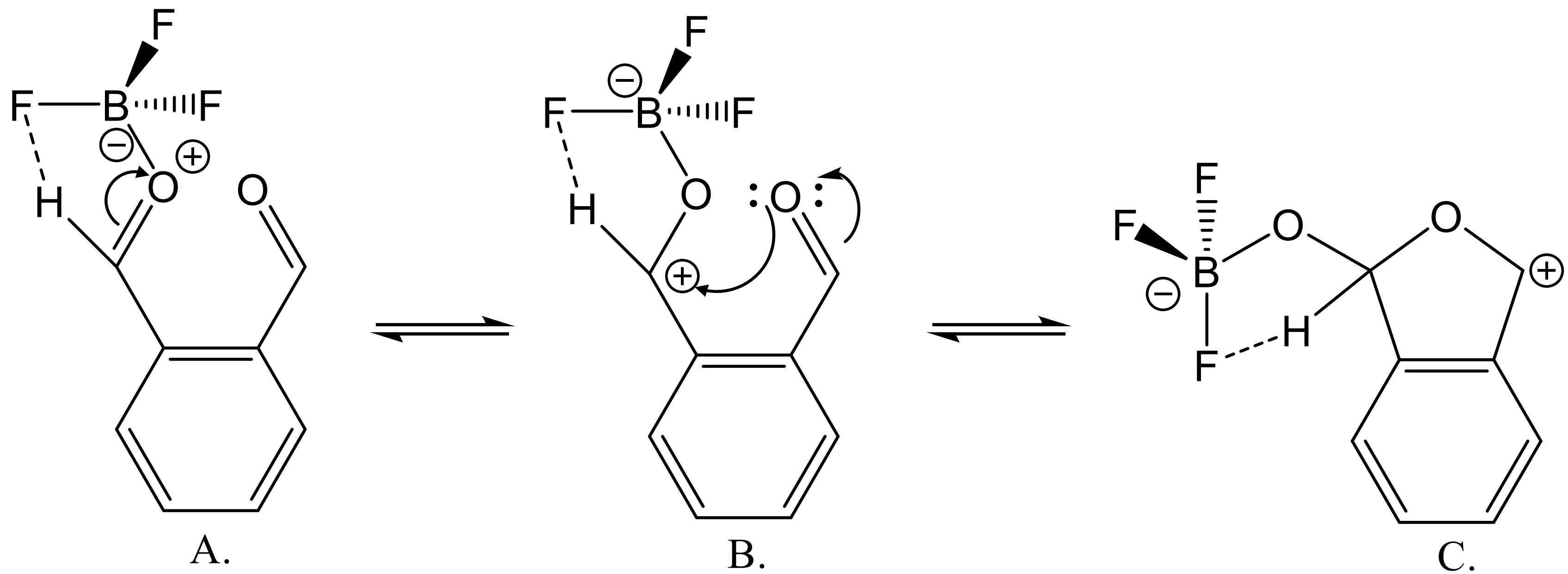
Application – Disappearing Parachute

- Foldable
- Flexible at low temperature
- Tough
- Photosensitive

Cationic Polymerization of PPHA

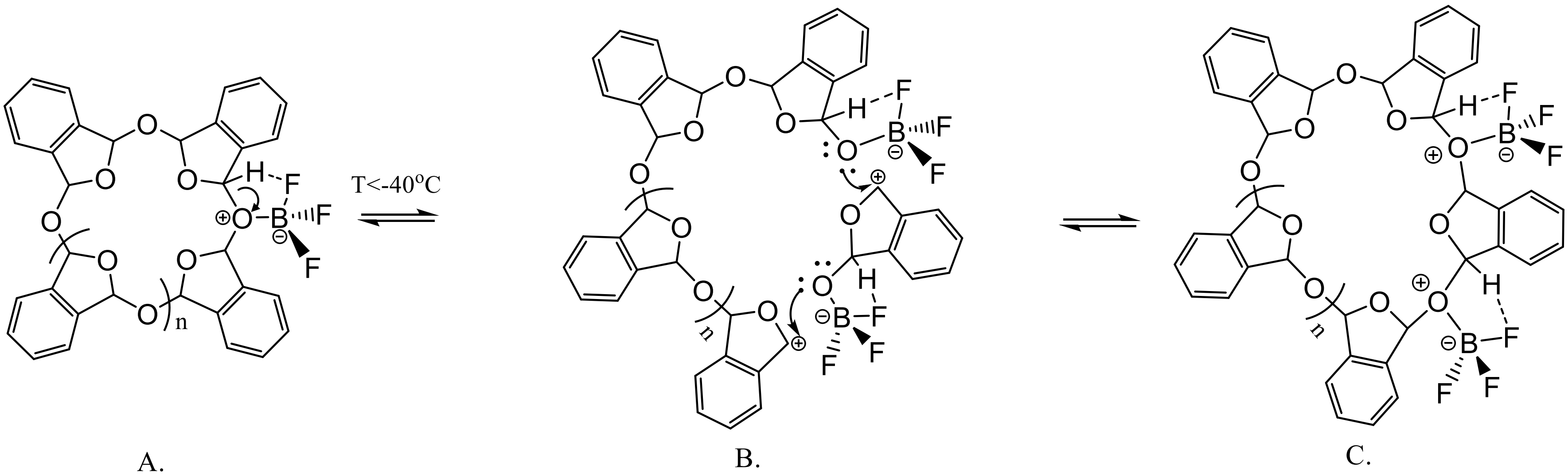


Polymer Synthesis Route



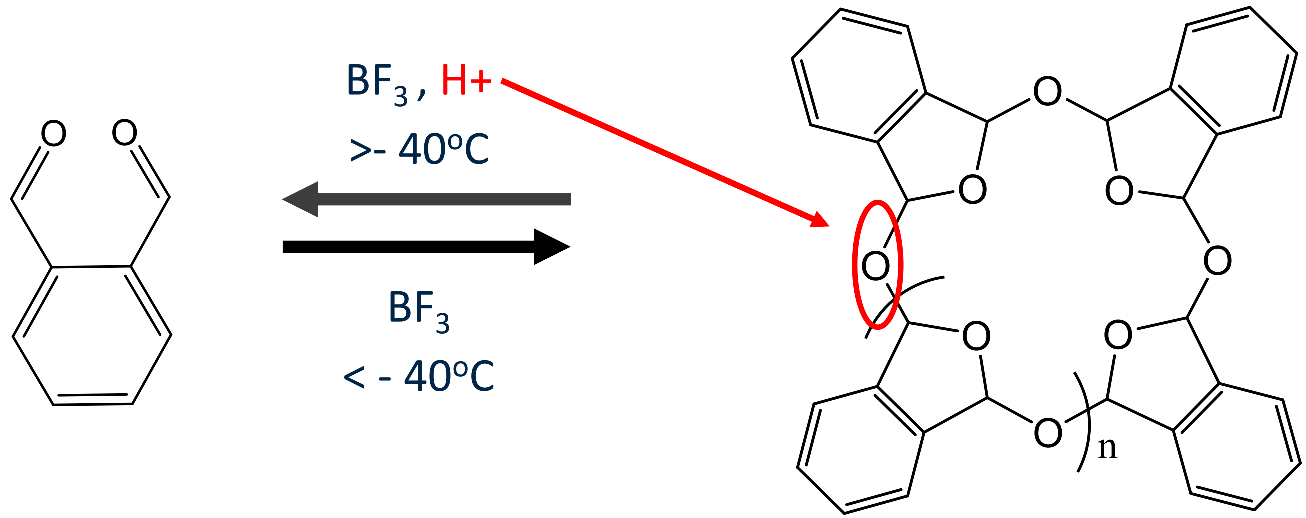
Initial PHA-BF_3 complexation (A), rearrangement of the cation to the formyl carbon (B), and the cyclized monomer cation (C)

Polymer Growth



BF_3 complexes with existing polymer backbone (A). Rearrangement and opening of polymer chain (B) allows another monomer to insert itself. Both BF_3 complexes allow closing of polymer chain (C).

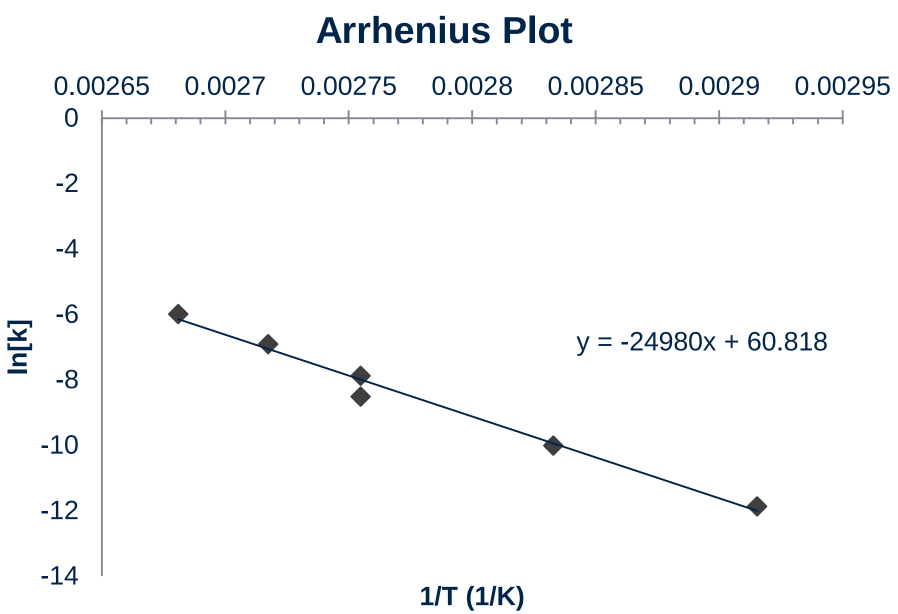
Low Ceiling Temperature Polyphthalaldehyde (PPHA)



- Can be cationically synthesized below T_c (-40 °C)
- Cyclic chain affords thermal stability up to 150 °C
- Acetal linkages are susceptible to acidic protonation
- Ideal material for transient (disposable) electronics

Thermally Stable (Months at 30ºC)

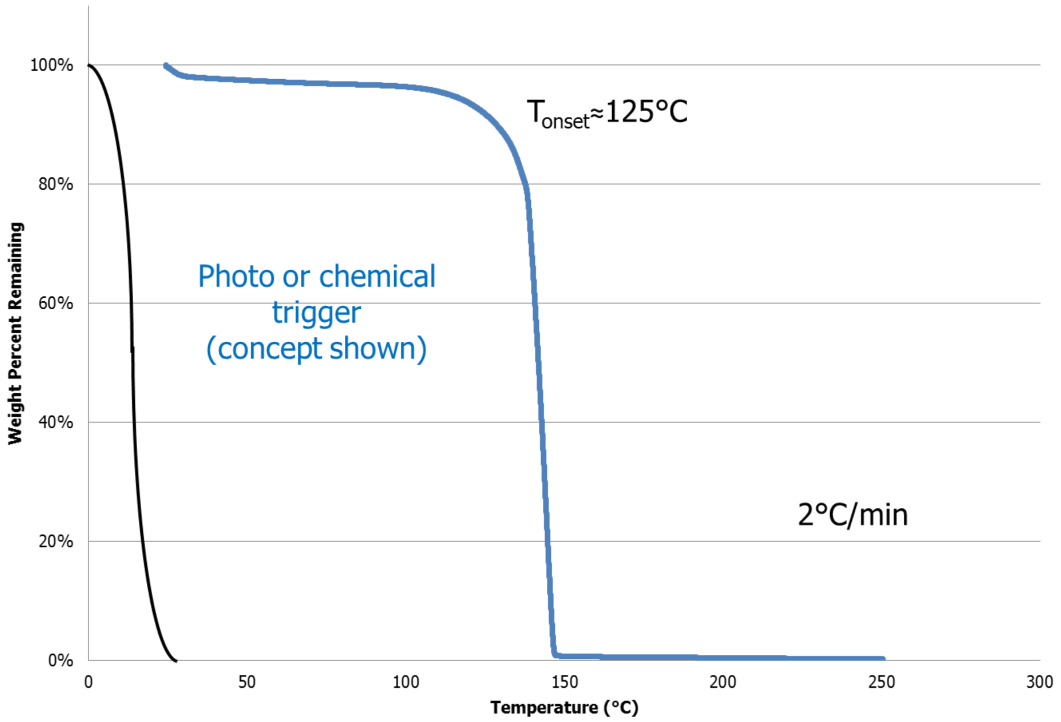
Georgia Tech

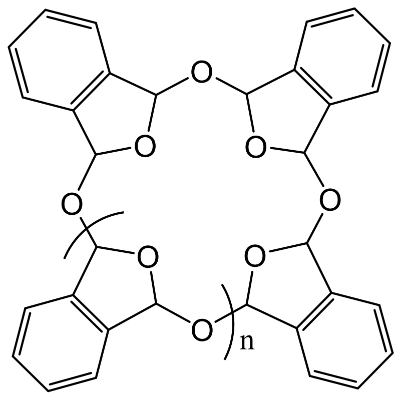


- Isothermals: 100°C, 95°C, 90°C, 80°C, 70°C
- Arrhenius Parameters:
  - $A = 2.6 \times 10^{26}$
  - E_a = 50 kcal/mol

Temperature (°C)	1% loss
Ambient: 20˚C	13 years
Hot Desert - 40˚C (continuous)	21 days

Polymer is Thermally Stable



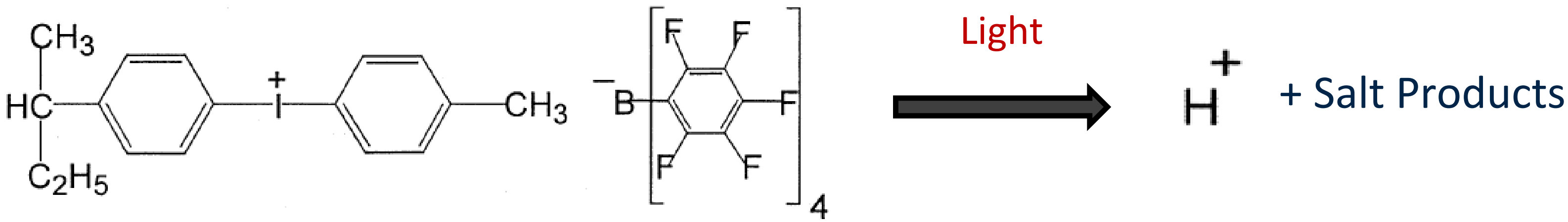


Cyclic PPHA, n>1000

Rupture a single bond and depolymerization at T > -40°C

Photo-Triggering: Two Part Photopackage

(a) Depolymerization at any temperature –reuse acid

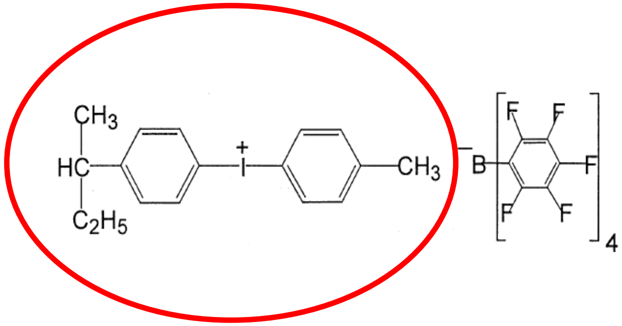


(b) Sensitizer: Pick the wavelenths you want

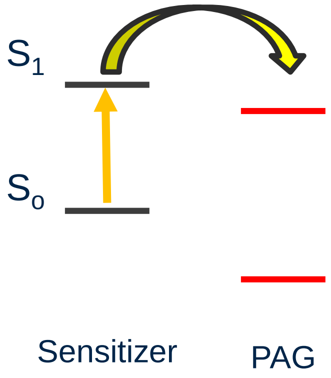
Optical Trigger and Sensitizers

Optical Trigger- photo-acid generator absorbs short wavelengths

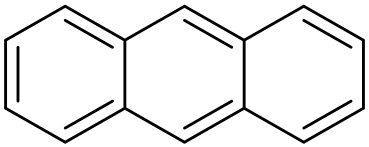
Absorbs < 300nm of light



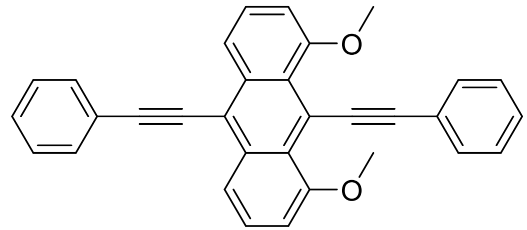
Sensitize to longer wavelengths



Modified Sensitizers: Red Shift and Solubility

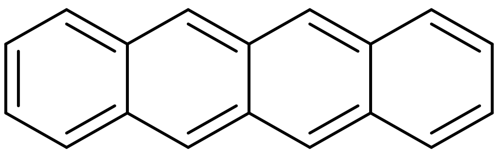


Anthracene
200 – 400 nm

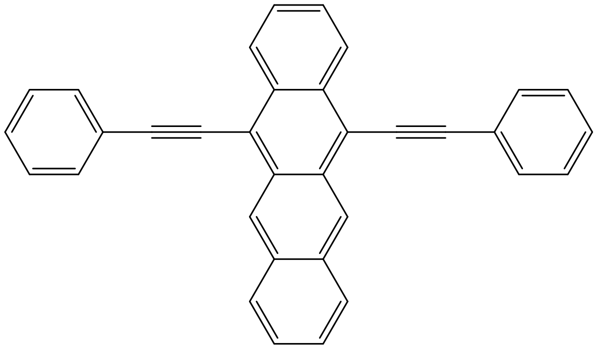


1,8-dimethoxy-9,10-bis(phenylethynyl)anthracene – **DMBA**

Yellow

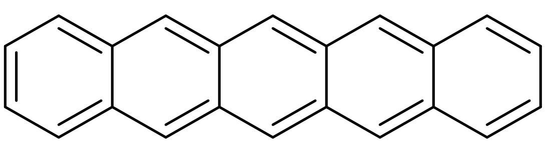


Tetracene
280 – 500 nm

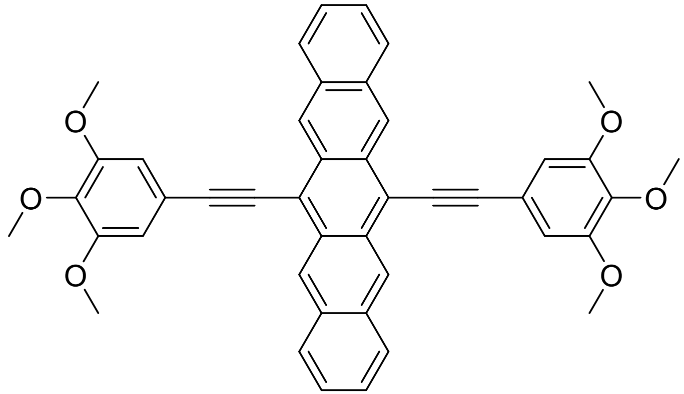


5,12-bis(phenylethynyl)tetracene – **BPET**

Red-orange



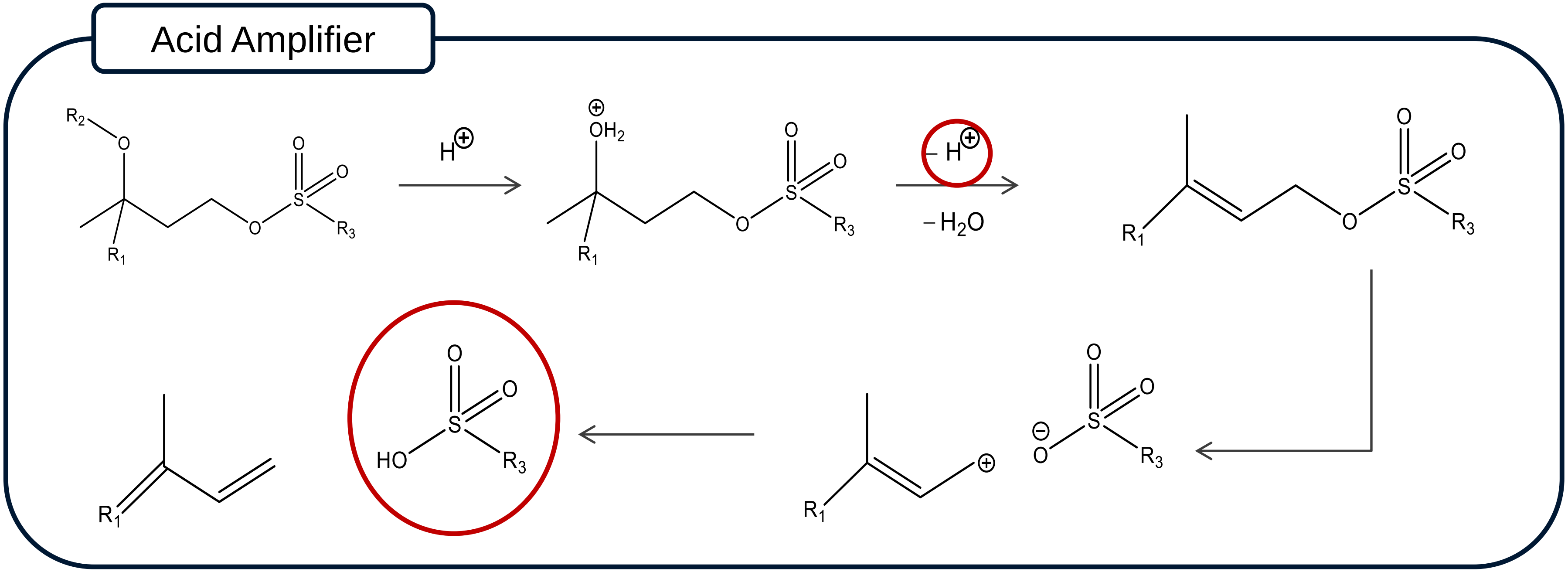
Pentacene
450 – 600 nm

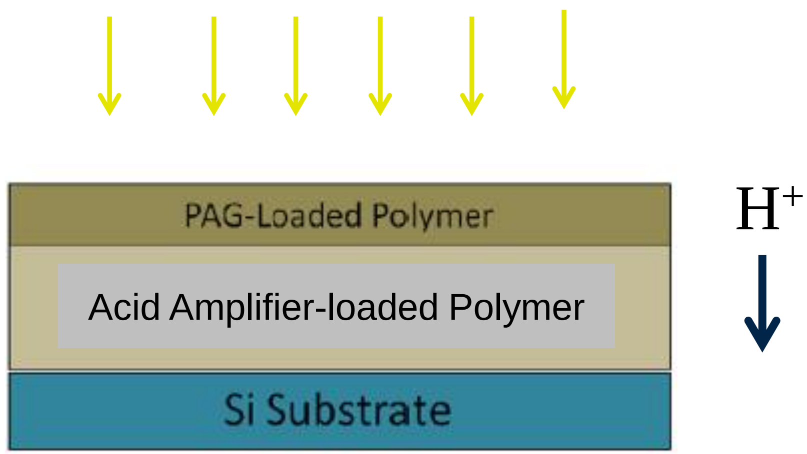


6,13-bis(3,4,5-trimethoxyphenylethynyl)pentacene – **BTMP**

Dark blue

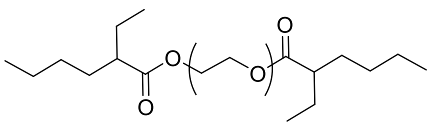
Acid Amplification



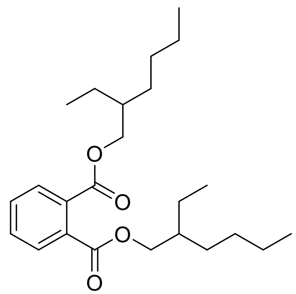


Mechanical Properties: Rigid to Flexible

Non-Ionic Plasticizers



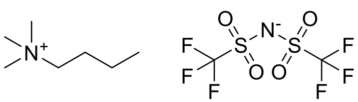
Poly(ethylene glycol)
PEO



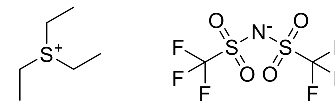
Bis(2-ethylhexyl) phthalate
BEHP

- Low melting points
- Higher plasticizing effect
- Phase segregation at relatively low loadings (30 to 20 wt%)
- Higher likelihood of leaching
- May interact with free acid

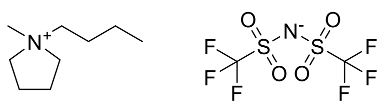
Ionic Plasticizers



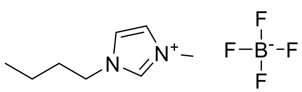
AMM TBFSI



SF TBFSI



BMP TBFSI

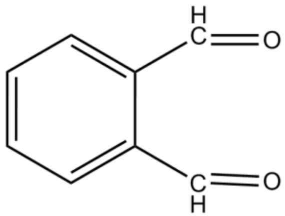


IM BF4

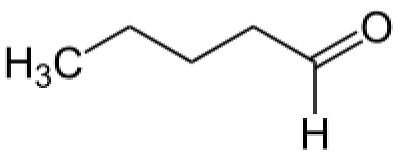
- Low melting Points
- Lower plasticizing effect
- No visible phase segregation at high loadings (>100 wt%)
- Low Leaching Rates
- Inert to free acid

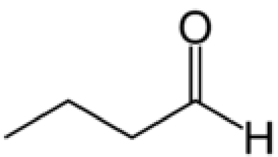
Co-polymer Components and Their Properties

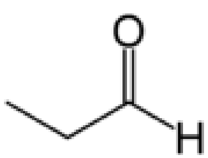
Substance	Freezing Point	Boling Point
Phthalaldehyde	55^{o}C	266^{o}C
Pentanal	-60^{o}C	102^{o}C
Butanal	-97^{o}C	75^{o}C
Propanal	-81^{o}C	46^{o}C
Acetaldehyde	-123^{o}C	20^{o}C



Homopolymer





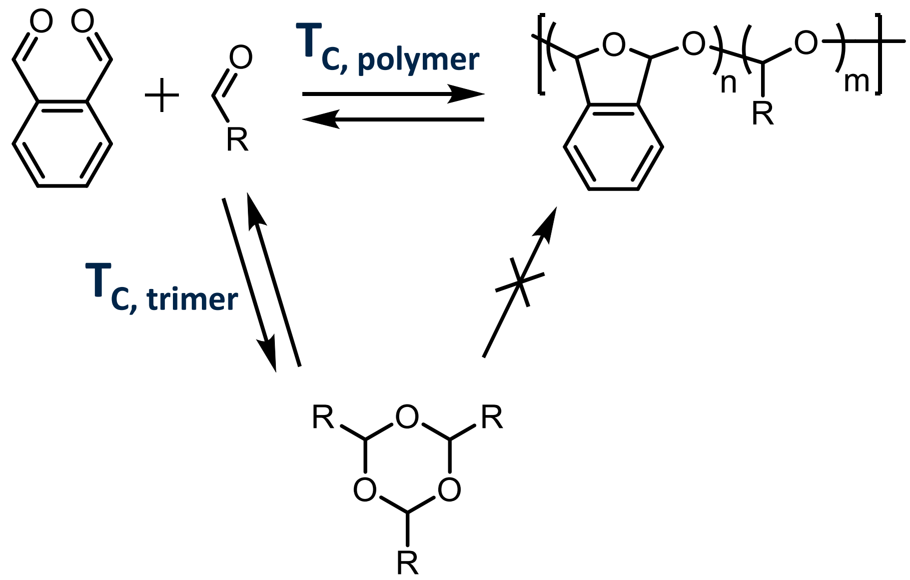


Mechanical Properties

Material	Modulus	Elongation to Break
PHA Homopolymer	2.0-2.5 GPa	1%
PHA-Butanal Copolymer	1.6-2.0 GPa	0.6-1.0%
PHA-Heptanal Copolymer	1.1-1.5 Gpa	0.6%

Traditional plasticizers used to improve toughness.

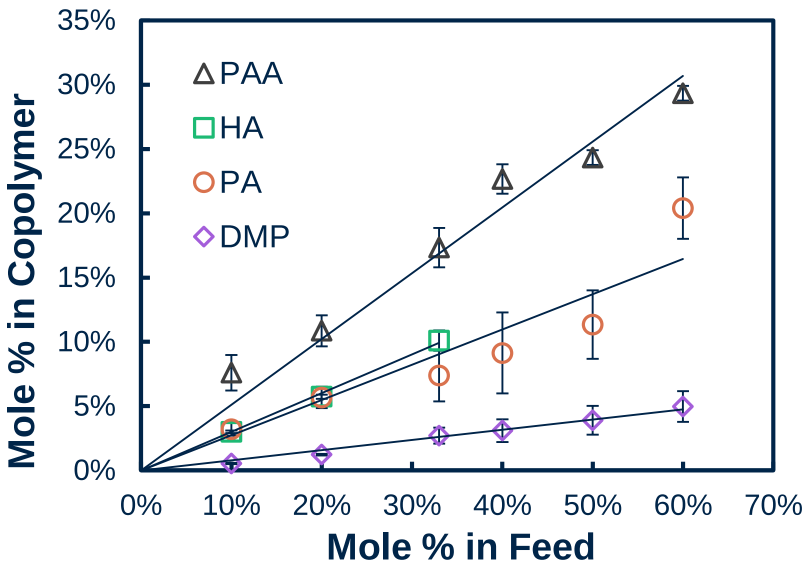
Phthalaldehyde Copolymerization

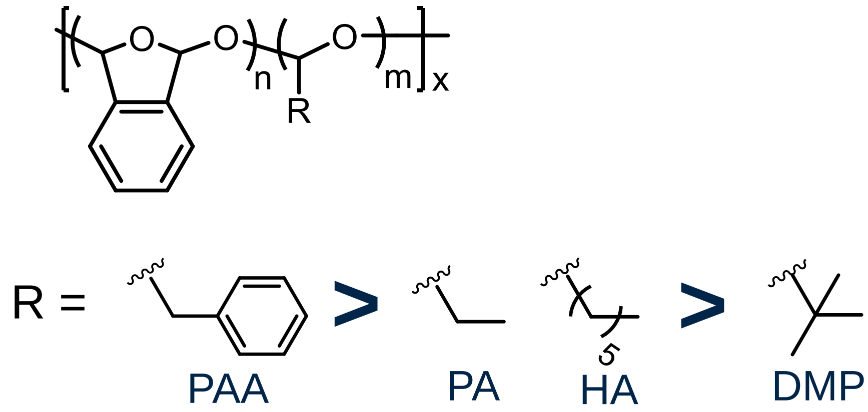


$T_{C,\,trimer} > T_{C,\,polymer}$

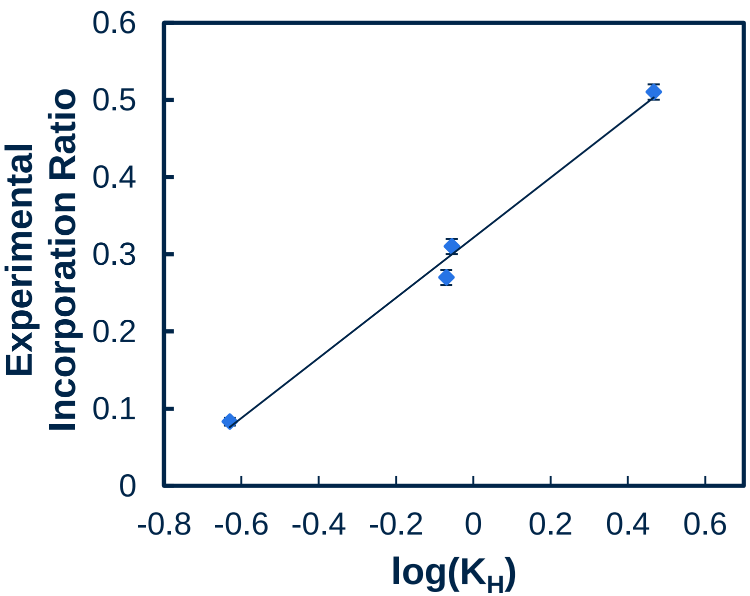
Alkyl aldehydes can form trioxanes, which do not polymerize

Effects of Comonomer Structure

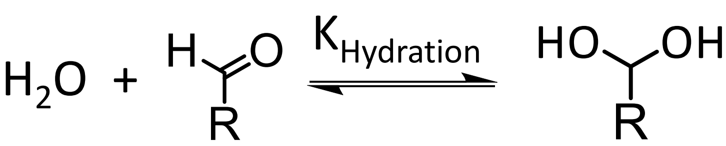




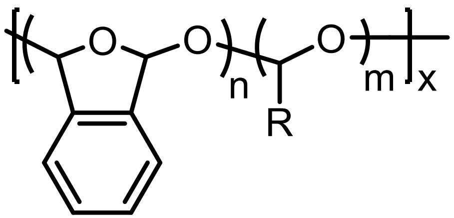
$\log K_H = 0.47 > -0.07, -0.055 > -0.63$

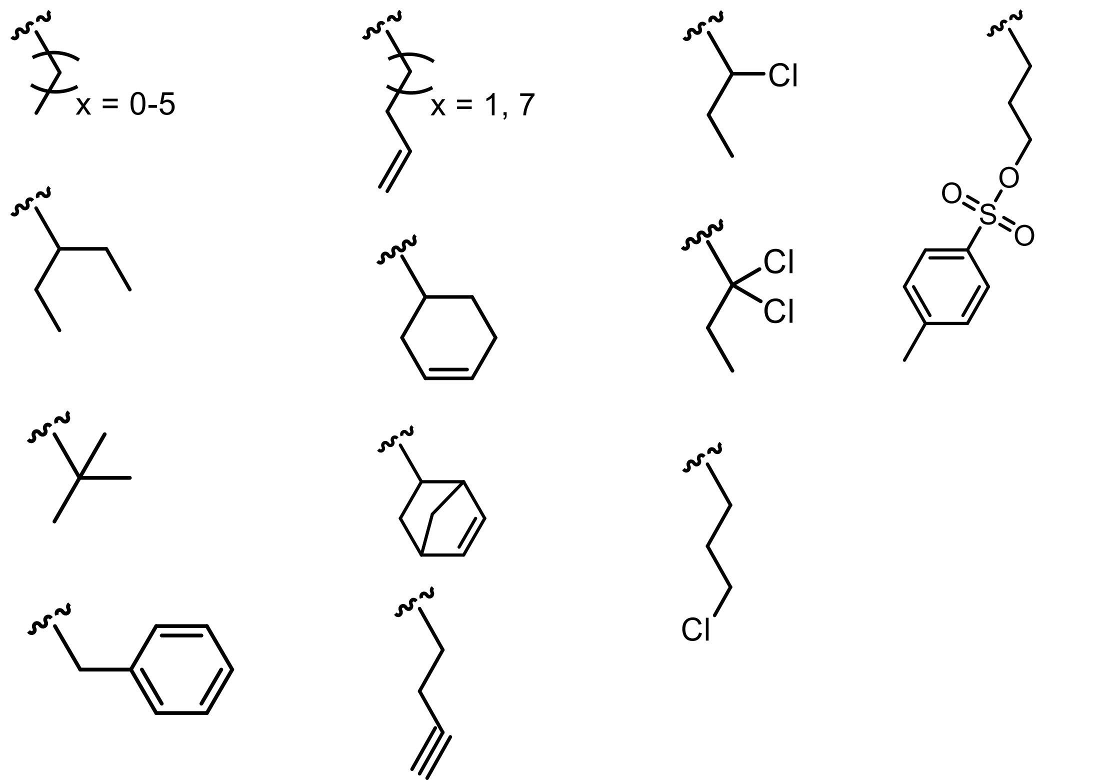


Increasing electron-deficiency of aldehyde

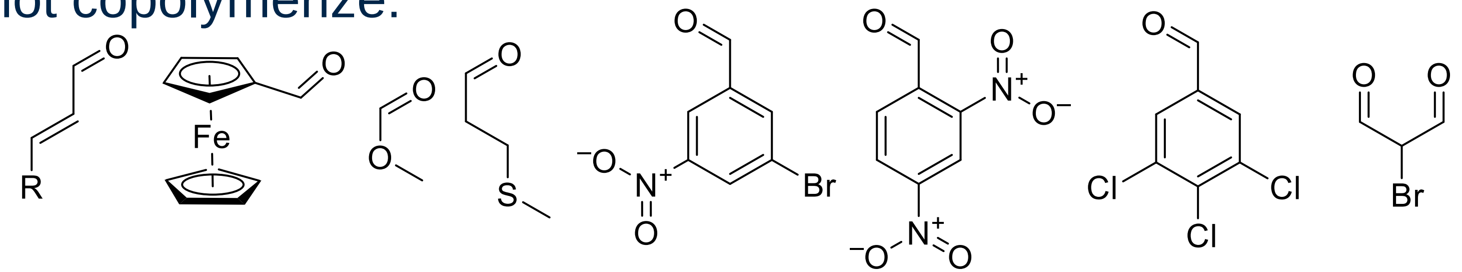


Copolymer Variety



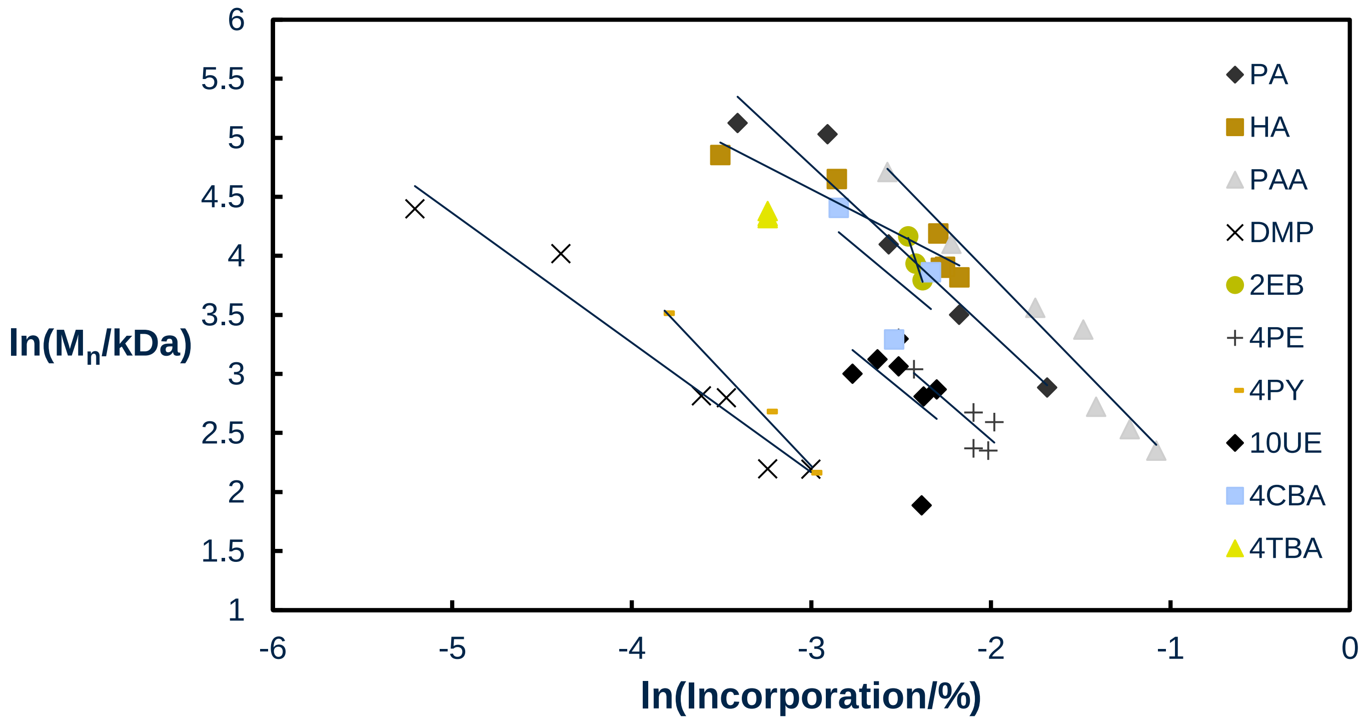


Will not copolymerize:

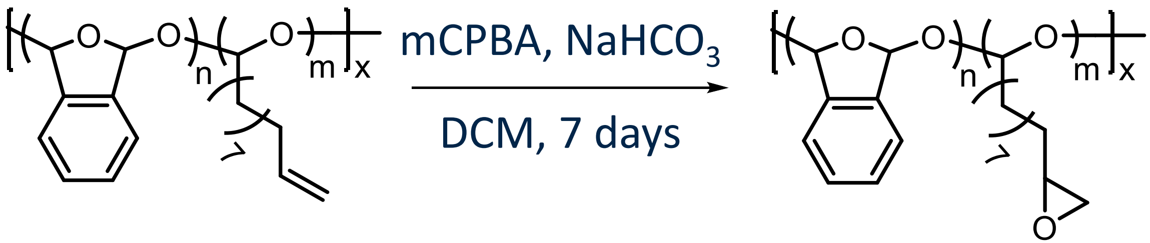


Copolymer Molecular Weight

- Molecular weight appears to be thermodynamically controlled
- MW decreases as more aliphatic aldehyde is incorporated into the copolymer

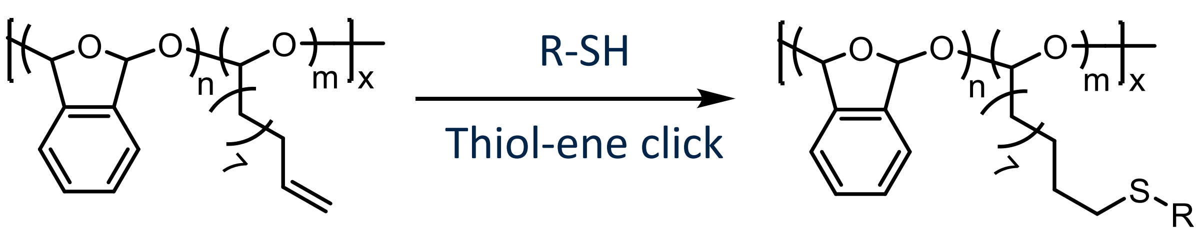


Post-Polymerization Modification

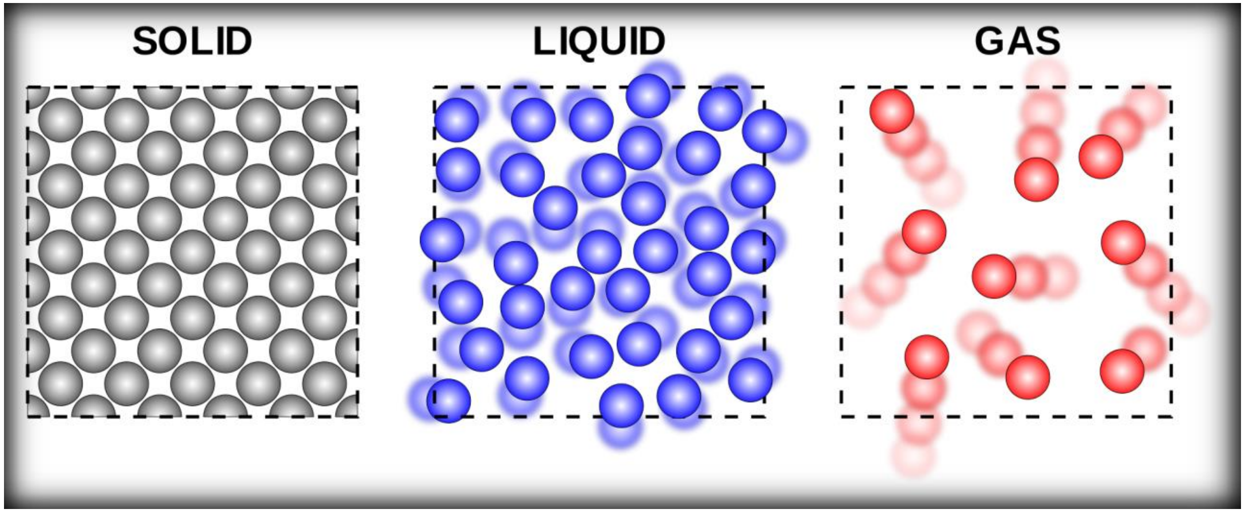


50% polymer yield
100% conversion

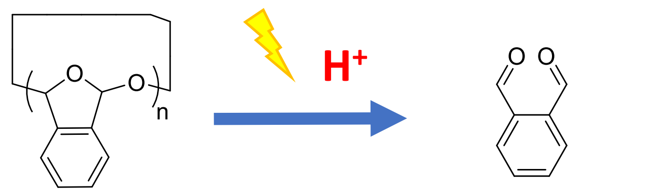
33% polymer yield
100% conversion



Delayed Photo-response



Solid-State Kinetics (QCM)



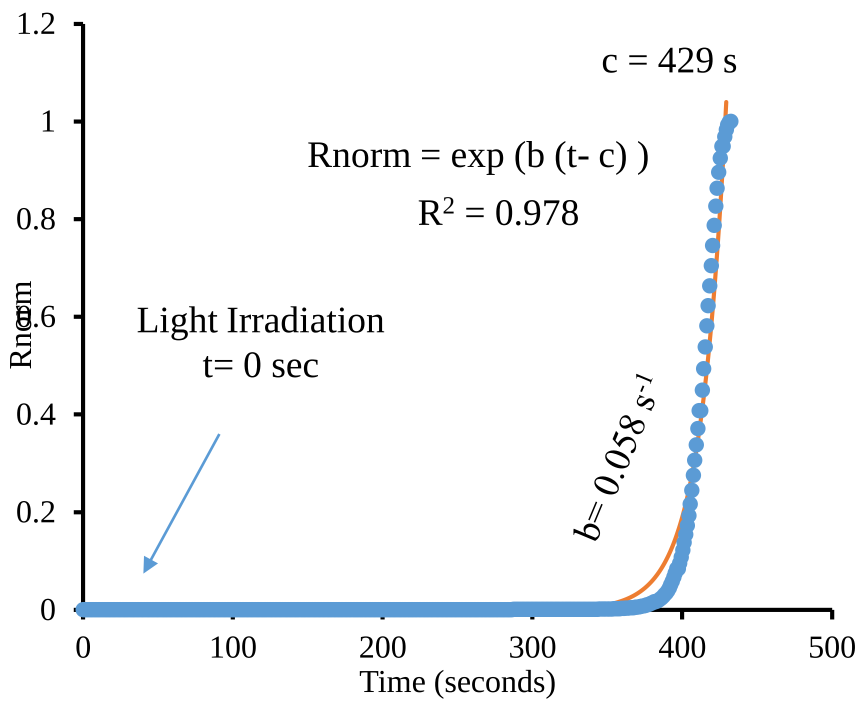
Solid Polymer

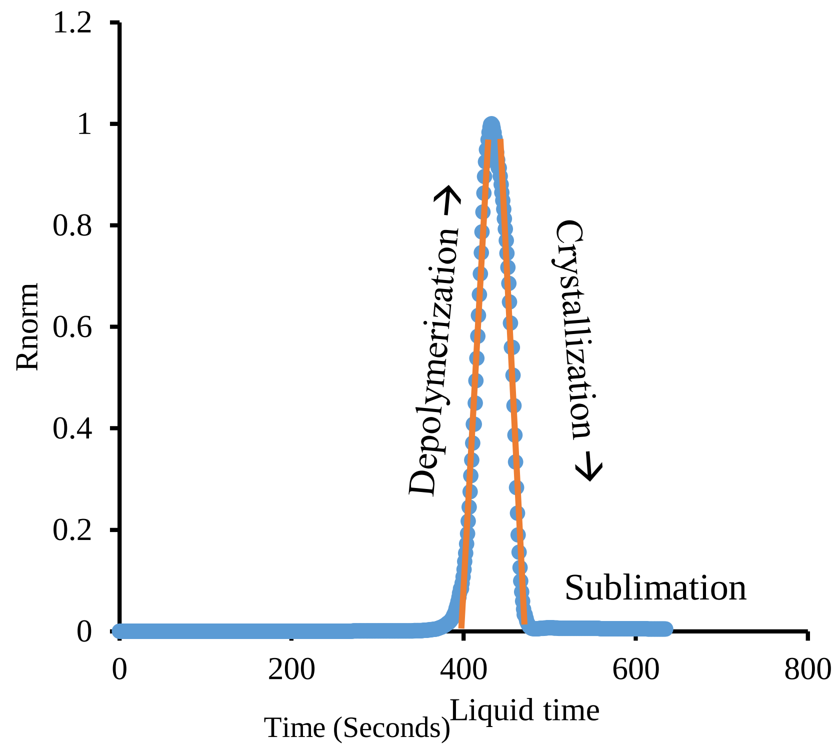
Liquid Monomer

I. 1 second

II. 6 minutes

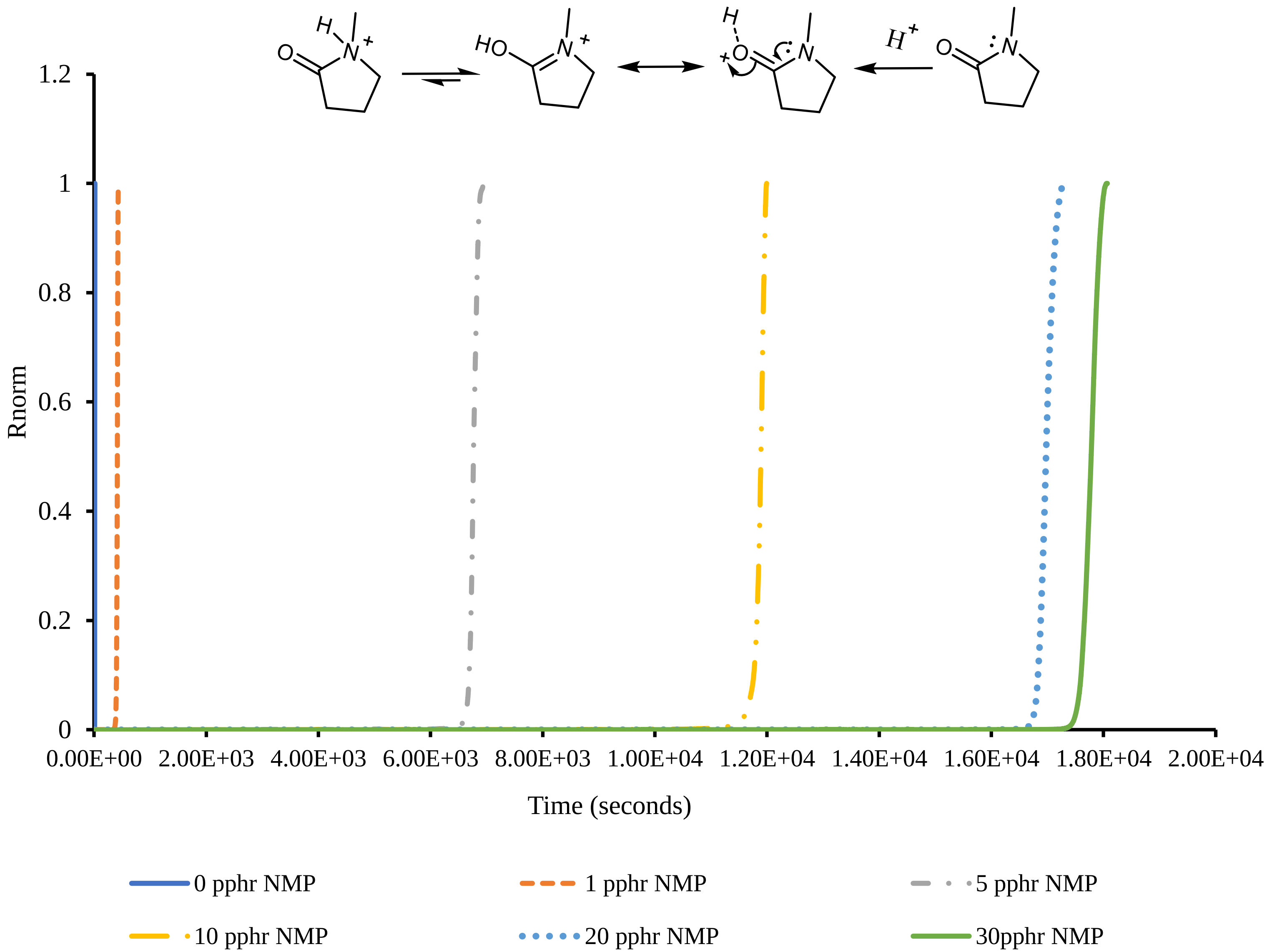
III. 10 minutes





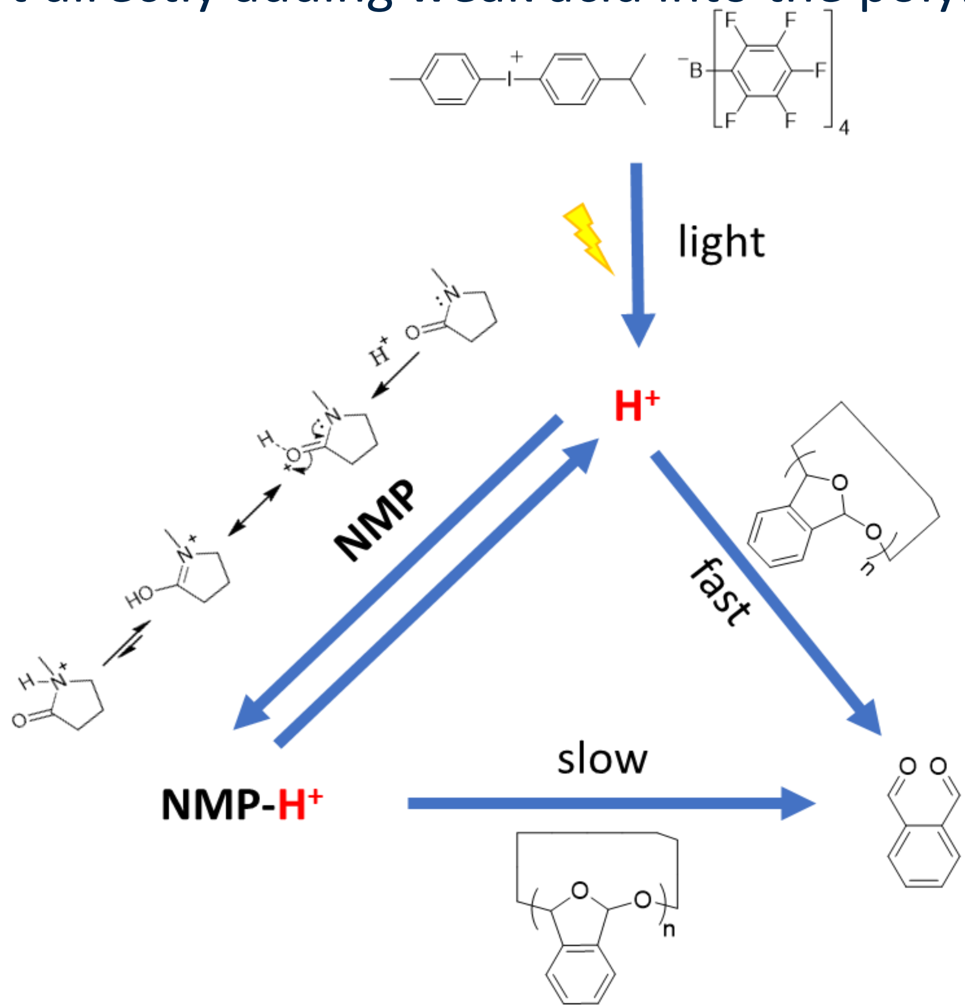
*Acknowledge Dr. Jared Schwartz for developing exponential fit model

Time-Delayed Depolymerization of PPHA

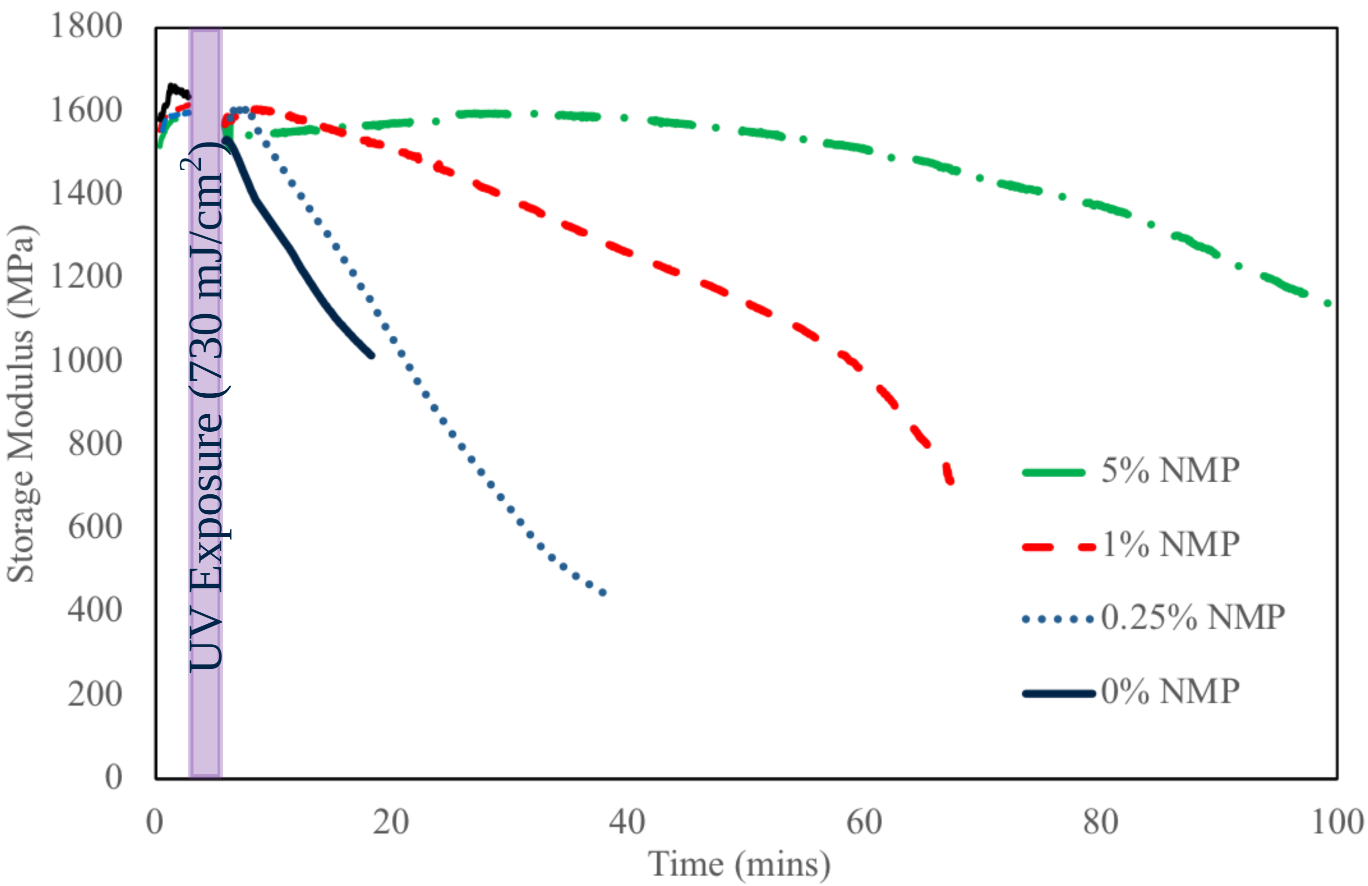


Mechanism of Controlled Depolymerization

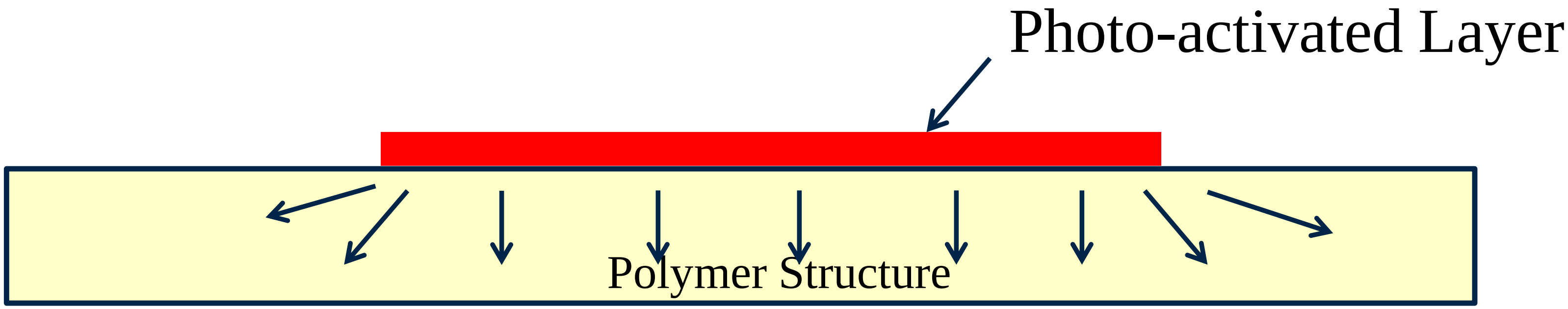
- In-situ generation of weaker acid
  - Cannot directly adding weak acid into the polymer formulation

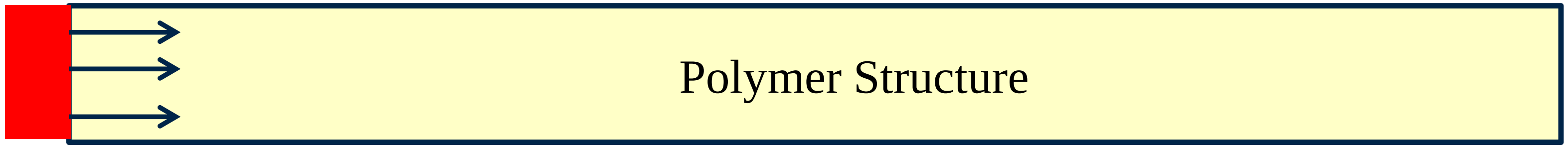


Modulus During Delay Time

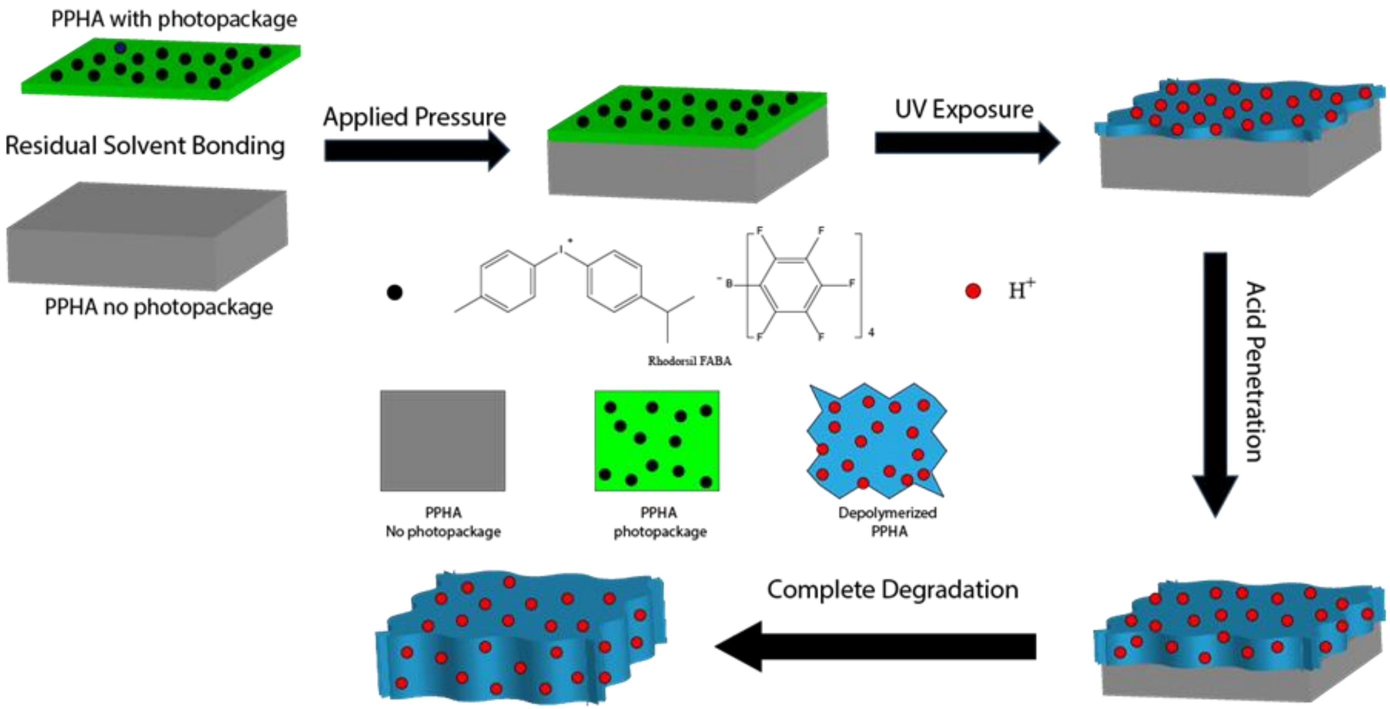


Catalyst Propagation





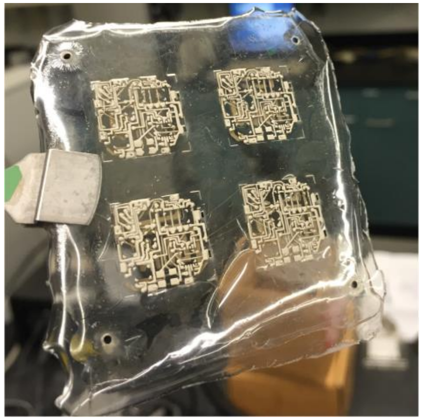
Bilayer Fabrication and Working Mechanism



Conclusions

- Understand and control the thermal degradation mechanisms of PPHA and Copolymers
  - Widened the thermal process window for sacrificial applications
- Modify mechanical properties from flexible to rigid
- Expand the spectral sensitivity of decomposable polymers into the entire visible spectrum
  - Understanding the thermodynamics and kinetics of photo-catalysts
  - Faster photolysis speeds for transient and lithographic sacrificial-applications
- Delay the photoresponse and achieve liquification
  - Introducing competitive-hydrogen bonding effects of weak bases
  - Depressing the freezing point of phthalaldehyde with ionic liquids to sub-zero temperatures.

Transient Printed Wiring Board on PPHA substrate



Transient LED on sensitized PPHA substrate

Princeton University Dr. Barry Rand Group

Transient UAVs – Flights in August!

DARPA ICARUS Program