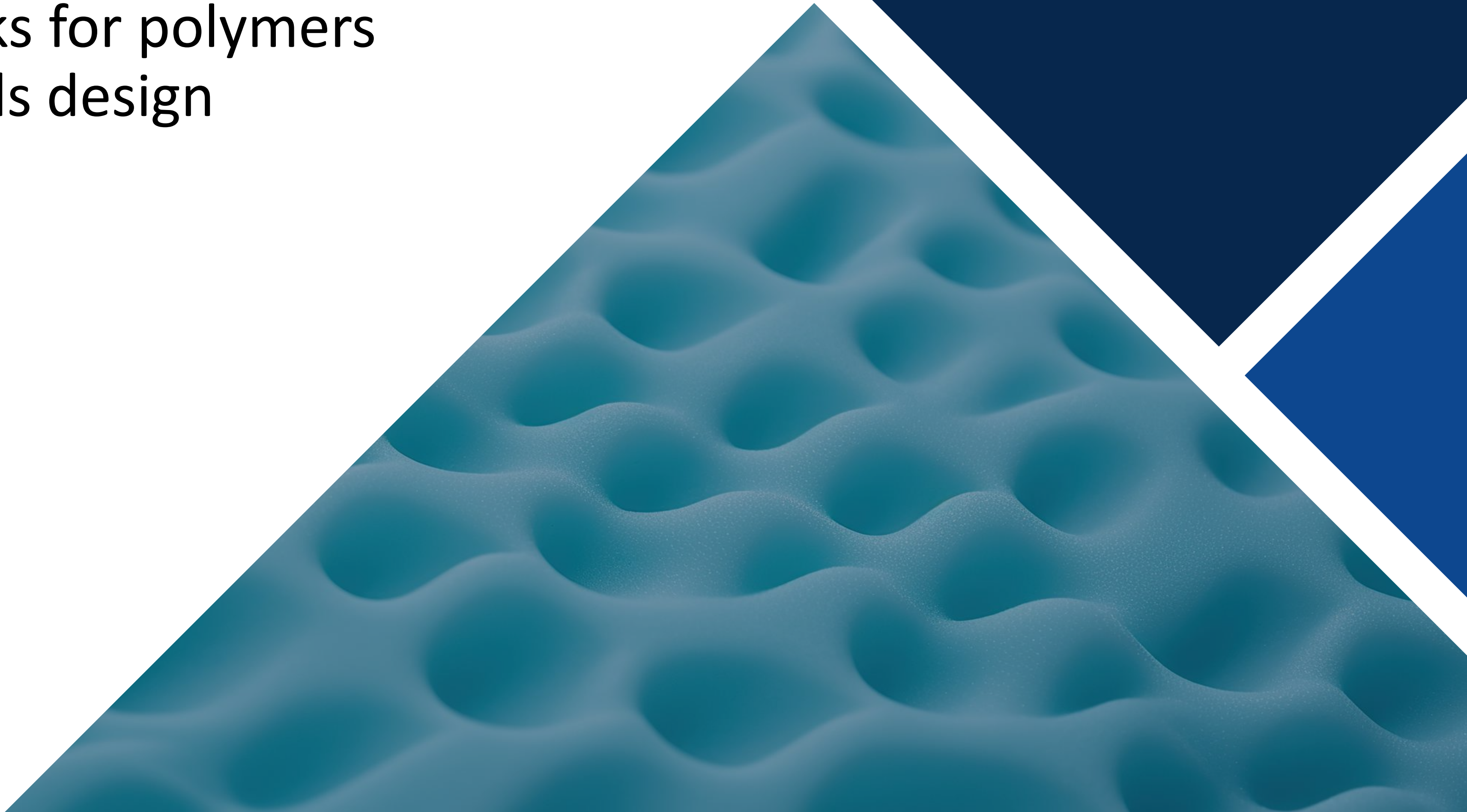
CO_2-based exovinylene cyclic carbonates: versatile building blocks for polymers and advanced materials design

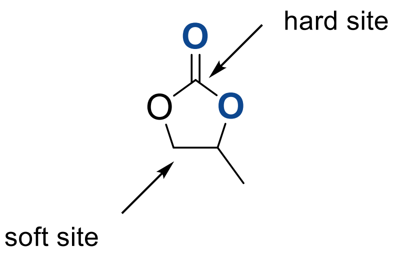
LIÈGE université
FRITCO₂T

September 10th 2025



Polymers from CO_2-based 5-membered cyclic carbonates

Reactivity



HSAB theory of Pearson

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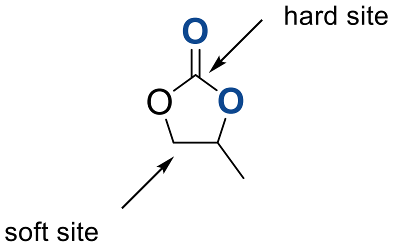

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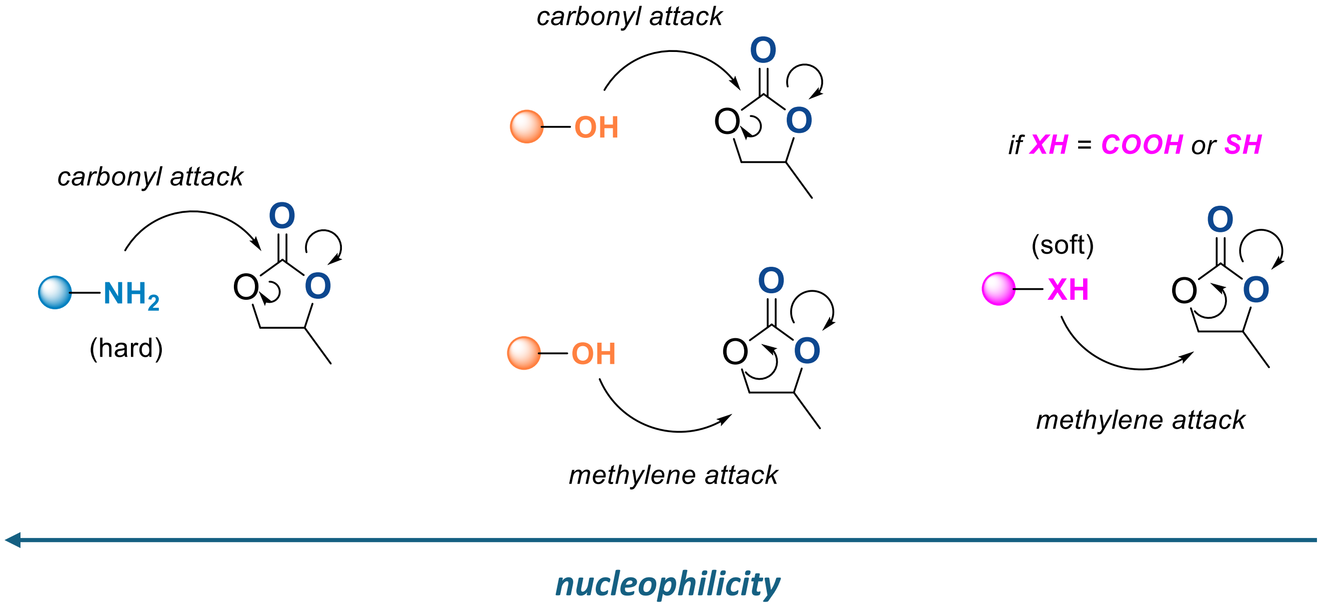

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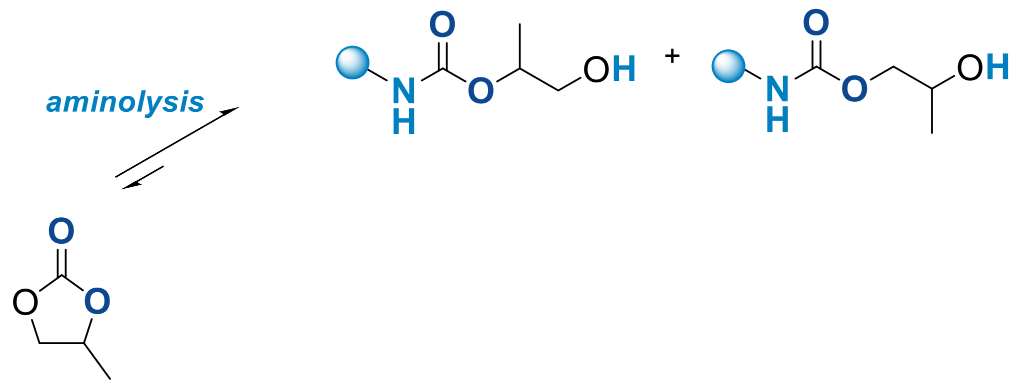

Moderate T (80-140 °C)
2 regioisomers
High conversion (> 95%)
Moderate reactivity

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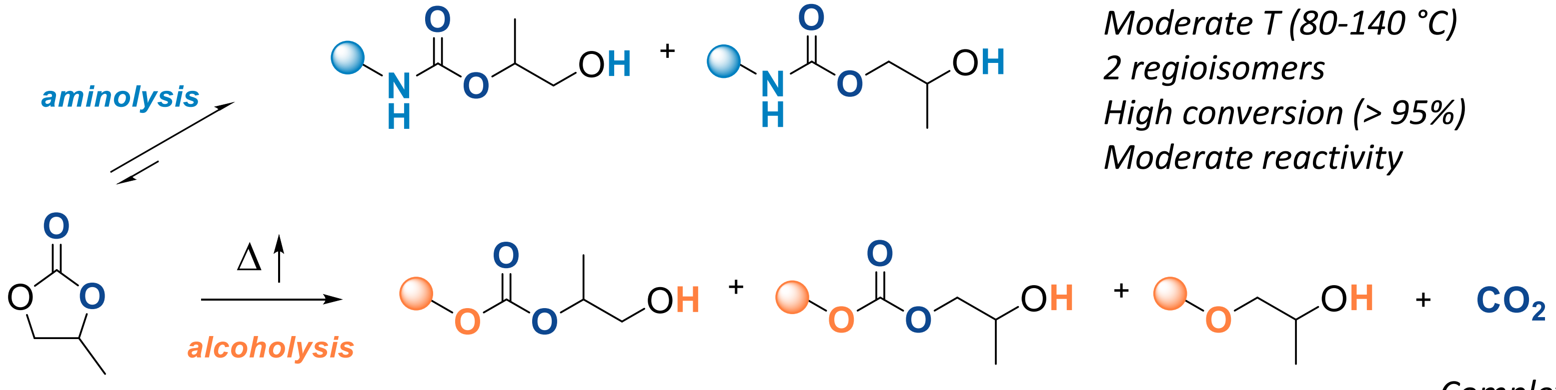

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Complex product mixture
Very high T (> 140-180 °C)

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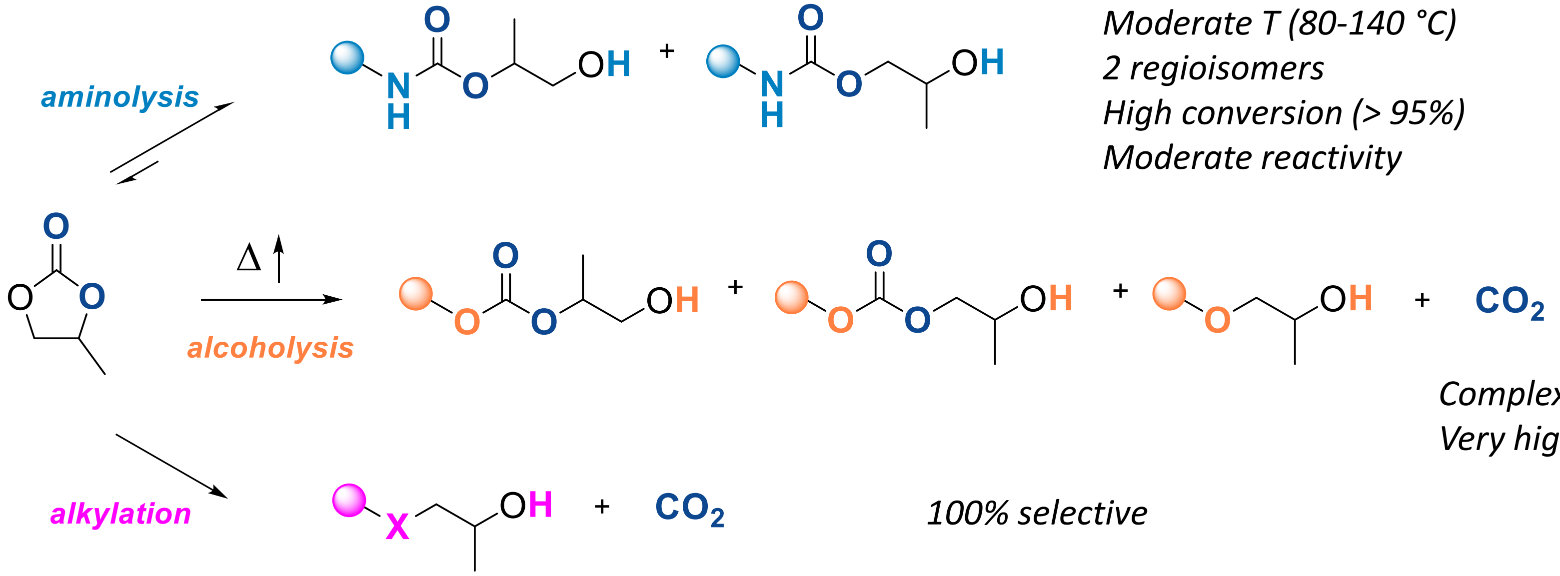


Moderate T (80-140 °C)
2 regioisomers
High conversion (> 95%)
Moderate reactivity

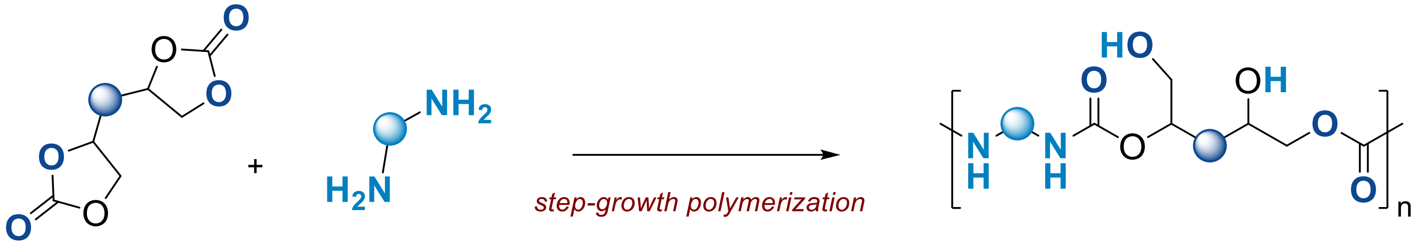
Complex product mixture
Very high T (> 140-180 °C)

100% selective

Polymers from CO_2-based 5-membered cyclic carbonates

Poly(hydroxyurethane)

Isocyanate-free



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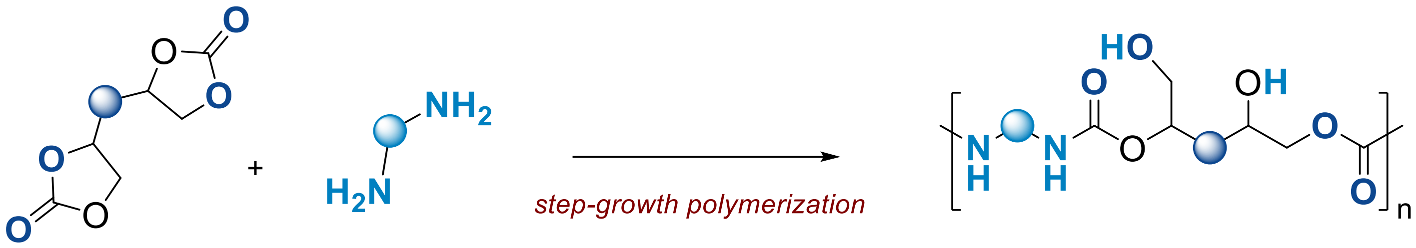
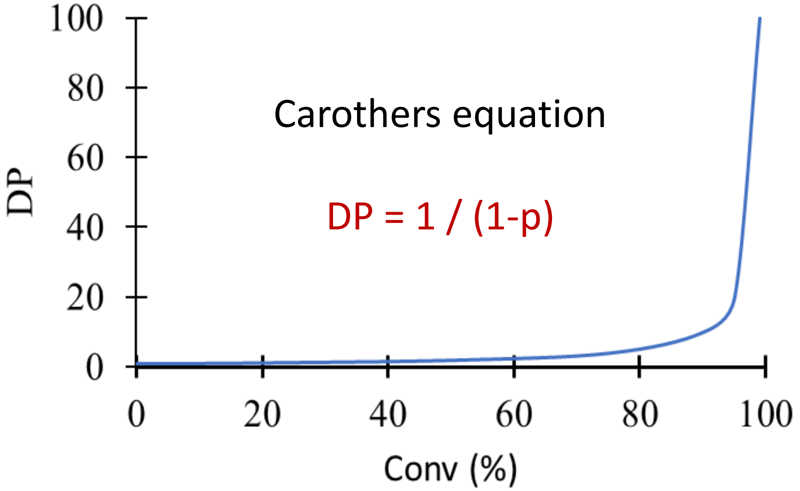


Challeging access to thermoplastics



Prog Polym Sci, 2025, 165, 101968; *Chem. Rev.* 2015, 115, 22, 12407–12439; ChemSusChem, 2019, 12, 3410-3430

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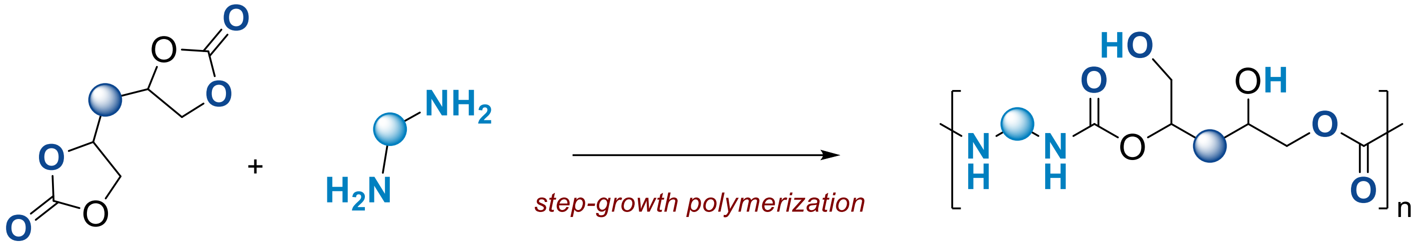
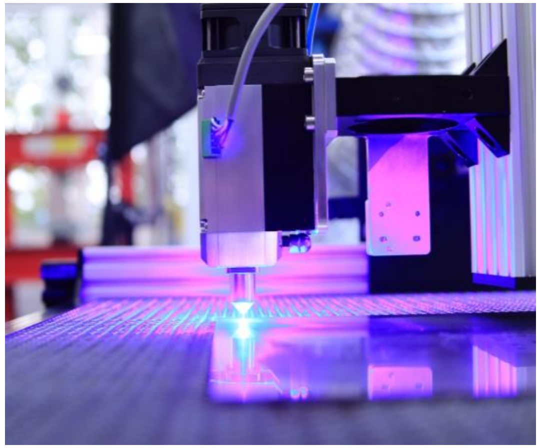
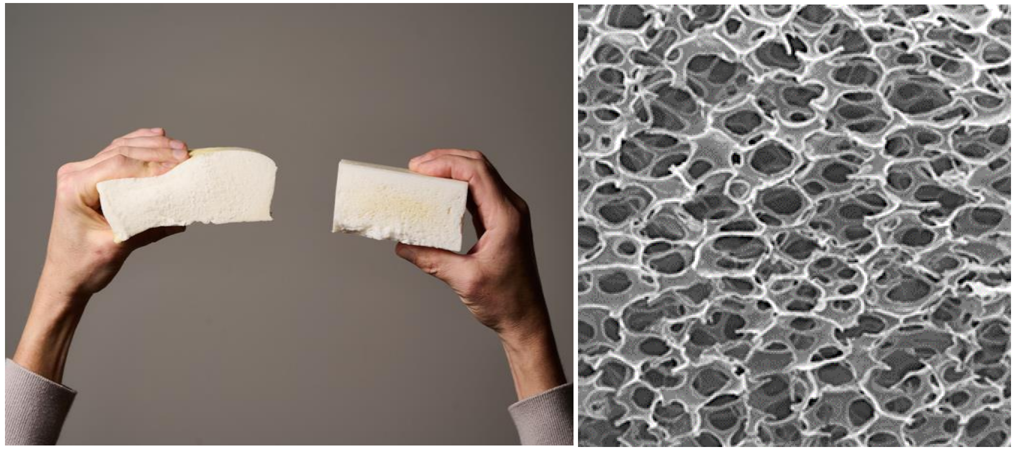
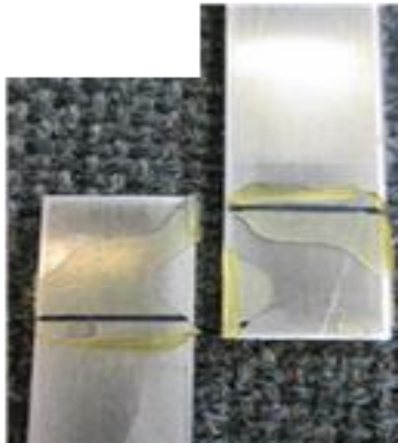


Thermosetting applications





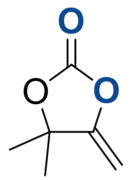


Ink | *r.T. CO_2-self-blown NIPU foams* | *Glue* | *Hydrogel*

Biomacromolecules 2024, 25, 3, 1810–1824; . *Am. Chem. Soc.* 2024, 146, 1, 988–1000; ACIE, 2022, 61, e202213422; *ACS Sustainable Chem. Eng.* 2021, 9, 29, 9541–9562; ACS Appl Mater Interfaces, 2021, 17, 54396-54408

Polymers from CO_2-based exovinylene cyclic carbonates (αCC)

Reactivity of αCC



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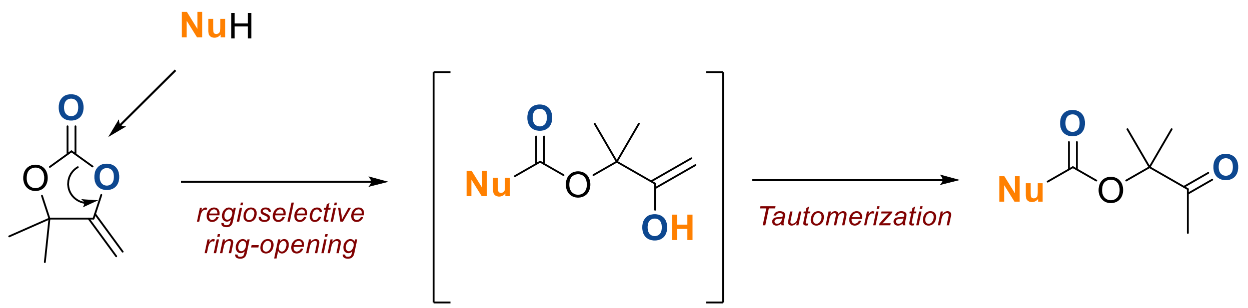

r.T. reactivity
(ultra) Fast reaction
Quantitative
No side-product

ACIE, 2022, 61, e202116066

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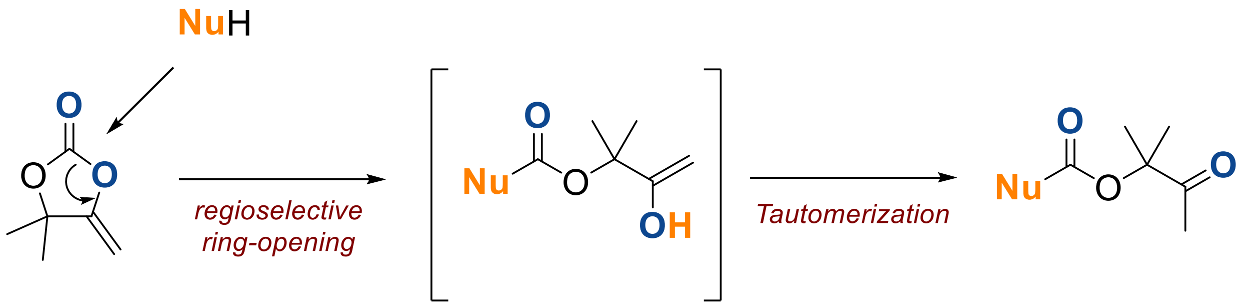

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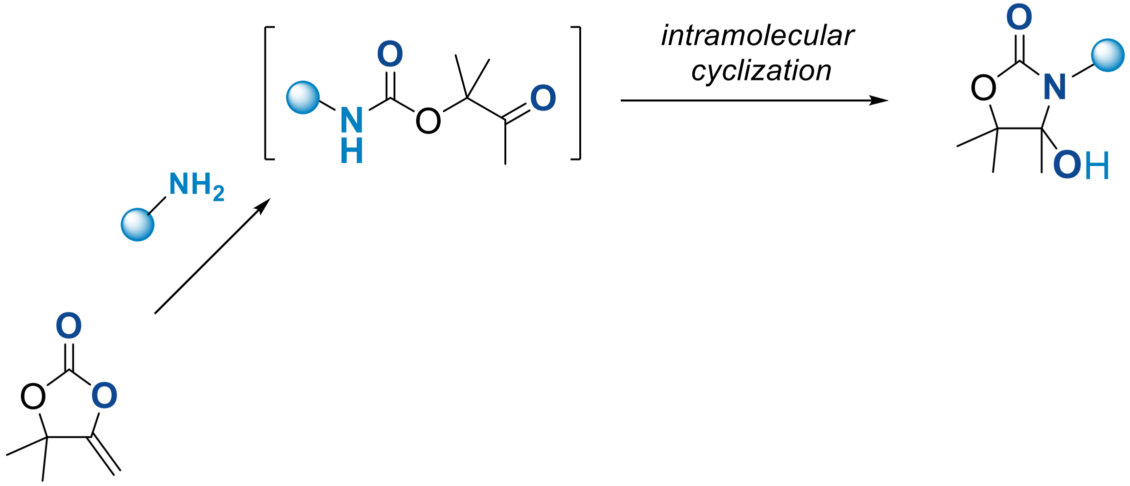

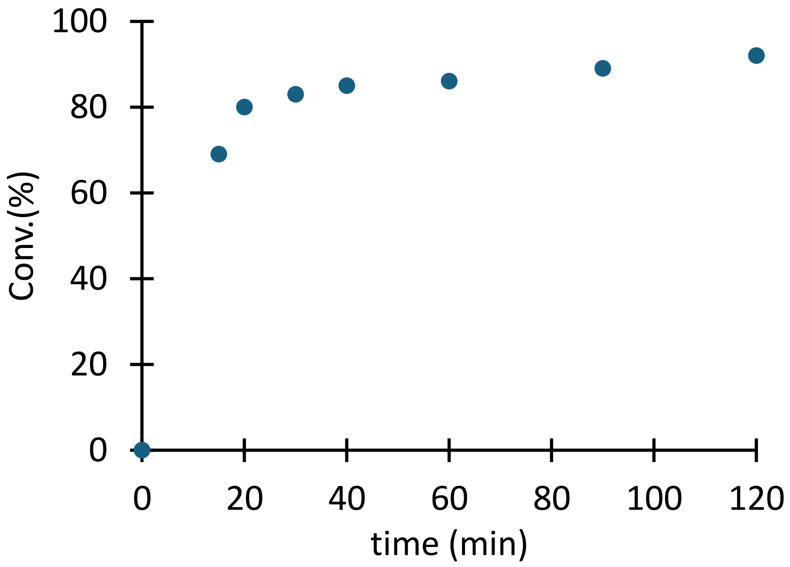

ACIE, 2022, 61, e202116066; ACIE, 2017, 56, 10394-10398, Macromolecules 2020, 53, 15, 6396–6408

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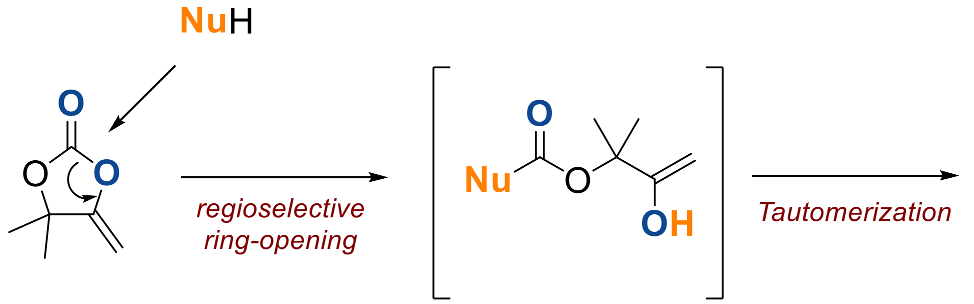

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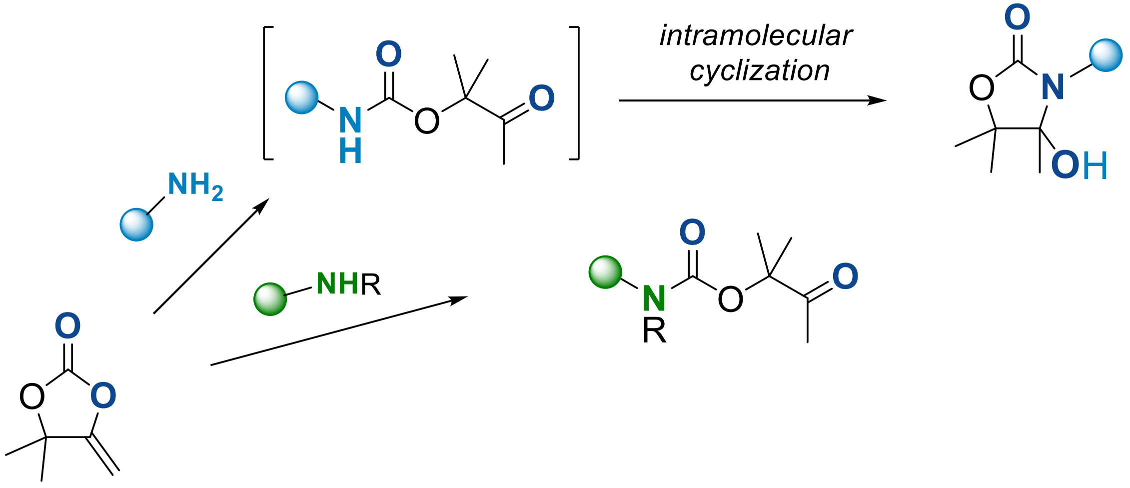

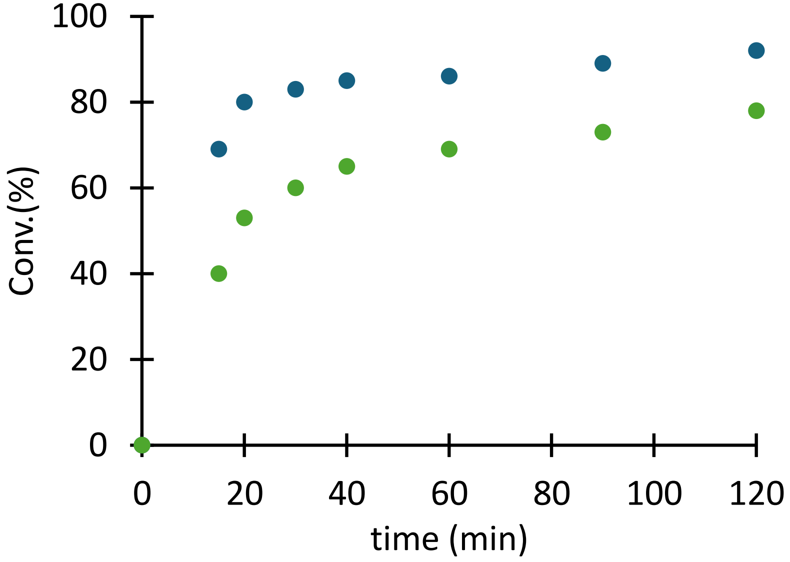

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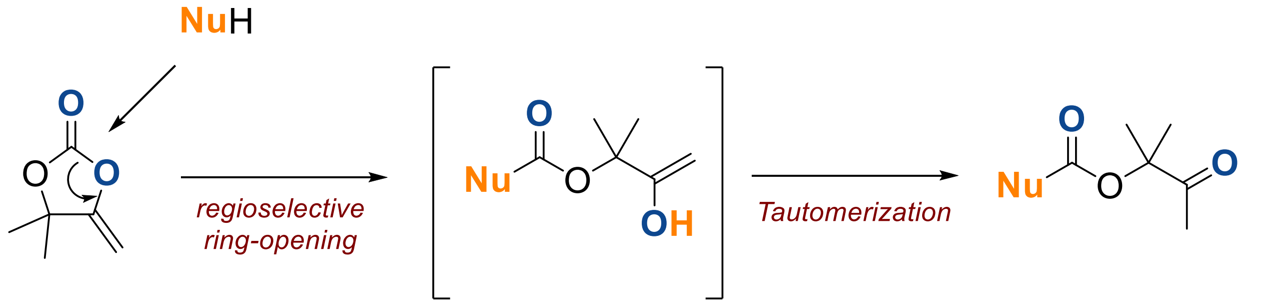

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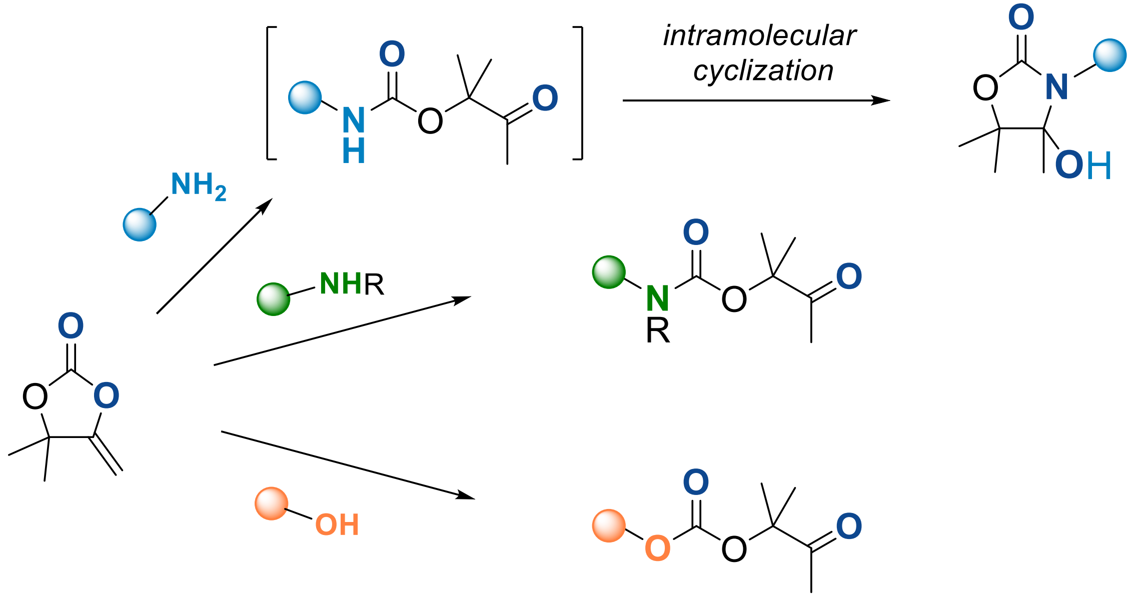

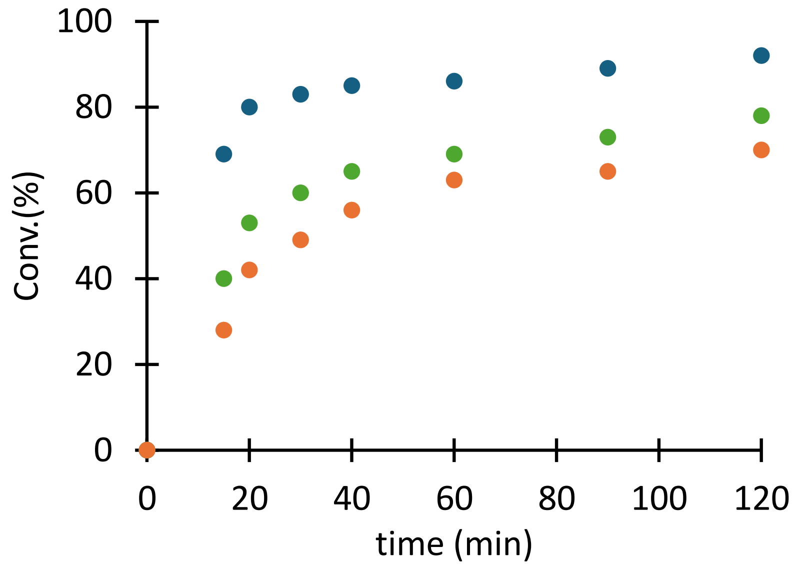

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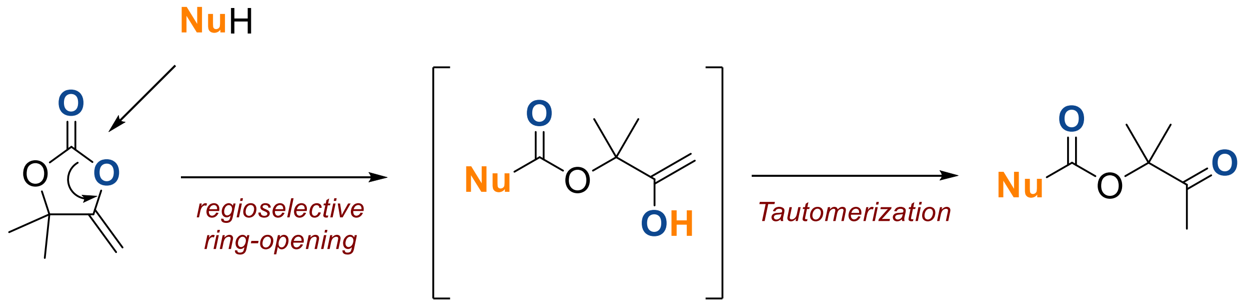

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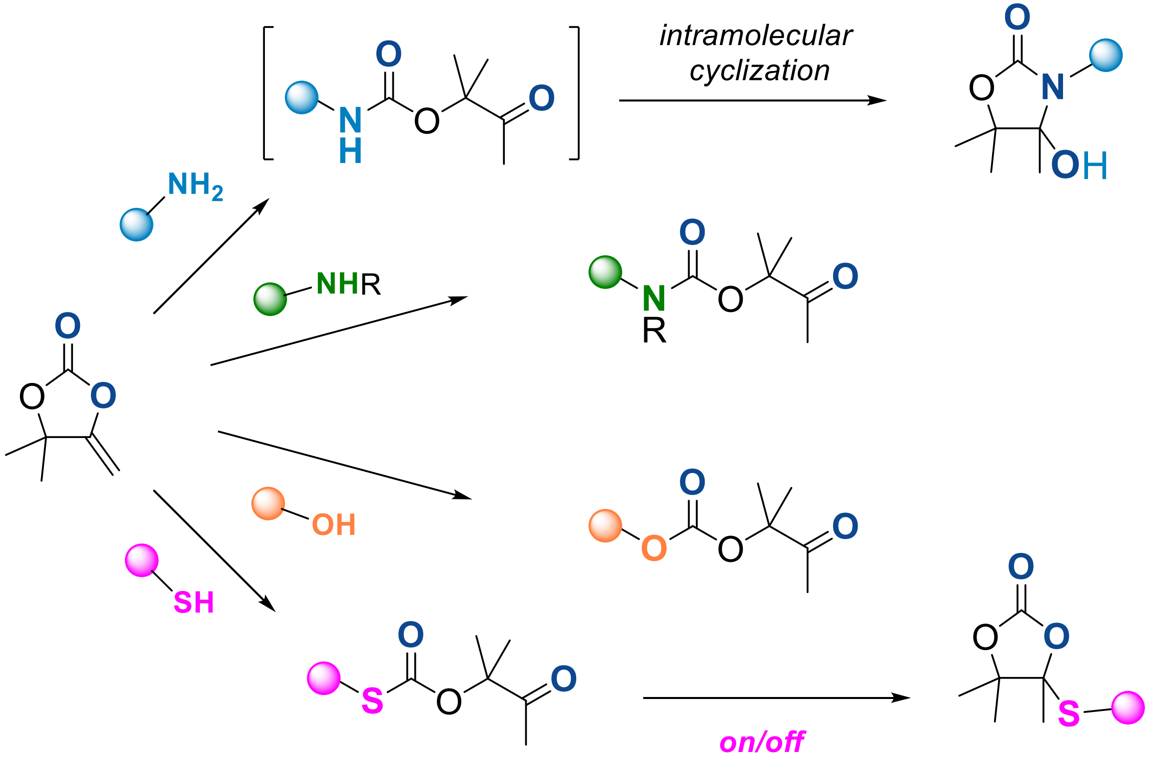

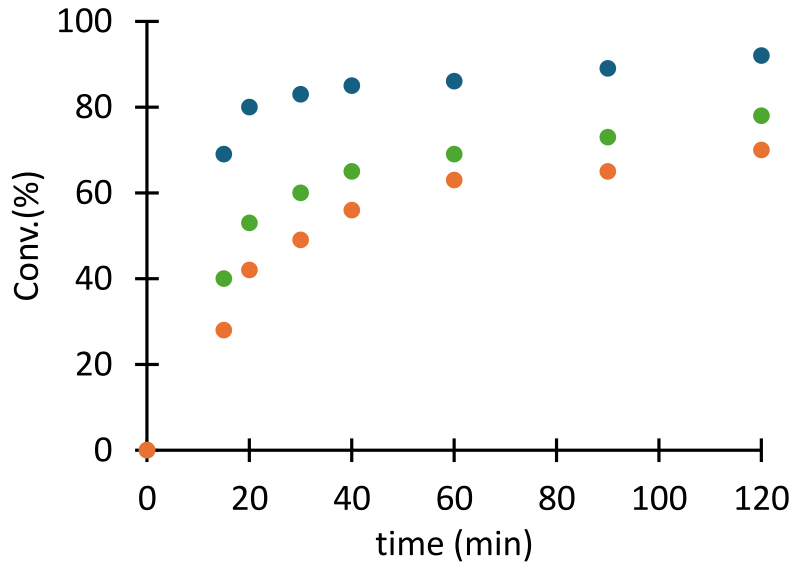

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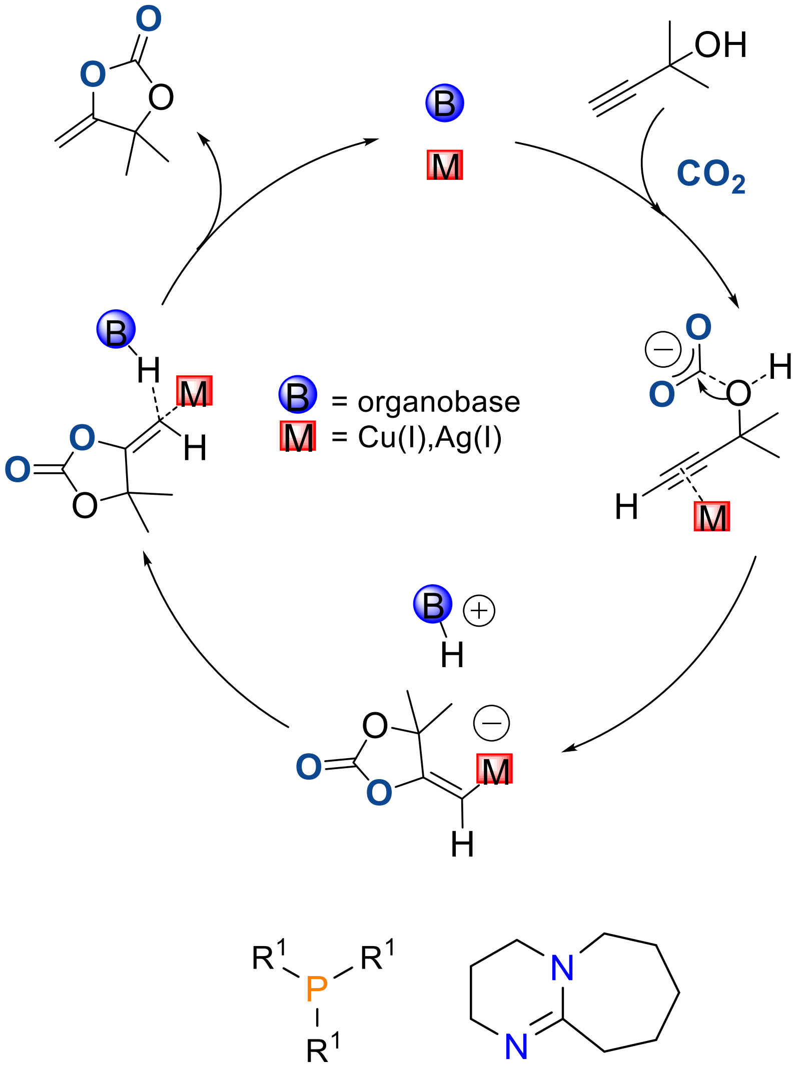
Polymers from CO_2-based exovinylene cyclic carbonates (αCC)

αCC synthesis



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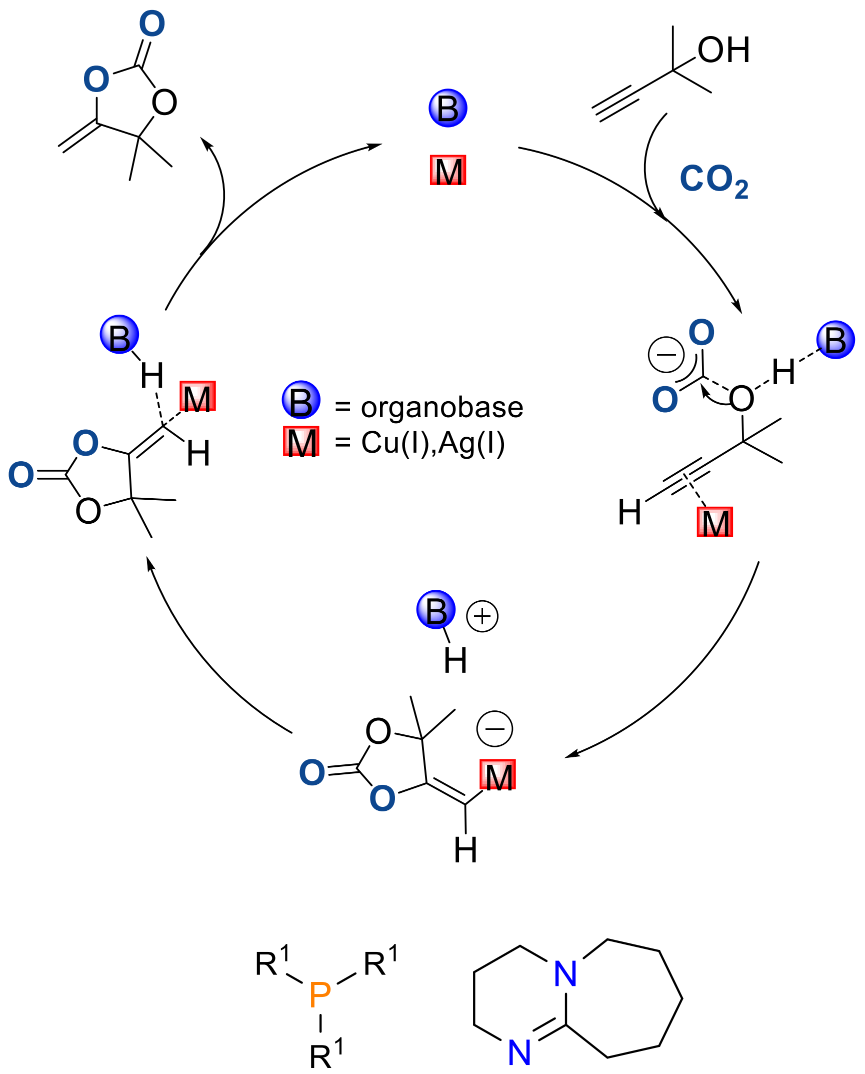
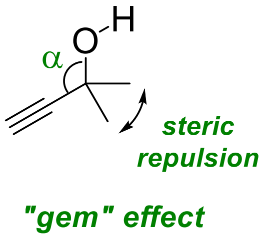


Tertiary propargylic alcohol



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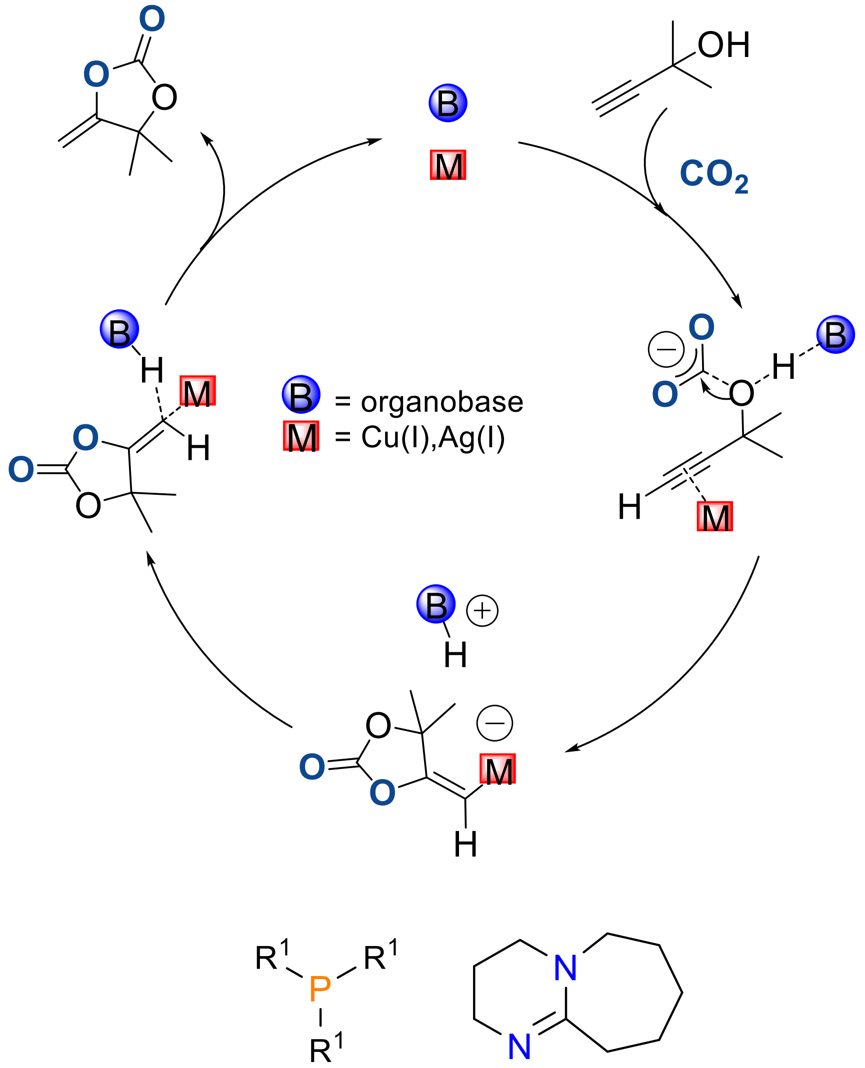

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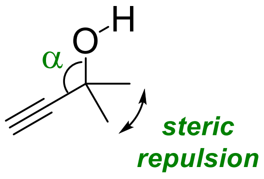
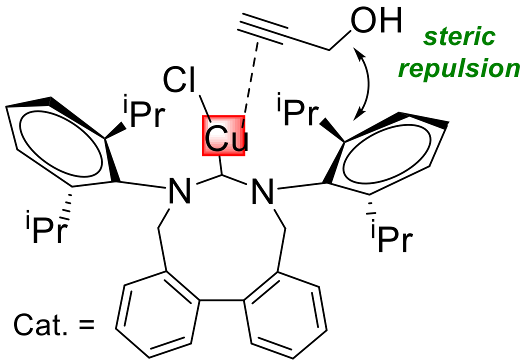


"gem" effect

Primary propargylic alcohol



Angle compression by bulky catalyst

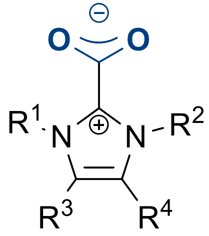
Combined with a weak base (CsF)

ACIE, 2022, 61, e202116066; Green Chem., 2021,23, 889-897

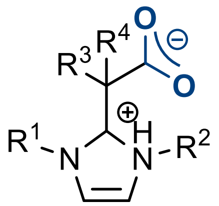
Polymers from CO_2-based exovinylene cyclic carbonates (αCC)

αCC synthesis

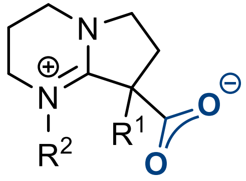
NHC-CO_2

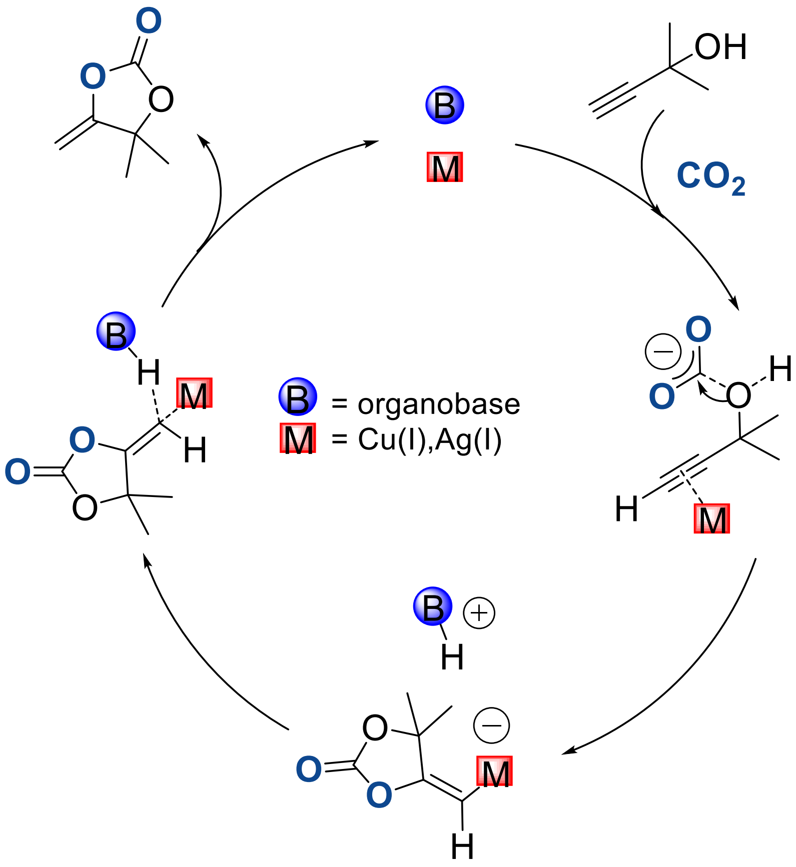


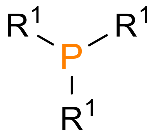
NHO-CO_2

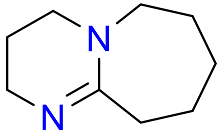


DBN-CO_2

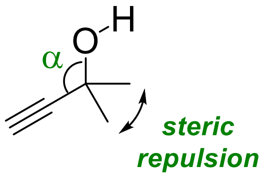








Tertiary propargylic alcohol



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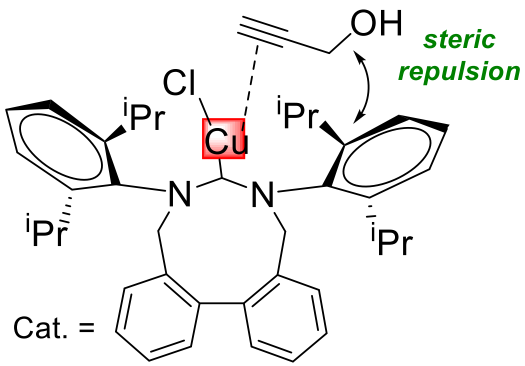

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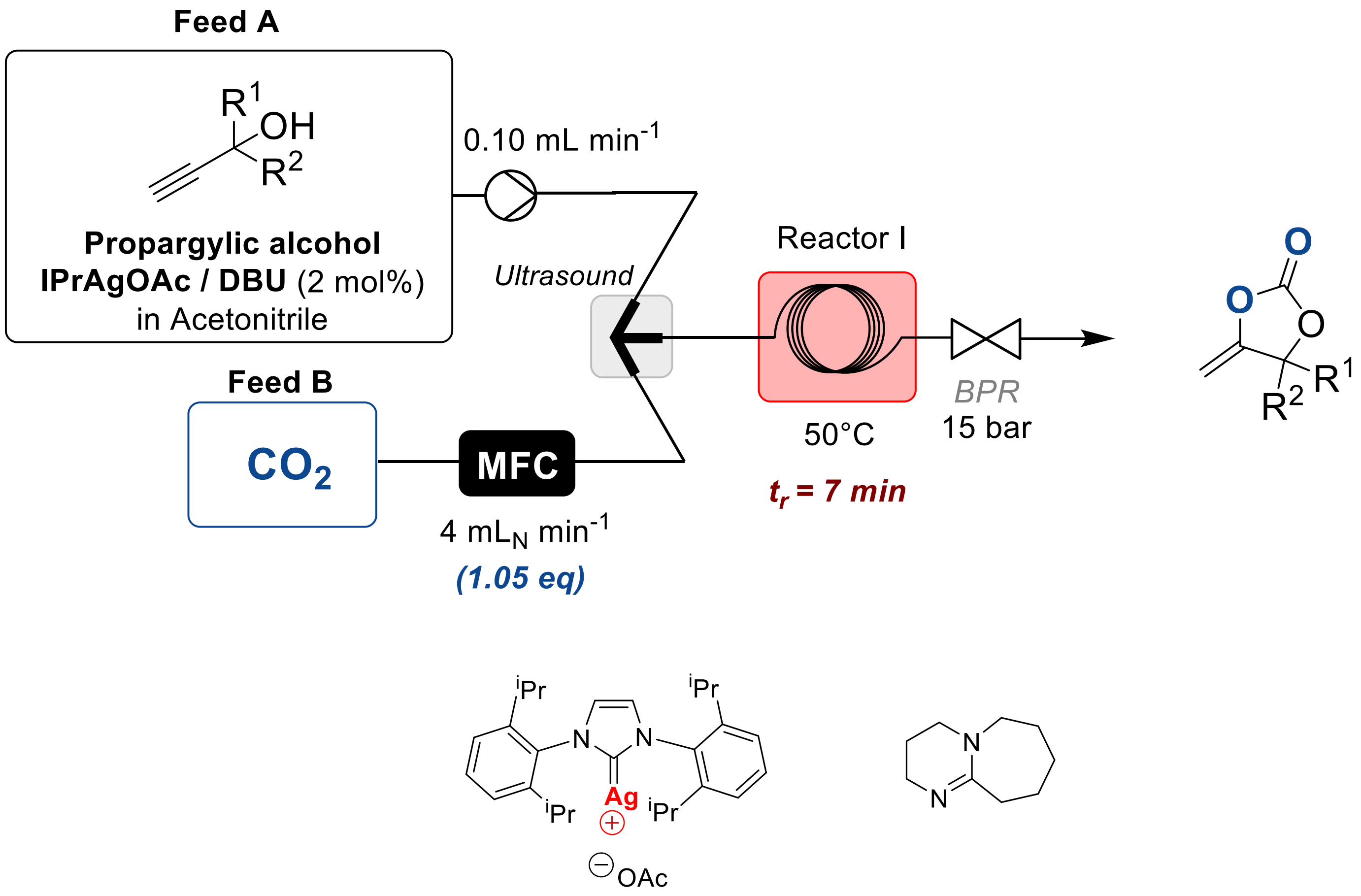
Flow synthesis of αCC



Green Chem., 2020, 22, 1553-1558; Green Chem., 2025,27, 722-730

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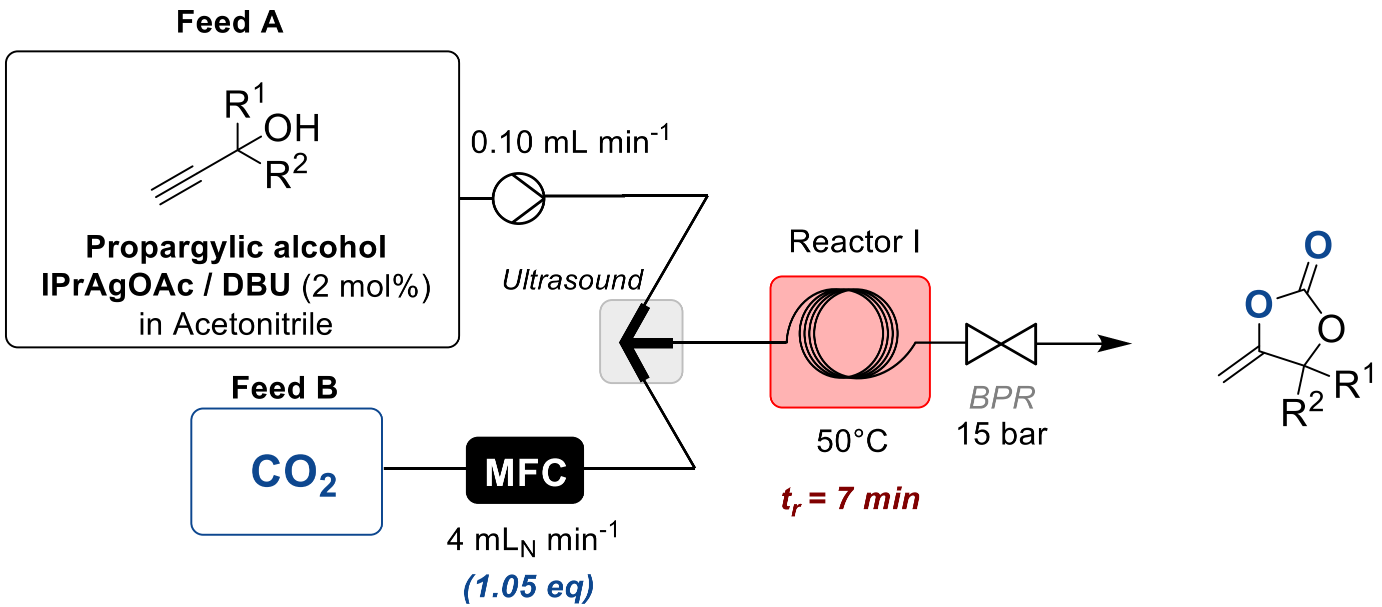
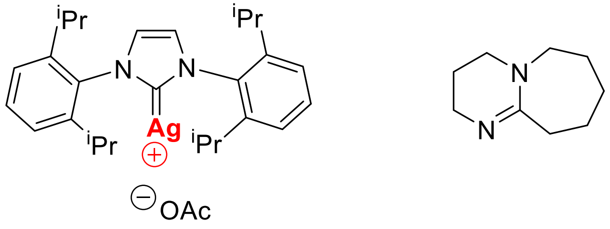
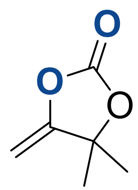
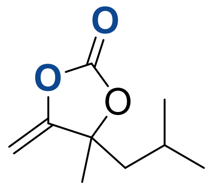


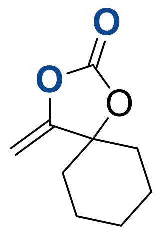




Conv.: 99%
Select.: >99%
Prod.: 31 g day^{-1}
STY: 0.76 kg h^{-1} L^{-1}



Conv.: 99%
Select.: >99%
Prod.: 41 g day^{-1}
STY: 1.01 kg h^{-1} L^{-1}



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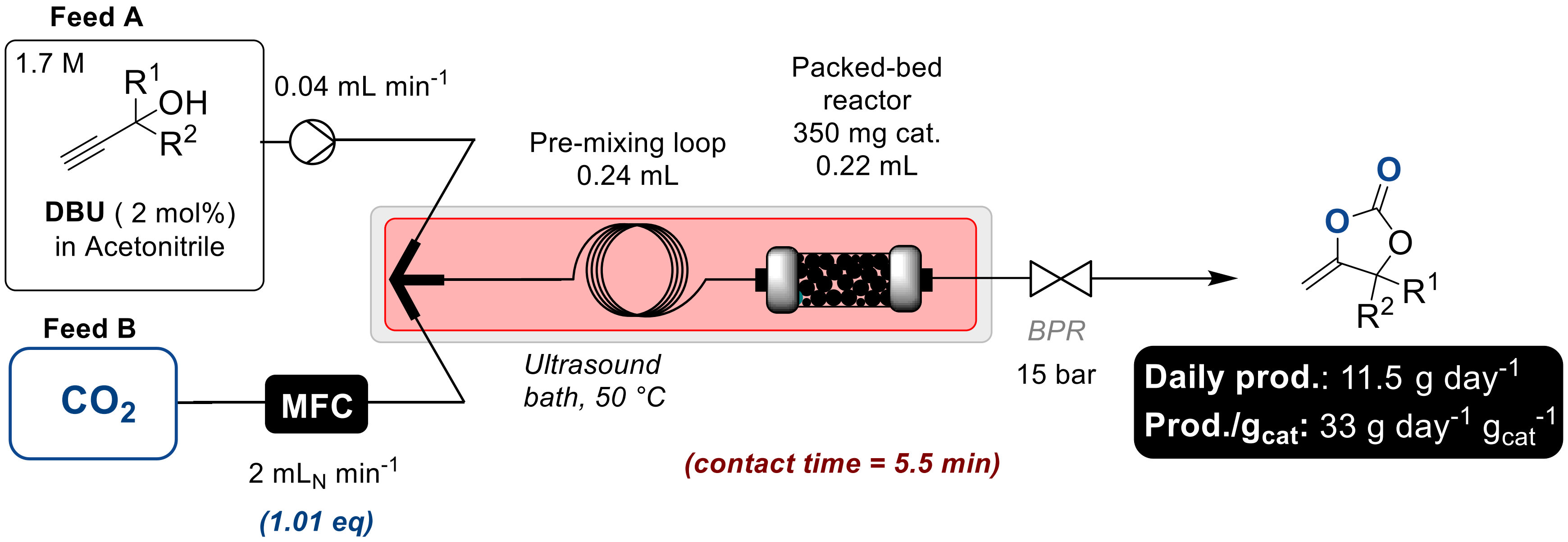
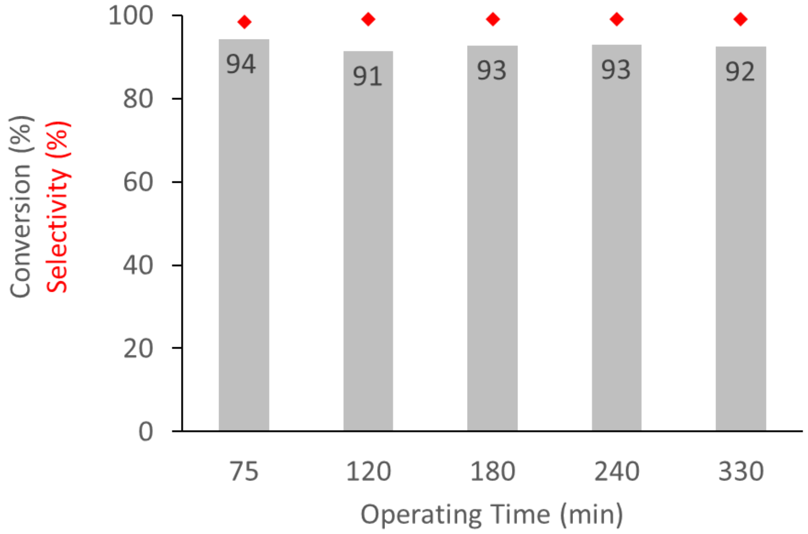
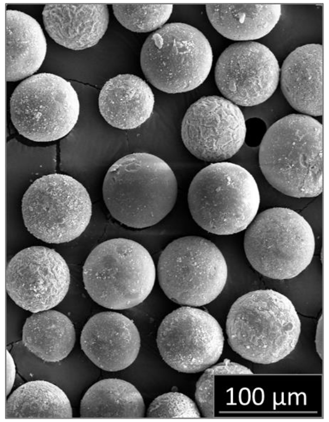
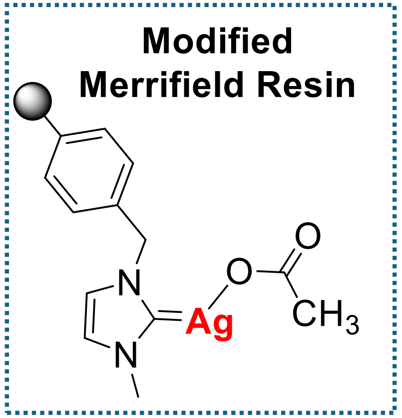




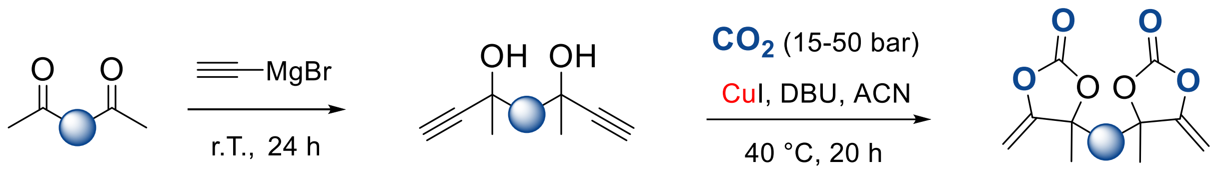




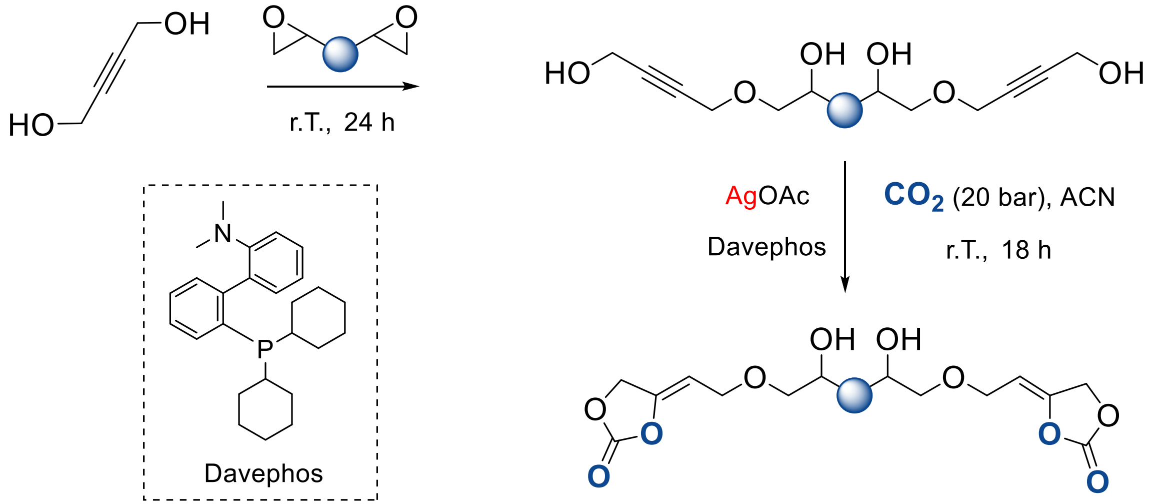
Green Chem., 2020, 22, 1553-1558; Green Chem., 2025,27, 722-730

Polymers from CO_2-based exovinylene cyclic carbonates (αCC)

Design of bis-αCC



Carboxylative cyclization :



Green Chem., 2020, 22, 1553-1558; ACIE, 2022, 61, e202116066; ACIE, 2022, 61, e202116066

Polymers from CO_2-based exovinylene cyclic carbonates (αCC)

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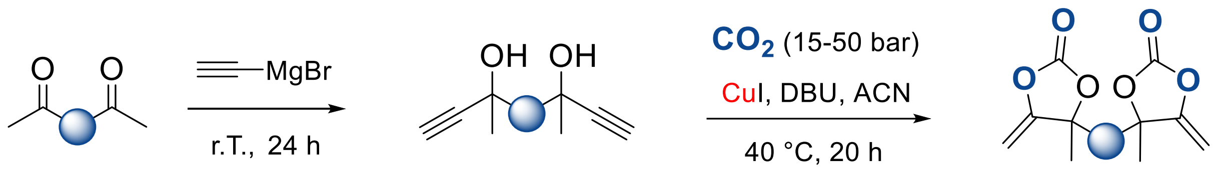

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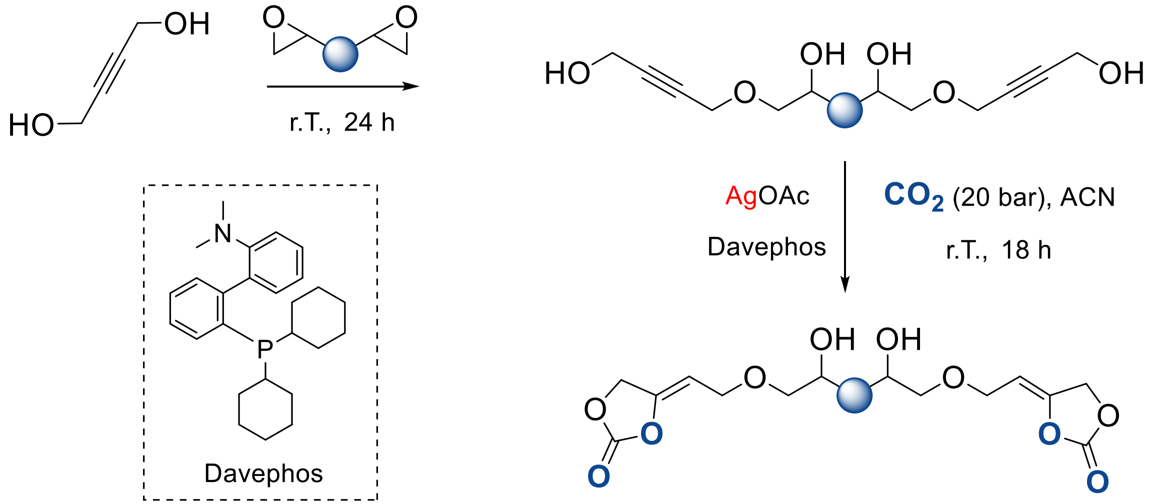
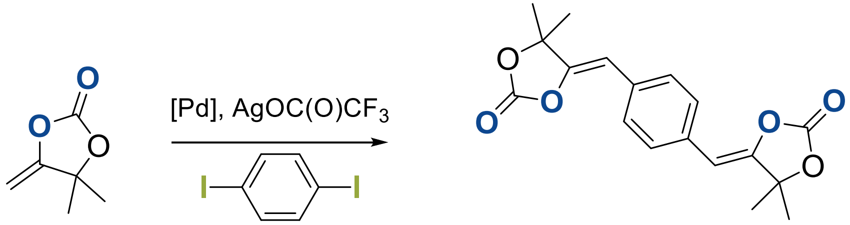


Heck coupling :

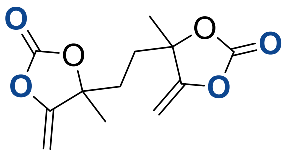


Green Chem., 2020, 22, 1553-1558; ACIE, 2022, 61, e202116066; ACIE, 2017, 56, 10394-10398

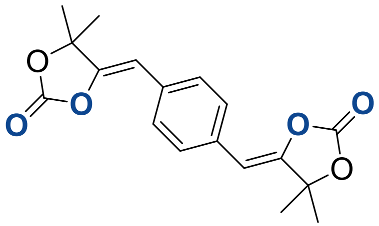
Polymers from CO_2-based exovinylene cyclic carbonates (αCC)

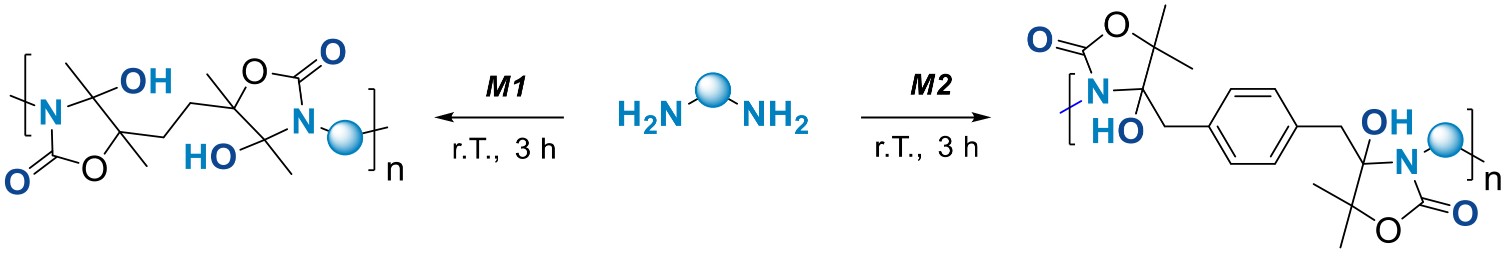
Polymers from bis-αCC

***M1* =**



***M2* =**





Mw < 40,000 g/mol

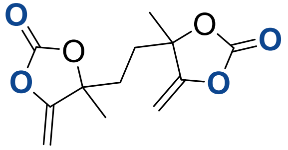
Mw < 77,000 g/mol

ACIE, 2022, 61, e202116066; ACIE, 2017, 56, 10394-10398 66

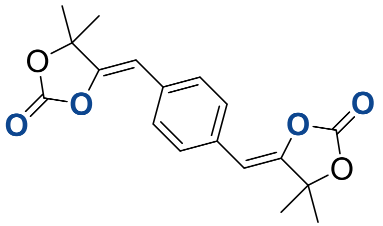
Polymers from CO_2-based exovinylene cyclic carbonates (αCC)

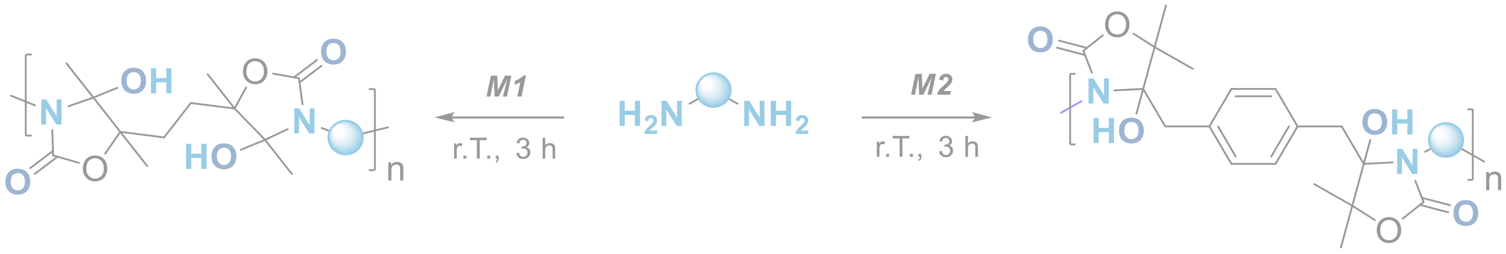
Polymers from bis-αCC

***M1* =**



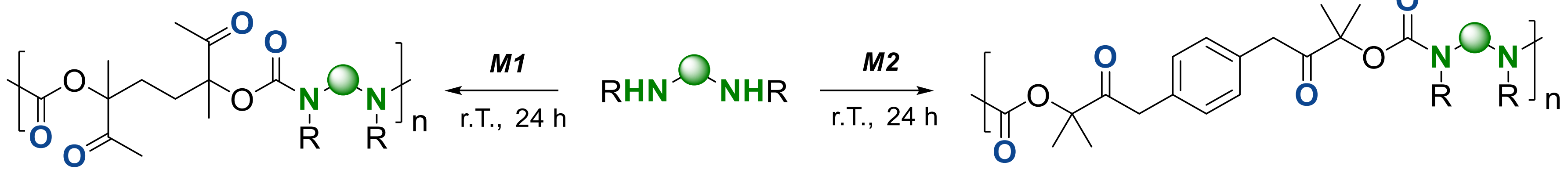
***M2* =**





Mw < 40,000 g/mol

Mw < 77,000 g/mol



7000 g/mol < Mw < 16,000 g/mol (with DBU)

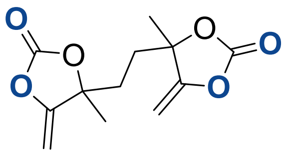
40,000 g/mol < Mw < 73,000 g/mol (with DBU)

ACIE, 2022, 61, e202116066; ACIE, 2017, 56, 10394-10398 66

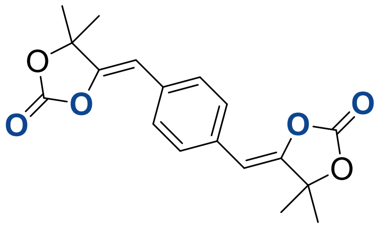
Polymers from CO_2-based exovinylene cyclic carbonates (αCC)

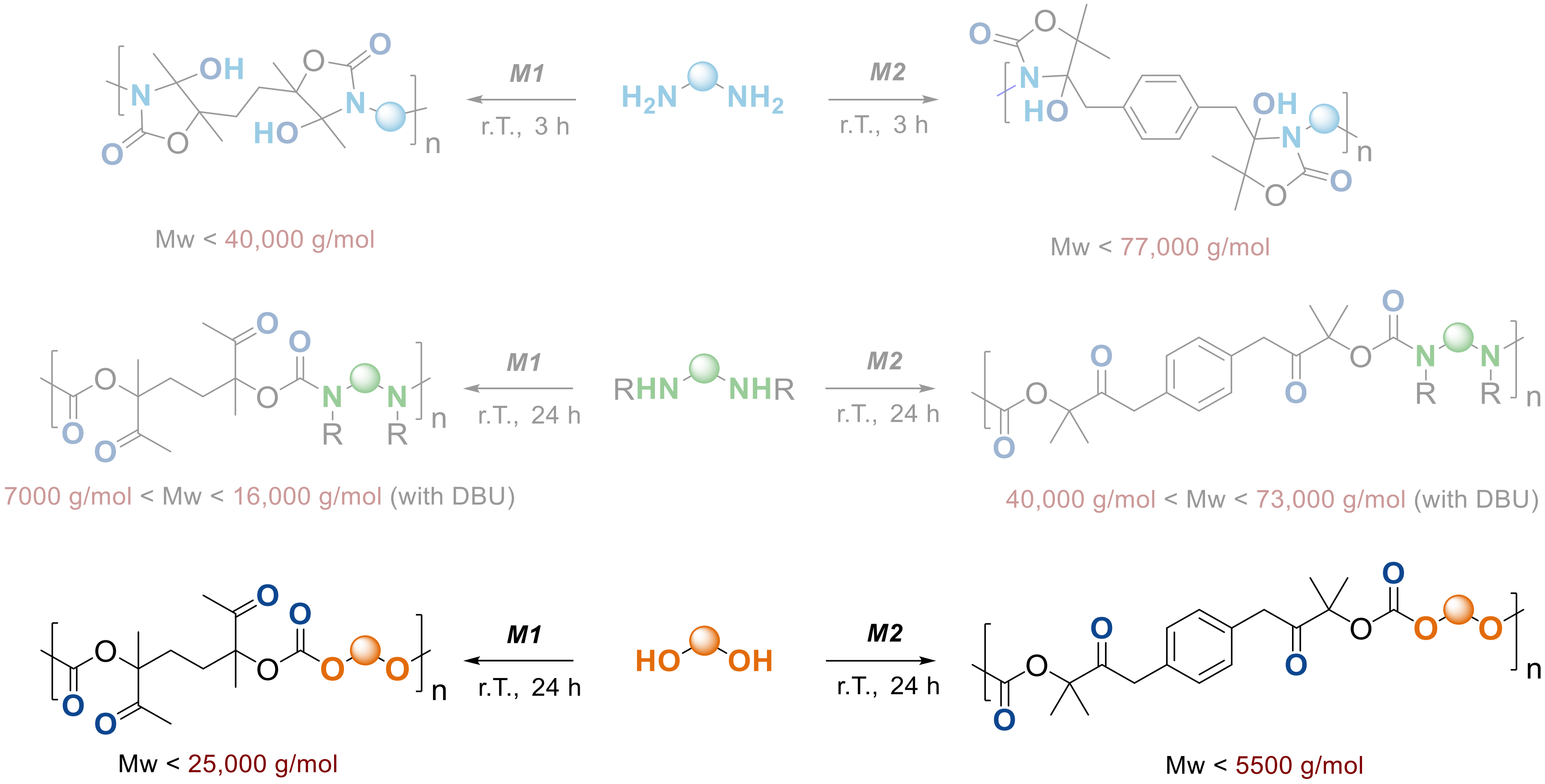
Polymers from bis-αCC

***M1* =**



***M2* =**



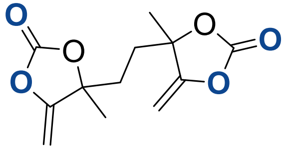


ACIE, 2022, 61, e202116066; ACIE, 2017, 56, 10394-10398 66

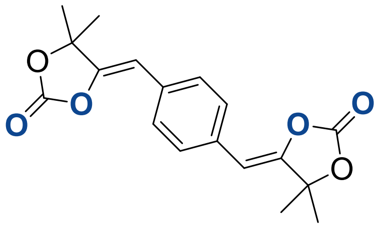
Polymers from CO_2-based exovinylene cyclic carbonates (αCC)

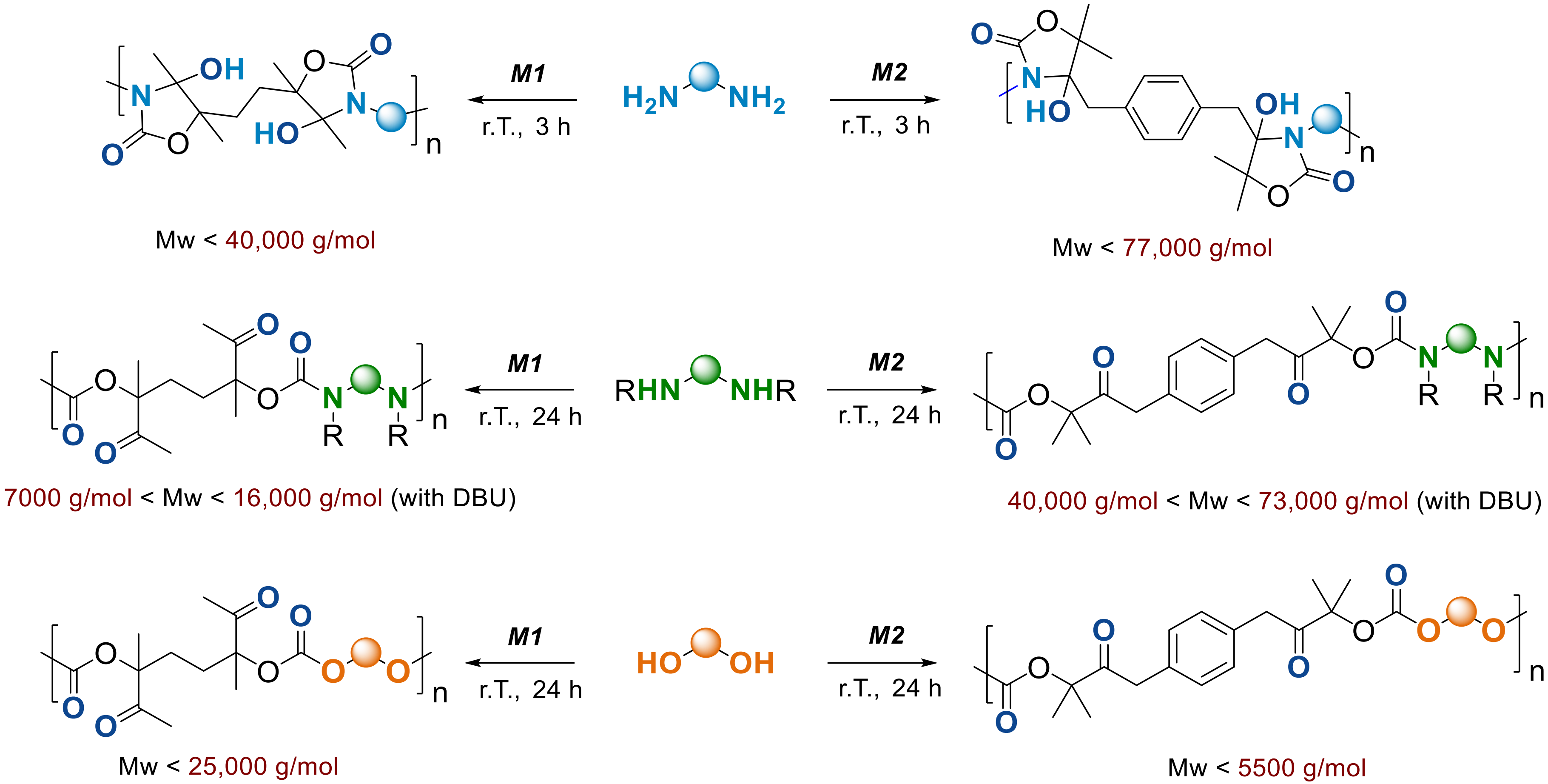
Polymers from bis-αCC

***M1* =**



***M2* =**

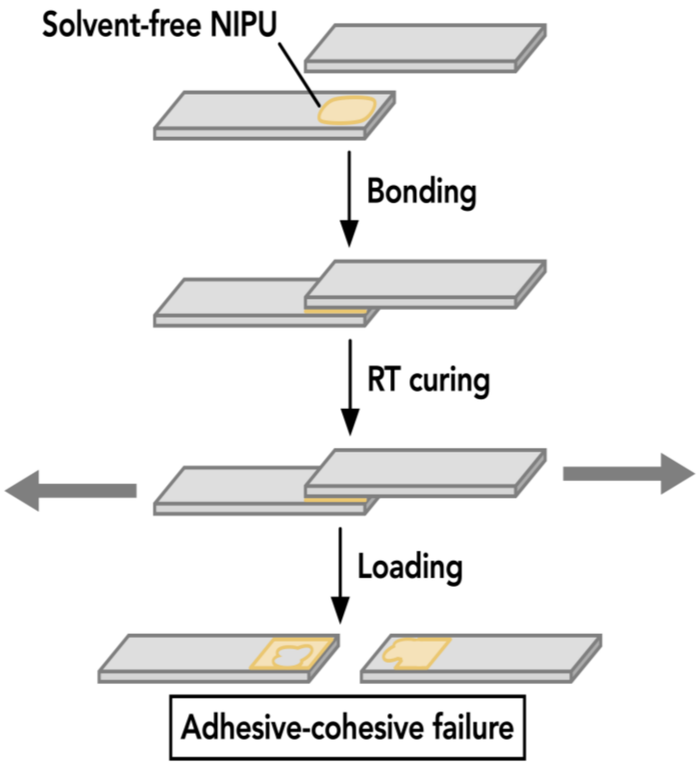




ACIE, 2022, 61, e202116066; ACIE, 2017, 56, 10394-10398 66

Advanced materials Design

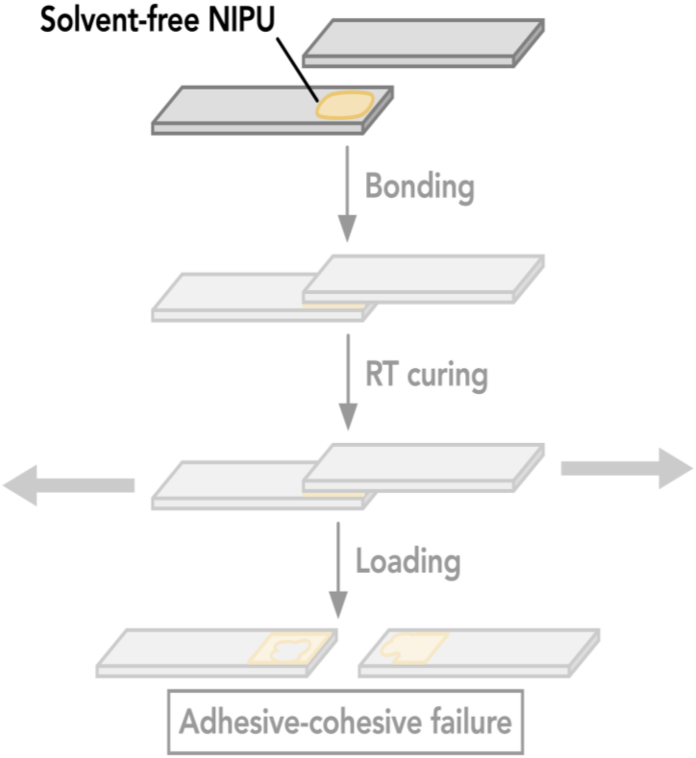
Poly(oxazolidinone) adhesives



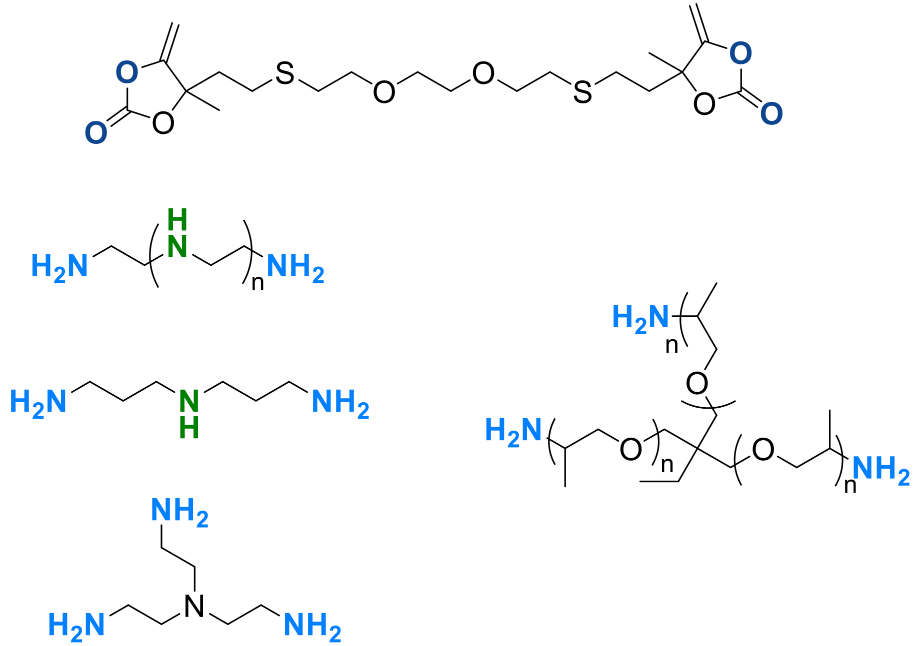
Macromolecules 2025, 58, 13, 6452–6465

Advanced materials Design

Poly(oxazolidinone) adhesives



Thermosetting adhesive formulation : pot-life



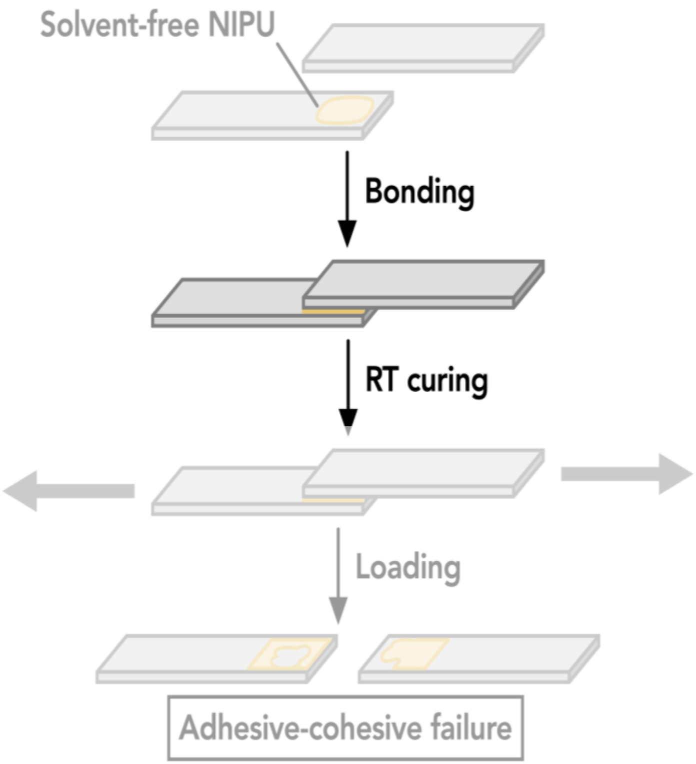
Instant gel formation ← → Moderate reactivity

Gel time (r.T.)	Few sec.	> 10 h

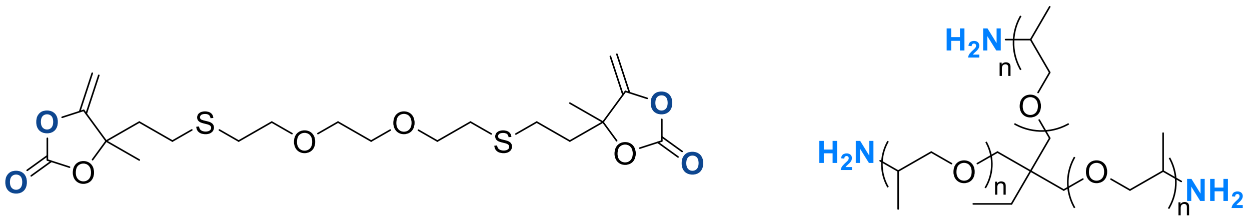
Macromolecules 2025, 58, 13, 6452–6465

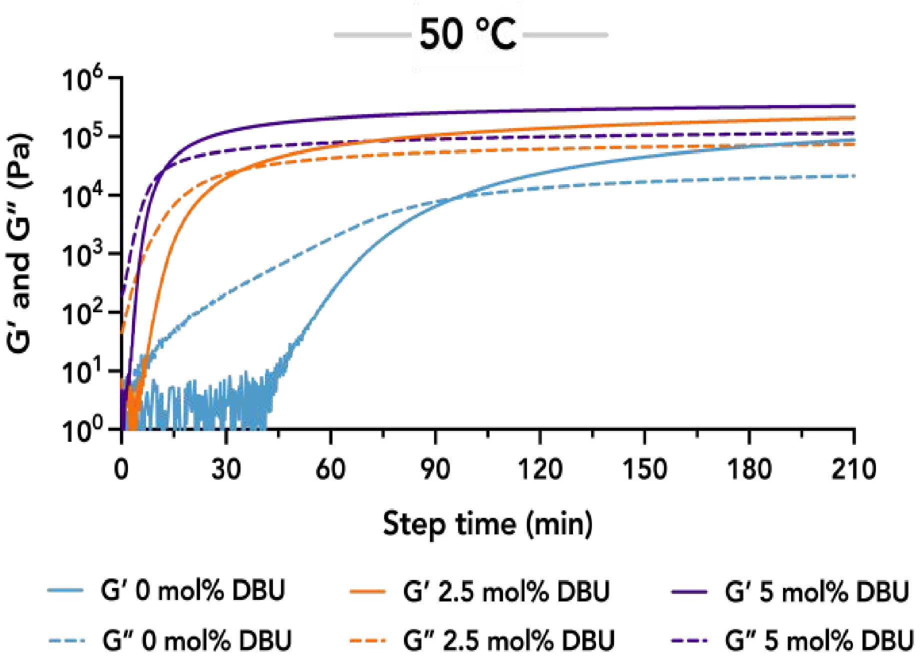
Advanced materials Design

Poly(oxazolidinone) adhesives



Rheology



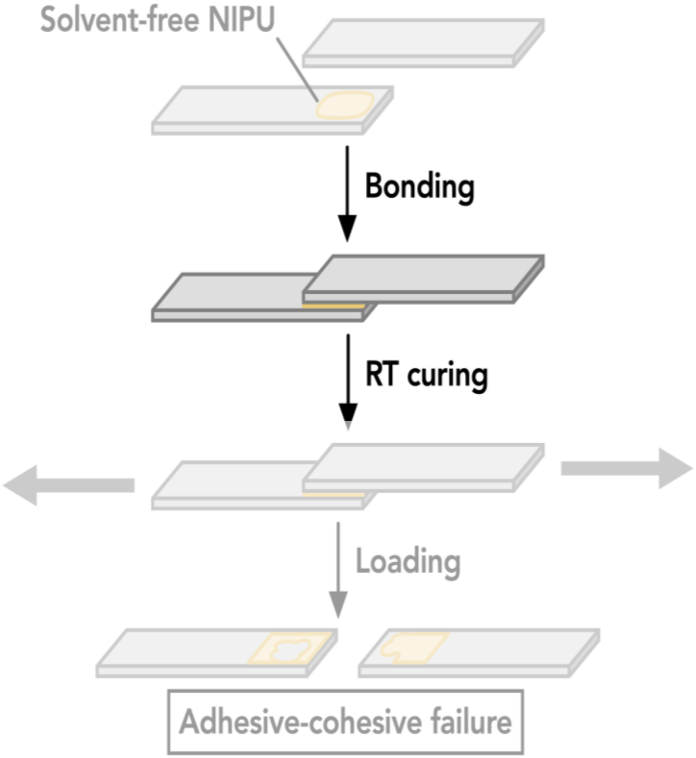


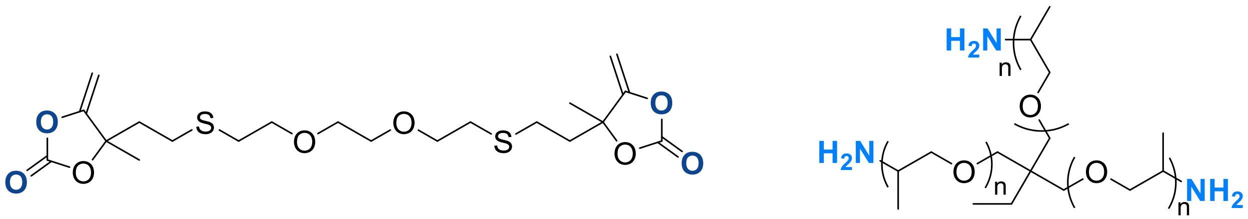
Macromolecules 2025, 58, 13, 6452–6465

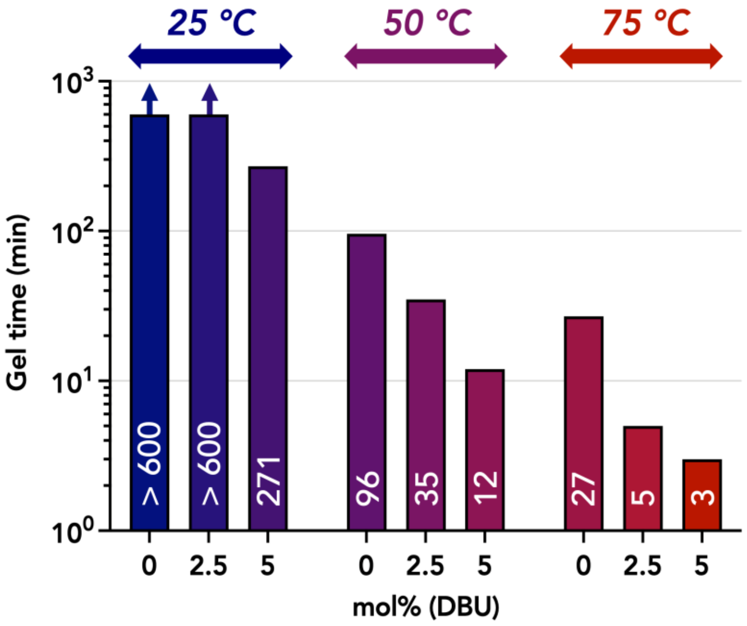
Advanced materials Design

Rheology

Poly(oxazolidinone) adhesives



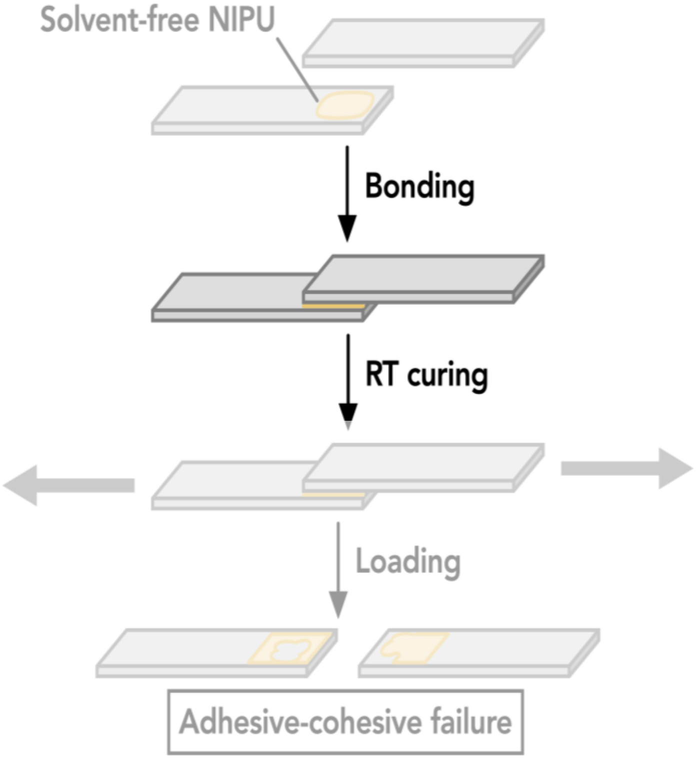




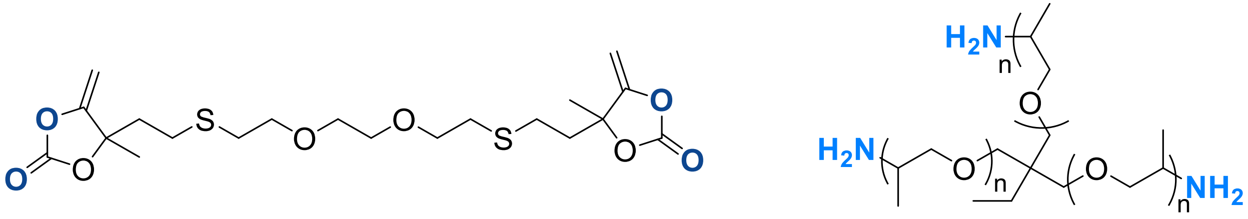
Macromolecules 2025, 58, 13, 6452–6465

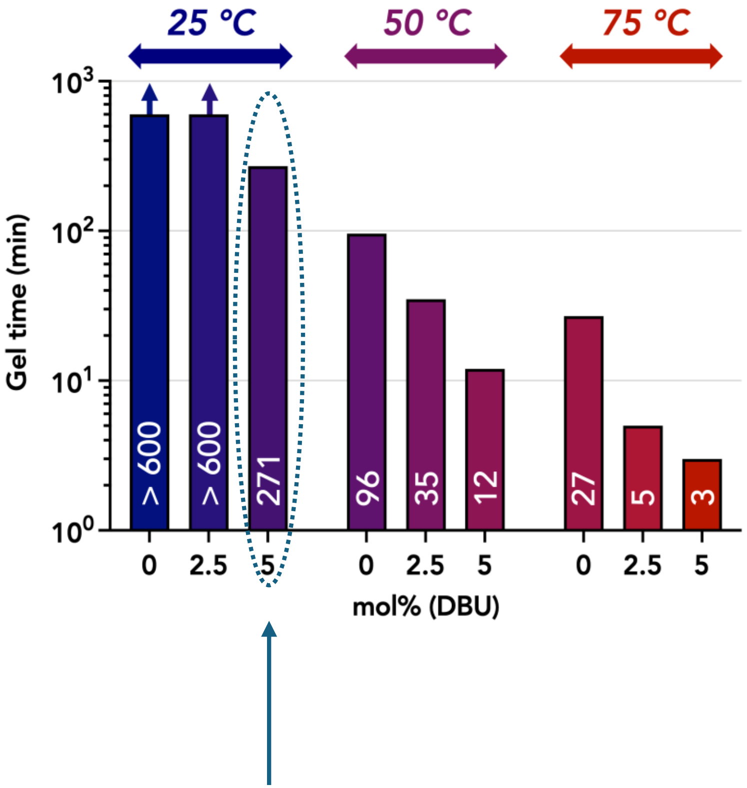
Advanced materials Design

Poly(oxazolidinone) adhesives



Rheology

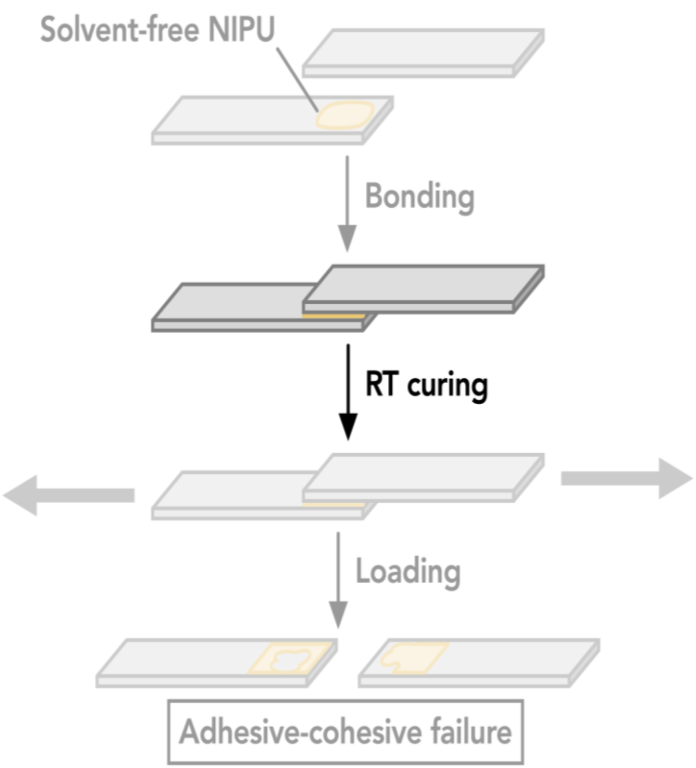




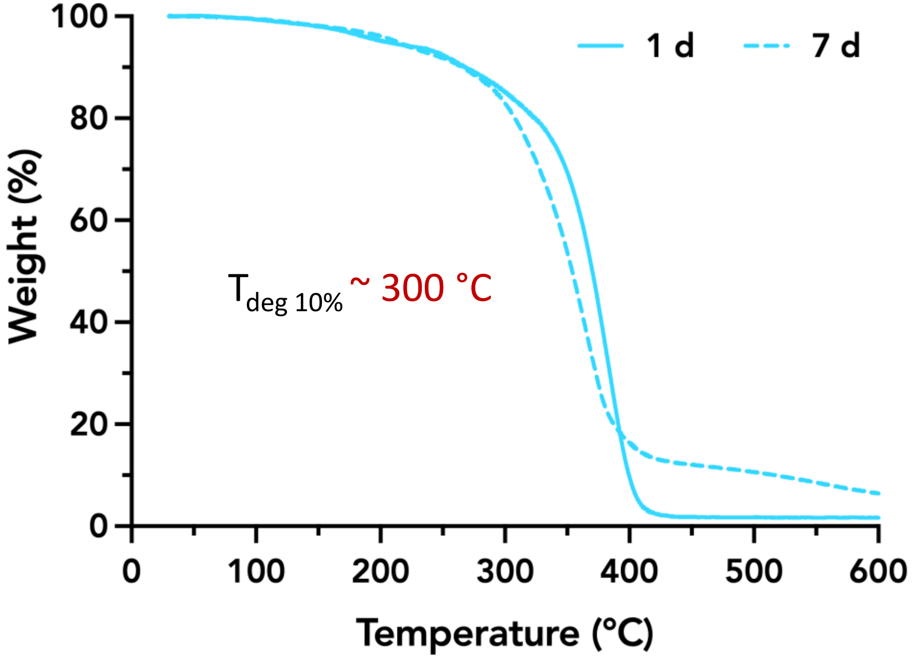
Macromolecules 2025, 58, 13, 6452–6465

Advanced materials Design

Poly(oxazolidinone) adhesives



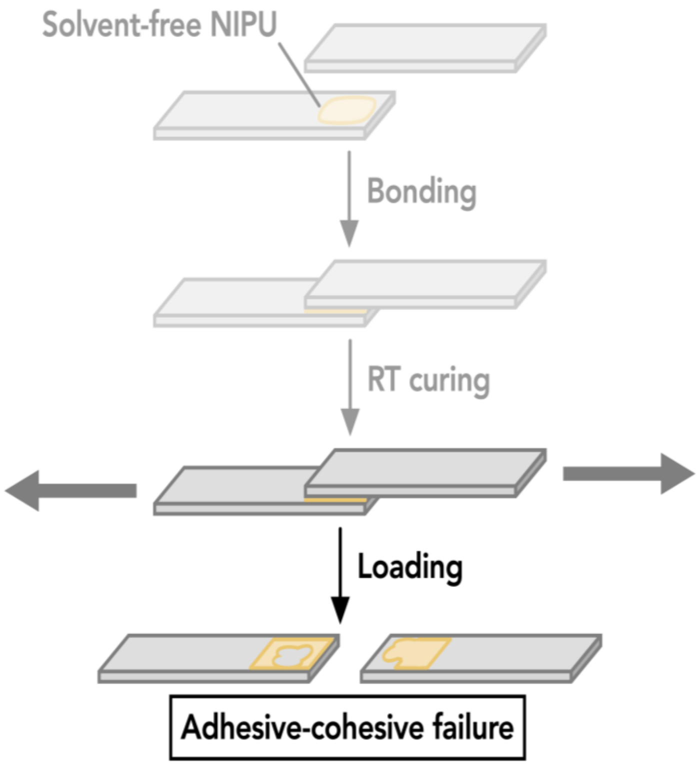
Thermal stability



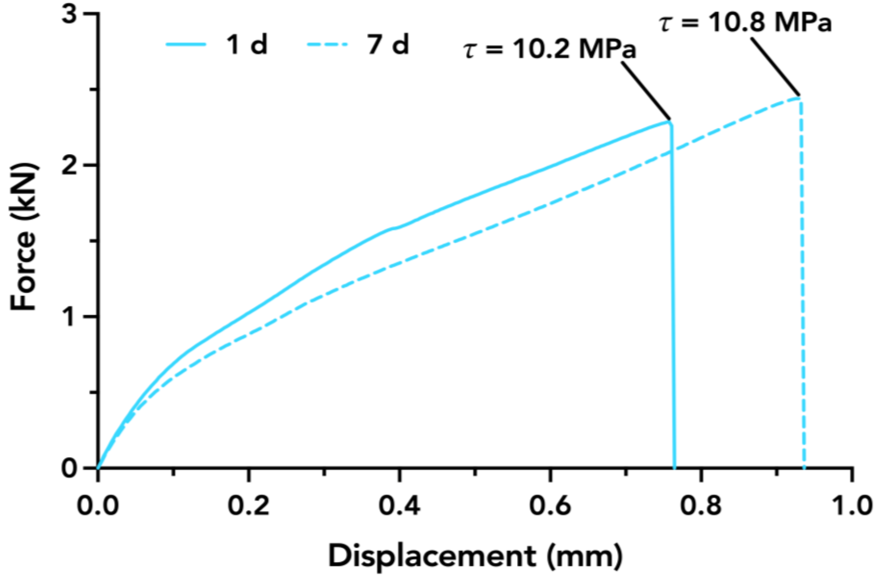
Macromolecules 2025, 58, 13, 6452–6465

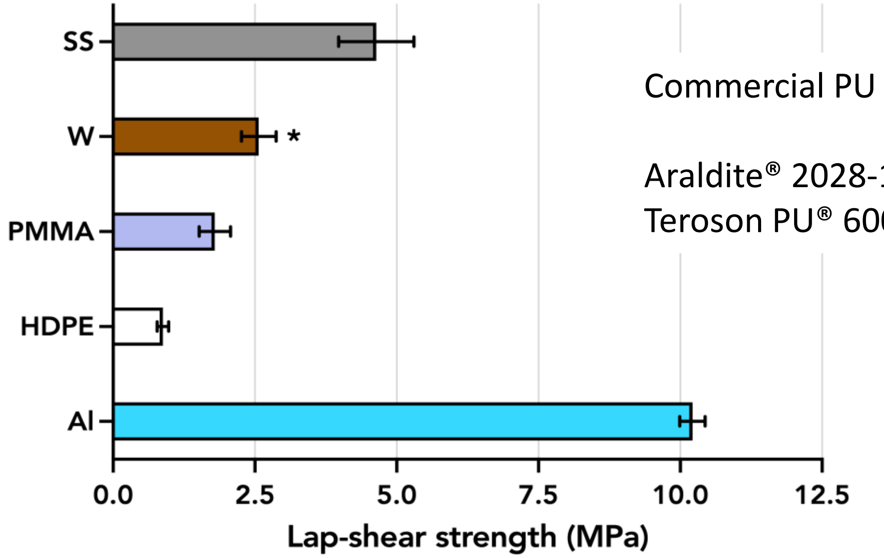
Advanced materials Design

Poly(oxazolidinone) adhesives



Lap shear adhesion





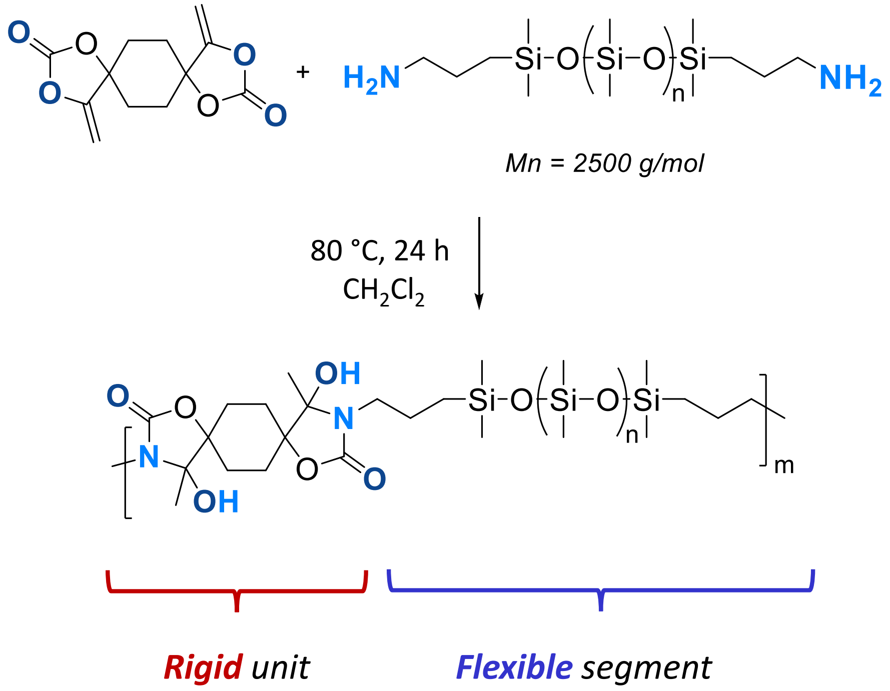
Commercial PU glues:

Araldite® 2028-1 = 8 Mpa
Teroson PU® 600 = 10 MPa

Macromolecules 2025, 58, 13, 6452–6465

Advanced materials Design

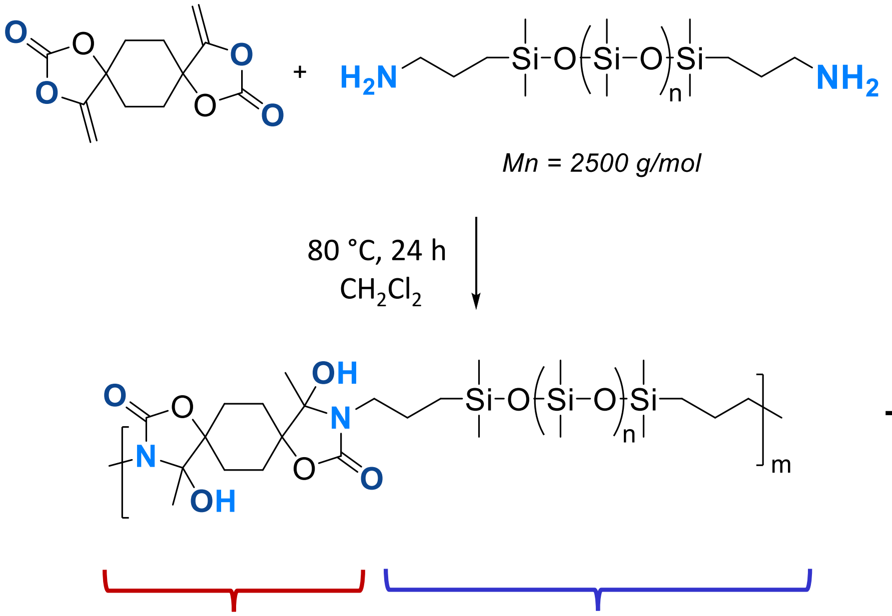
TPE for blood contact applications



Adv Health Mater, 2025, doi.org/10.1002/adhm.202502670

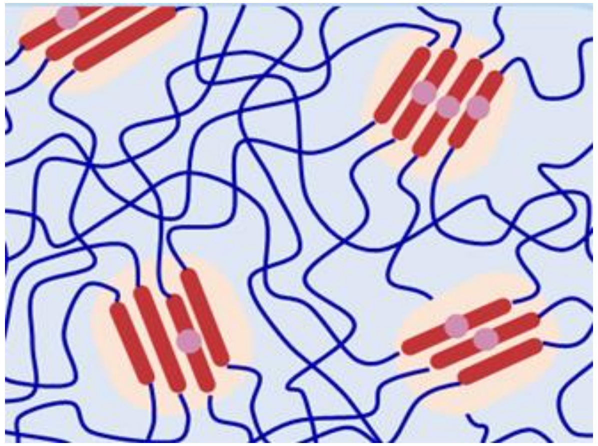
Advanced materials Design

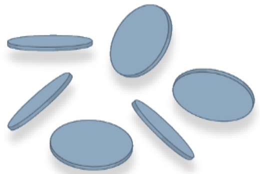
TPE for blood contact applications



***Rigid** unit*   ***Flexible** segment*

Thermoplastic elastomers





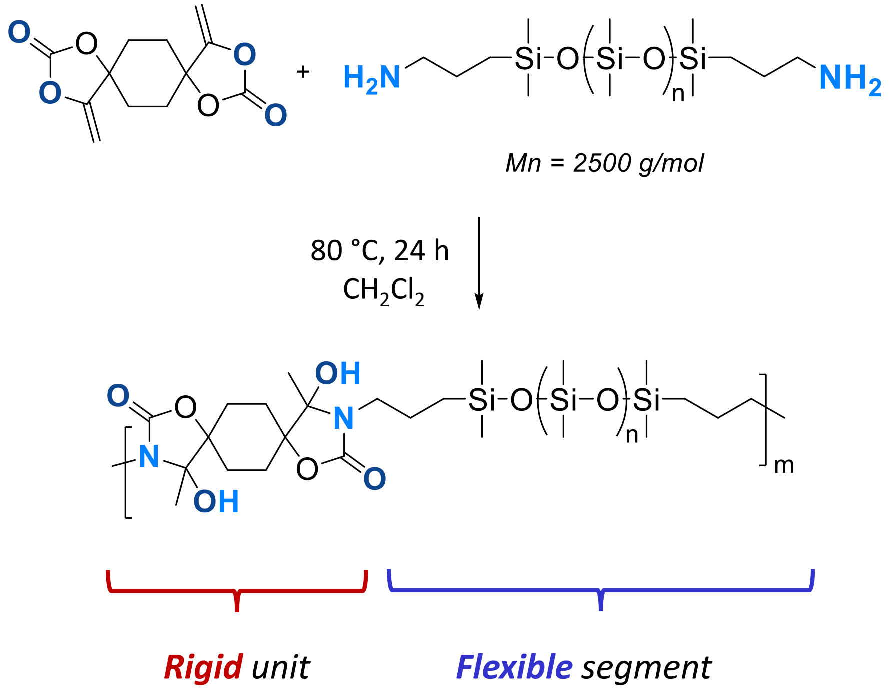
Proccessable pellets

*Self-assembly in **hard** and **soft** domains*
Reversible physical crosslinks

Adv Health Mater, 2025, doi.org/10.1002/adhm.202502670

Advanced materials Design

TPE for blood contact applications

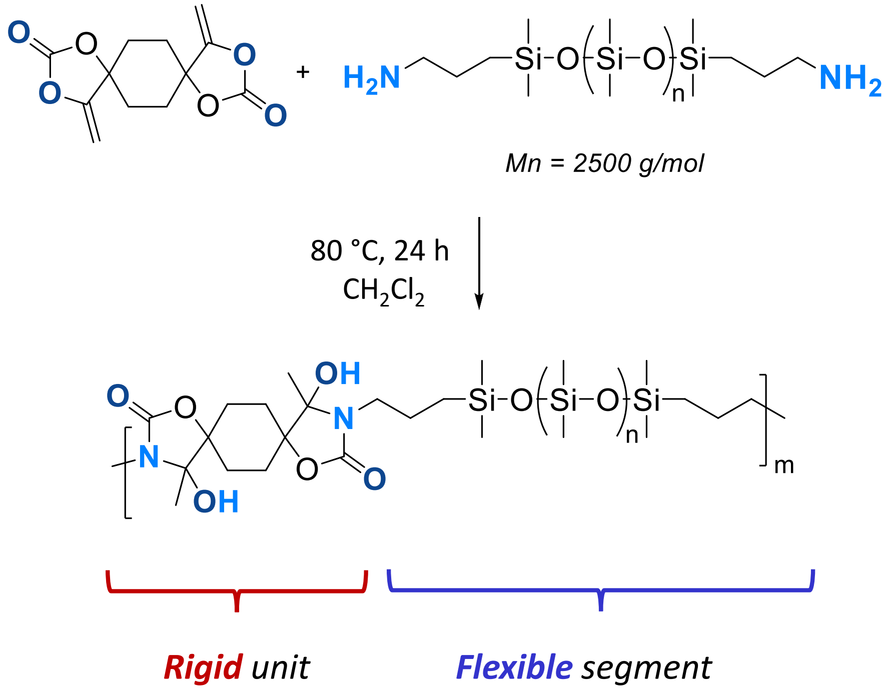


Films

Adv Health Mater, 2025, doi.org/10.1002/adhm.202502670

Advanced materials Design

TPE for blood contact applications



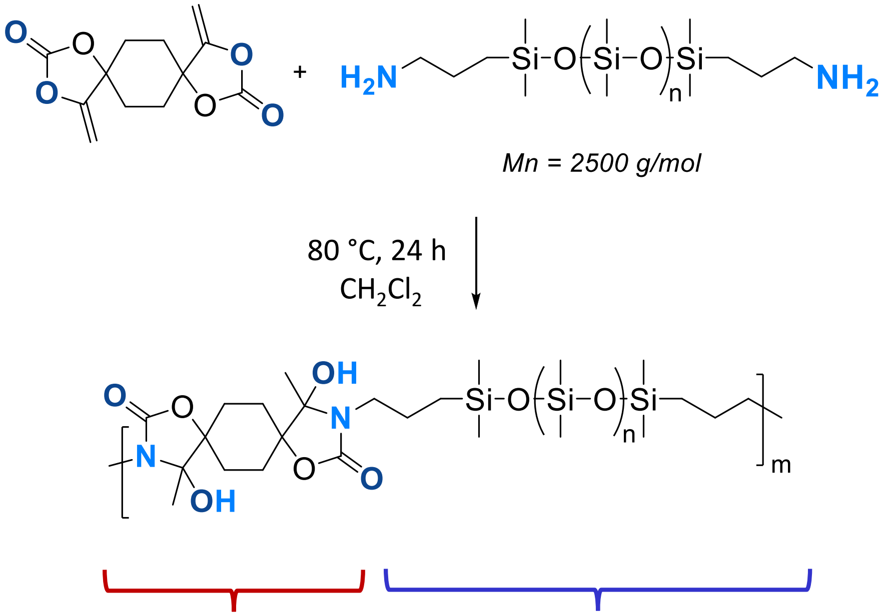
Films

Injection molding (heart valve)

Adv Health Mater, 2025, doi.org/10.1002/adhm.202502670

Advanced materials Design

TPE for blood contact applications

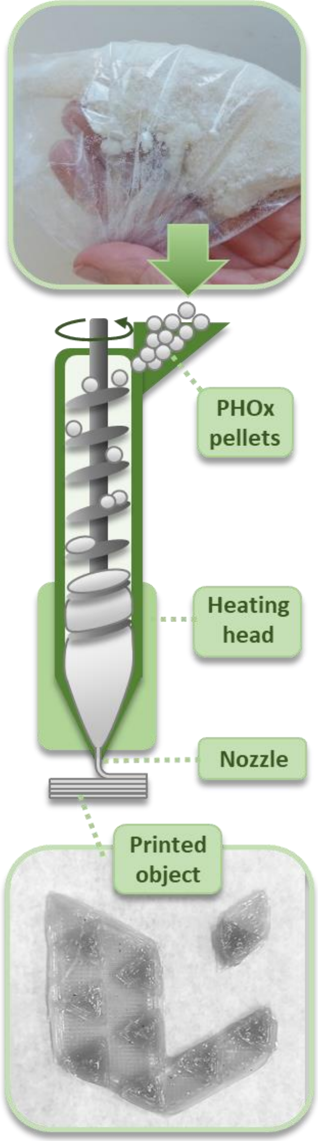


Rigid *unit* ***Flexible*** *segment*

Films

Injection molding (heart valve)

3D printing



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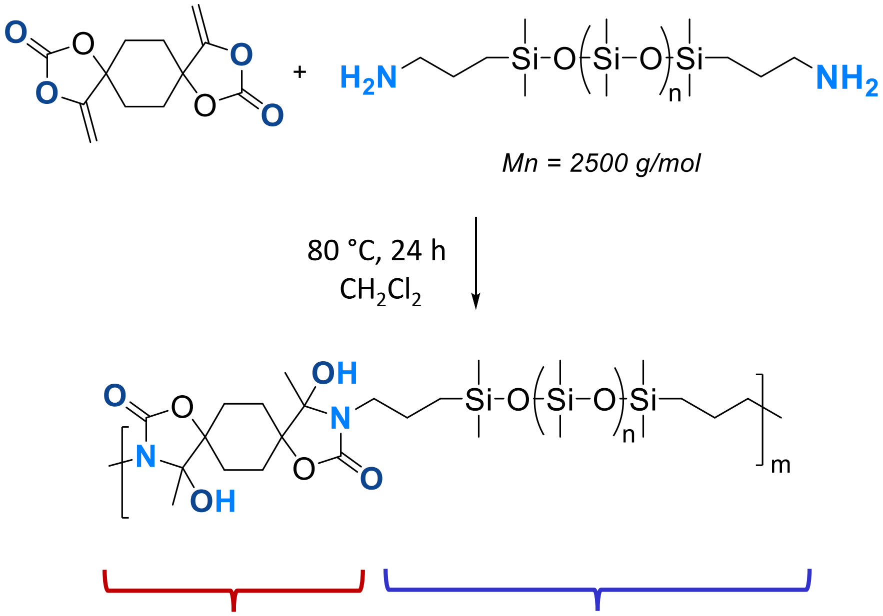
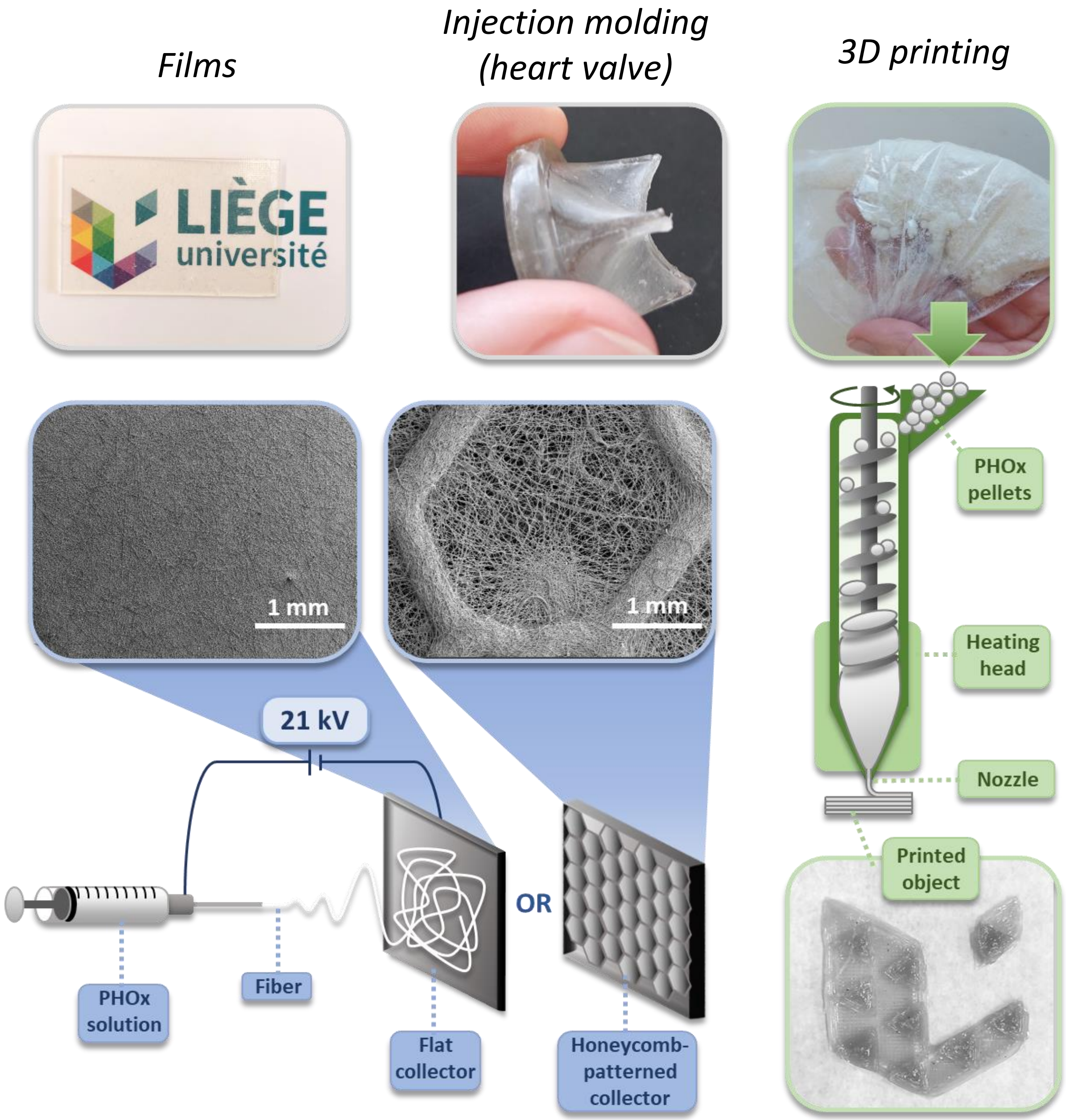
Advanced materials Design

TPE for blood contact applications



Rigid *unit*   ***Flexible*** *segment*



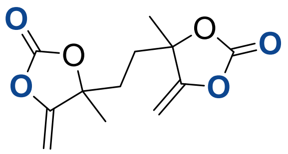
Electrospun mats for tissues engineering

Adv Health Mater, 2025, doi.org/10.1002/adhm.202502670

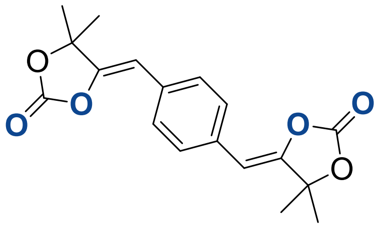
Polymers from CO_2-based exovinylene cyclic carbonates (αCC)

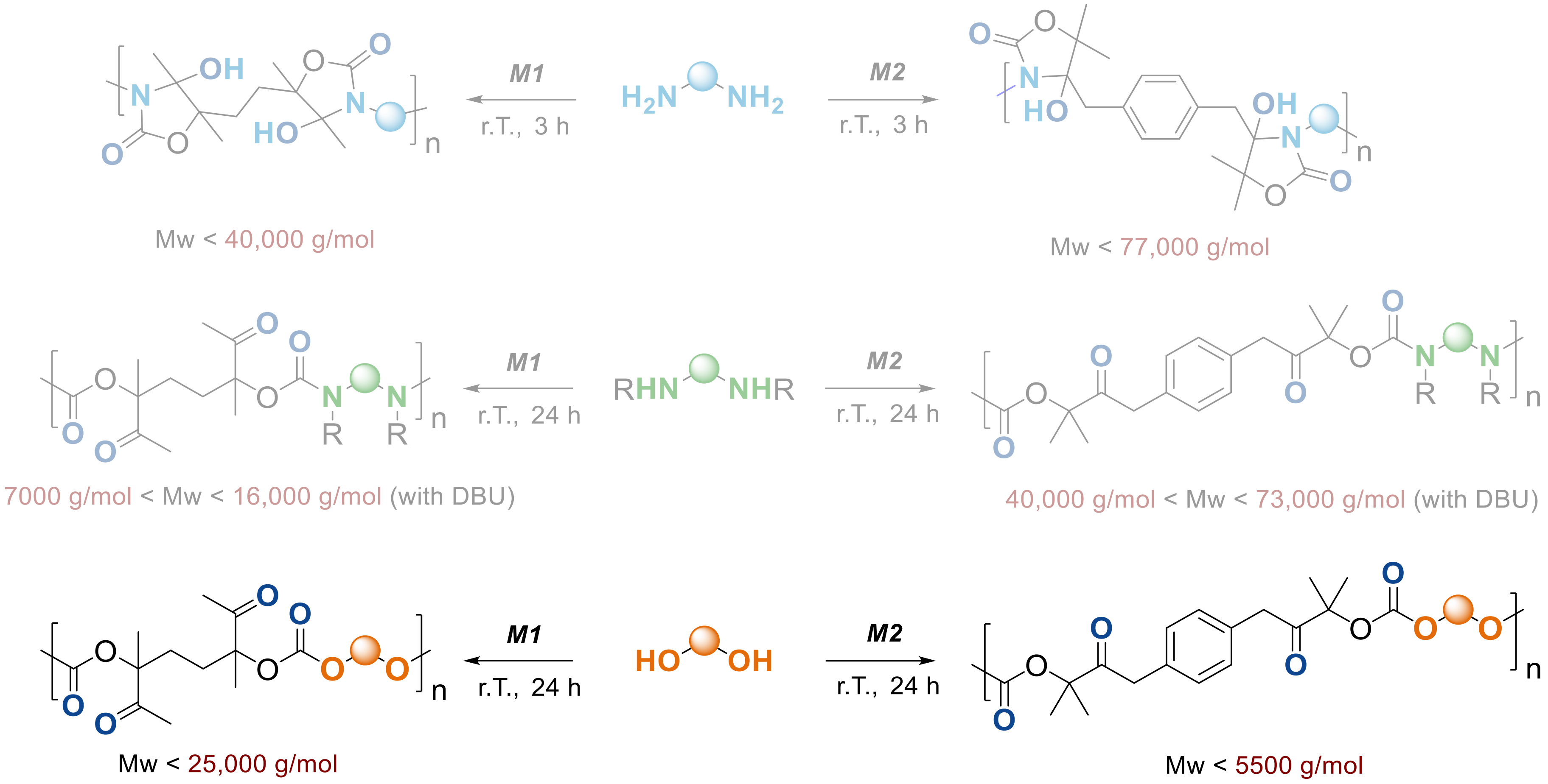
Polymers from bis-αCC

***M1* =**



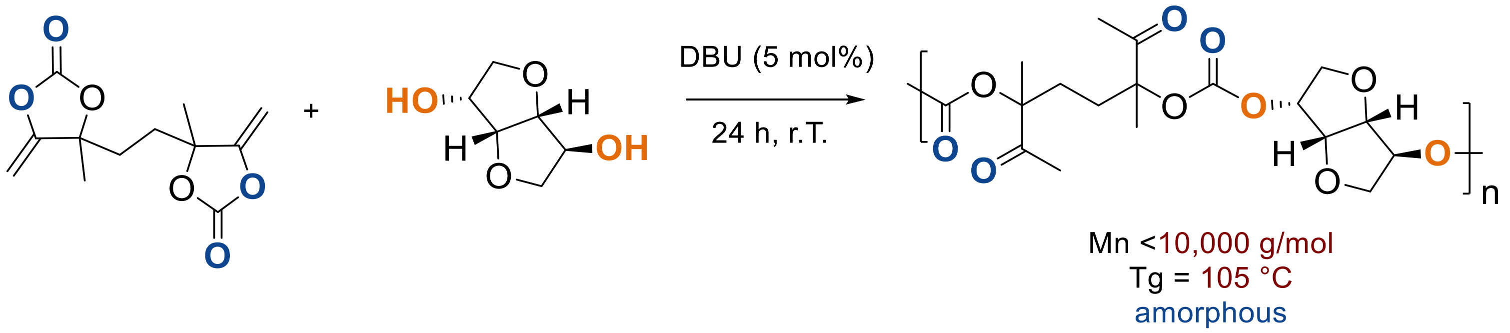
***M2* =**





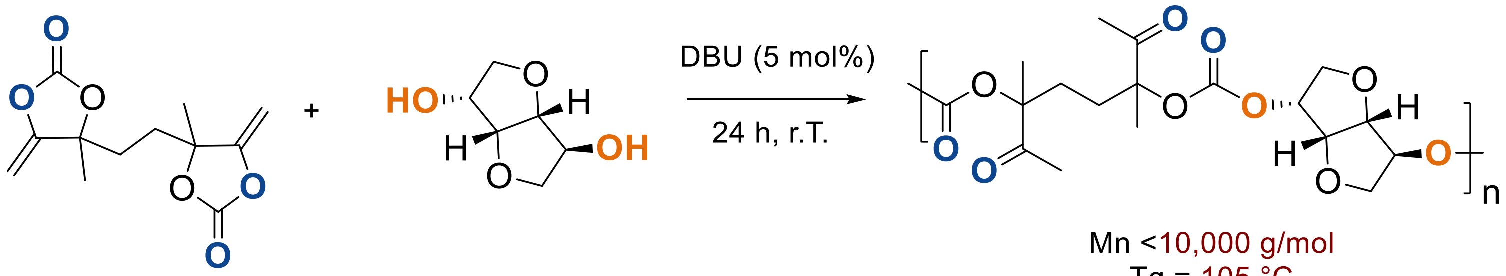
Advanced materials Design

Tissues engineering

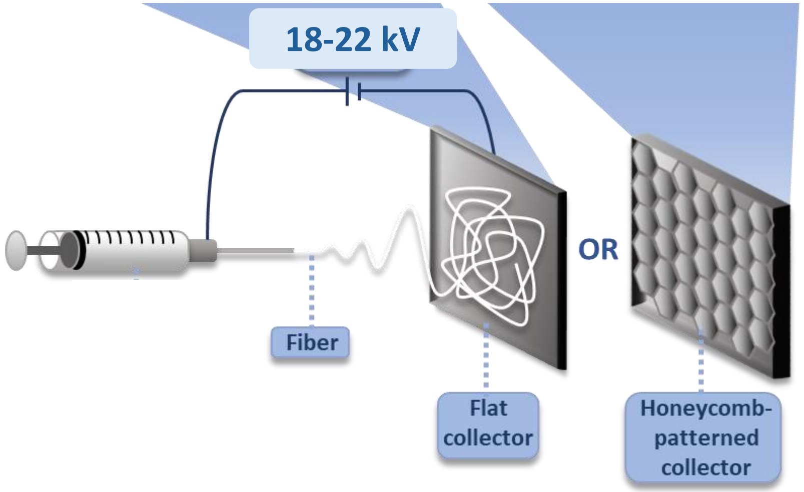


Advanced materials Design

Tissues engineering

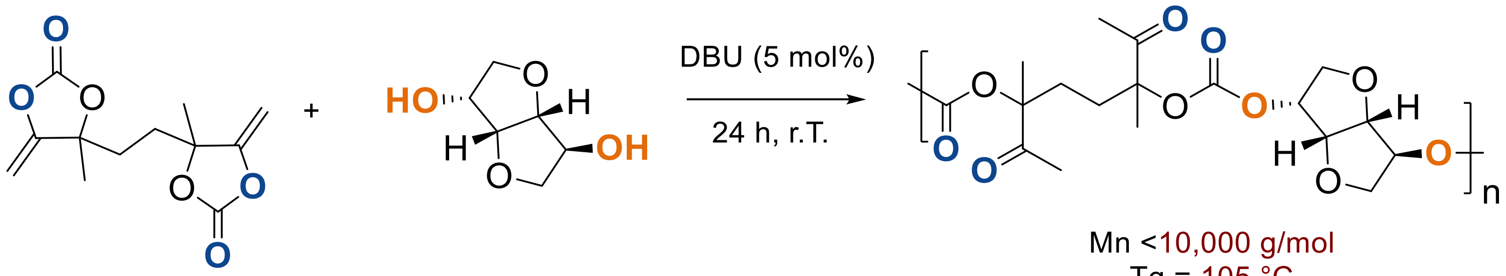


Mn <10,000 g/mol
Tg = 105 °C
amorphous



Advanced materials Design

Tissues engineering

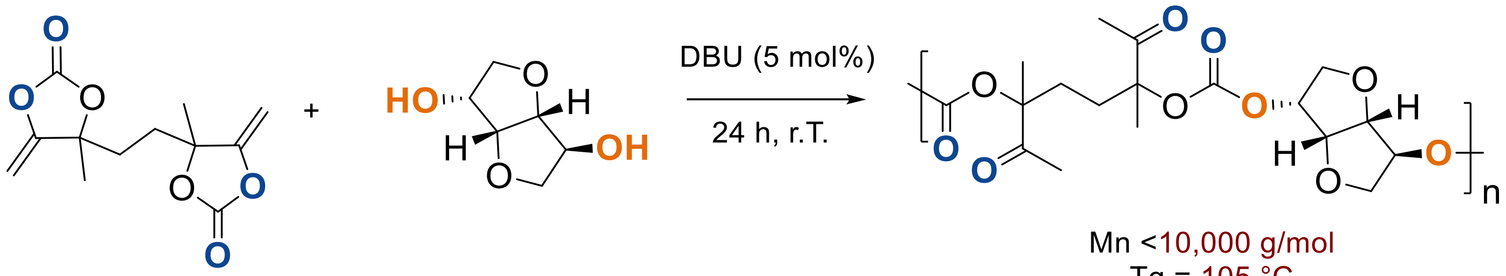


Mn <10,000 g/mol
Tg = 105 °C
amorphous

Human fibroblasts
proliferation

Advanced materials Design

Tissues engineering



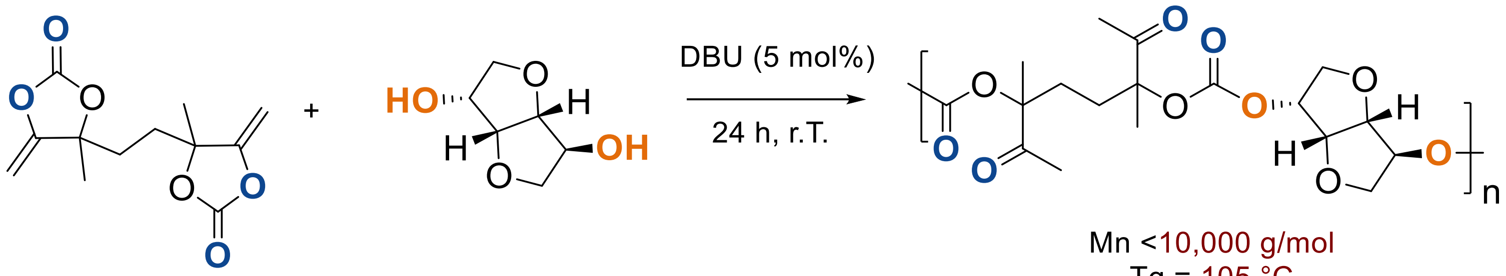
Mn <10,000 g/mol
Tg = 105 °C
amorphous

Human fibroblasts
proliferation

Human mesenchymal stem cells
proliferation

Advanced materials Design

Tissues engineering



Mn <10,000 g/mol
Tg = 105 °C
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Human fibroblasts
proliferation

Human mesenchymal stem cells
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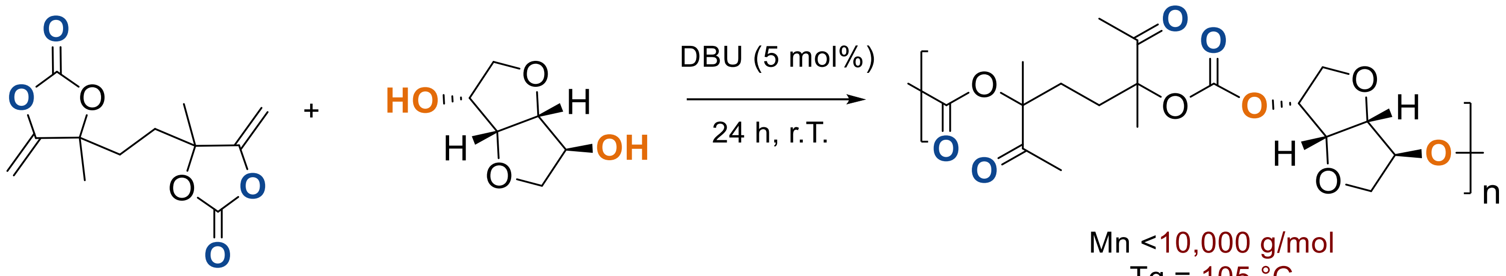
Advanced materials Design

Tissues engineering



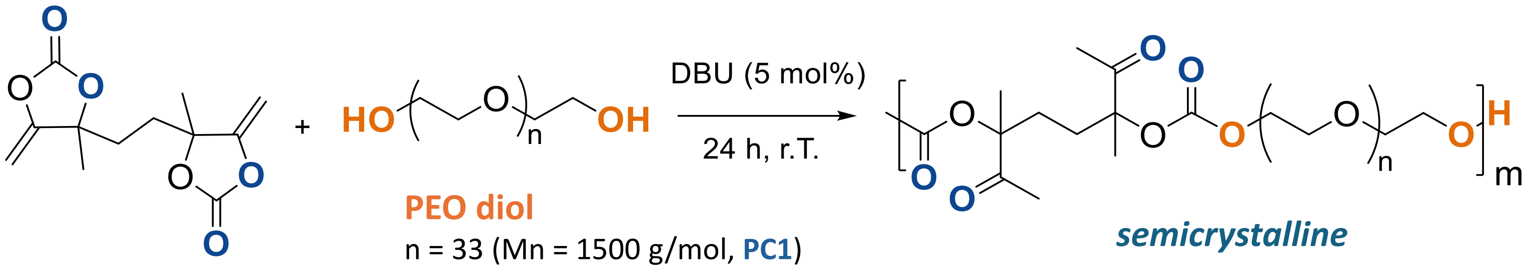
Mn <10,000 g/mol
Tg = 105 °C
amorphous

In Vivo testing in mice

***No inflammatory response** after 80 days*
Biocompatibility

Advanced materials Design

Solid electrolyte for Li-ion battery



PEO diol

n = 33 (Mn = 1500 g/mol, **PC1**)

n = 44 (Mn = 2000 g/mol, **PC2**)

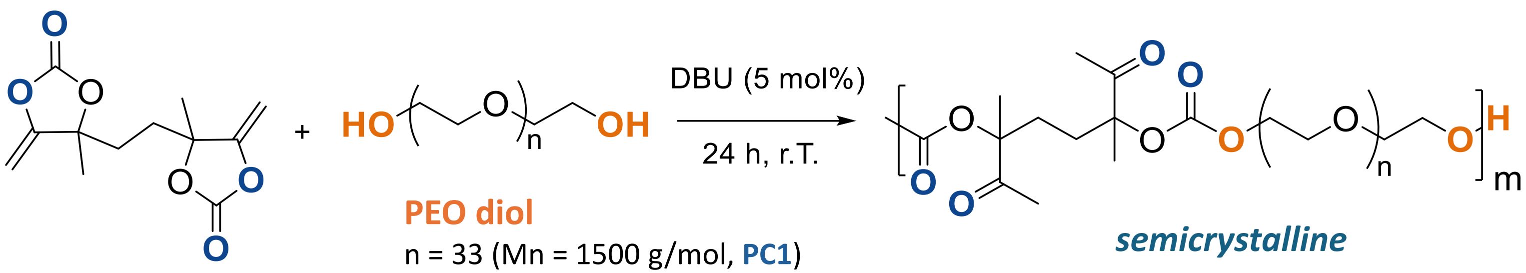
n = 89 (Mn = 4000 g/mol, **PC3**)

semicrystalline

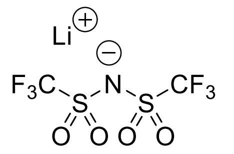
J. Mater. Chem. A, 2019,7, 9844-9853

Advanced materials Design

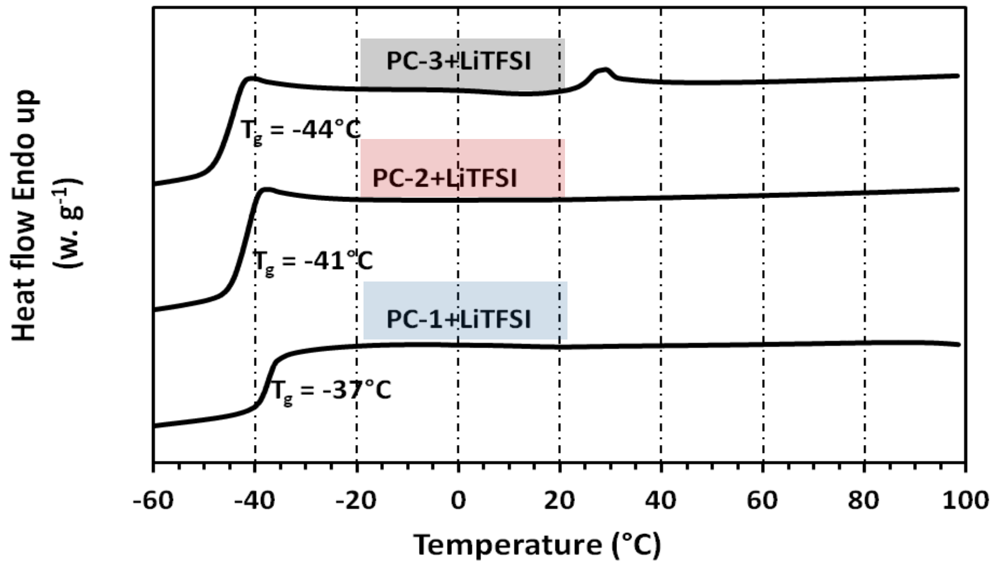
Solid electrolyte for Li-ion battery

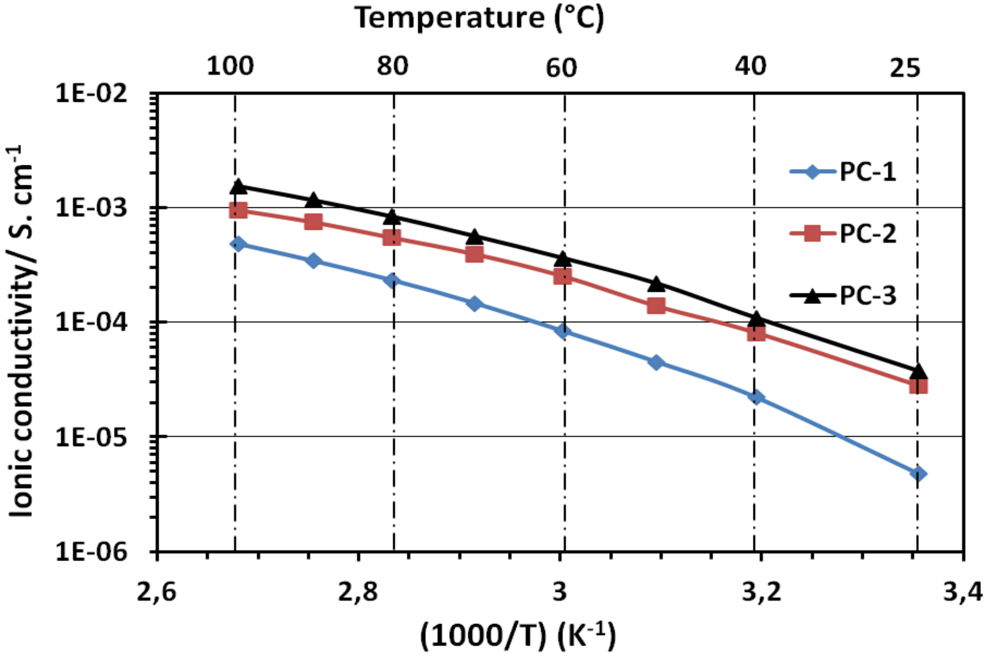


PEO diol
n = 33 (Mn = 1500 g/mol, PC1)
n = 44 (Mn = 2000 g/mol, PC2)
n = 89 (Mn = 4000 g/mol, PC3)



LiTFSI





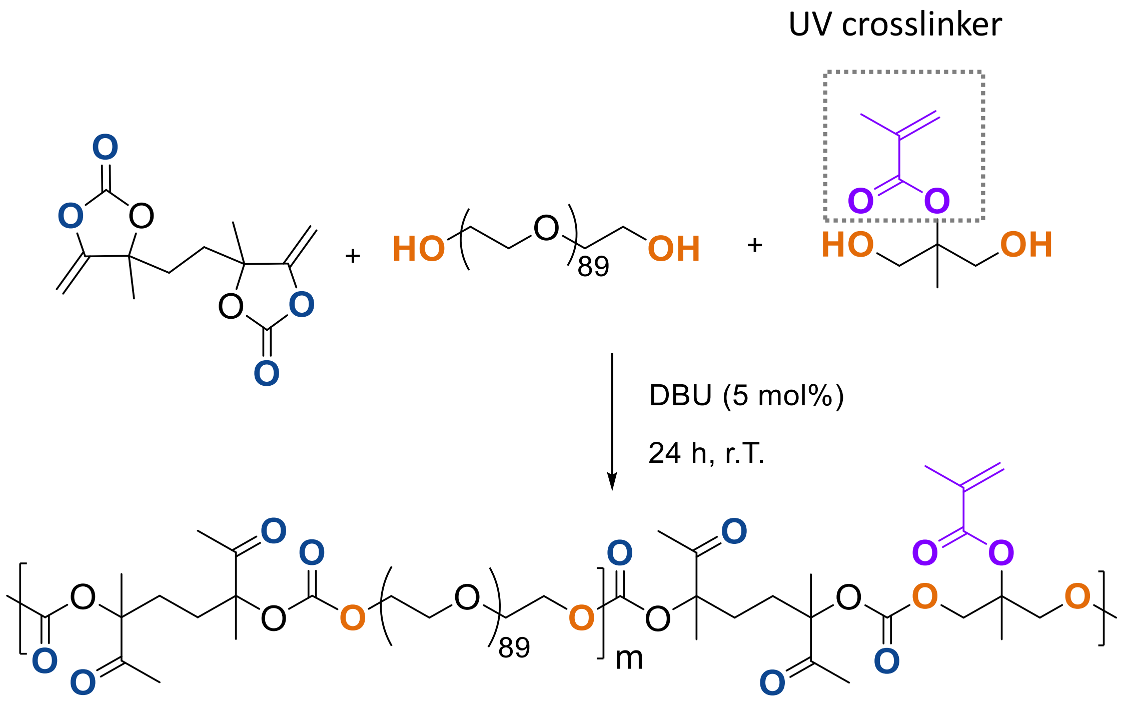
Amorphous PCs (30 wt% LiTFSI)

4.86×10^{-6} S.cm^{-1} < Ionic conductivity < 3.75×10^{-5} S.cm^{-1} (at 25 °C)

J. Mater. Chem. A, 2019,7, 9844-9853

Advanced materials Design

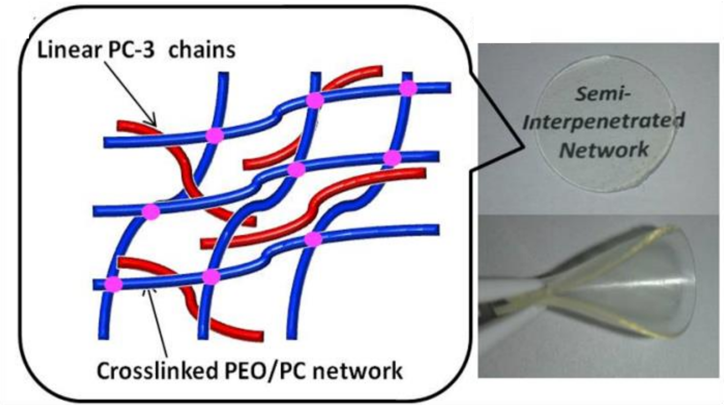
Solid electrolyte for Li-ion battery

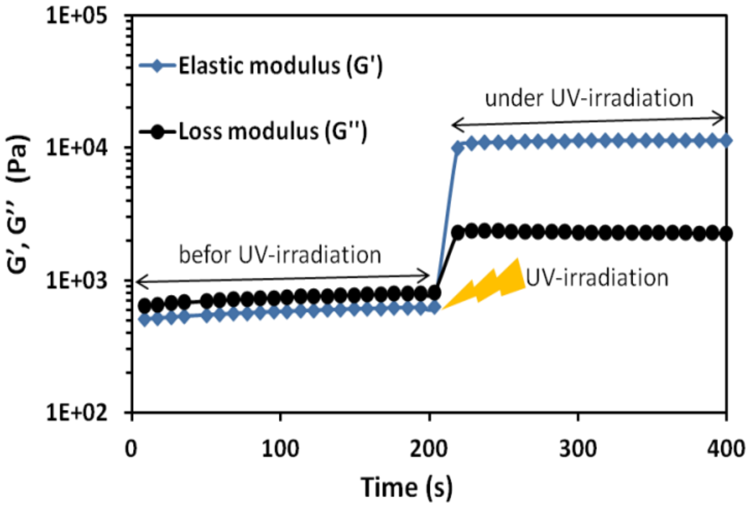


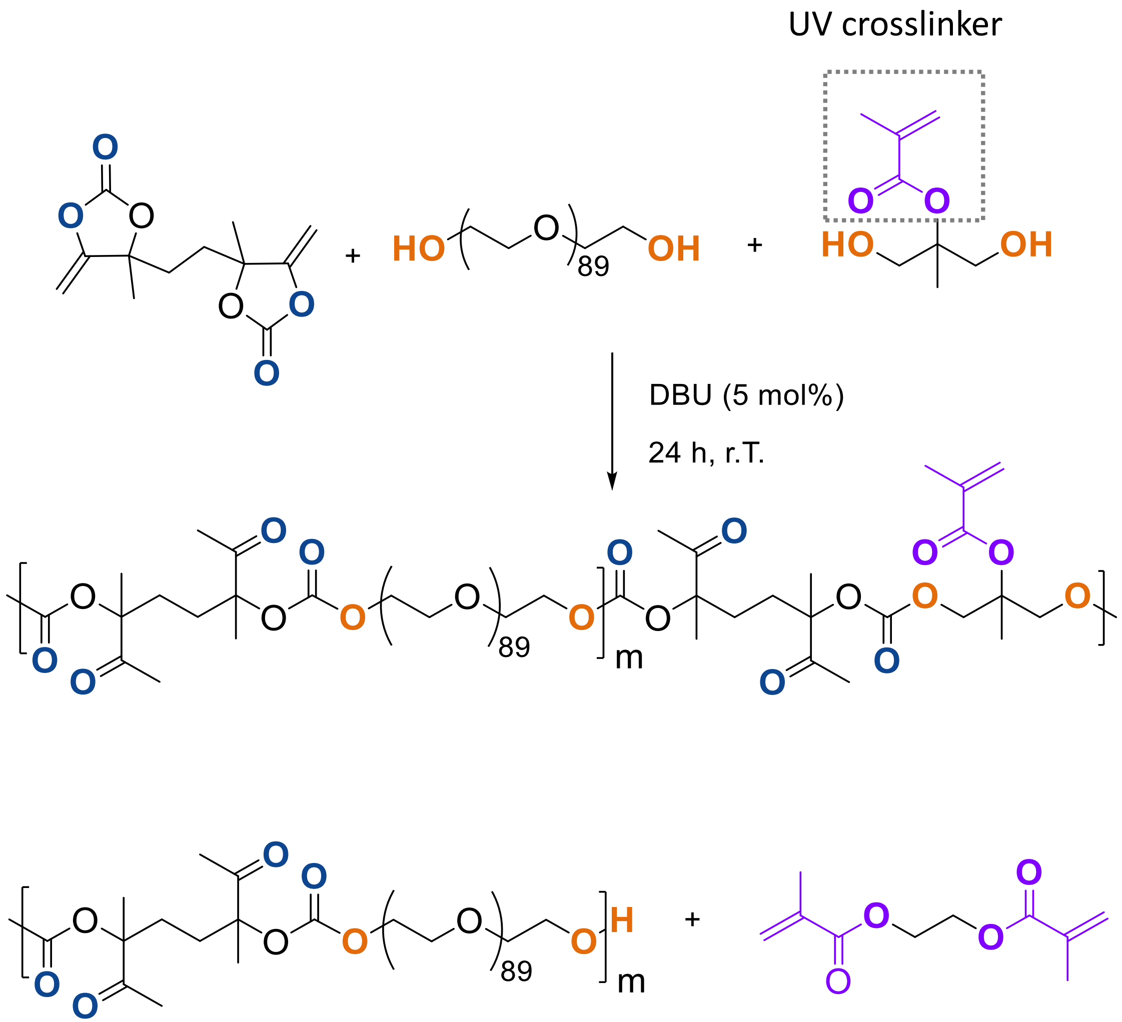
J. Mater. Chem. A, 2019,7, 9844-9853

Advanced materials Design

Solid electrolyte for Li-ion battery



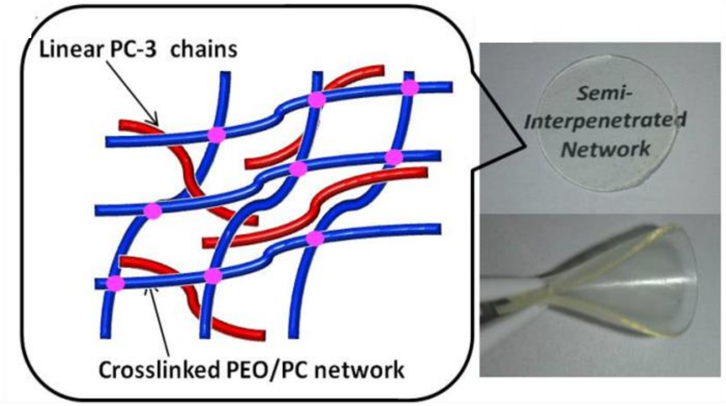


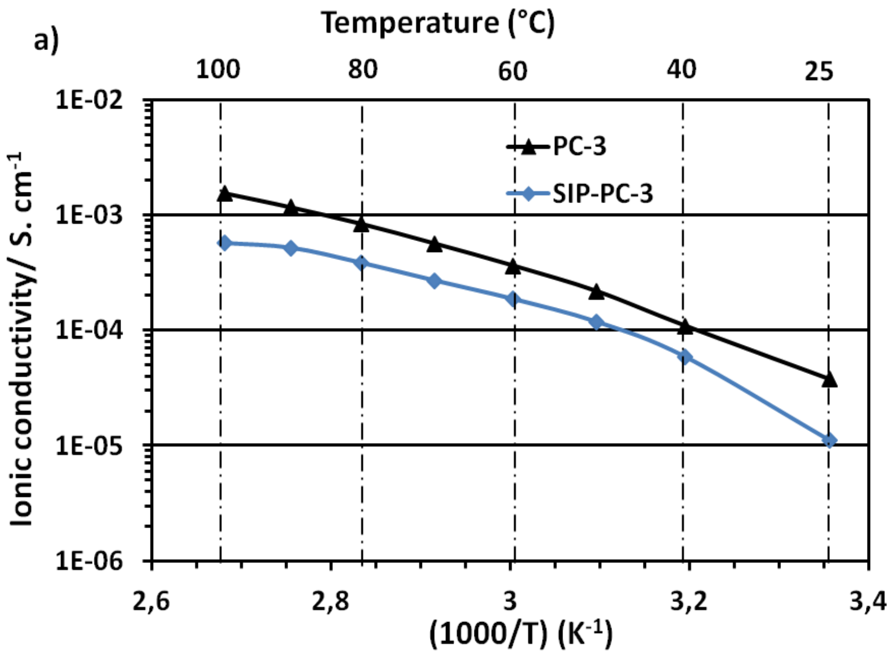


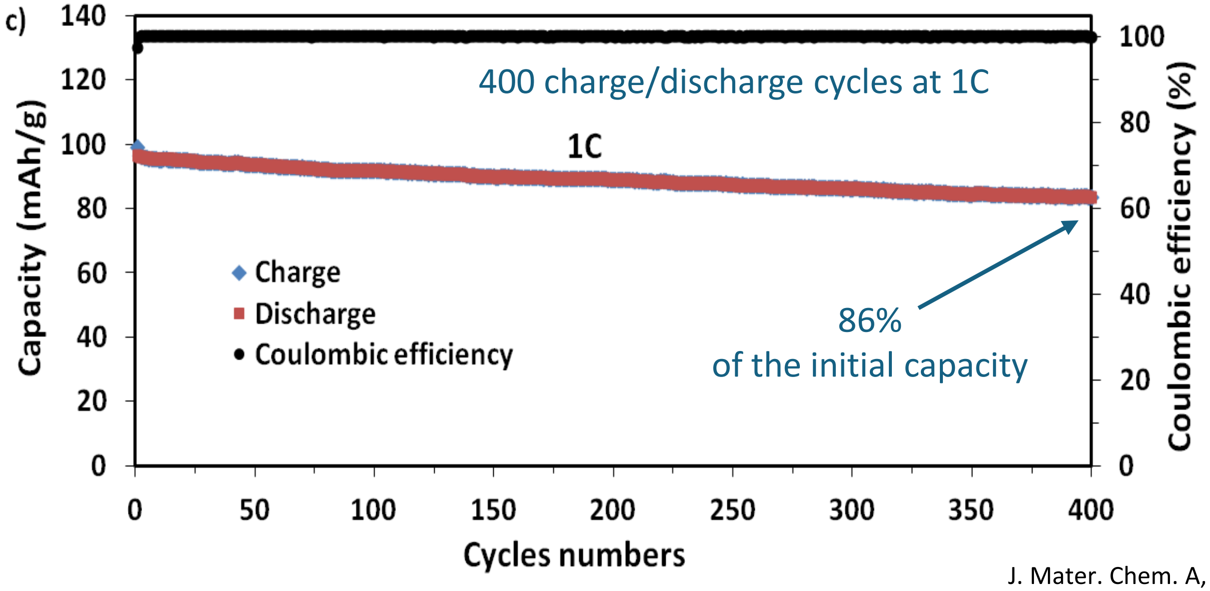
J. Mater. Chem. A, 2019,7, 9844-9853

Advanced materials Design

Solid electrolyte for Li-ion battery







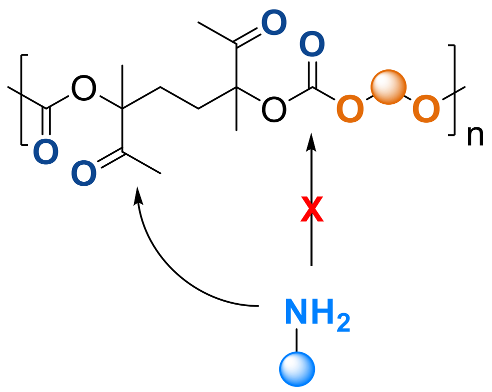
C rate = 1C : current to completely charge/discharge the battery in 1 h (fast charge/discharge)

J. Mater. Chem. A, 2019,7, 9844-9853

Polymer end-of-life

Polycarbonates aminolysis

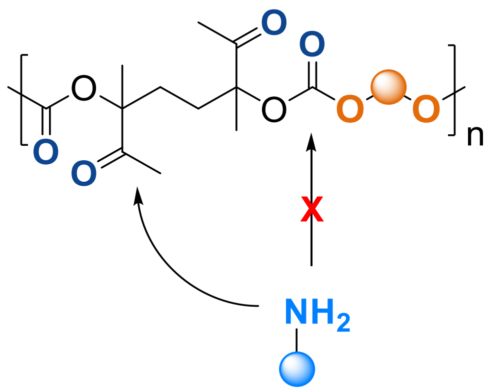
2 electrophilic carbonyl sites



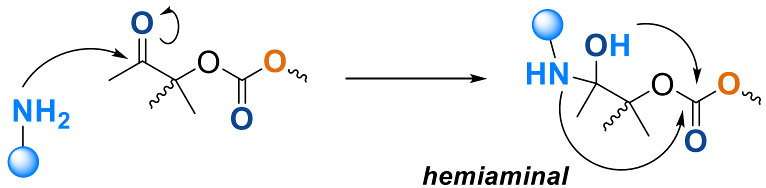
ACS Sustainable Chem. Eng. 2022, 10, 27, 8863–8875

Polymer end-of-life

2 electrophilic carbonyl sites



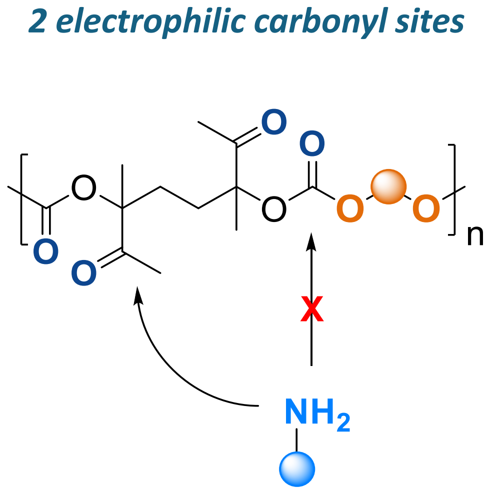
Polycarbonates aminolysis

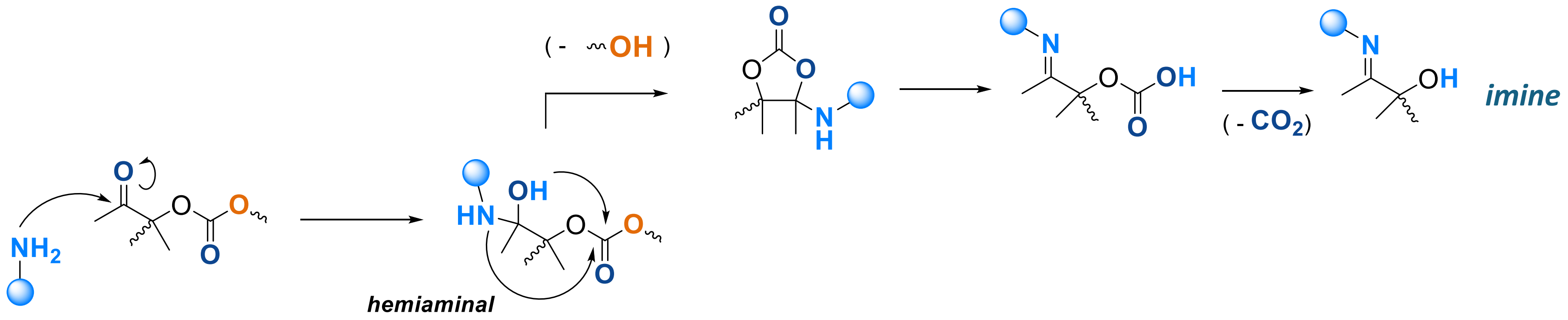


ACS Sustainable Chem. Eng. 2022, 10, 27, 8863–8875

Polymer end-of-life

Polycarbonates aminolysis



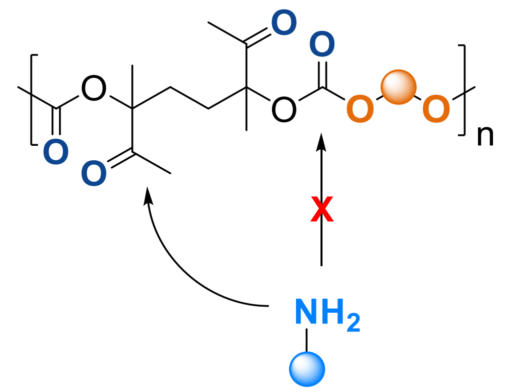


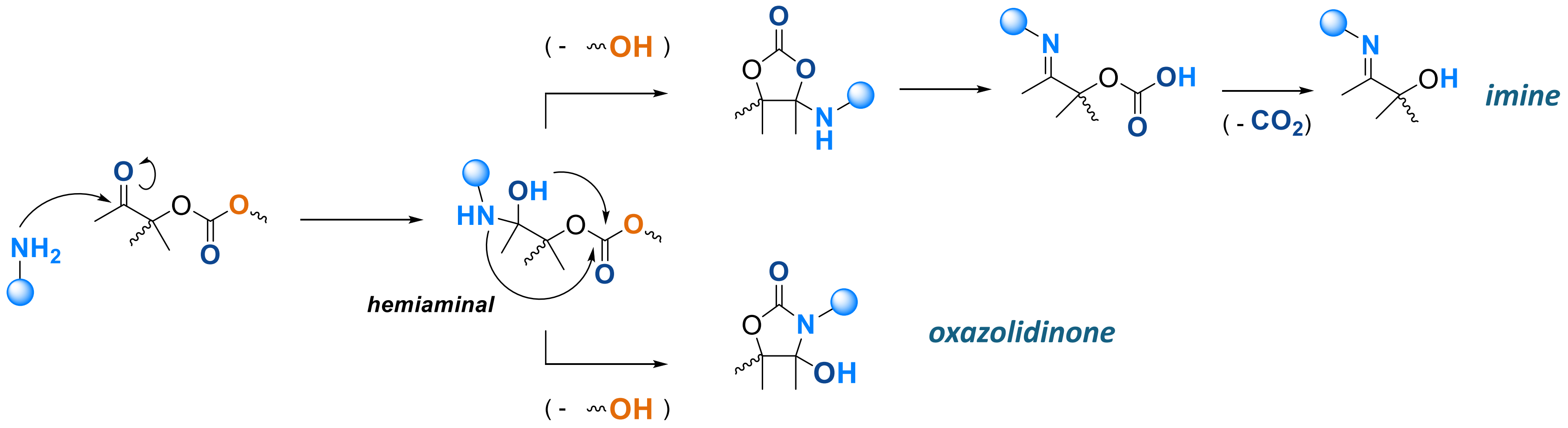
ACS Sustainable Chem. Eng. 2022, 10, 27, 8863–8875

Polymer end-of-life

Polycarbonates aminolysis

2 electrophilic carbonyl sites





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Polymer end-of-life

Polycarbonates aminolysis

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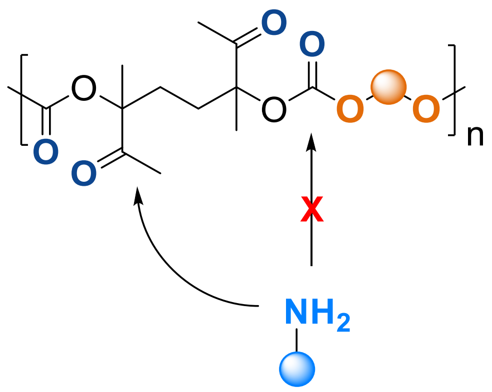

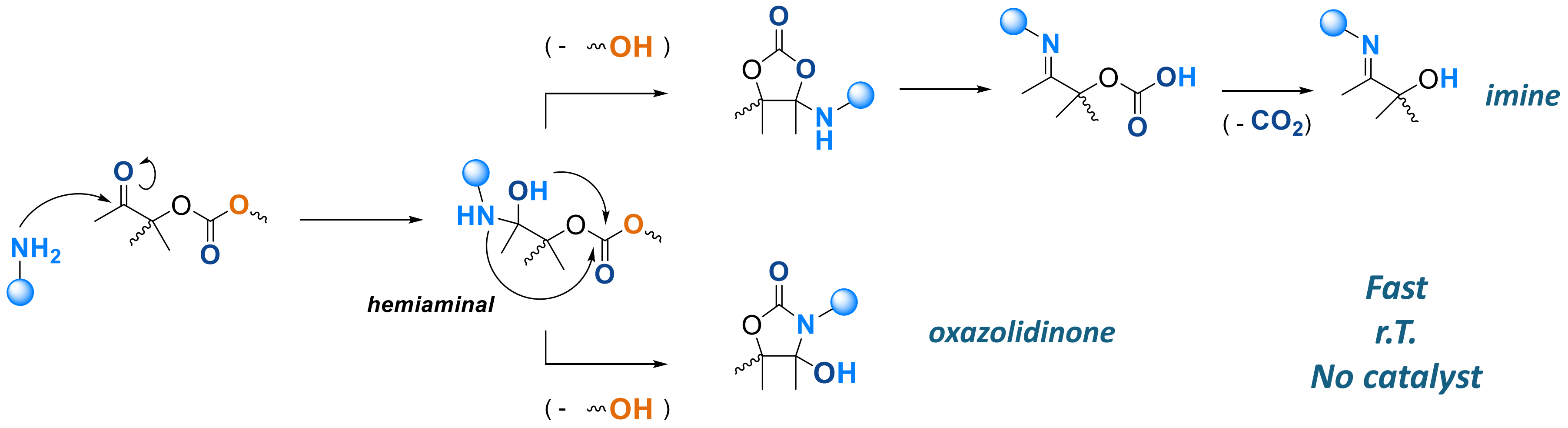

ACS Sustainable Chem. Eng. 2022, 10, 27, 8863–8875

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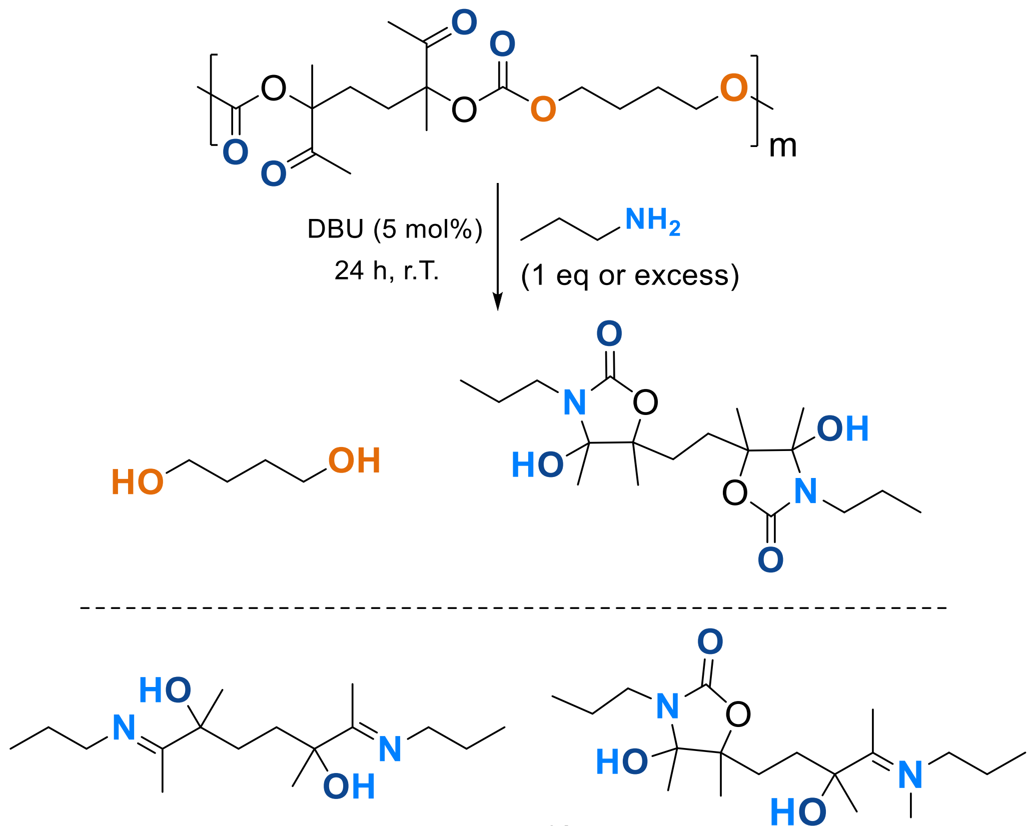
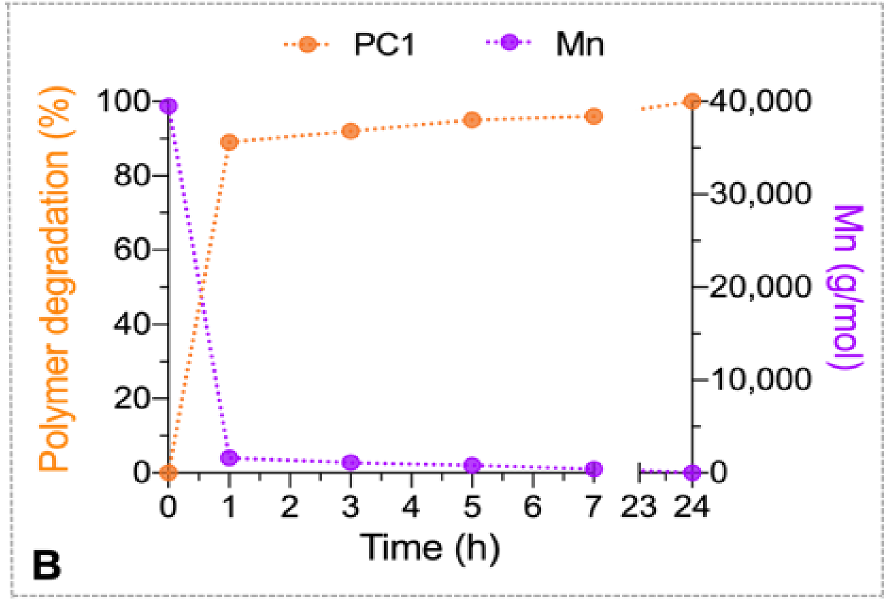
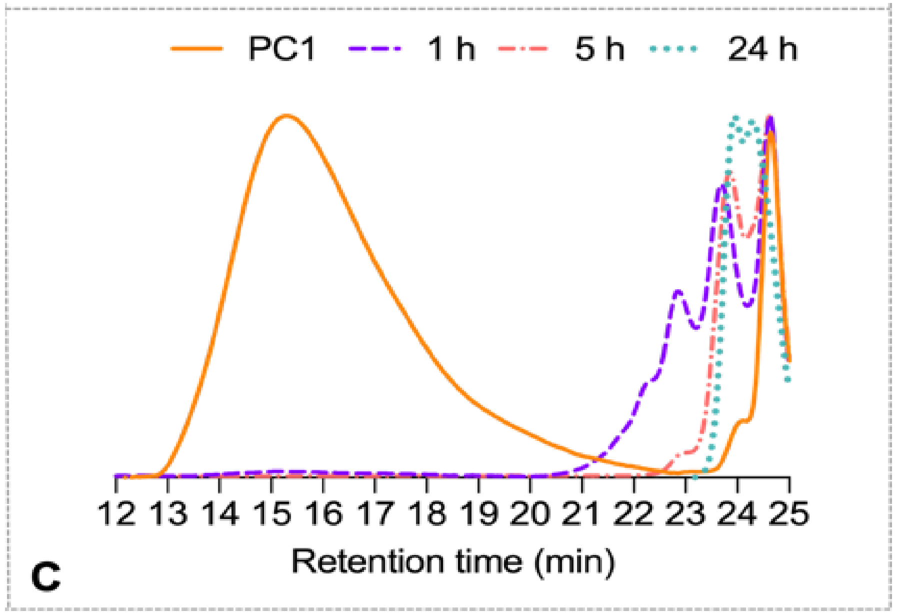
Polycarbonates aminolysis



17%

(reduced to 5% with 1 eq. of amine)

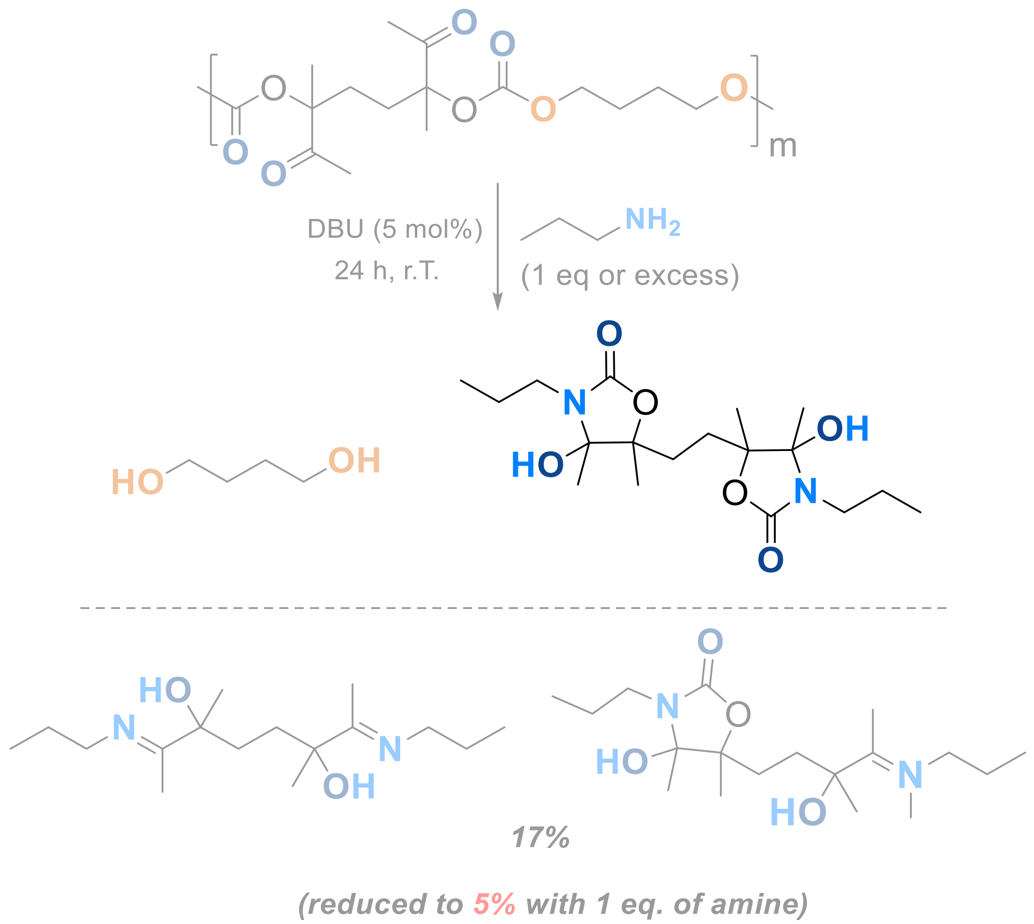


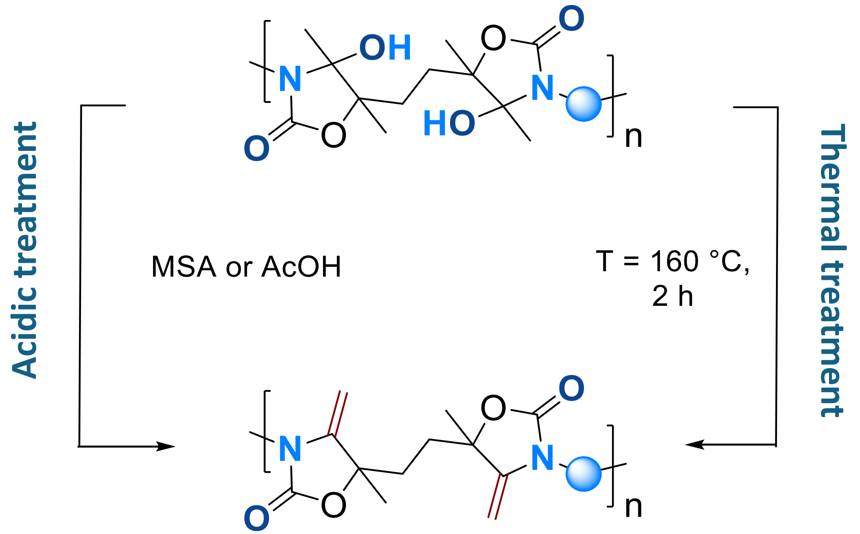


ACS Sustainable Chem. Eng. 2022, 10, 27, 8863–8875

Polymer end-of-life

Polycarbonates aminolysis

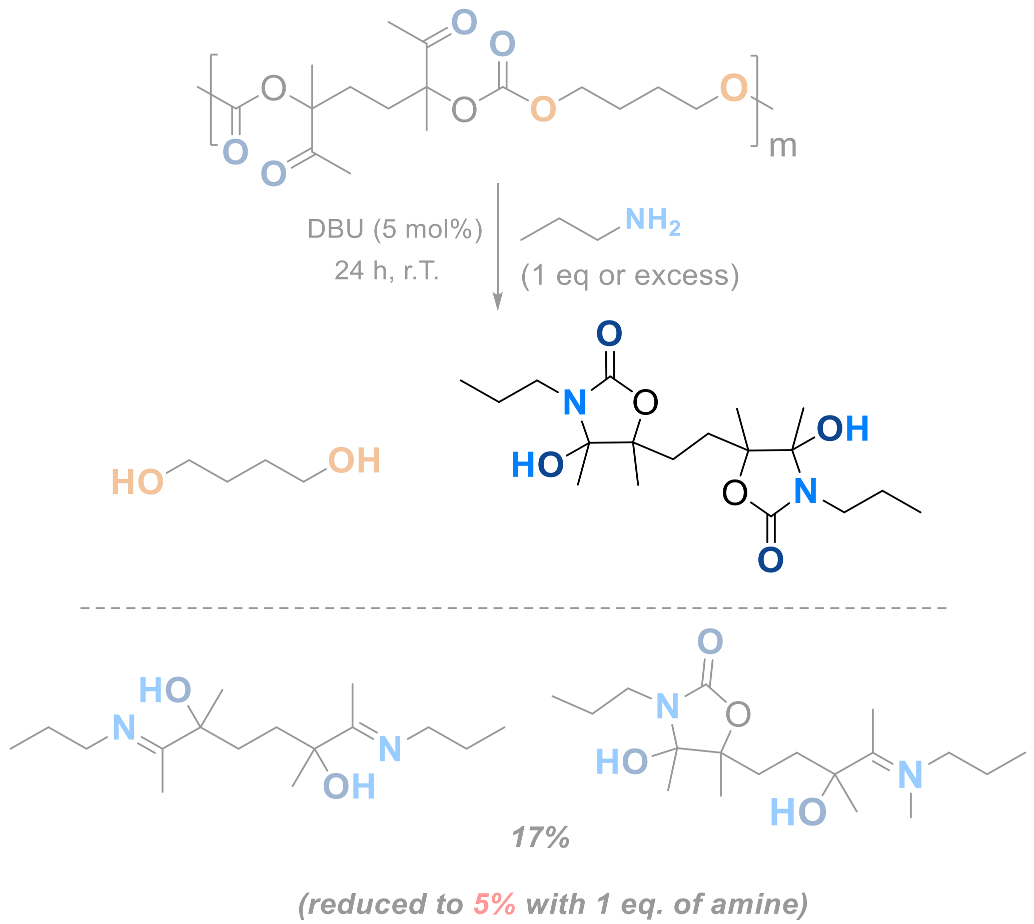


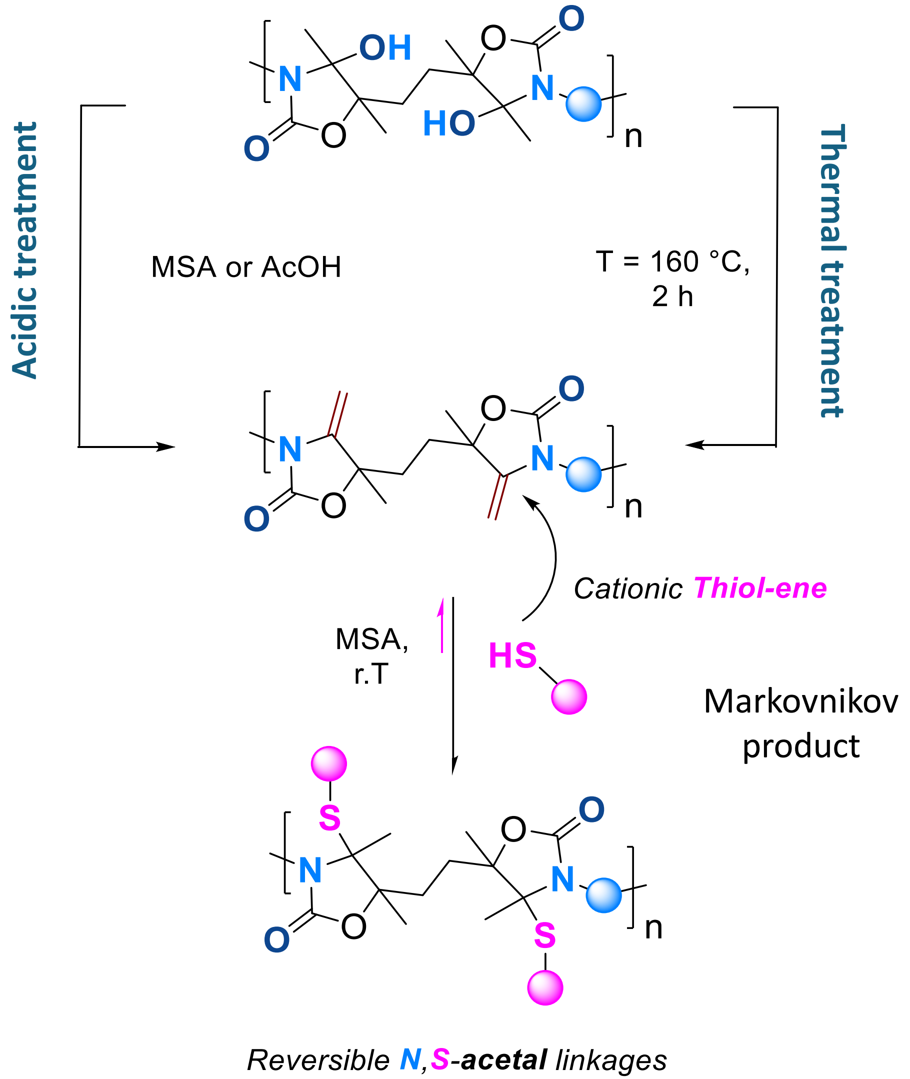


Polym. Chem., 2022,13, 3076-3090

Polymer end-of-life

Polycarbonates aminolysis

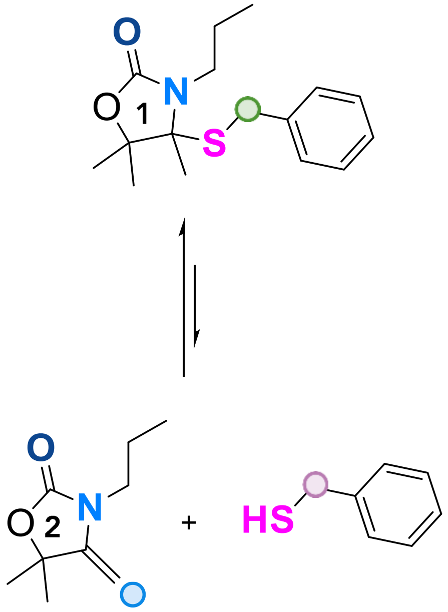


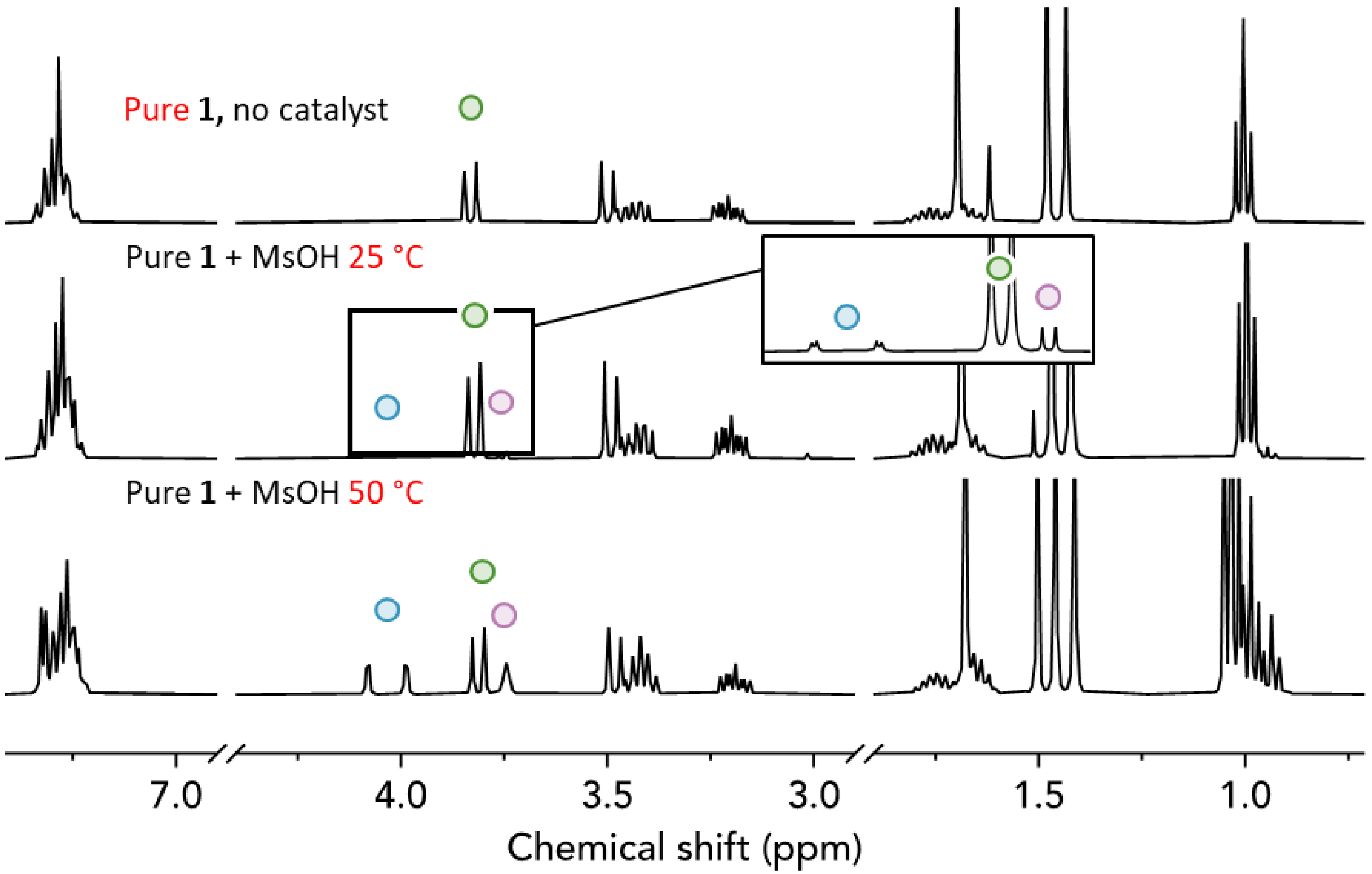


Polym. Chem., 2022,13, 3076-3090; J. Am. Chem. Soc. 2023, 145, 46, 25450–25462

Polymer end-of-life

N,S-acetal dissociation

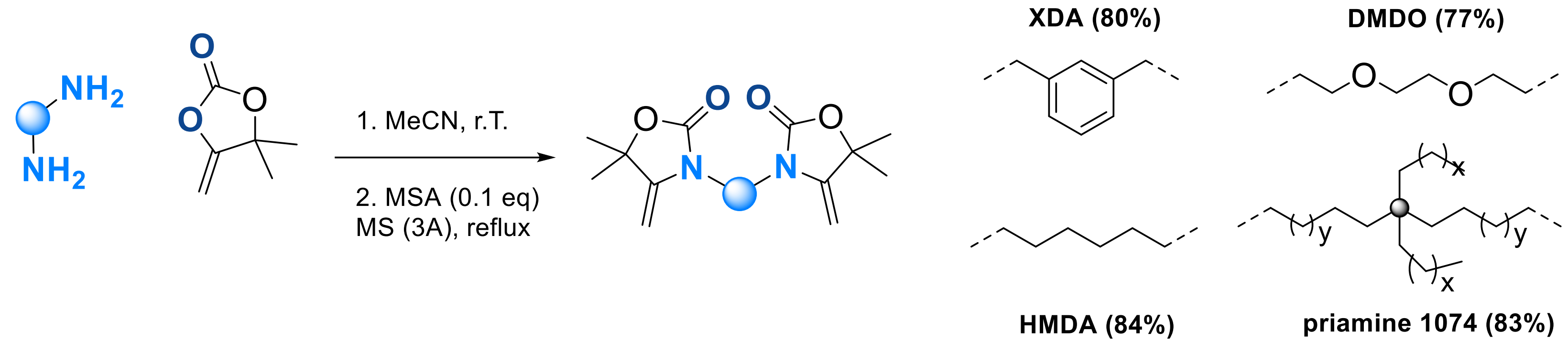




J. Am. Chem. Soc. 2023, 145, 46, 25450–25462

Polymer end-of-life

Covalent adaptable *N,S*-acetal networks



J. Am. Chem. Soc. 2023, 145, 46, 25450–25462

Polymer end-of-life

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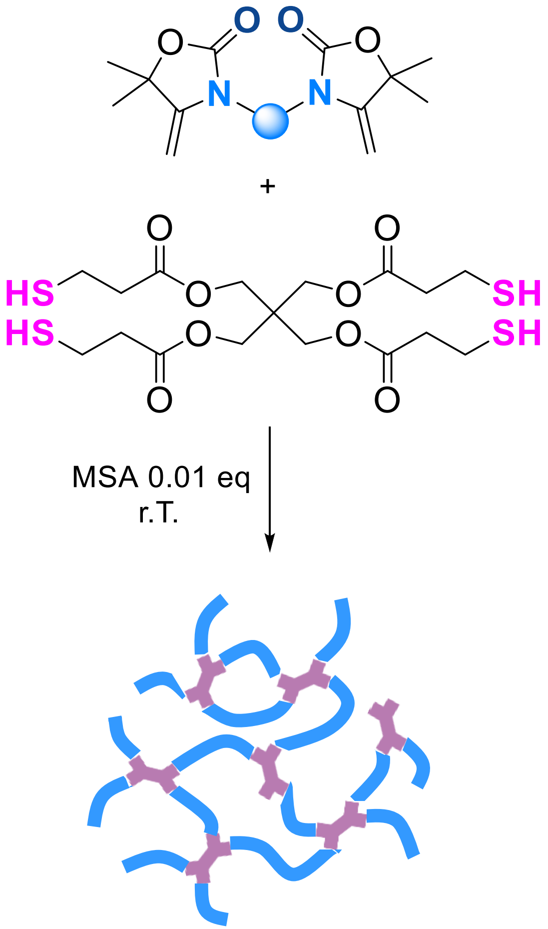
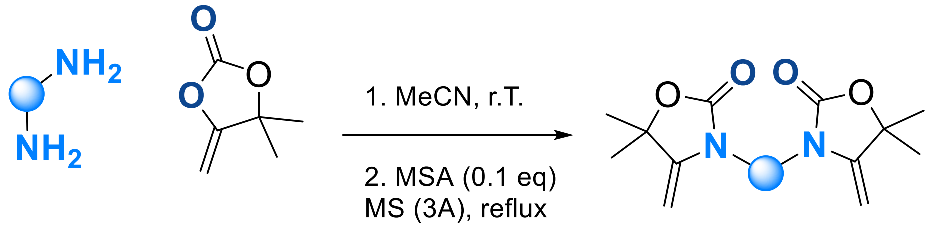
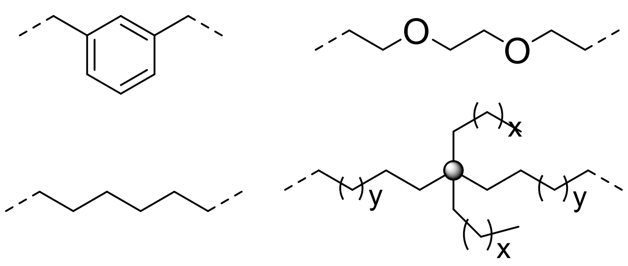




XDA (80%) DMDO (77%)

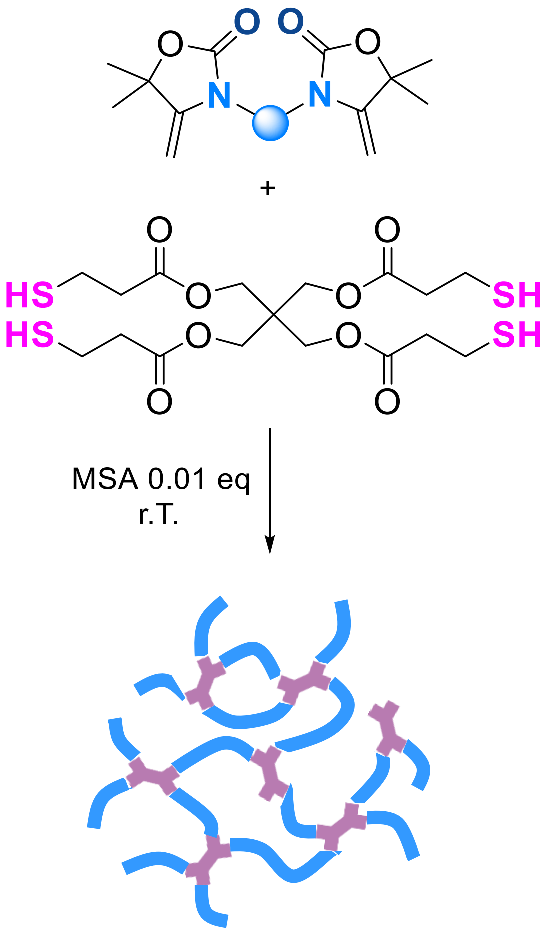


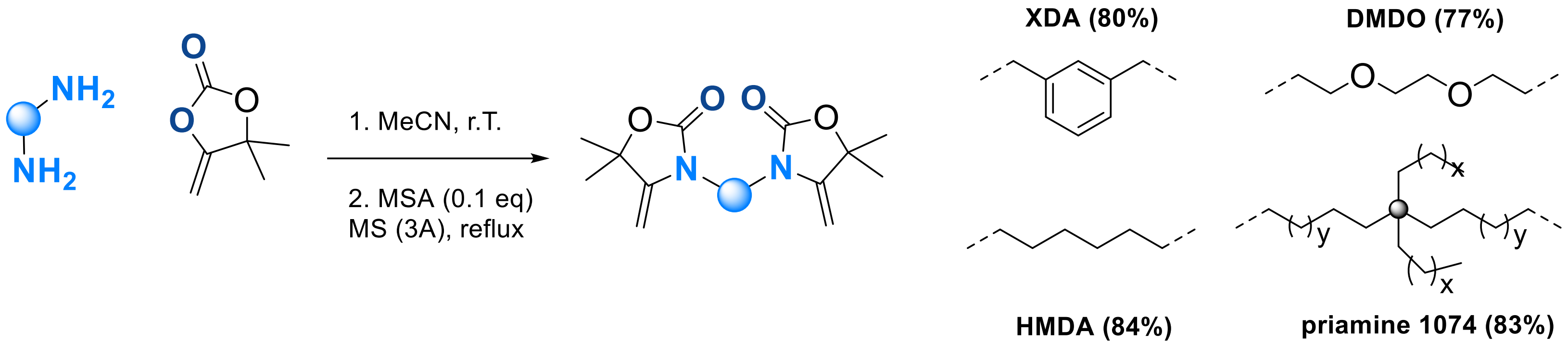
HMDA (84%) priamine 1074 (83%)

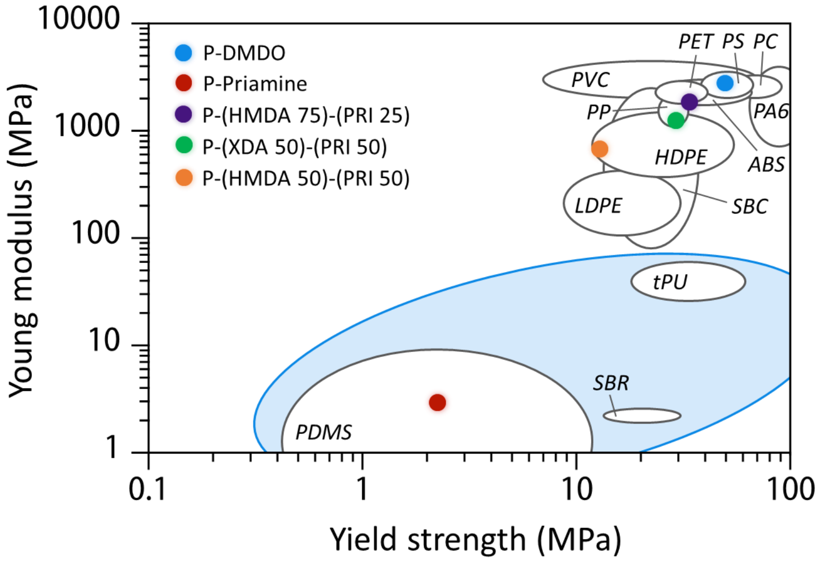
J. Am. Chem. Soc. 2023, 145, 46, 25450–25462

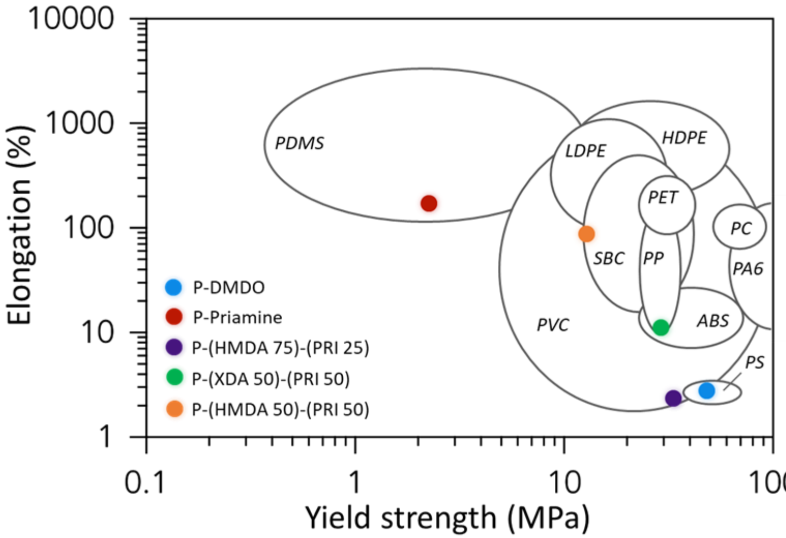
Polymer end-of-life

Covalent adaptable *N,S*-acetal networks







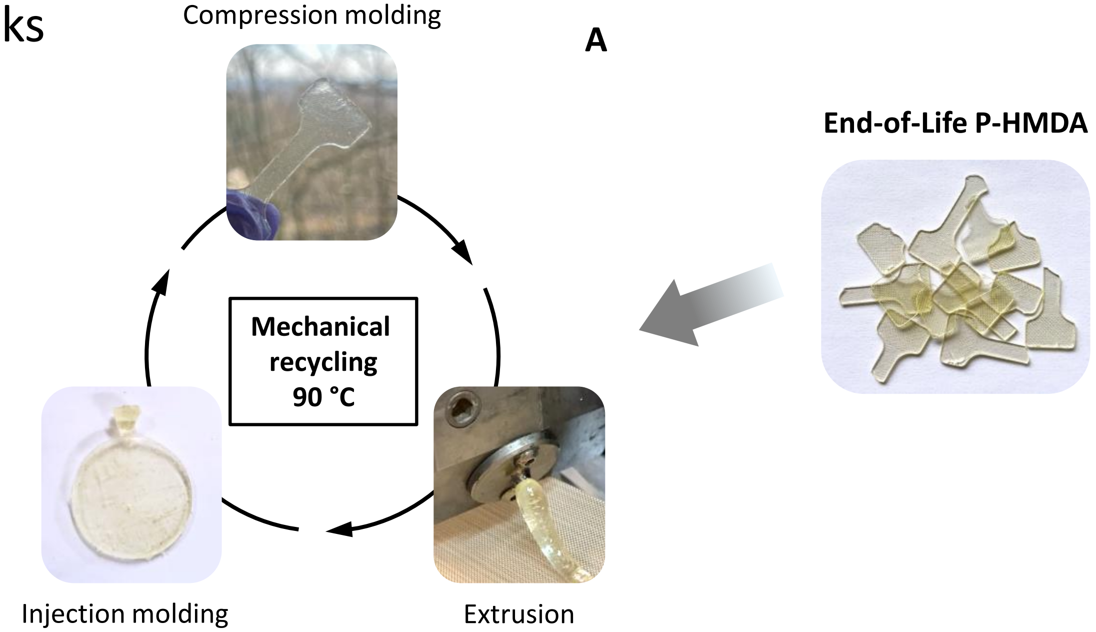


Analogues to comodity polymers

J. Am. Chem. Soc. 2023, 145, 46, 25450–25462

Polymer end-of-life

Recycling *N,S*-acetal networks



J. Am. Chem. Soc. 2023, 145, 46, 25450–25462

Polymer end-of-life

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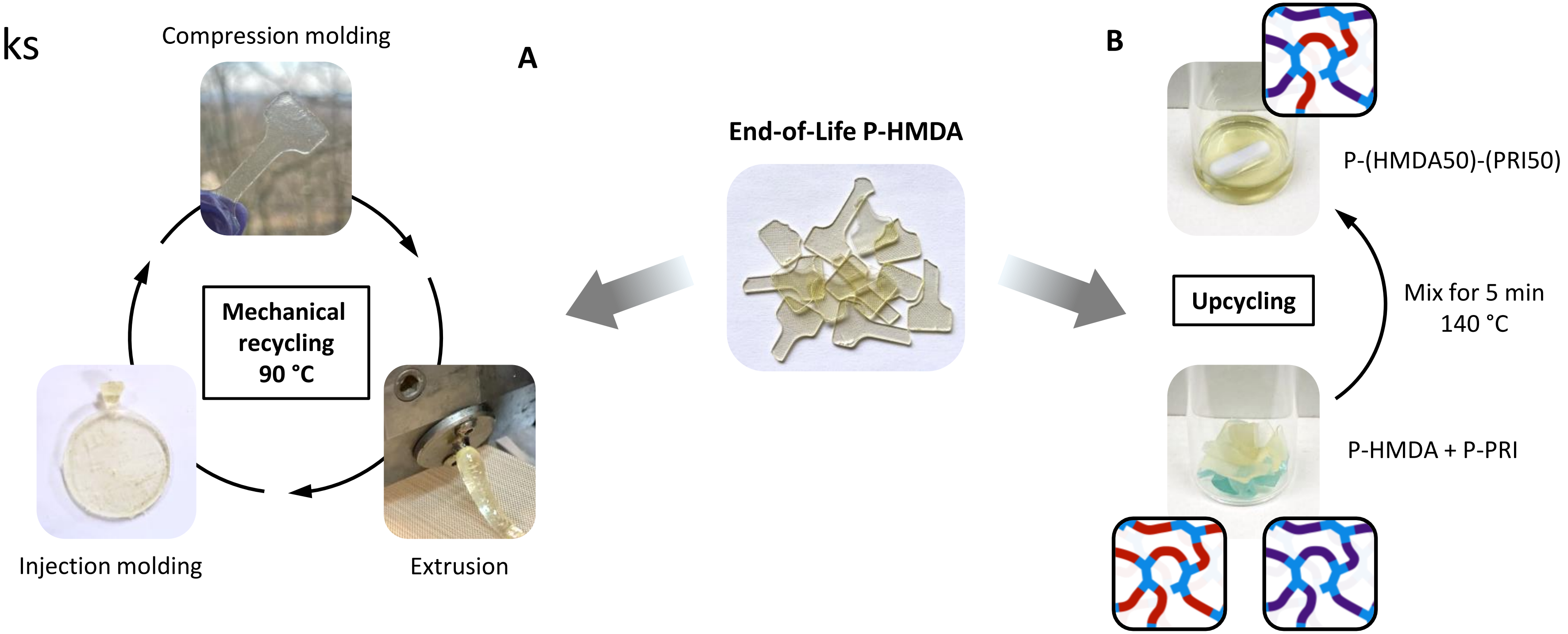
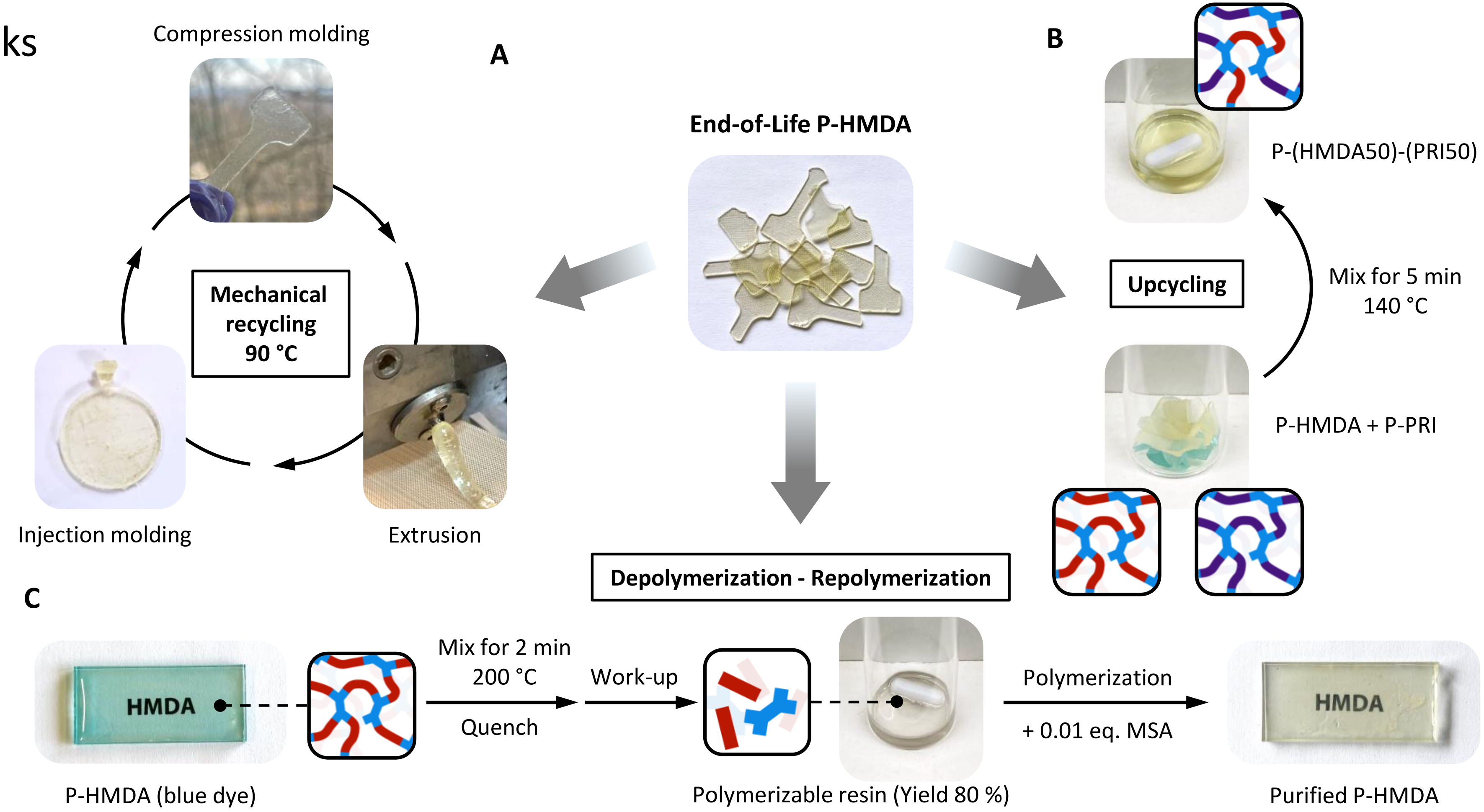


J. Am. Chem. Soc. 2023, 145, 46, 25450–25462

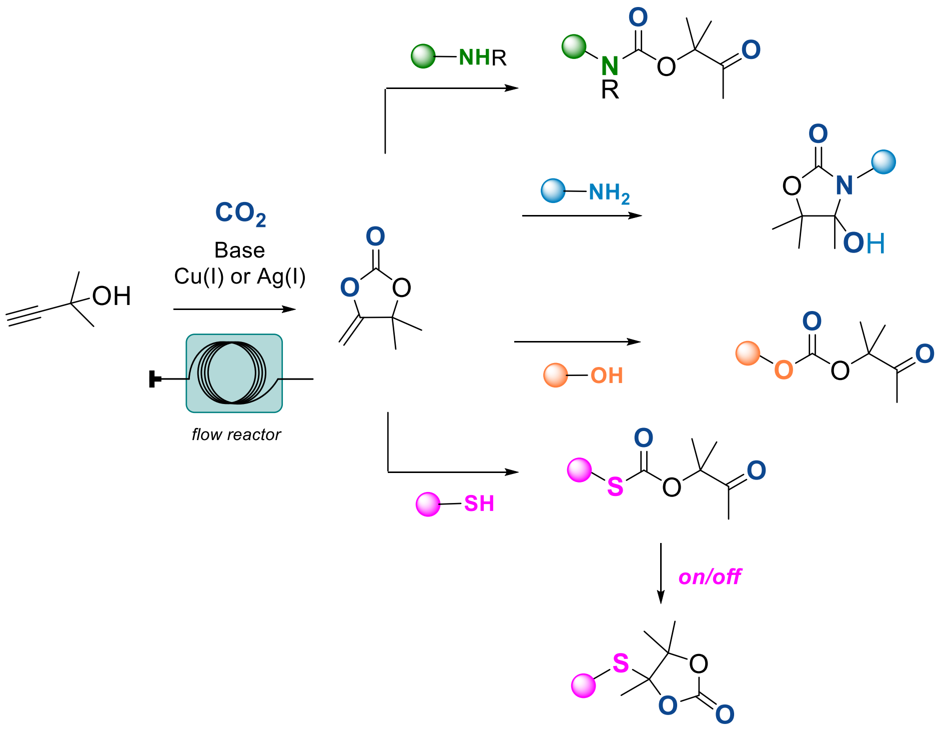
Polymer end-of-life

Recycling *N,S*-acetal networks

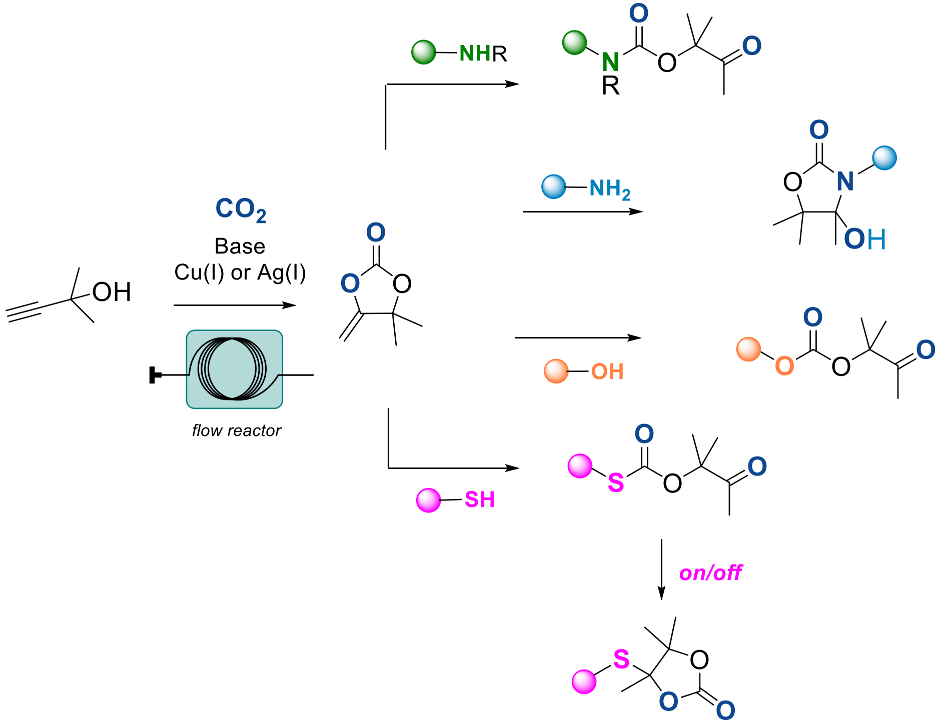


J. Am. Chem. Soc. 2023, 145, 46, 25450–25462

Conceptual approaches to CO_2 polymers



Conceptual approaches to CO_2 polymers



Advanced materials design

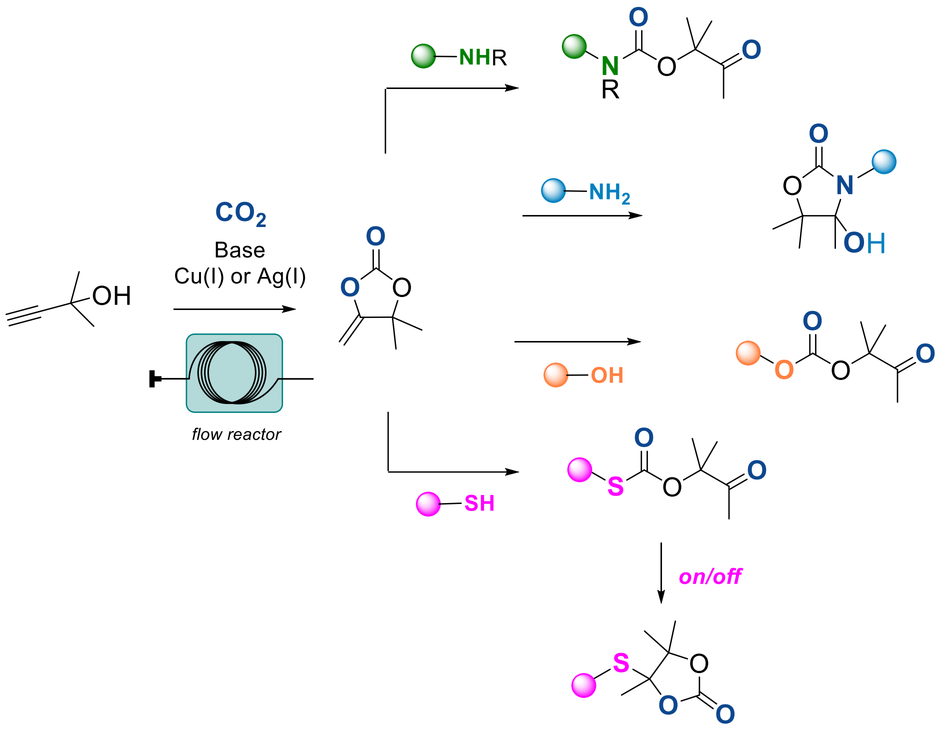
Glues

Heart valves

Tissues
engineering

Solid electrolytes
Li-ion Batteries

Conceptual approaches to CO_2 polymers



Advanced materials design

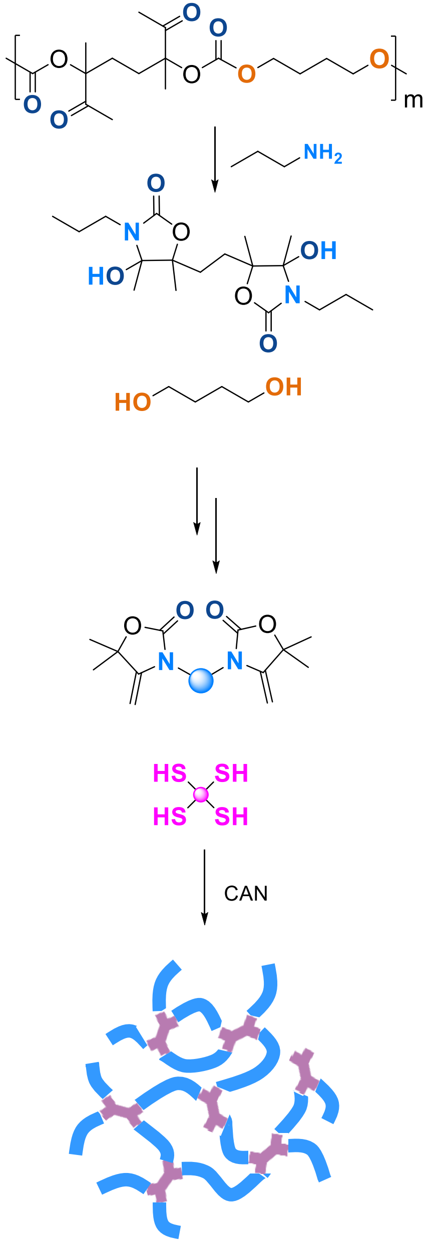

Glues


Heart valves


Tissues engineering

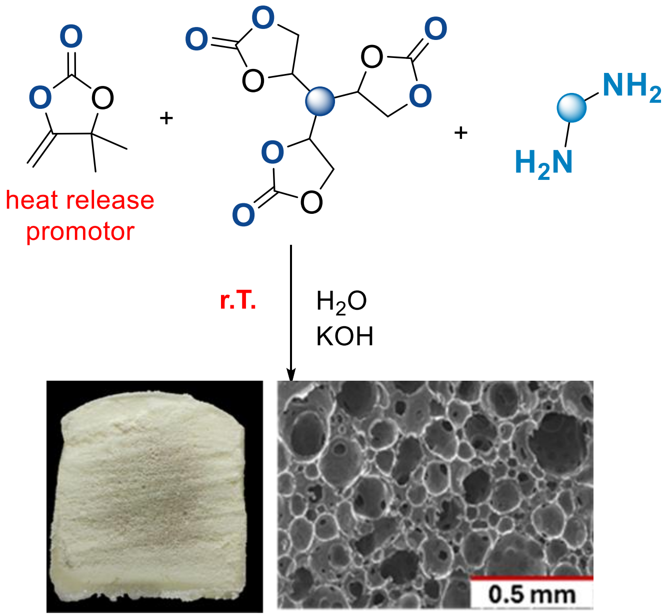

Solid electrolytes Li-ion Batteries

End-of-Life



Future directions

CO_2-self foaming NIPUs

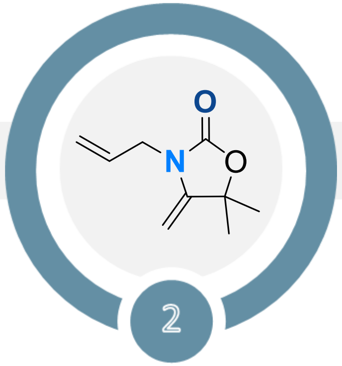


Ultrafast foaming (< 1-5 min)

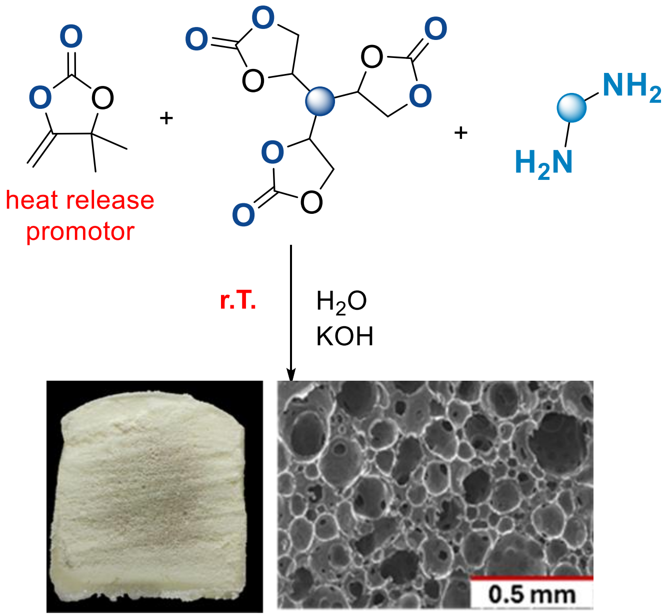
Macromolecules 2025, 58, 3, 1673–1685

Future directions

Adv Mater, 2025, 37, 2417355



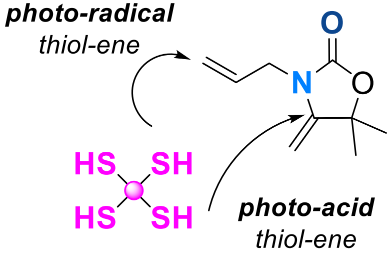
CO_2-self foaming NIPUs



Ultrafast foaming (< 1-5 min)

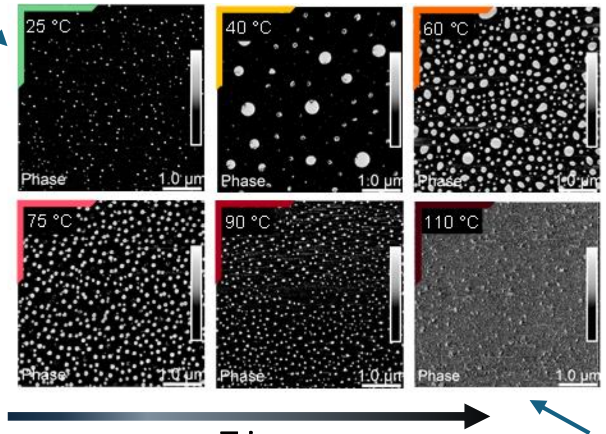
Macromolecules 2025, 58, 3, 1673–1685

Pluripotent materials

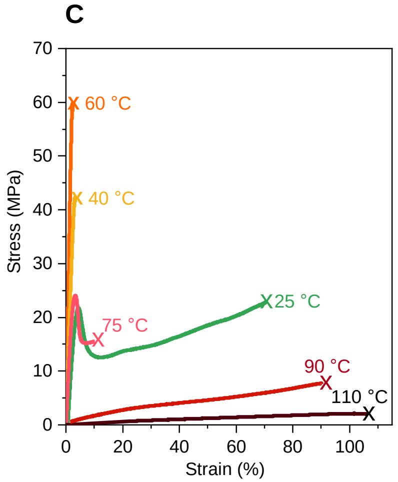


Locked phase

Phase change



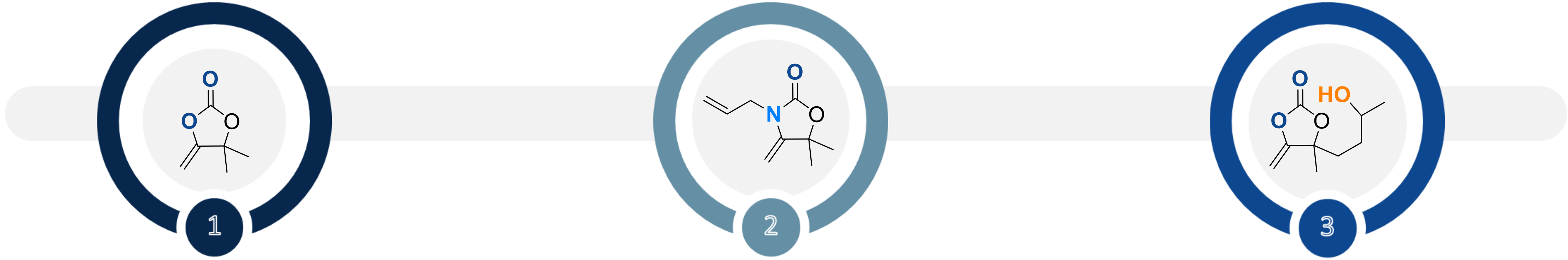
Erased phase



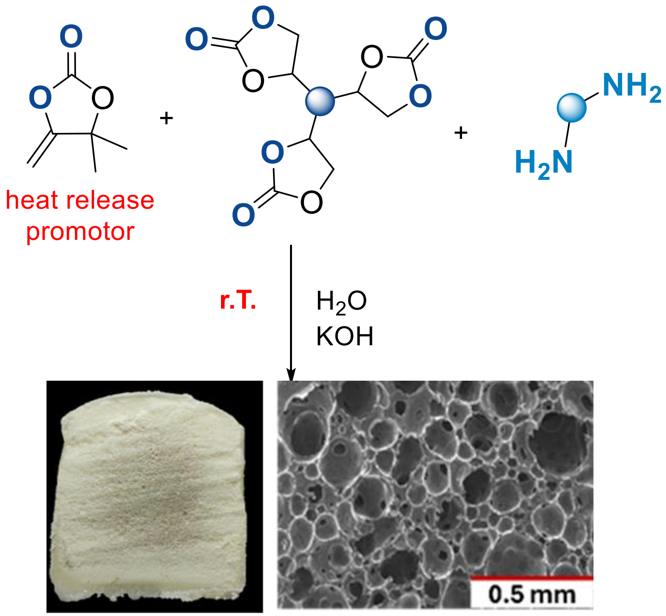
Future directions

Adv Mater, 2025, 37, 2417355

Nature Comm, 205, 16, 1372



CO_2-self foaming NIPUs



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Macromolecules 2025, 58, 3, 1673–1685

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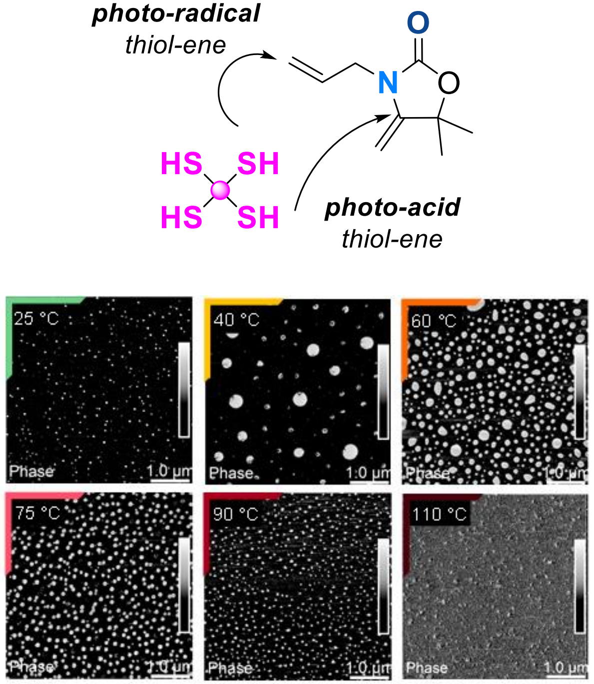
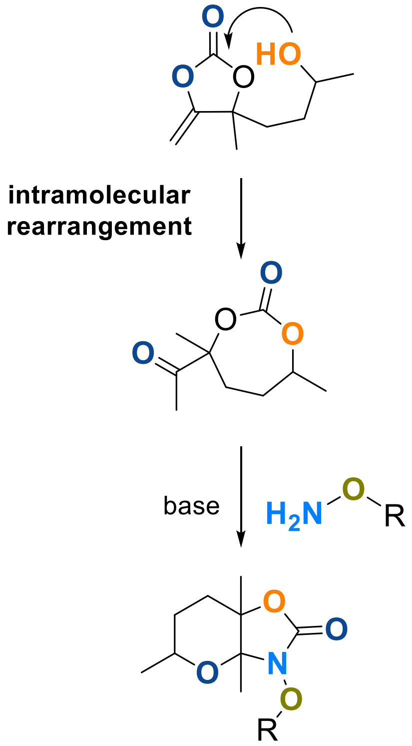


New pharmacores



Acknowlegments

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ET LA WALLONIE INVESTISSENT DANS VOTRE AVENIR

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Thank you