Chemically recyclable elastomers from low-ceiling temperature β-methyl-δ-valerolactone monomer

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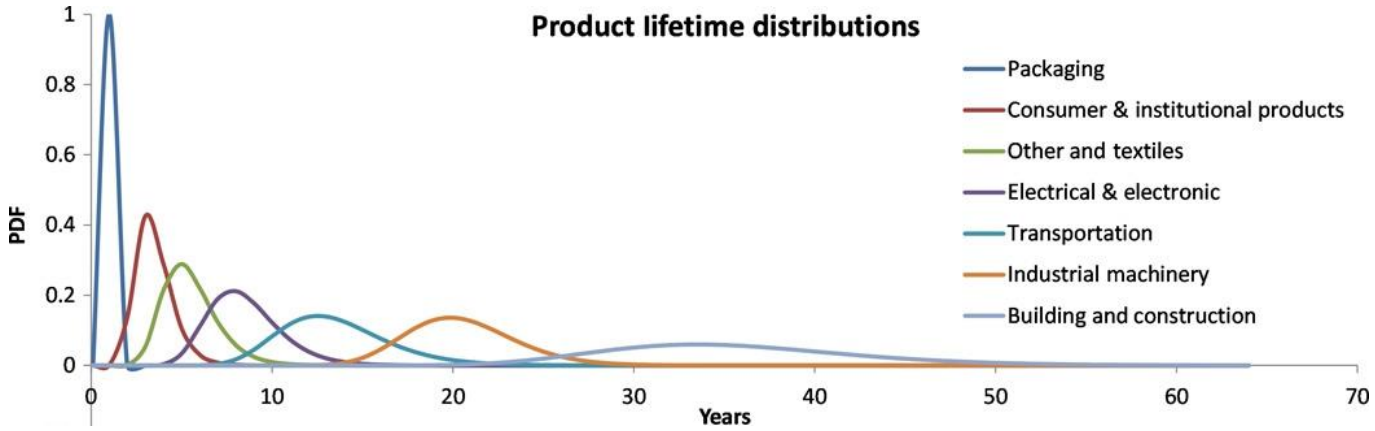
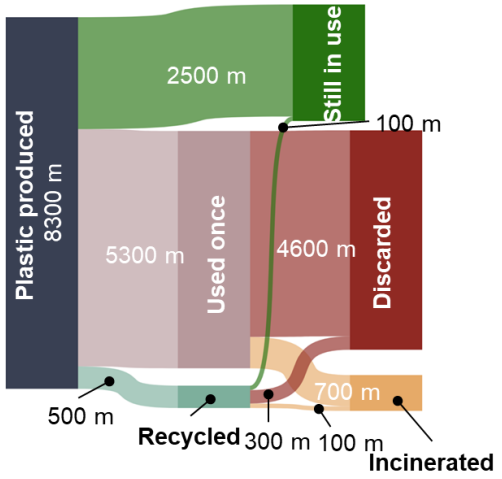
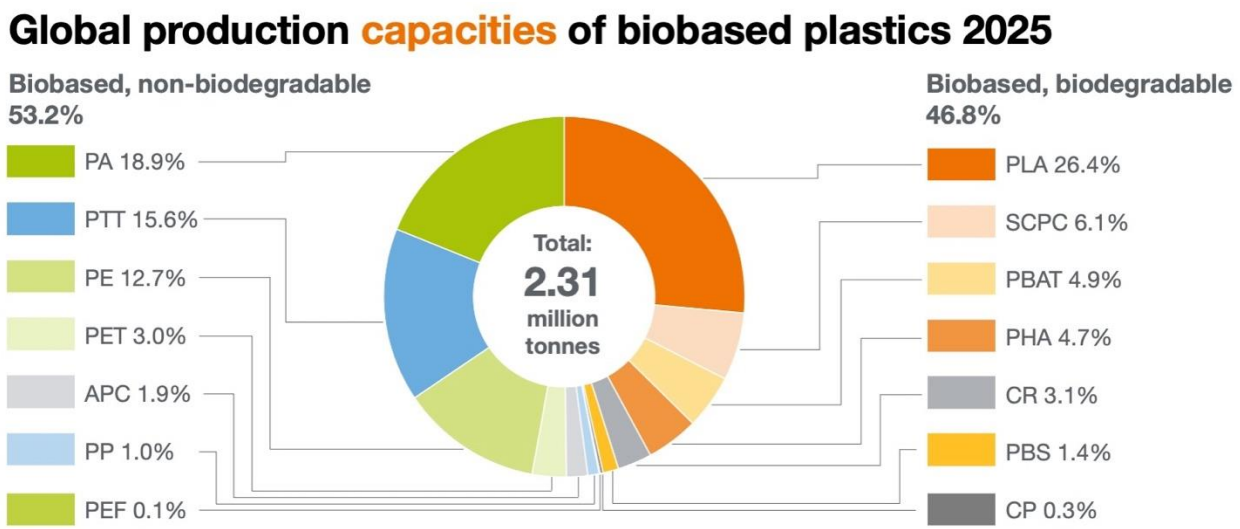
Current approach to plastics is limited

Plastic lifetimes exceed desired use window, contributing to waste





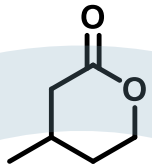


Only 0.5% of annual plastic production

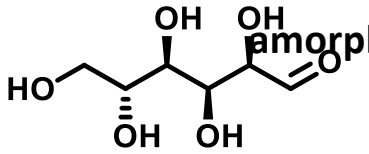
Geyer, R.; Jambeck, J. R.; Law, K. L. Sci Adv 2017, 3, e1700782; https://www.european-bioplastics.org/market/

PβMVL as a sustainable soft segment

β-methyl-δ-valerolactone (βMVL)



engineered *E.coli*



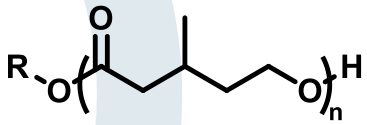
amorphous polyol (T_g = -60 °C)

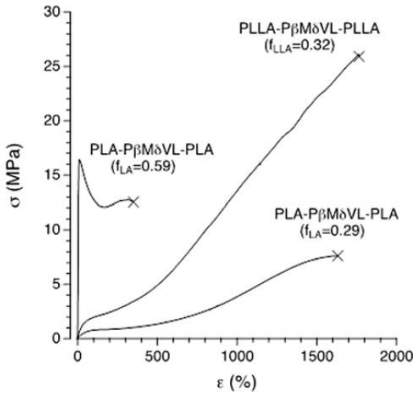
- Renewable feedstock
- Economically competitive (<$2/kg)

Xiong et al. *PNAS* **2014**, *111*(23), 8357–8362.

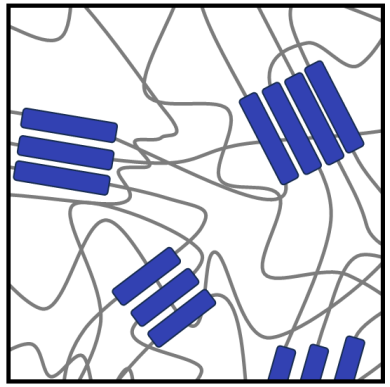
Poly(β-methyl-δ-valerolactone) (PβMVL)

bulk T_c = 227 °C

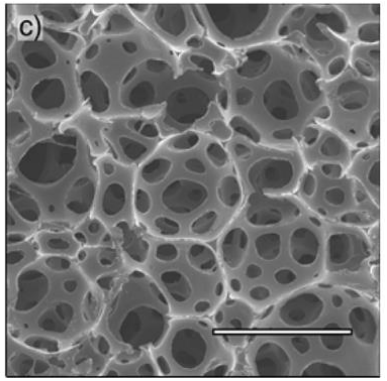




thermoplastic elastomers



thermoplastic polyurethanes



polyurethane foams (thermoset)

elastomers

Xiong et al. *PNAS* **2014**, *111*(23), 8357–8362.
Schneiderman et al. *ACS Macro Lett.* **2016**, *5*(4), 515-518.

Ceiling temperature dictates polymerizability

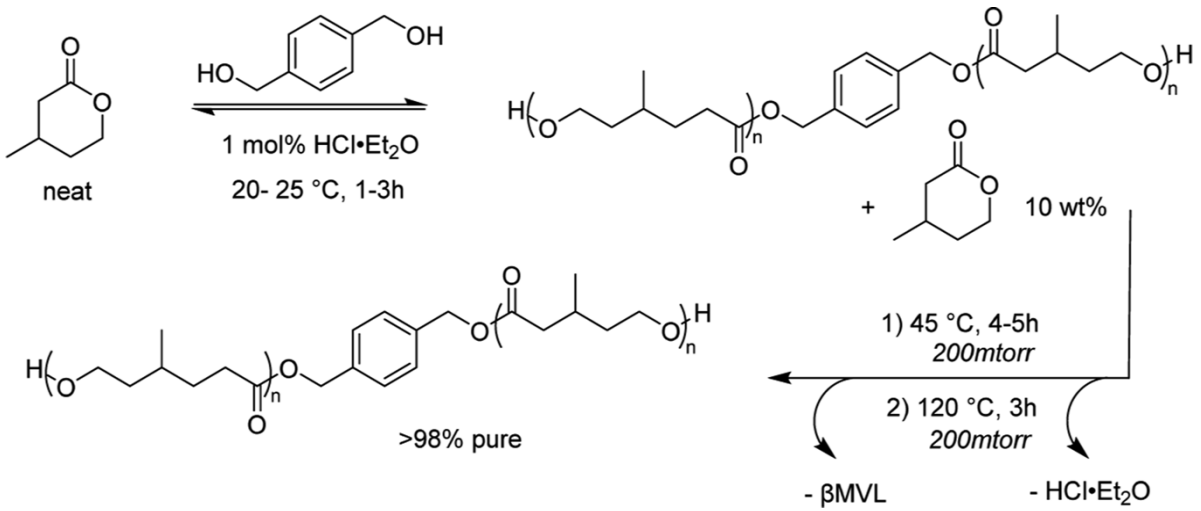
How can we manage $[M]_{eq}$?

$T > T_c$ $T = T_c$ $T < T_c$

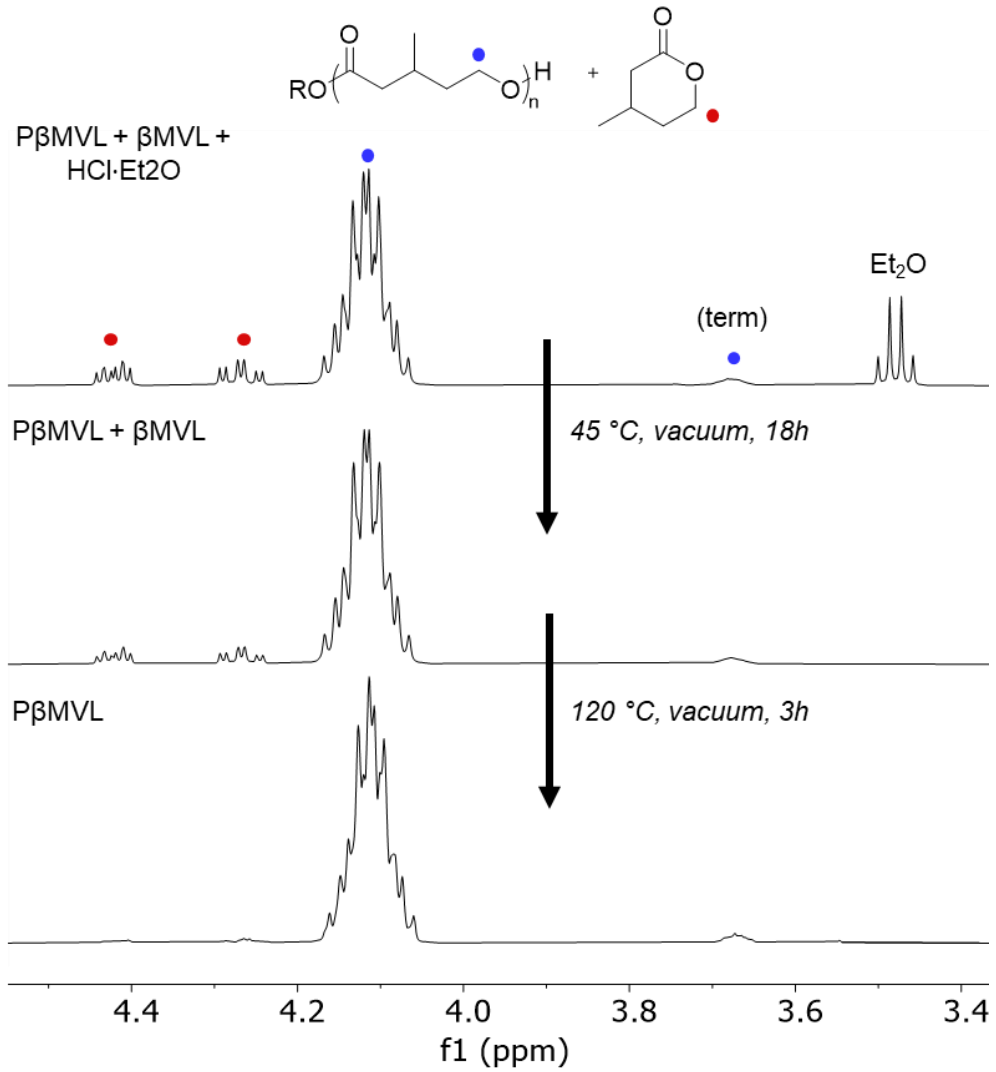
$k_{polym} < k_{depolym}$ $k_{polym} = k_{depolym}$ $k_{polym} > k_{depolym}$

$$T_c = \frac{\Delta H_p}{R\ln\left([M]_{eq}/[M]_{ss}\right) + \Delta S_p}$$

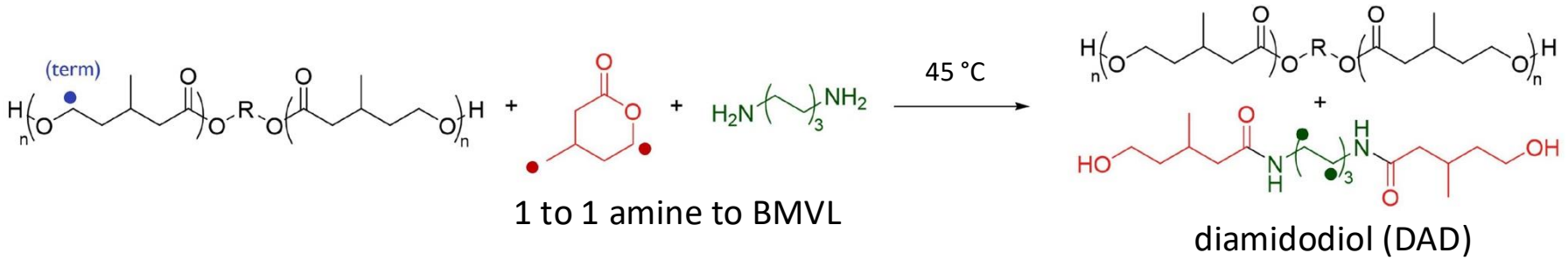
Distillation approach to residual monomer

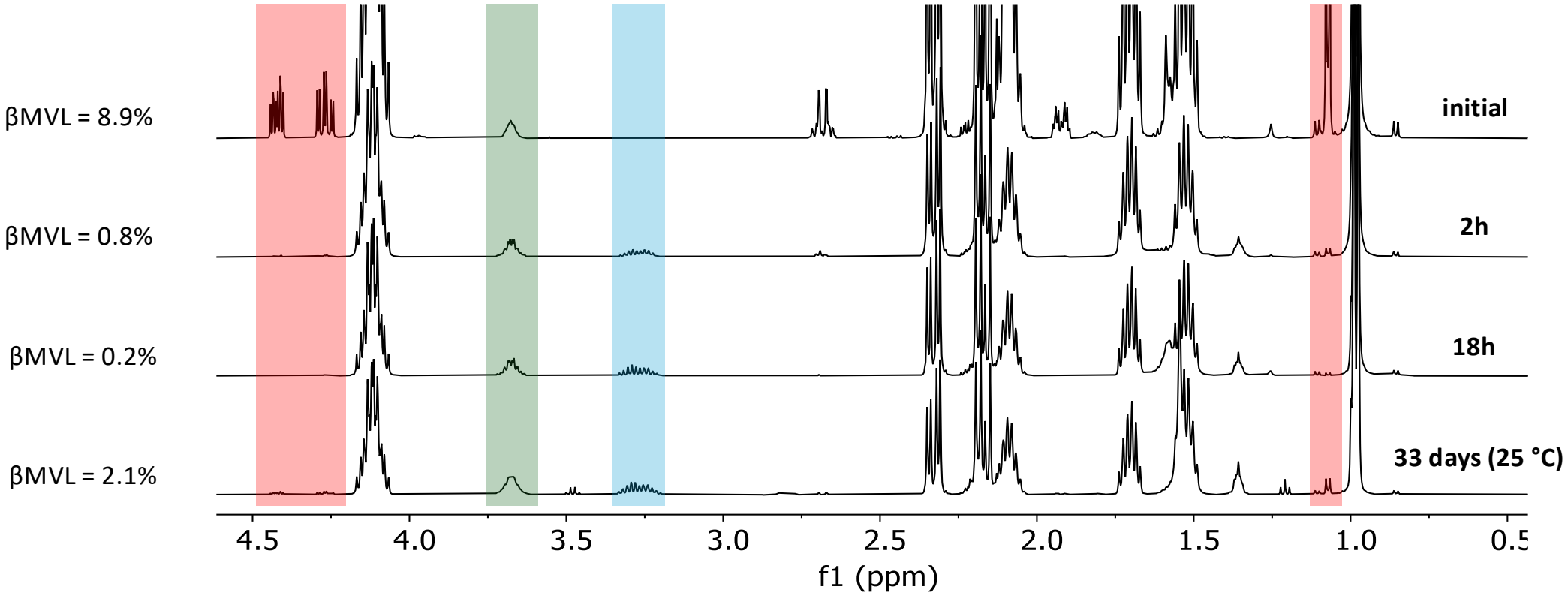


Restores equilibrium in glass vial after one month

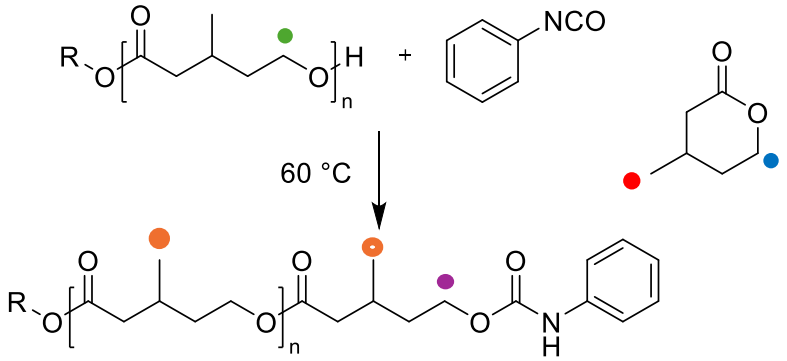


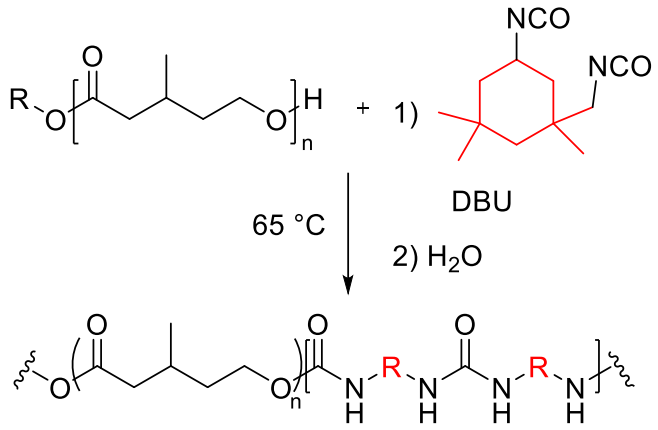
Sequestration approach to residual monomer

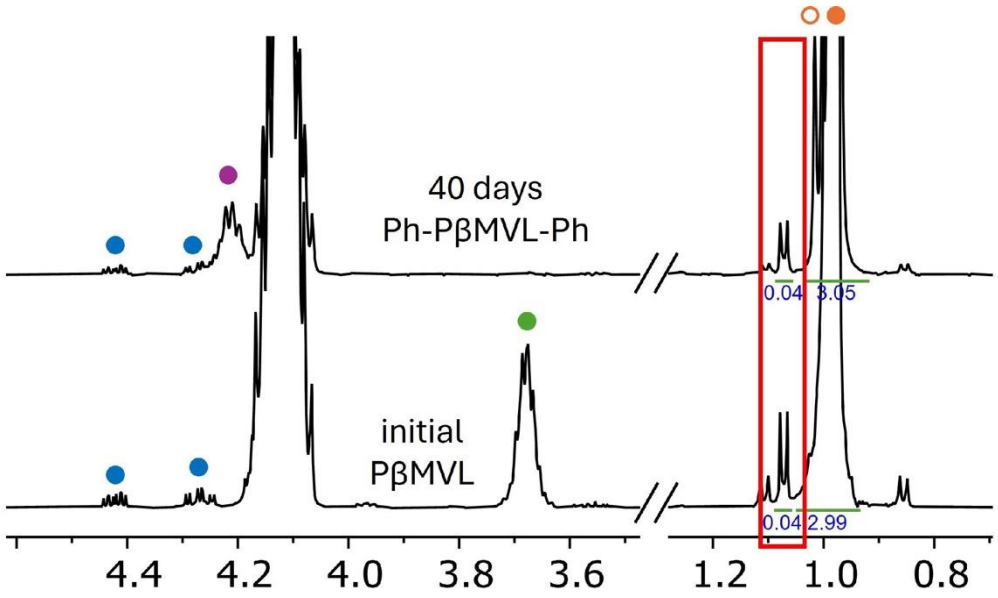


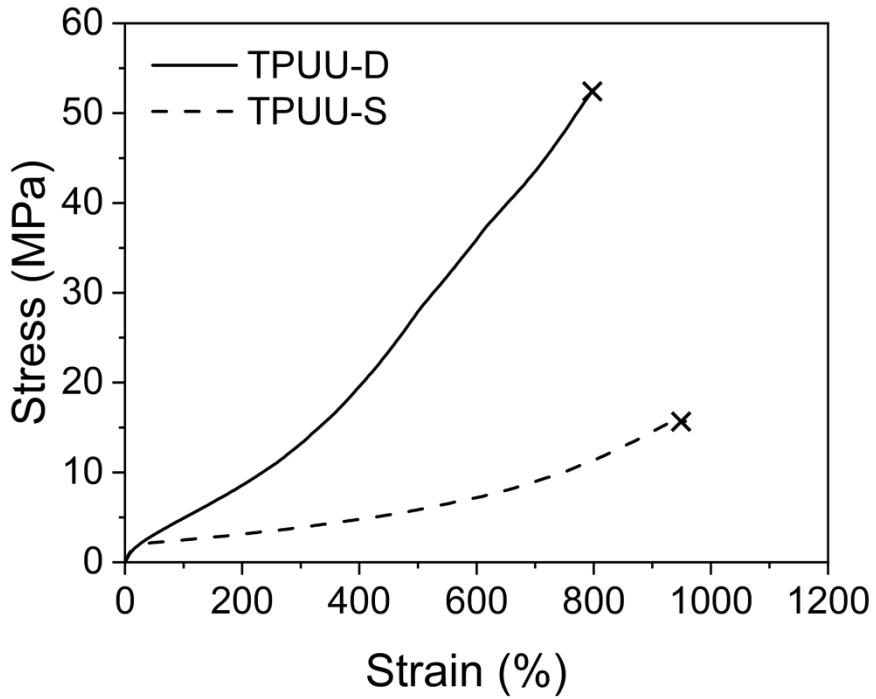


Endcapping enhances PβMVL stability

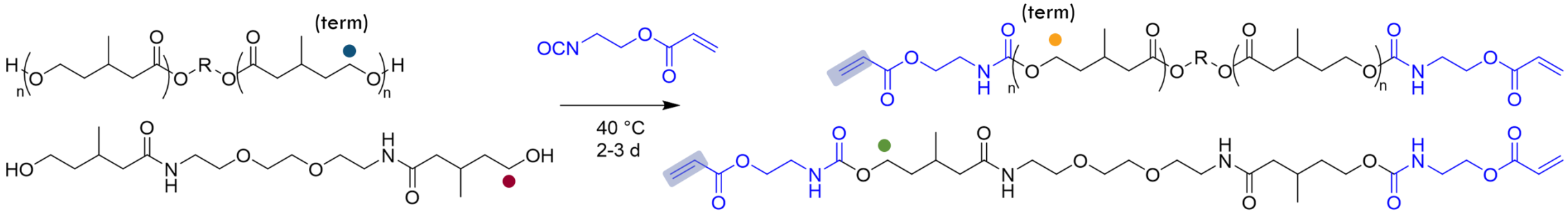


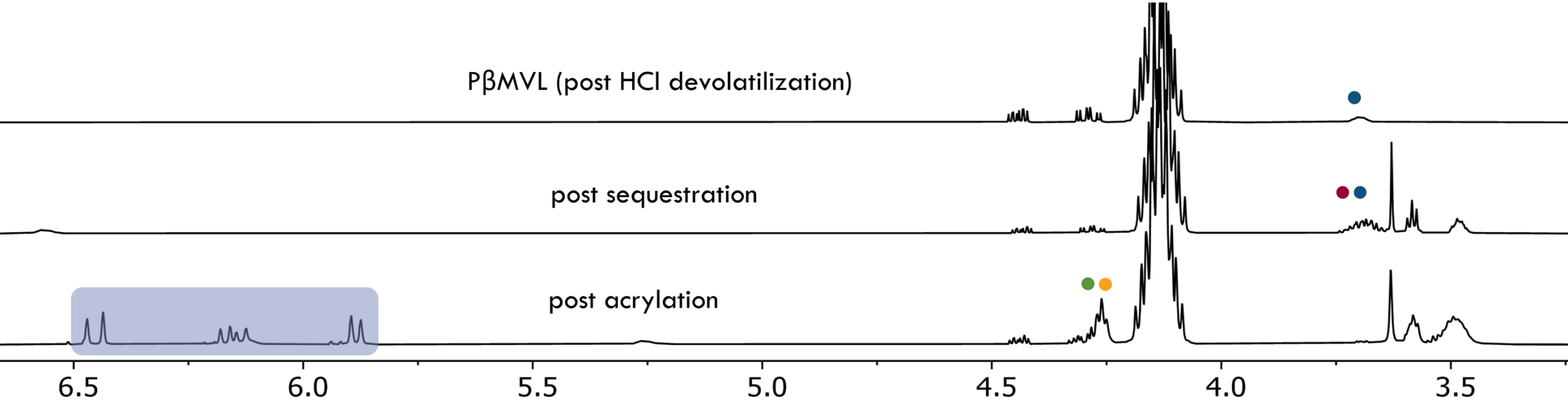




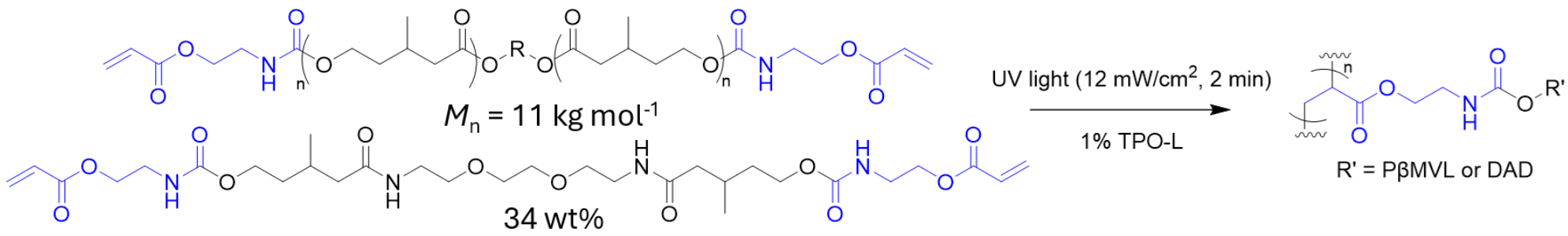


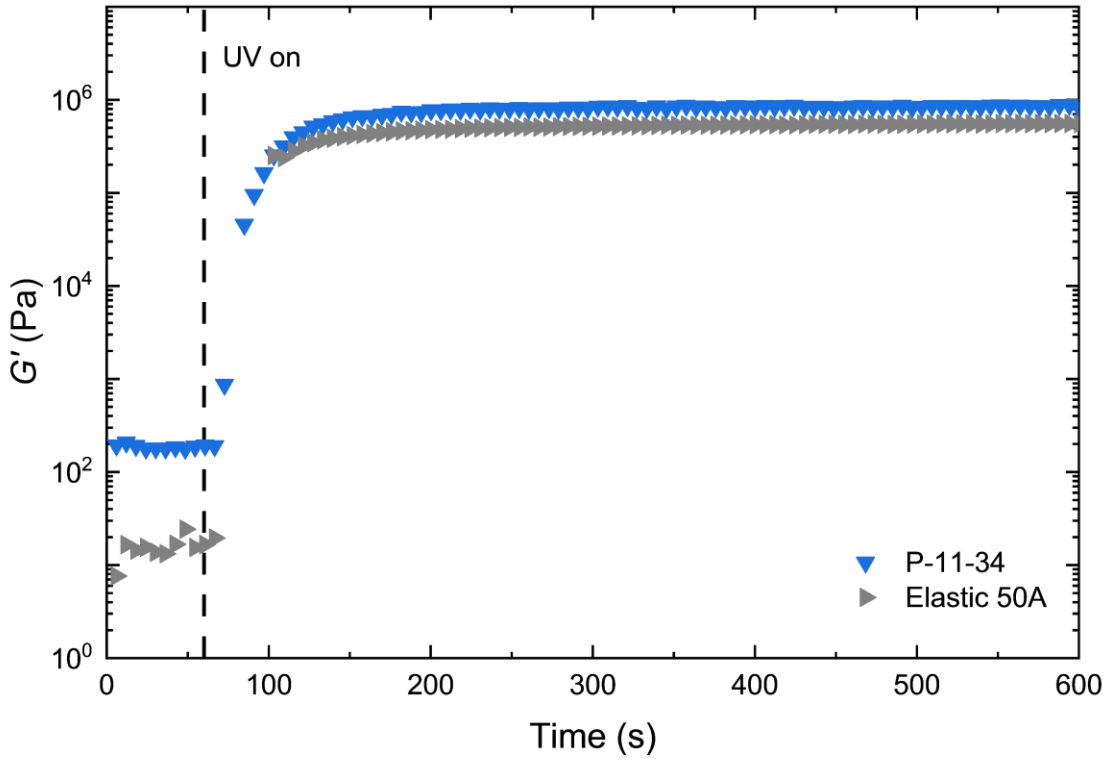
Acrylation for 3D printing capabilities



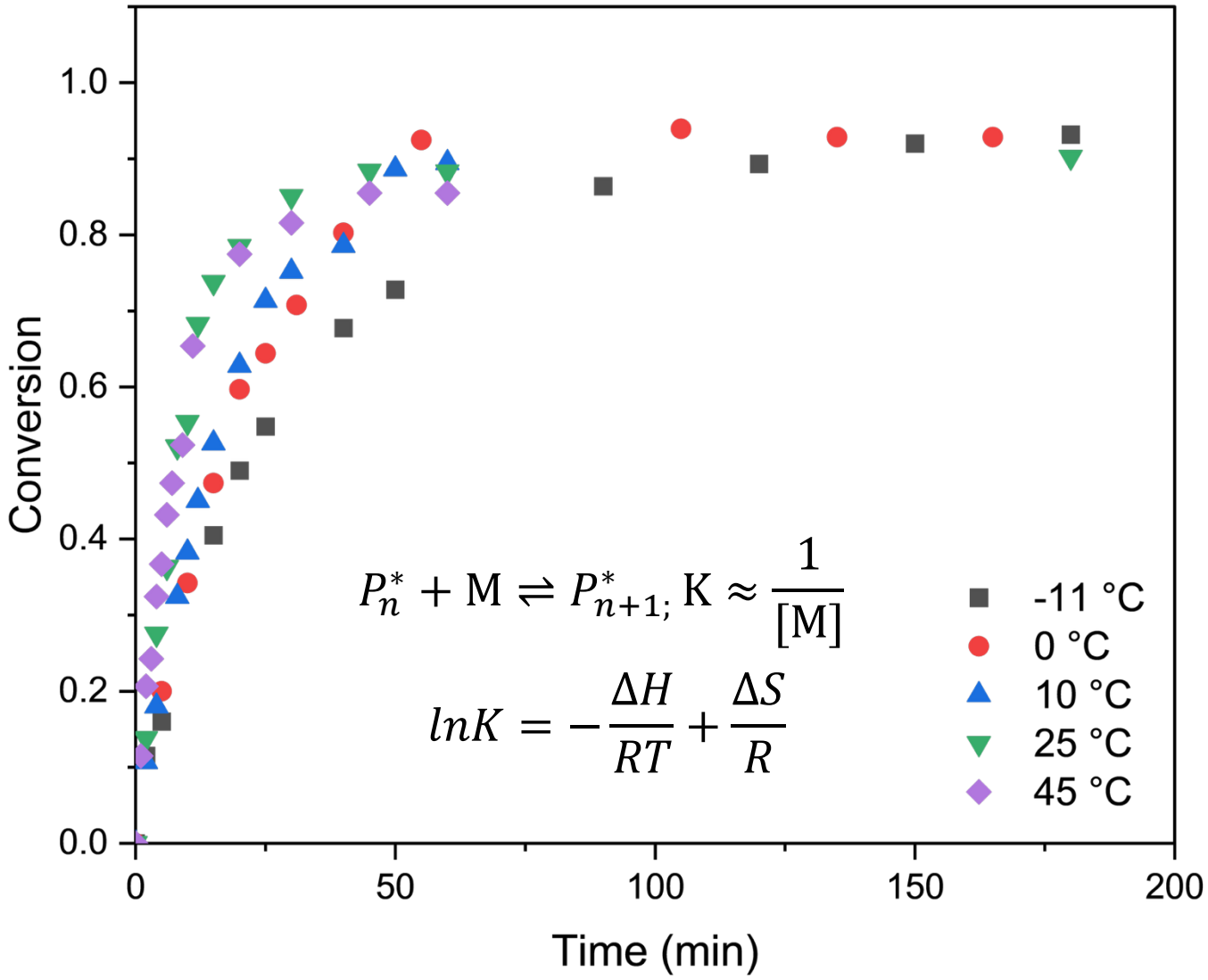


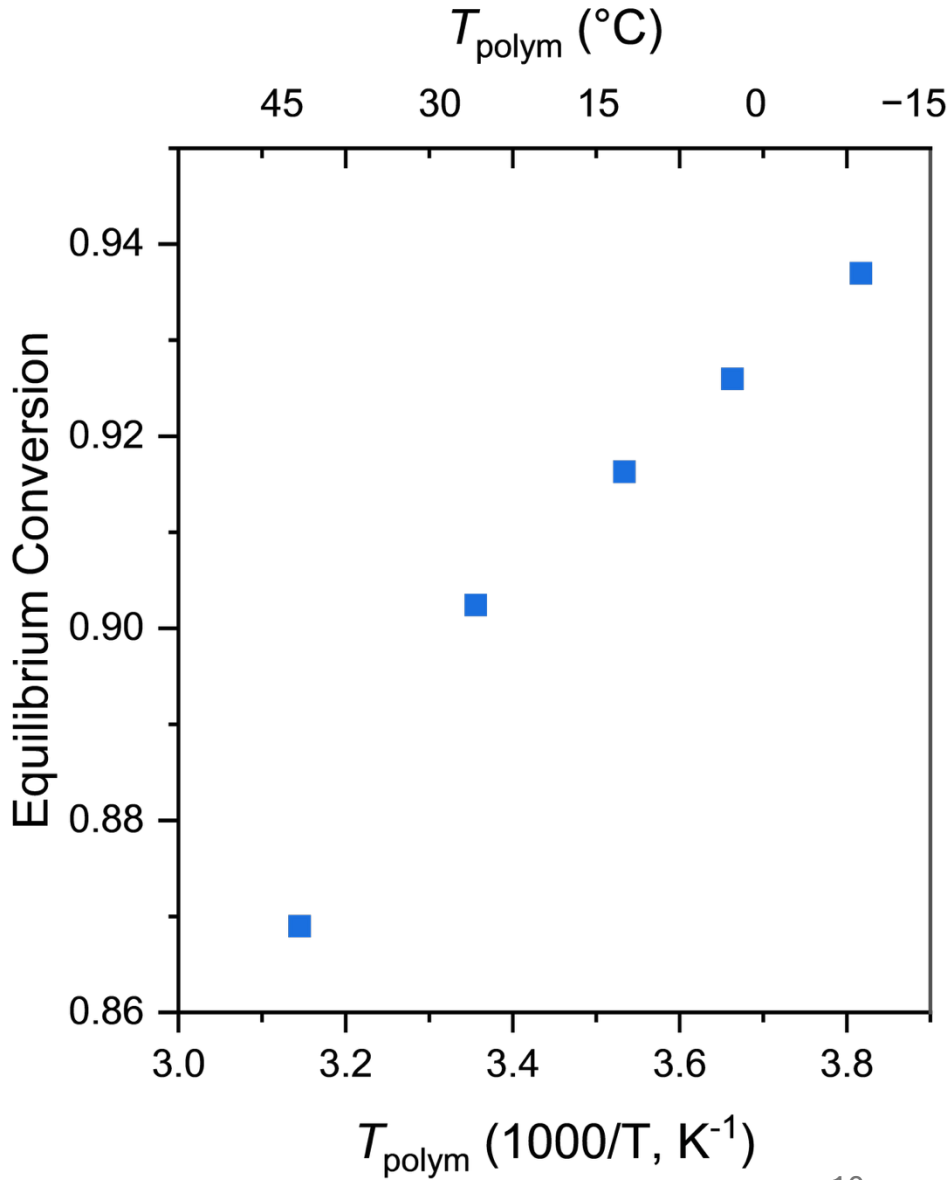
Rapid photocuring kinetics





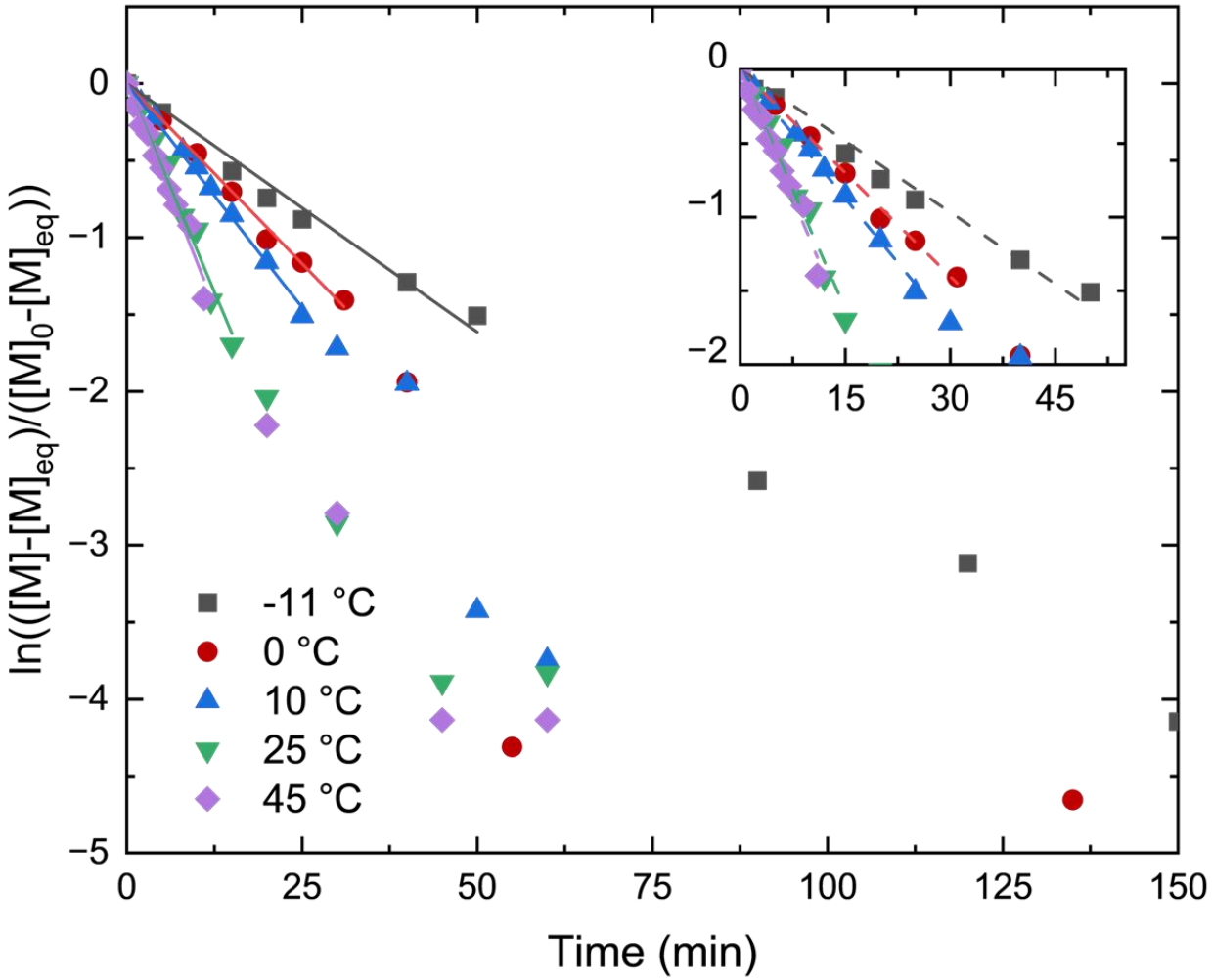
T_{polym} to control $[\beta MVL]_{eq}$ for sequestration to DAD

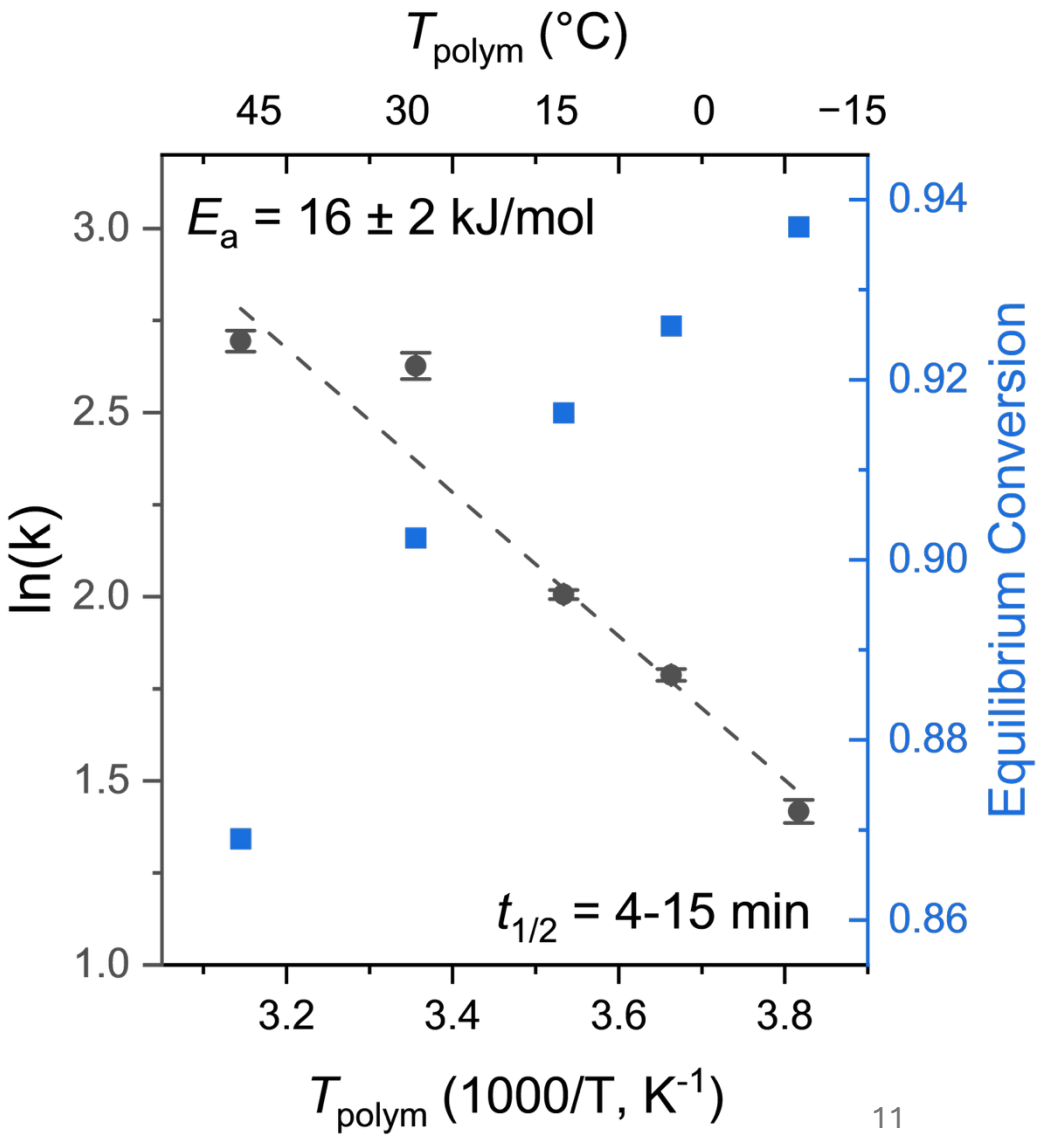




Extracting kinetic data

$$\frac{-d[\beta MVL]}{dt} = k_{app}\,[\beta MVL]^x \; where \; k_{app} = \mathrm{k[HCl]}^y[\mathrm{ROH}]^z$$





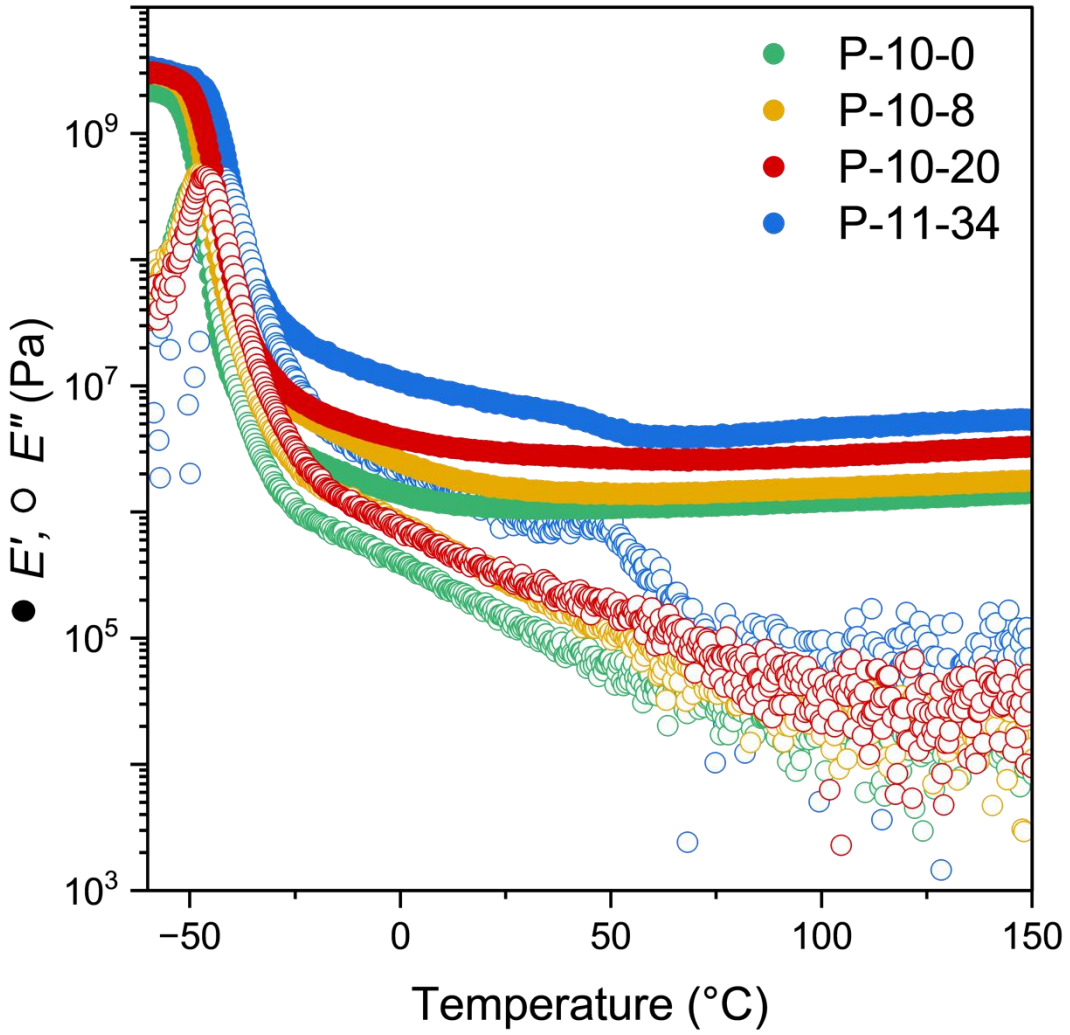
Library of polymers

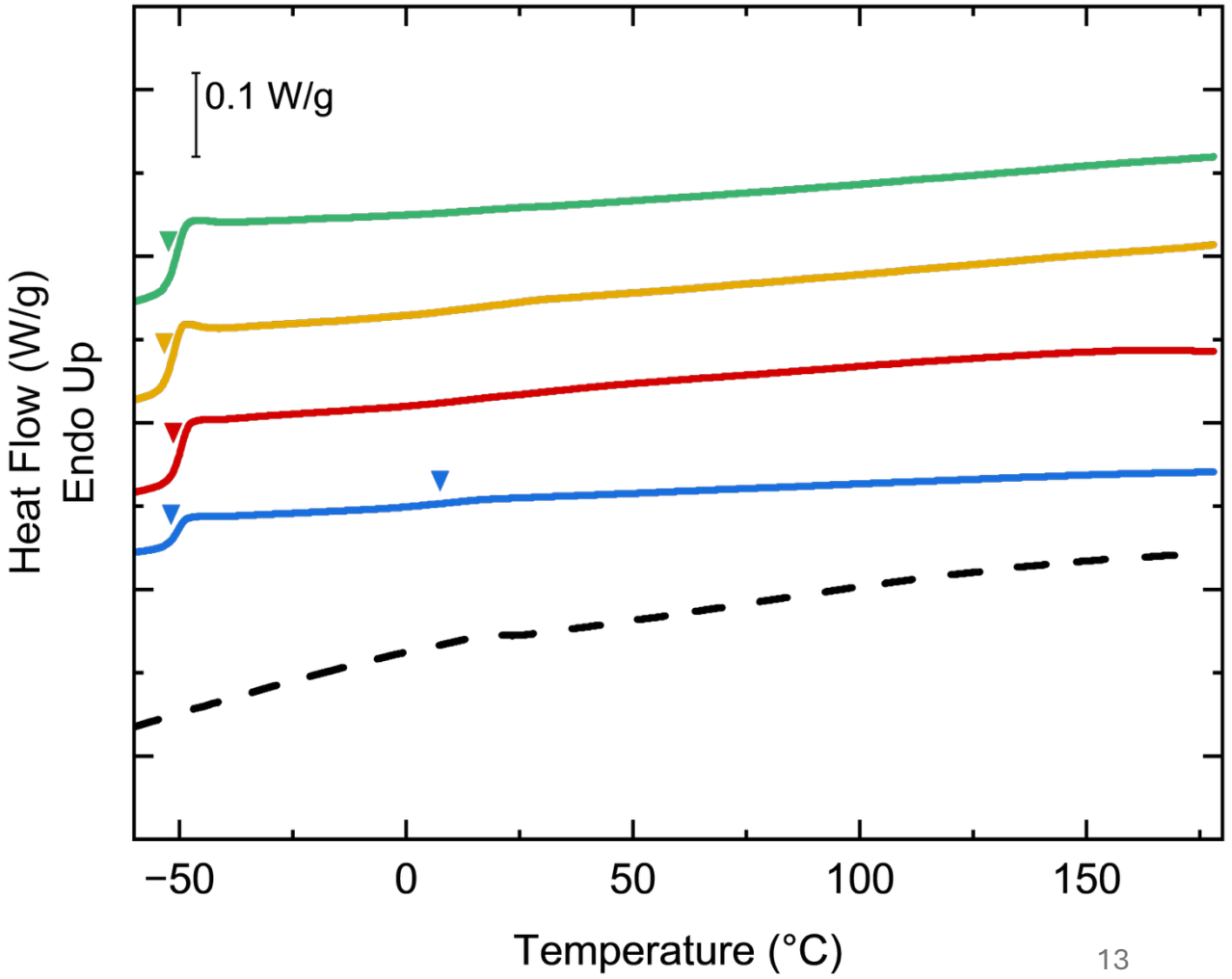
P-$M_{n,P\beta MVL}$-DAD (wt%)

Sample	PβMVL M_n (kg mol^{-1})	T_{polym} (°C)	DAD (wt%)	BBC	Gel Frac (%)	Degree of Swelling
P-10-0	10.2	22	0	0.98	85 ± 3	7.4 ± 0.4
P-10-8	9.5	–4	8.2	0.95	90 ± 10	6.4 ± 0.5
P-10-20	10.2	22	20.1	0.92	98 ± 8	5.0 ± 0.2
P-11-34	10.7	45	34.4	0.88	91 ± 2	5.1 ± 0.9
P-5-20	5.0	22	20.3	0.90	87 ± 1	4.79 ± 0.03
P-28-23	28.0	22	23.2	0.92	77 ± 1	6.5 ± 0.1

Thermal properties of crosslinked materials

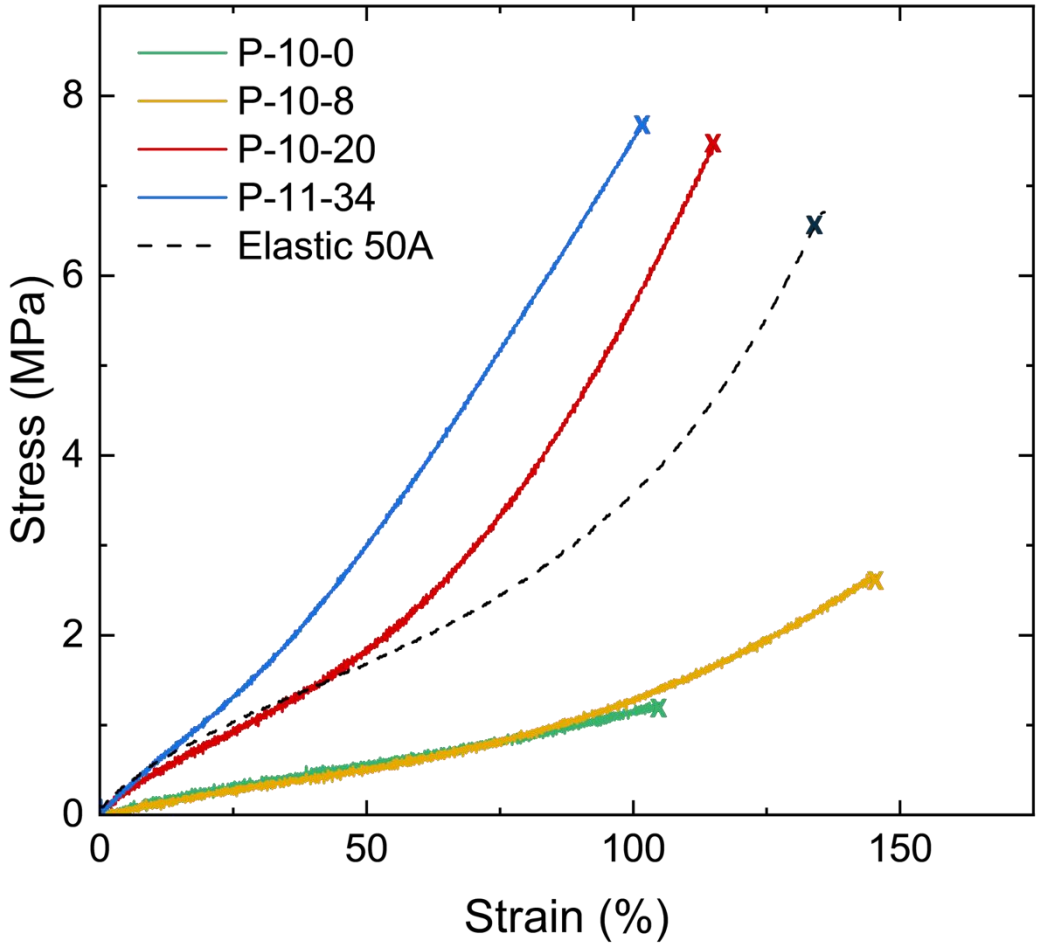
$$M_{x,eff} = \frac{\rho RT}{G_N}$$

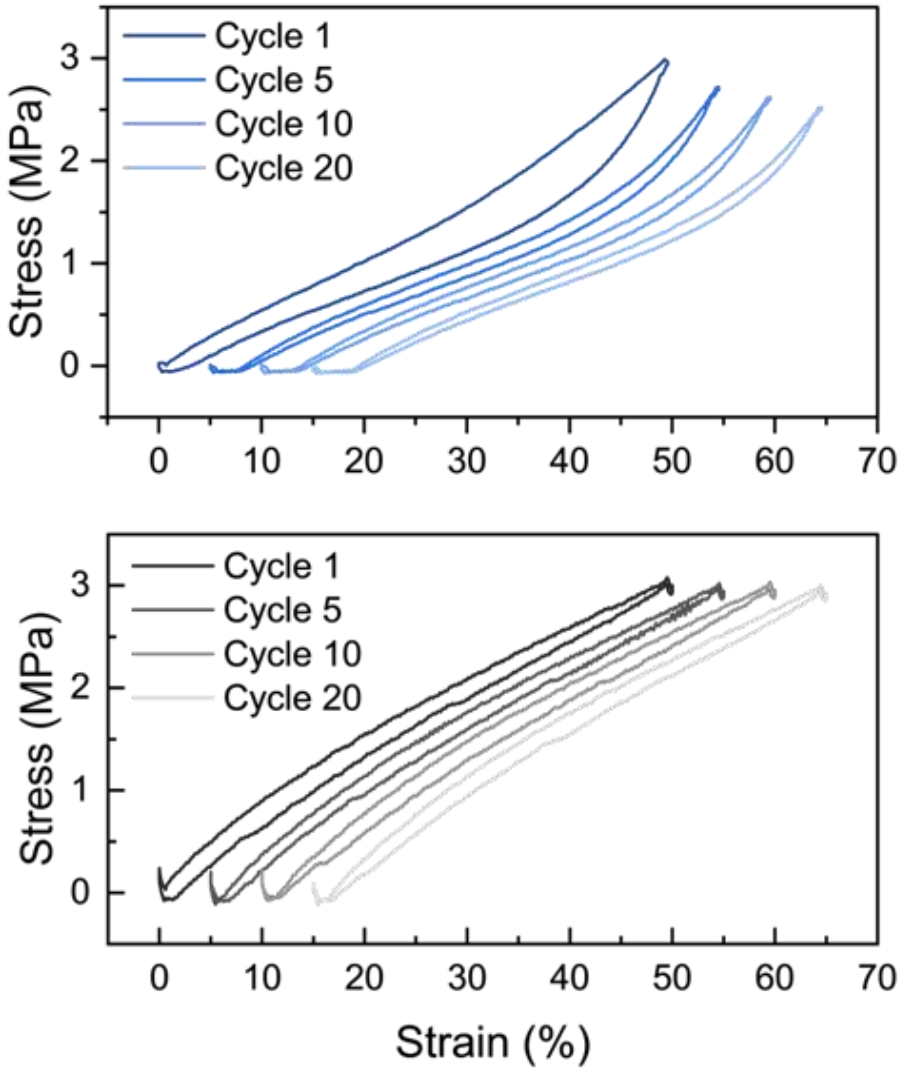




Mechanical performance enhanced by DAD

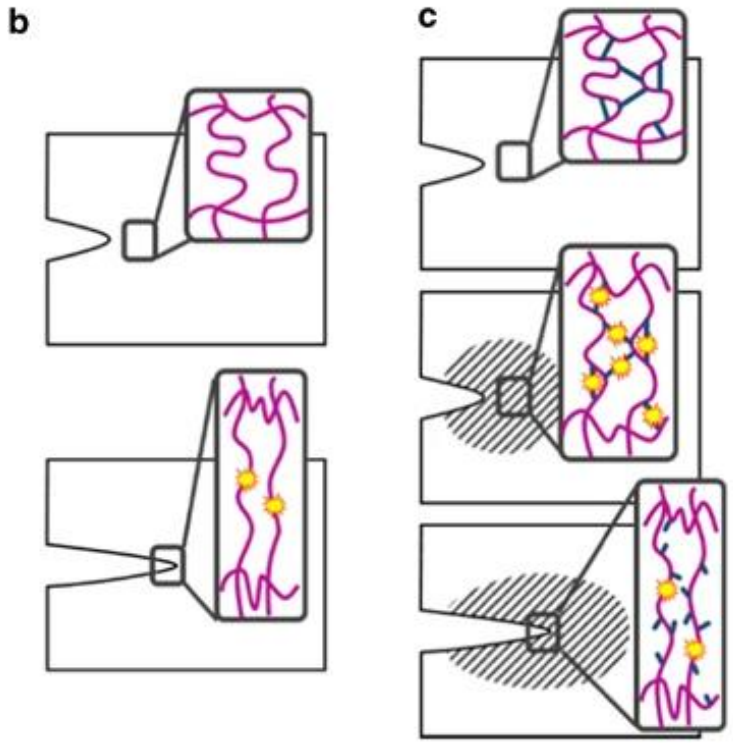
Sample	σ_b (MPa)	ε_b (%)	E_y (kPa)
P-10-20	6 ± 1	100 ± 20	48 ± 8
Elastic 50A	6 ± 3	130 ± 20	47 ± 3





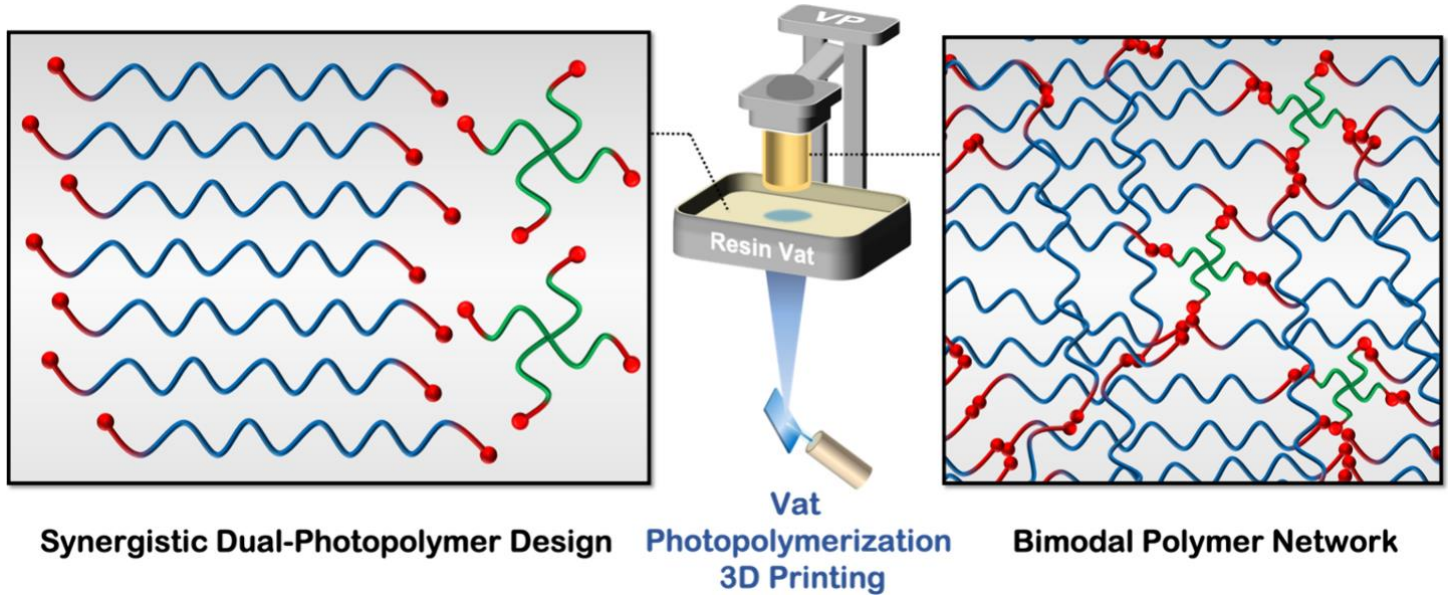
Literature precedent for DAD effects

Brittle hydrogen bonds in **stretchy matrix**



Nakajima, T. *Polym. J.* **2017**, 49, 477-485.

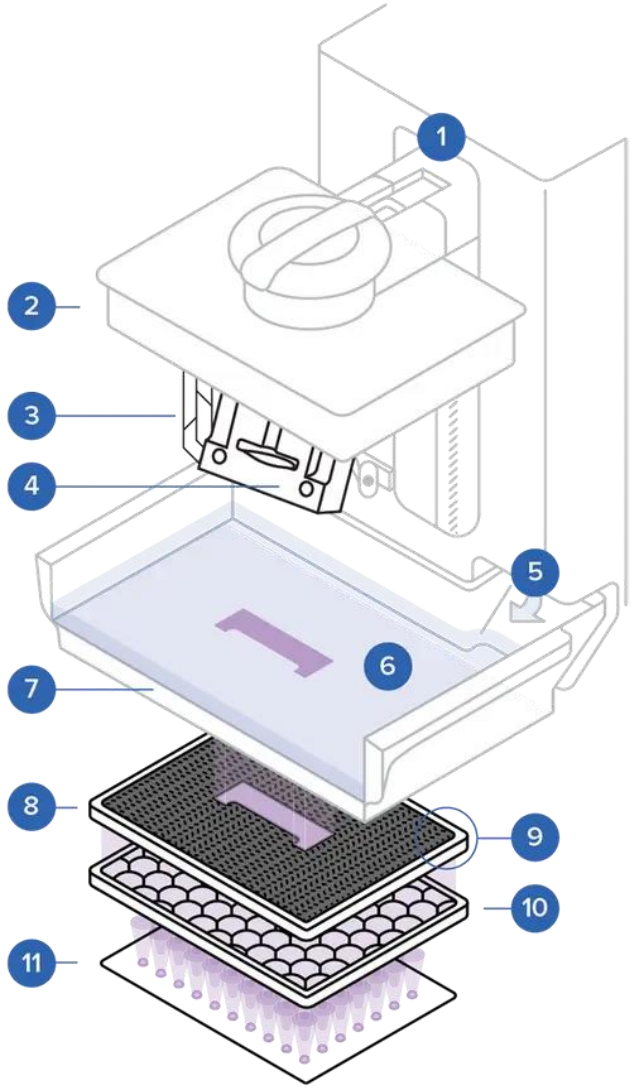
Strength from high crosslinking density and **flexibility from low crosslinking density**

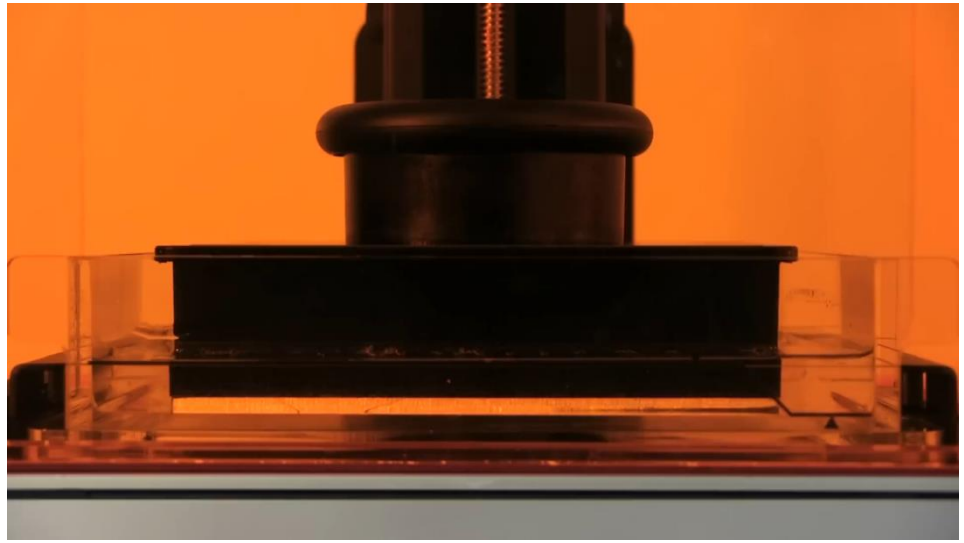


Bao, Y. *ACS Appl. Polym. Mater.* **2024**, *6*(23), 14026-14036.

Vat photopolymerization requirements

1. Six Control Systems
2. Build Platform
3. Supports
4. Printed Part
5. High-Speed Automatic Resin Handling
6. Resin
7. Flexible Film Resin Tank
8. Light Processing Unit 4
9. Release Texture
10. Collimating Lenses
11. LEDs

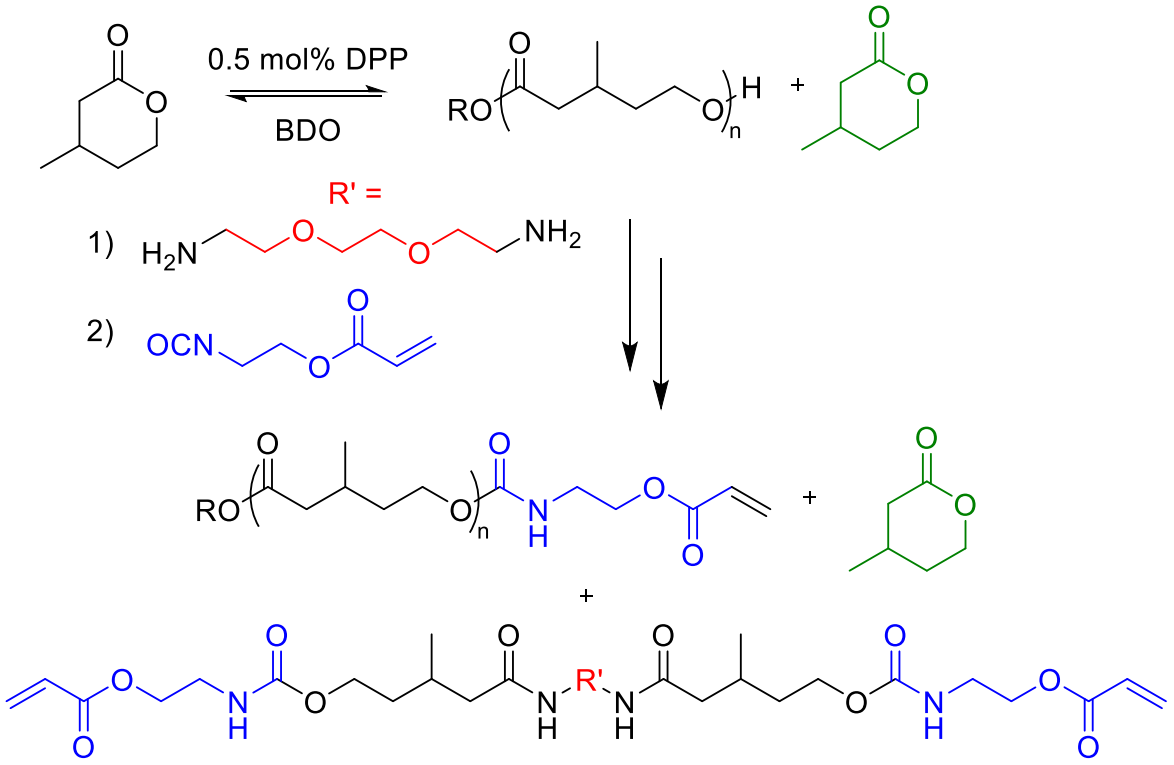




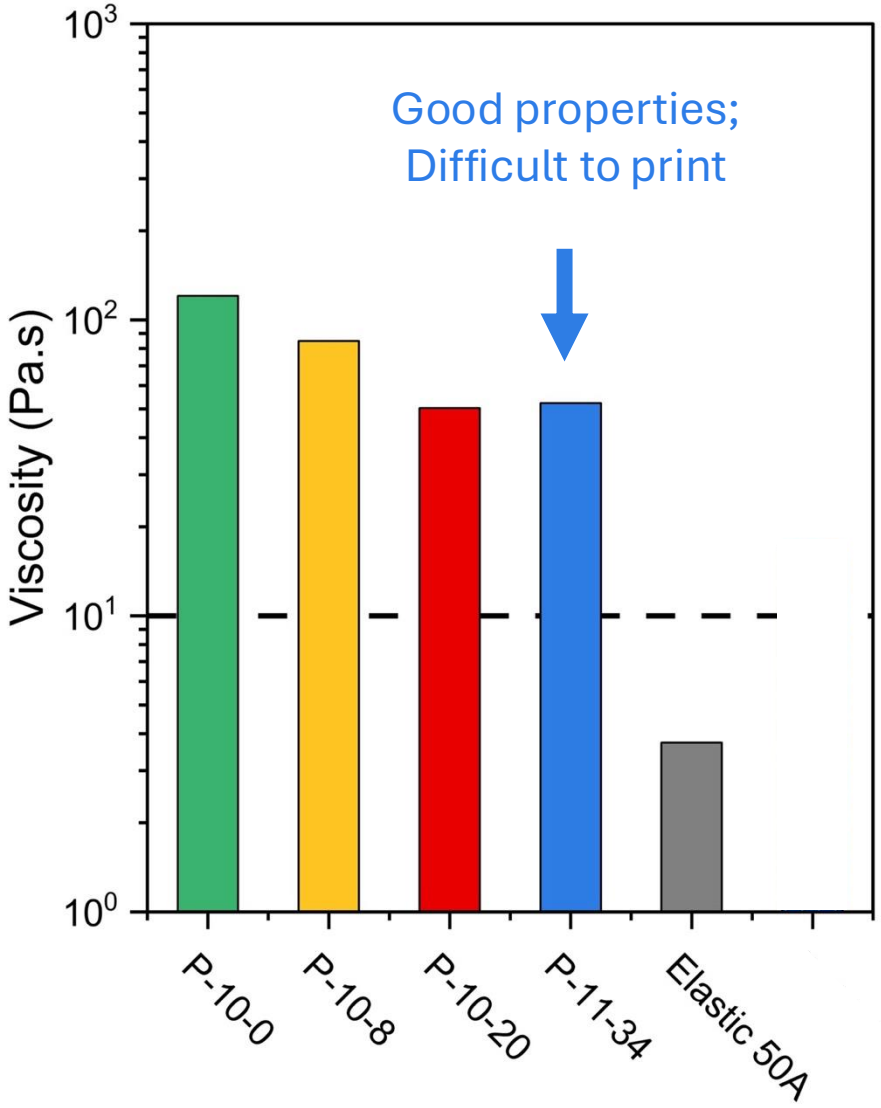
- Low viscosity
- Rapid photocuring

- Fast printing speed
- Customizable and complex geometries

Library of polymers

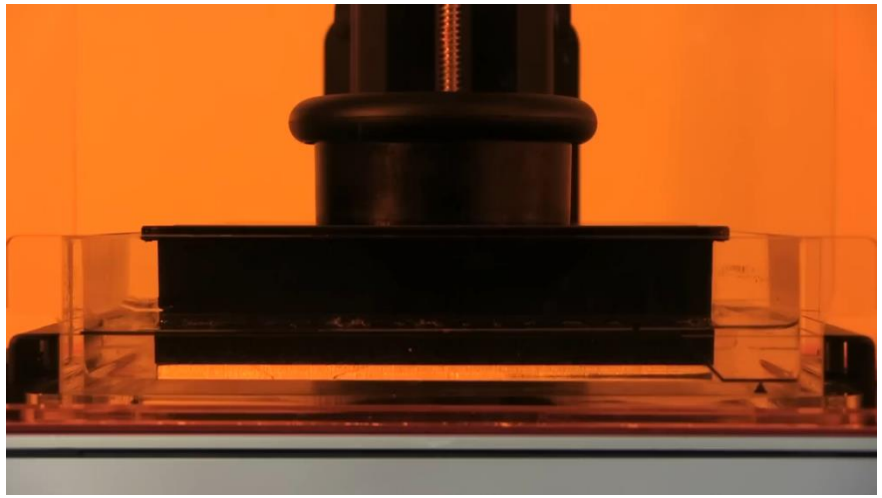


At 105 °C:
PβMVL + 40 wt% DAD + 15 wt% βMVL diluent



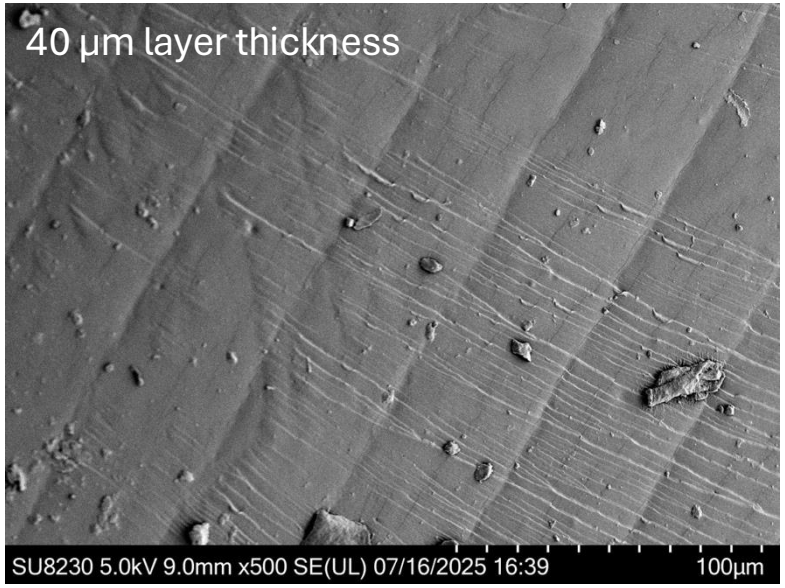
Can recover βMVL post print!

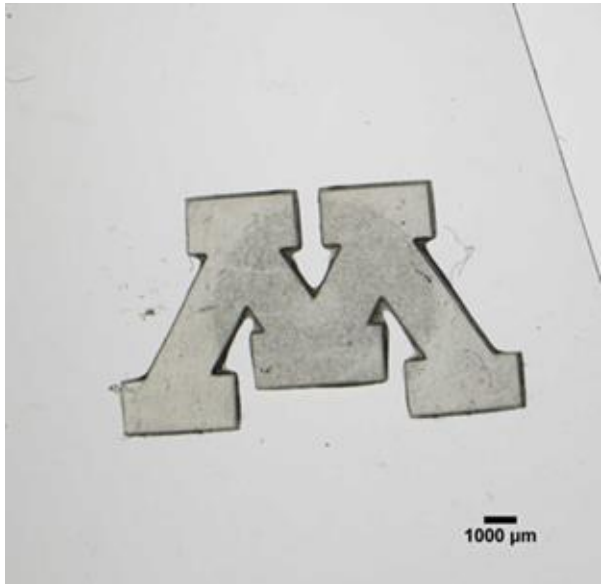
Rapid and high-resolution 3D printing

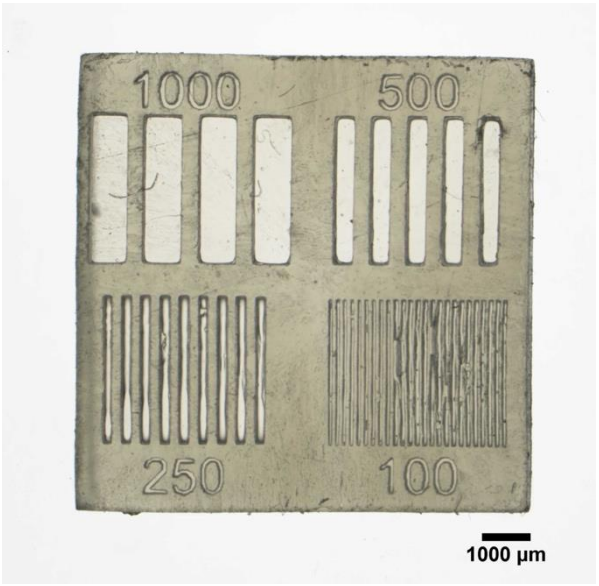


1.2 wt% TPO-L, 20 mW cm^{-2}

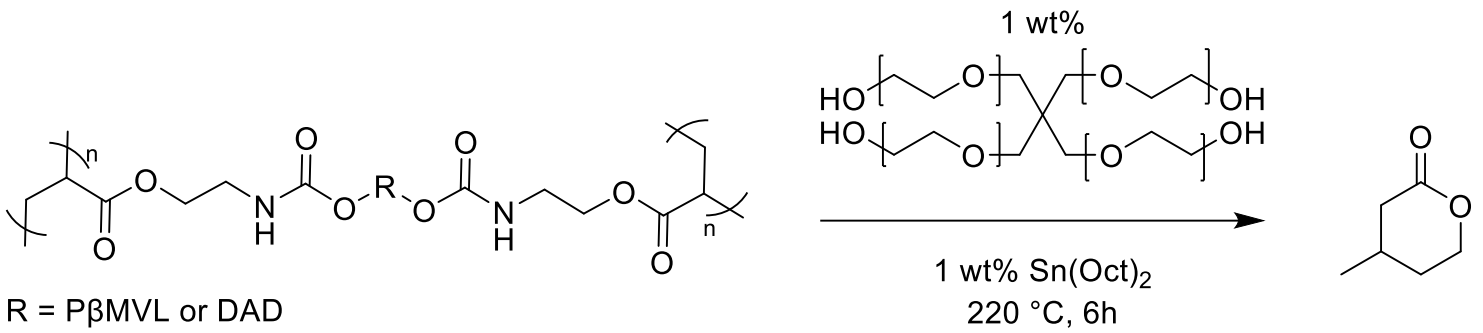
1 s per layer

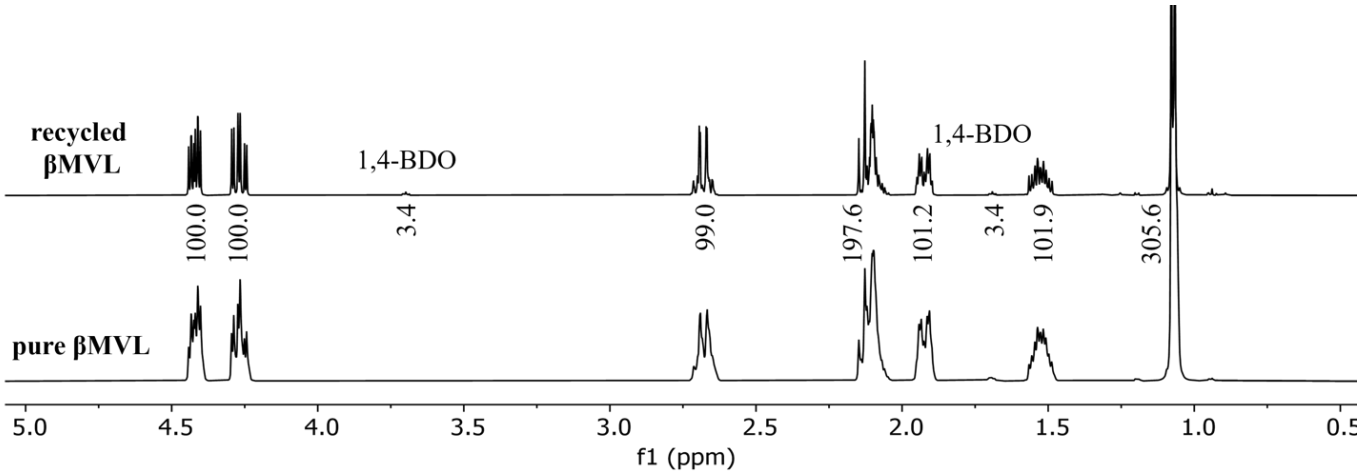


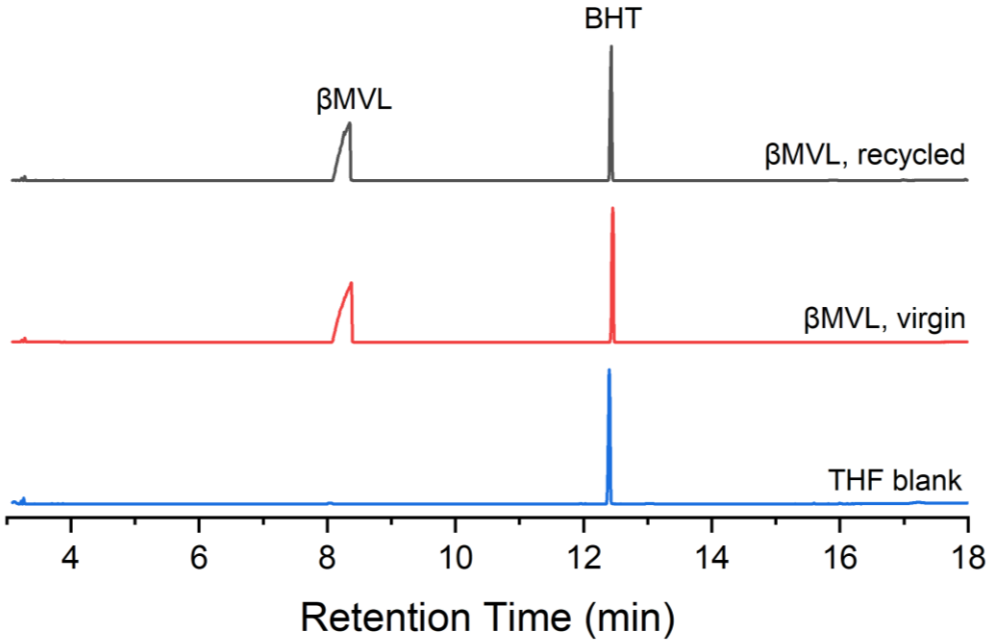




Chemical recycling recovers βMVL

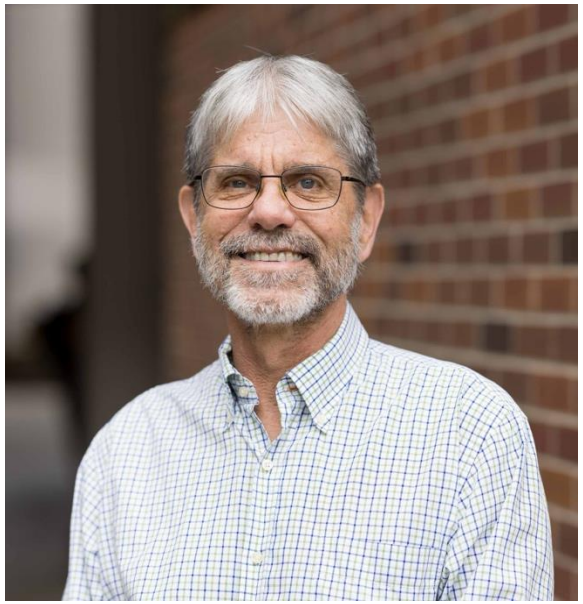






Acknowledgements

Prof. Marc Hillmyer



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