

Catalysis in Poly(hydroxy-urethane) Systems: Rheo-polymerization Testing

Authors:

Weronika M. Milanowska^a, Aleksandra M. Fage^{b*}, Ulrich Förter-Barth^b, Dominik Wołosz^a, Paweł G. Parzuchowskia*

Afiliations:

^aWarsaw University of Technology, Faculty of Chemistry, Noakowskiego 3, 00-664 Warsaw, Poland ^bFraunhofer Institute for Chemical Technology ICT, Josephvon-Fraunhofer-Straße 7, 76327 Pfinztal, Germany

6th most produced polymer globally with versatile applications

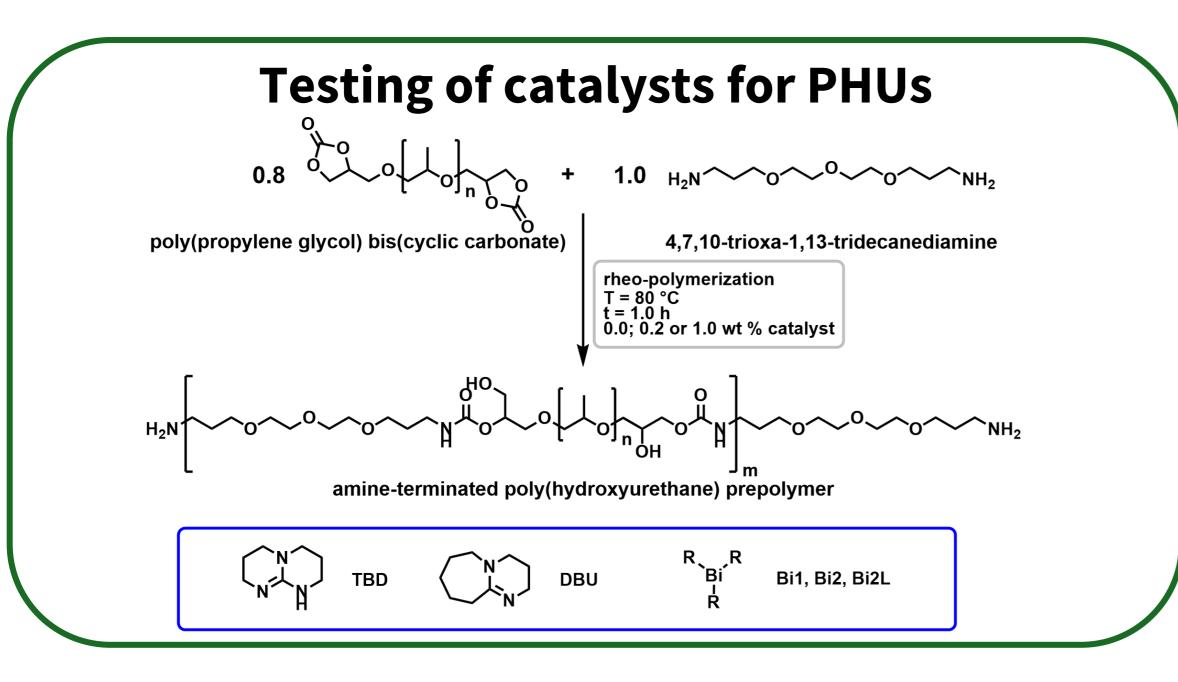
Urethane Synthesized from polyols and toxic diisocyanates

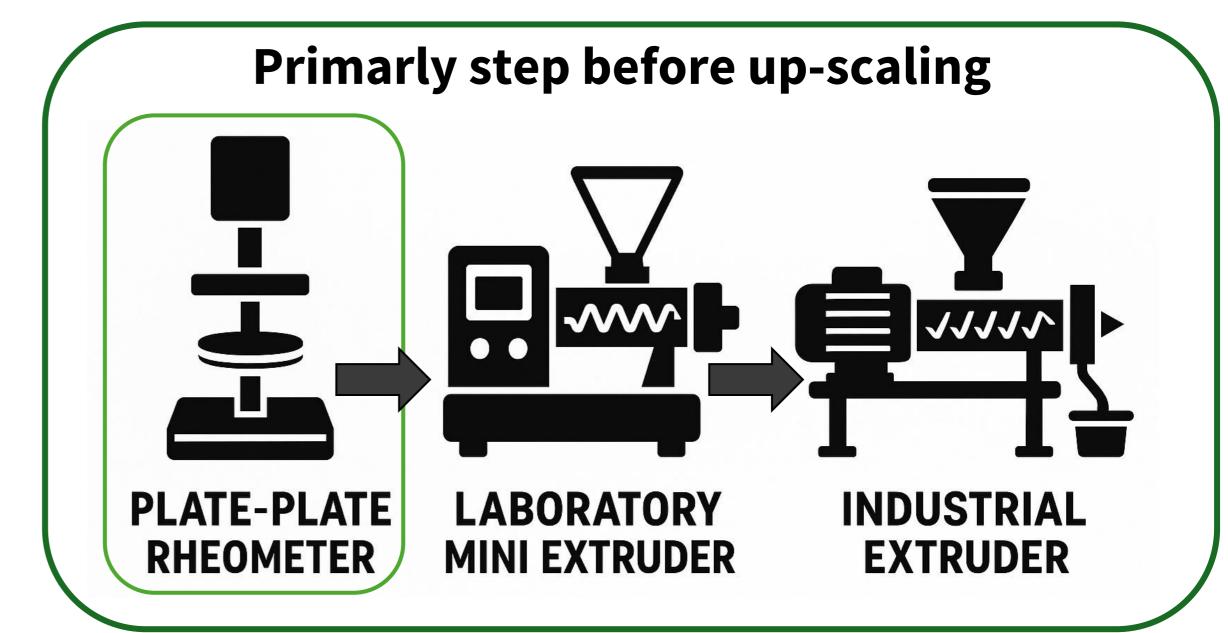
Alternative for polyurethanes

Synthesized from diamines and CO₂-based cyclic carbonates

> A novel solution - requires further investigation and optimization

A technology with decades of industrial use





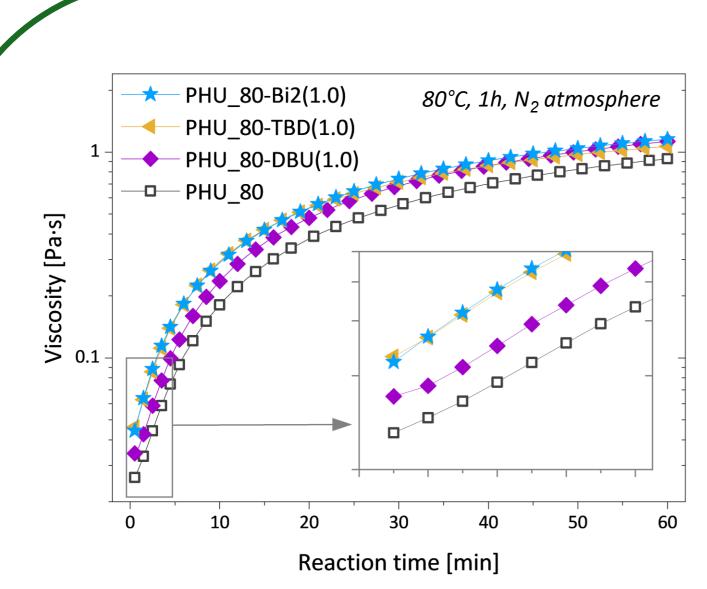
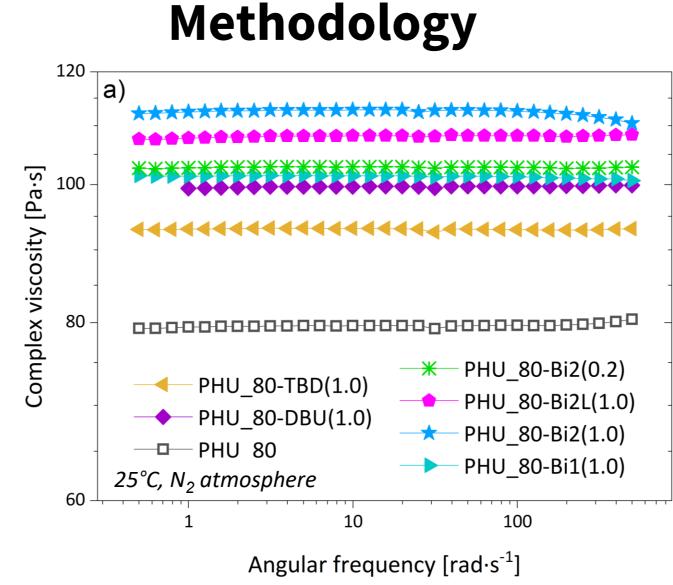
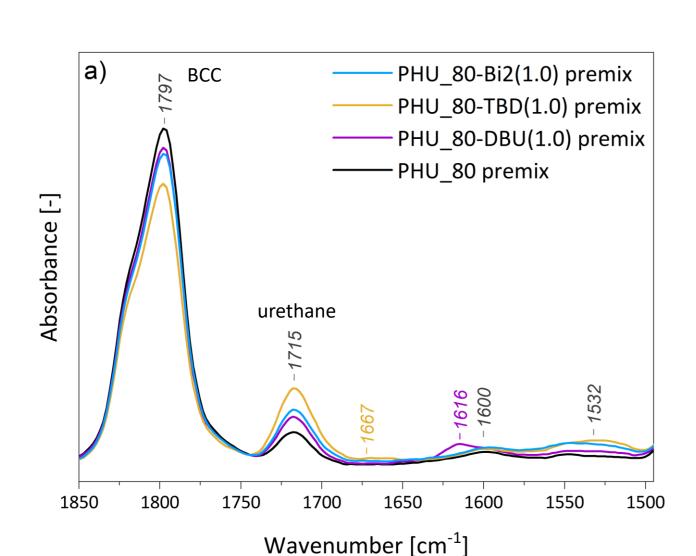


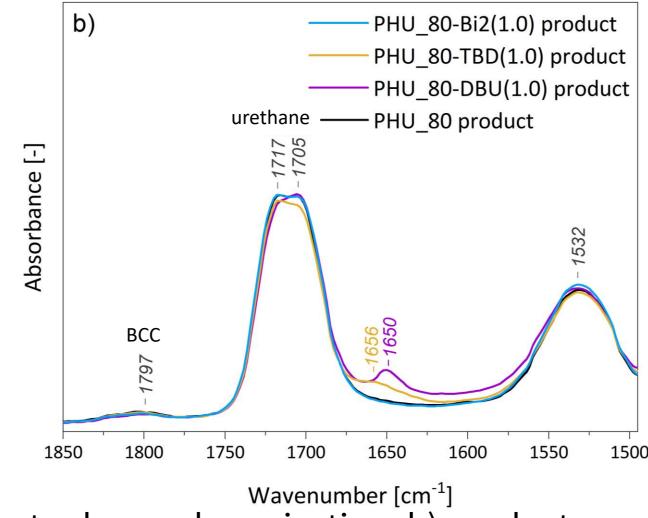
Figure 1. Rheo-polymerization, 1h, 80°C



10⁴ 10³ Modulus [Pa] 10^{-1} 10^{-2} 10^{-3} 25°C, N₂ atmosphere Angular frequency [rad·s⁻¹]

Figure 2. Comparison of diferences in performace of catalysts based on frequency sweep measurements at 25°C: a) complex viscosity, b) moduli





PHU_80-Bi2(1.0) product PHU_80-TBD(1.0) product 4.42 PHU_80-DBU(1.0) product no BCC - PHU_80 product

Figure 4: ¹H NMR spectra of products

Figure 3: FT-MIR spectra of: a) premixes prior to rheo-polymerization, b) products.

Conclusions

Rheo-polymerization:

Efficient approach for screening polymerization conditions with Low-viscosity system: various formulations of monomers and catalysts

Post-polymerization:

- 1h of rheo-polymerization is insufficient to reach full convertion (BCC residuals in FT-MIR of products),
- Full consumption of BCC in ¹H NMR conducted after storing,
- Oscillatory rheological measurements performed immediately after synthesis as a reliable analytical method

 Ideal coating precursor providing uniform coverage, after siloxane modification enabling moisture curing

Bi-based catalysts vs amine-based catalysts:

- Comparable performance, even at lower concentrations,
- Lower toxicity and greater stability under reaction condition

Bibliography:

- Plastics the fast Facts 2024 Plastics Europe, https://plasticseurope.org/knowledge-hub/plastics-the-fast-facts-2024/, (accessed June 12, 2025). S. Benyahya, B. Boutevin, S. Caillol, V. Lapinte and J.-P. Habas, Polym. Int., 2012, 61, 918–925.
- A. Gomez-Lopez, S. Panchireddy, B. Grignard, I. Calvo, C. Jerome, C. Detrembleur and H. Sardon, ACS Sustain. Chem. Eng., 2021, 9, 9541–9562.