Synthesis of bio-based polyurethanes with photolabile functionalities for degradation on demand

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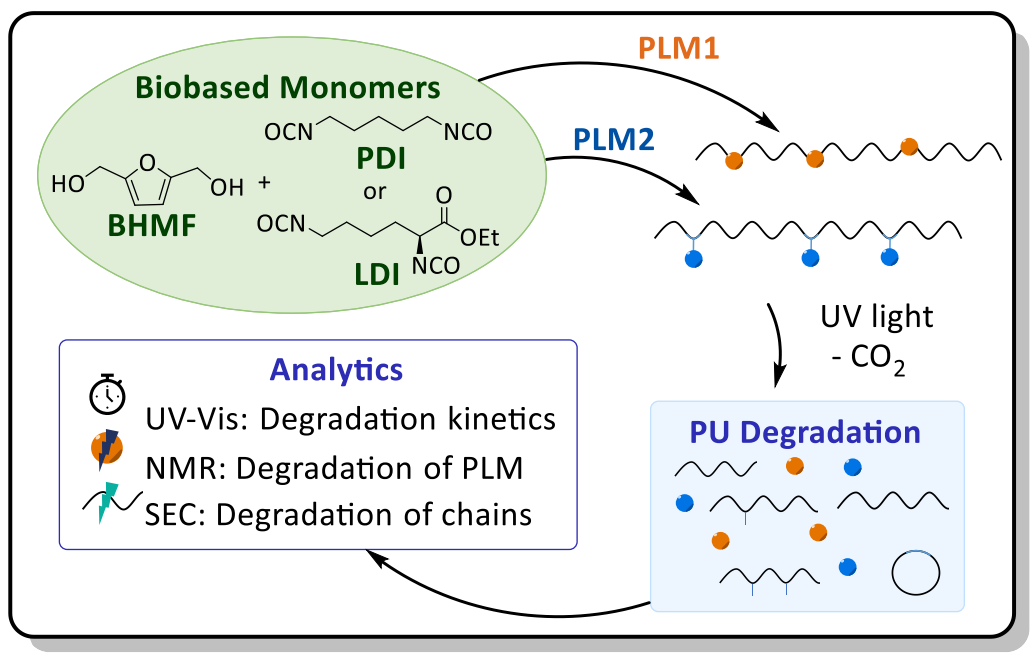
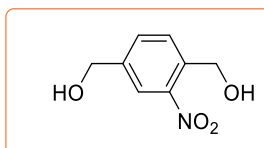
Introduction

Polyurethanes (PUs) are widely used but largely rely on petrochemicals and are poorly recycled (29.7%).[1] To improve recyclability, an eco-design approach is considered in this work. This project aims to incorporate photolabile molecules (PLMs) into bio-based PU structures, enabling degradation under UV light and possible recovery of reusable oligomers. Studies have proven the efficiency of photodegradation of conventional polymers using PLM.[2,3,4] To produce recyclable and bio-based PUs, the following monomers are involved: 2,5-bis(hydroxymethyl)furan (BHMF) and 1,5-pentane diisocyanate (PDI), derivates of cellulose, and L-lysine diisocyanate (LDI) coming from protein sources. The PLM and PU degradation are characterized by ultraviolet-visible absorption spectroscopy (UV-Vis), nuclear magnetic resonance spectroscopy (NMR), and size exclusion chromatography (SEC).

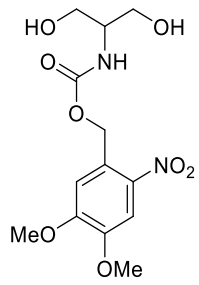


Photolabile molecules (PLMs)



Yield = 75 wt%

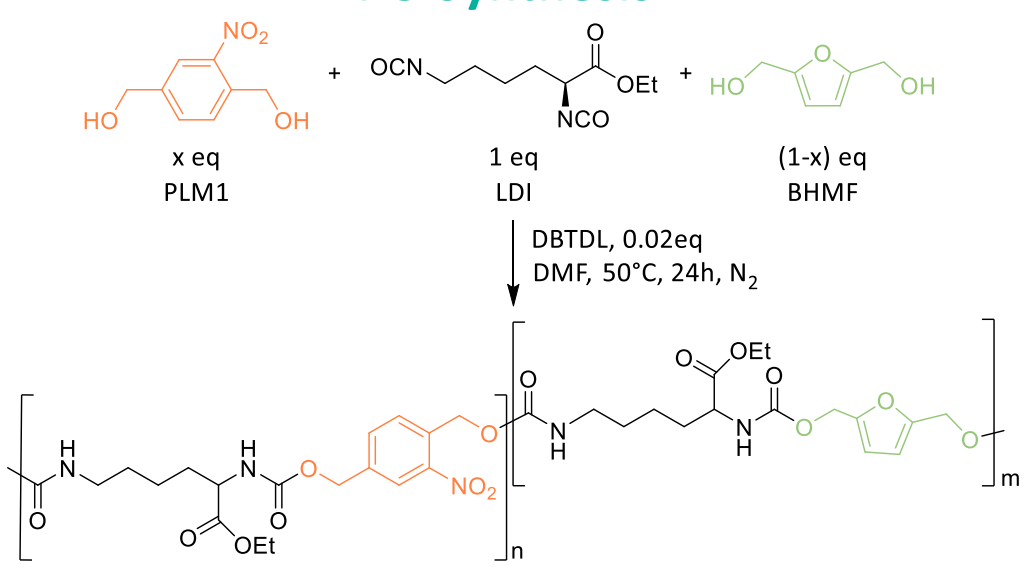
Purity = 99 %



Yield = 62 wt%, Pure

With 2 diisocyanates and 2 PLMs, 4 different systems are studied: {PDI-PLM1}; {PDI-PLM2}; {LDI-PLM1}; {LDI-PLM2}.

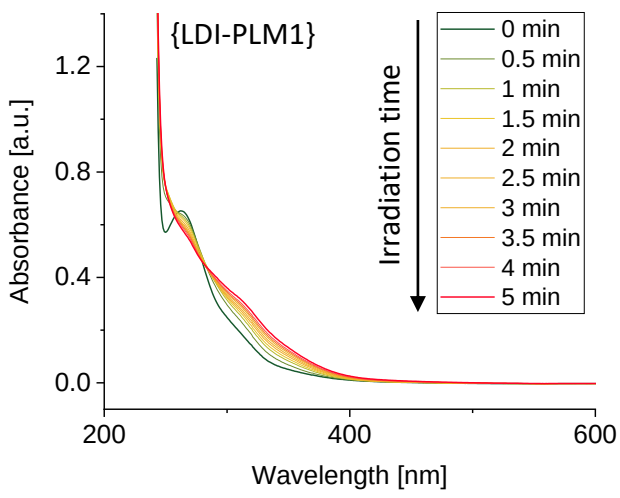
PU Synthesis



Schema of the synthesis of the system {LDI-PLM1}

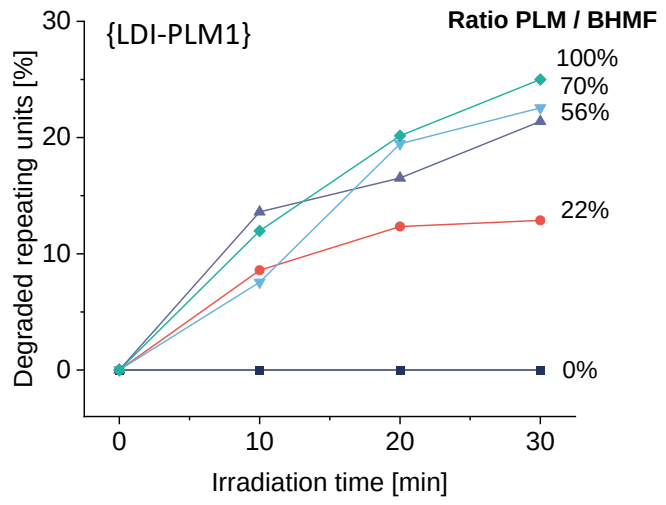
PU Degradation

Kinetics of degradation



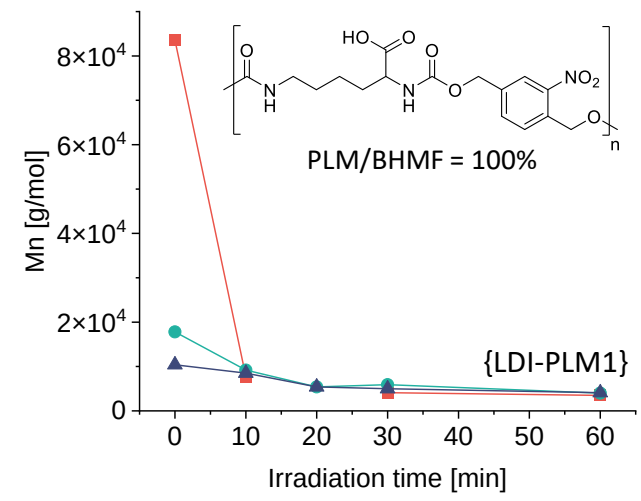
- 1st order reactions (PLM1 & PLM2)
- Degradation kinetics only depends on the nature of PLM (UV-Vis Absorbance)

Influence of PLM/BHMF ratio



- No significant amelioration of degradation for PU having between 56 and 100% PLM/BHMF (NMR)

Influence of initial molar mass



- Degradation to oligomers
- Resulting chain length (SEC) independent of the initial M_n

Influence of the diisocyanate

- No influence of the diisocyanate on the PLM-degradation kinetics
- After 30 min irradiation: 50% chain degradation for PU having no BHMF co-monomer for both diisocyanates

Summary

- Successful PLM synthesis and their implementation in bio-based PU chains
- Complementary methods for degradation characterization: NMR, SEC and UV-Vis
- Independence of the diisocyanate nature and initial M_n on PU-degradation to oligomers whereas PLM amount is determinant

Outlook

- End-groups characterization of oligomeric degradation products for possible repolymerization
- Implementation of PLM in bio-based polyesters and polycarbonates

Acknowledgment

The authors thank D. Kuckling (University of Paderborn) for providing PLM2 precursor and H. Komber (IPF, NMR), A. Lederer, and A. Seifert (IPF, SEC) for their analytical support. This work is funded by the SAW-Project “SUSTAIN—from waste to value” from the Leibniz Association.

References

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