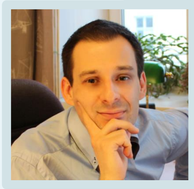
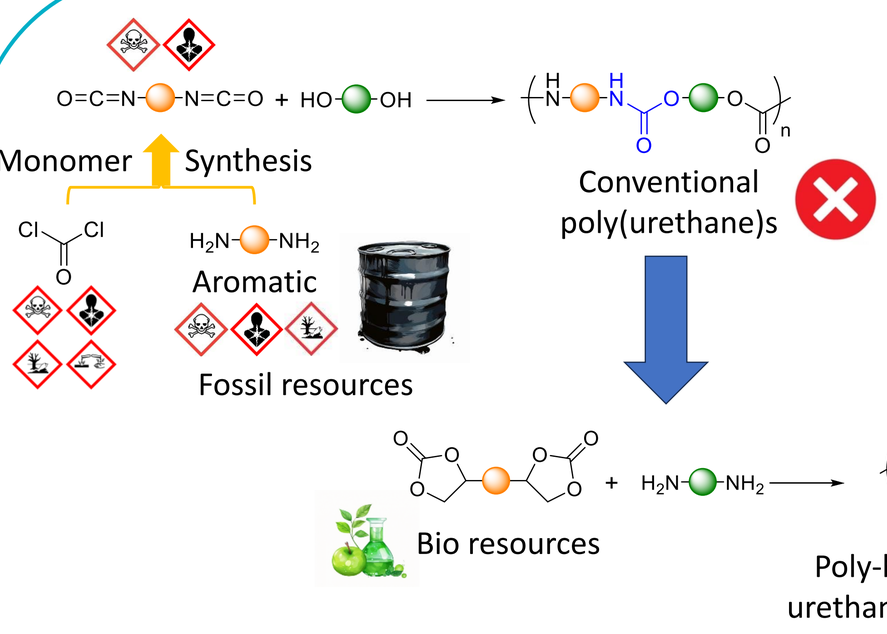
New perspectives for NIPUs : linear polyhydroxyurethanes (PHUs) of high-molecular weight obtained by fast polymerization



Abdurrahman Beter, Sergei V. Zubkevich, Arpan Datta Sarma, Vincent Berthé, Reiner Dieden, Daniel F. Schmidt and Alexander S. Shaplov[a]

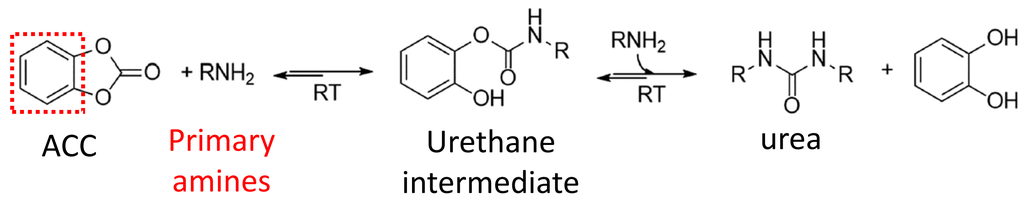
Introduction & problem to solve:



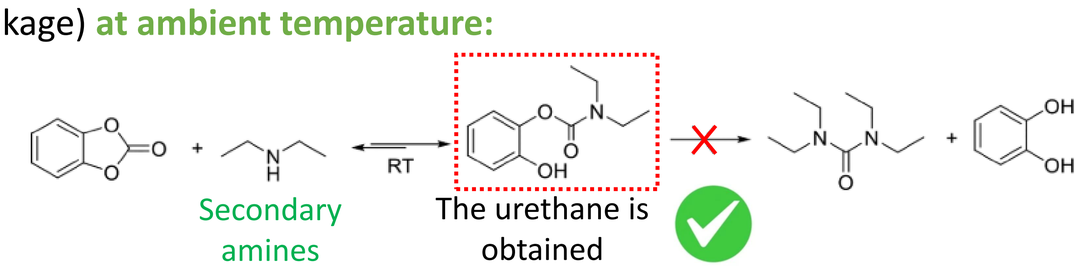
- Slow reaction rates (reaction takes hours at T > 100°C)
- Low Mn (average Mn = 8000 – 15000 g/mol)
- Low Tg values (typically <60°C)
- Significant moisture adsorption in humid environment
- Deterioration of mechanical properties upon storage

Hypothesis:

A recent study(*) evaluated the use of an **aromatic cyclic carbonate (ACC)** for the synthesis of organic ureas

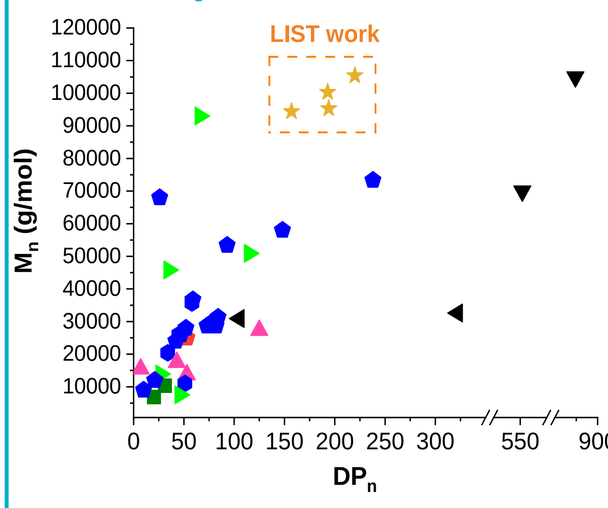


Secondary amines allow a **quick formation of urethane** (instead of urea linkage) **at ambient temperature:**



(*) *ACS Sustain. Chem. Eng.* ***2020****, 8 (41), 15640–15650.*

Comparison:



ROP of aziridine with carbon dioxide

ROP of cyclic carbamates

Polycondensation of biscarbamates and diols

Polycondensation of biscarbonates and diamines

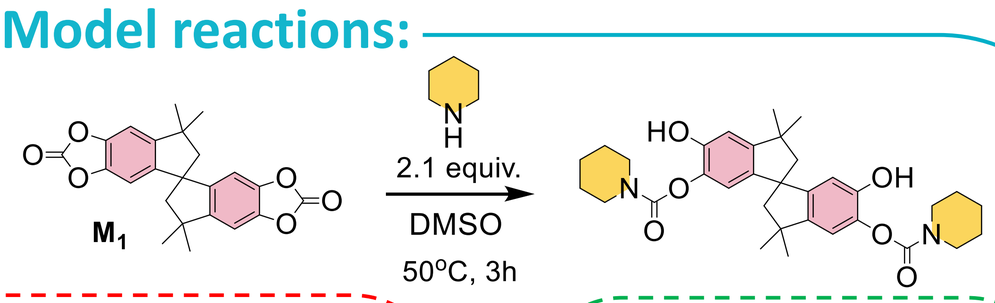
Curtius rearrangement of acyl azides

Polyaddition of 5-membered cyclic carbonates with primary diamines

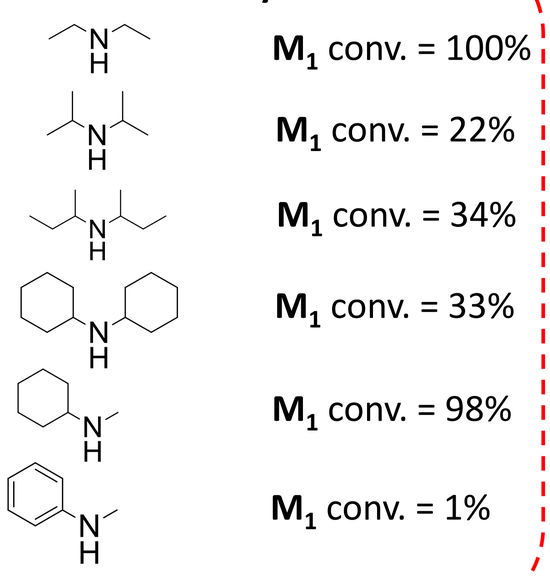
Polyaddition of 6/7/8-membered cyclic carbonates with primary diamines

Polyaddition of activated cyclic carbonates with secondary diamines

Model reactions:



Secondary amines



M_1 conv. = 100%

M_1 conv. = 22%

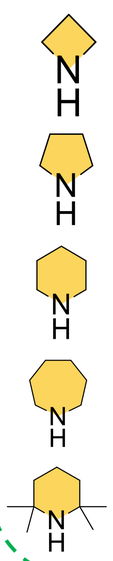
M_1 conv. = 34%

M_1 conv. = 33%

M_1 conv. = 98%

M_1 conv. = 1%

Alicyclic secondary amines



M_1 conv. = 88%

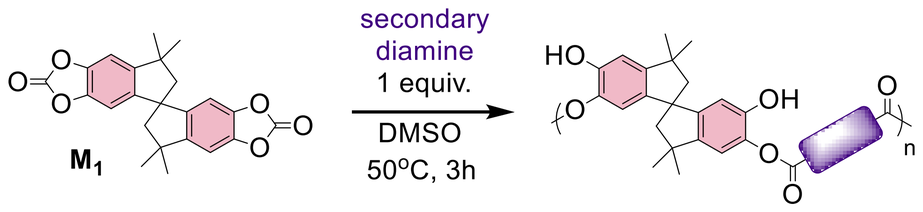
M_1 conv. = 100%

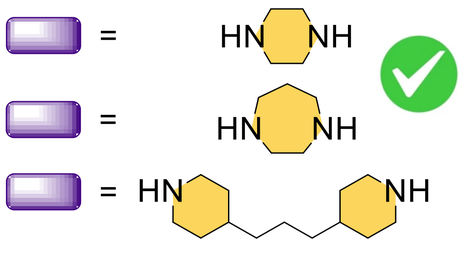
M_1 conv. = 100%

M_1 conv. = 100%

M_1 conv. = 95%

Novel method for PHU synthesis:



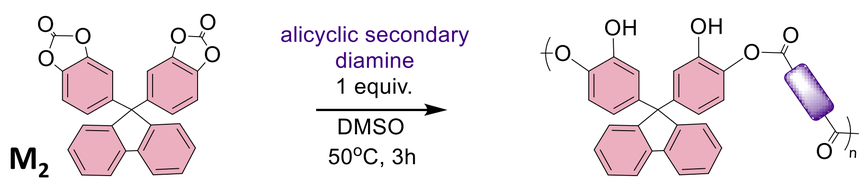


PHU_1 M_n = 120000 g/mol; M_w/M_n = 3.58

PHU_2 M_n = 95300 g/mol; M_w/M_n = 2.78

PHU_3 M_n = 56400 g/mol; M_w/M_n = 3.43

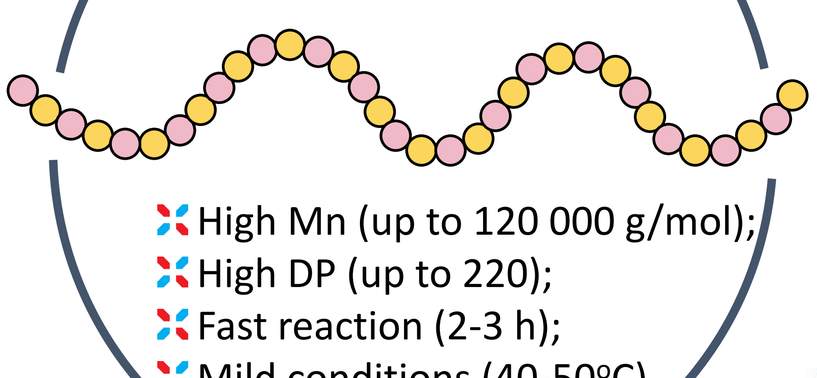
PHU_4 M_n = 29100 g/mol; M_w/M_n = 1.93



PHU_8 M_n = 100300 g/mol; M_w/M_n = 4.3

PHU_9 M_n = 28900 g/mol; M_w/M_n = 3.8

Conclusions:



- High Mn (up to 120 000 g/mol);
- High DP (up to 220);
- Fast reaction (2-3 h);
- Mild conditions (40-50°C).

"Method for synthesis of high molecular weight polyhydroxyurethanes and polyhydroxyurethanes thereof", **LU509504**, **2024**.

[a] Luxembourg Institute of Science and Technology (LIST), 5, Avenue des Hauts-Fourneaux, L-4362 Esch-sur-Alzette, Luxembourg

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Contact

Prof. Dr. Alexander S. Shaplov

alexander.shaplov@list.lu