Fully renewable NIPUs *via* thiol-ene polymerization

Luca Filippi[1], Michael A. R. Meier*[1,2]

[1]Karlsruhe Institute of Technology (KIT), Institute of Biological and Chemical Systems – Functional Molecular Systems (IBCS-FMS), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

[2]Karlsruhe Institute of Technology (KIT), Institute of Organic Chemistry, Straße am Forum 7, 76131 Karlsruhe, Germany

*E-mail: m.a.r.meier@kit.edu Internet: www.meier-michael.com

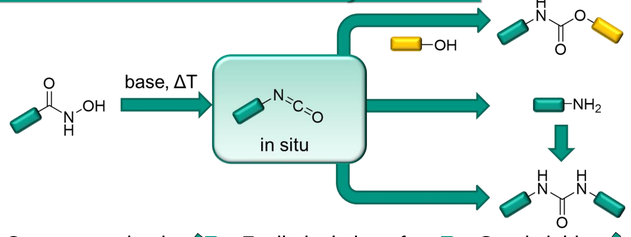
Institute of Biological and Chemical Systems
Functional Molecular Systems

Motivation

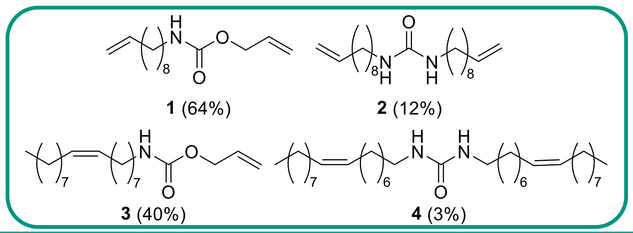
Polyurethanes (PU) are one of the most important class of polymeric materials, with applications ranging from insulation panels and foams to high performance adhesives and fibres. Industrially, PUs are synthesized by polyaddition of isocyanates with diols. Isocyanates have been not only been confirmed to be harmful for humans, but are also produced using highly toxic phosgene and amines. An alternative procedure toward PUs is therefore of utmost importance.

In this work, we present a different approach, in which the urethane monomer is prepared *via* the Lossen rearrangement[1] in a one-step synthesis and polymerized with both sustainable and commercially available dithiols[2] to produce a polyurethane chain with thioether linkages. The advantages of this method lie not only in the sustainable design during the preparation of the carbamate functionality, in the tunability of polymer properties by choice of dithiol moiety and the employment of the urea side-product, but also in the possibility to prepare block- and random copolymers with interesting thermal and mechanical properties.

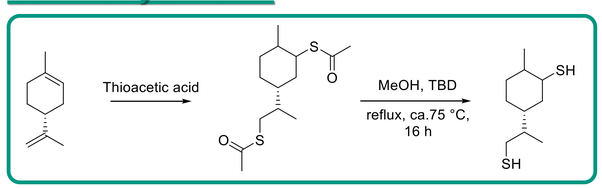
1 Carbamate and urea synthesis



- One-pot synthesis ✓
- Facile isolation of urea side product ✓
- Good yields ✓
- Hydroxamic acids from renewable feedstock ✓
- Solvent recycling ✓
- Catalytic amounts of base ✓

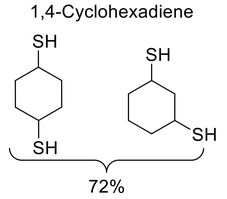


2 Dithiol synthesis



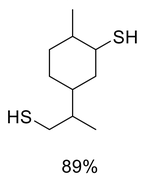
- Renewable starting materials ✓
- Simple procedure ✓
- Facile work-up ✓
- High yields ✓

1,4-Cyclohexadiene



72%

Limonene



89%

3 Polymerization of carbamates and ureas

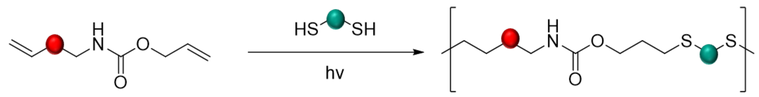


Table 1 : SEC and DSC results for different dithiols polymerized with either carbamate **1** or urea **2**

Diene	Dithiol[a)]	M_n [g/mol][b)]	$Đ_M$[b)]	T_g [°C]	T_m [°C]
1	1,2-Ethane	8000	1.50	.	80.4
	1,4-Butane	26600	1.87	-	73.3
	1,6-Hexane	33900	2.73	-	64.8/66.5
	1,10-Decane	5550	2.29	-	84.6
	Limonene	21150	2.08	-22.9	-
	1,3- and 1,4-Cyclohexane	6150	2.00	-14.6	-
	2,3-Butane	15650	1.88	-28.8	-
2	1,4-Butane	5750	2.24	-	137.4
	1,6-hexane	4850	2.32	-	136.3
	Limonene	7400	2.13	-	67.5

a) Conditions: 5 mol/L in THF, r.t., 3 h, 365nm, DMPA b) HFIP-SEC calibrated with PMMA standards

- Yields around 80% or higher ✓
- Simple purification of polymers ✓
- Short reaction times ✓
- Simple setup ✓
- Tunable polymer properties *via* monomer variation ✓
- Small scale ✓
- Good M_n and $Đ$ ✓

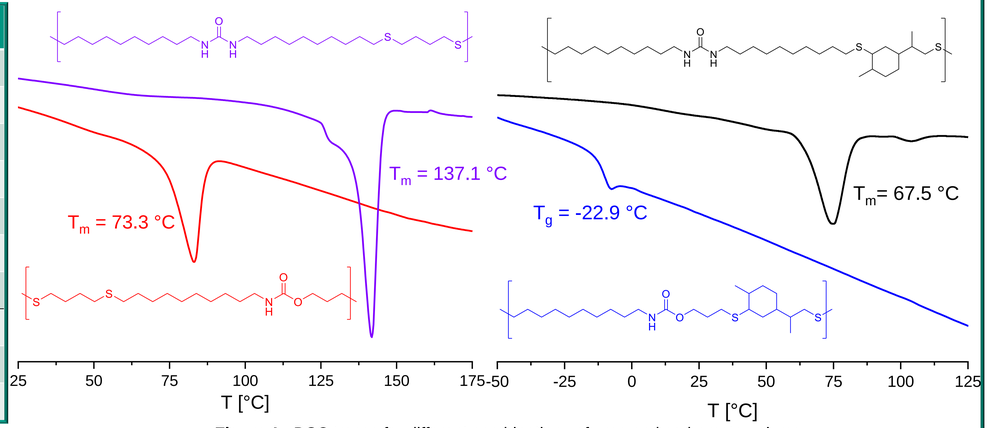
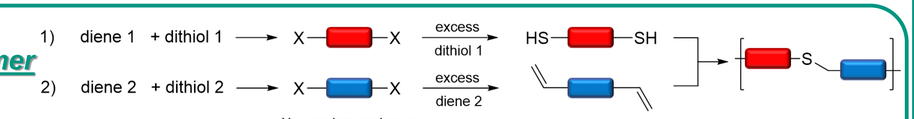


Figure 1 : DSC traces for different combinations of urea and carbamate polymers

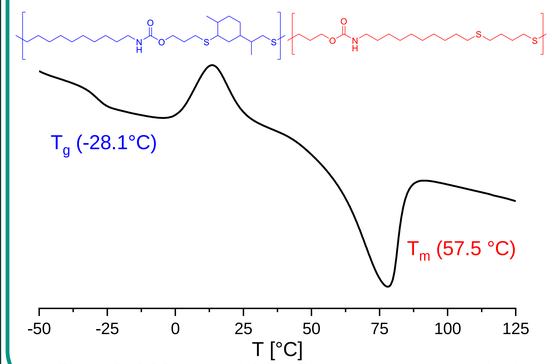
4 NIPU Copolymers

4.1 Block-copolymer synthesis:



Block-copolymer vs. random copolymers

Block - copolymer (A)



Random copolymer (B)

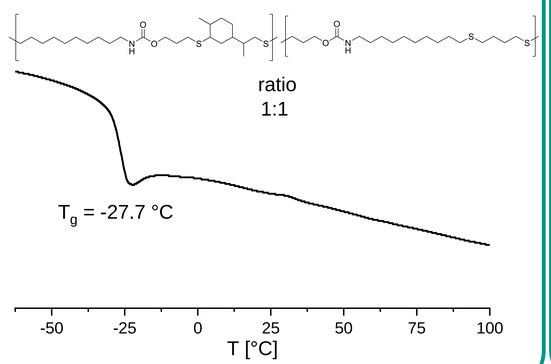
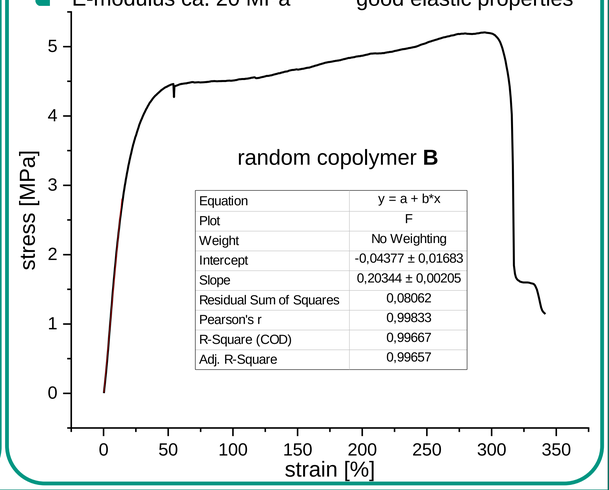


Figure 2 : DSC traces of **A** and **B** confirm the existence of differences in thermal properies between block- and random copolymers.

4.2 Tensile testing

- Max elongation of 300%
- Material hot pressed at just 85 °C
- E-modulus ca. 20 MPa
- Max force at 53 N
- Simple preparation
- Sustainable material with good elastic properties



Equation	y = a + b*x
Plot	F
Weight	No Weighting
Intercept	-0,04377 ± 0,01683
Slope	0,20344 ± 0,00205
Residual Sum of Squares	0,08062
Pearson's r	0,99833
R-Square (COD)	0,99667
Adj. R-Square	0,99657

References:

[1] O. Kreye, S. Wald, M. A. R. Meier, *Advanced Synthesis & Catalysis* **2013**, *355*, 81-86.

[2] M. Firdaus, M. A. R. Meier, U. Biermann, J. O. Metzger, *European Journal of Lipid Science and Technology* **2014**, *116*, 31-36.