PUReSmart

PolyUrethane Recycling Towards
a Smart Circular Economy

PUReSmart project results - Chemical recycling technologies for PU

Dirk De Vos – KU Leuven

Virtual Workshop –Chemical recycling and plastics
May 31, 2021

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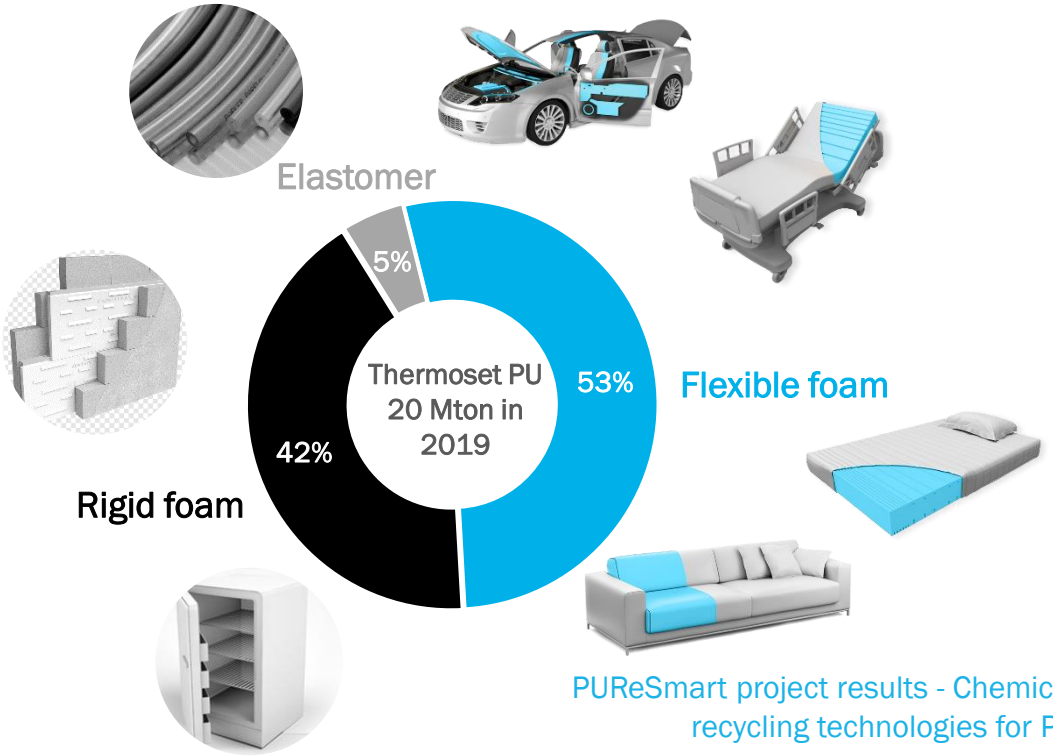
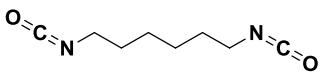
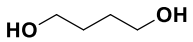
Polyurethane overview



Polyurethane history

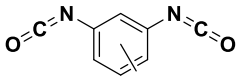
hexamethylene diisocyanate (HDI)

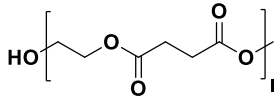




1,4-butanediol (BDO)

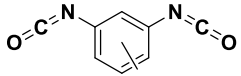
toluene diisocyanate (TDI)

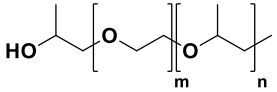




polyester polyol

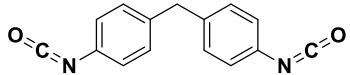
toluene diisocyanate (TDI)

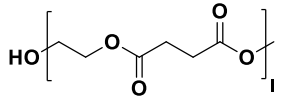




polyether polyol

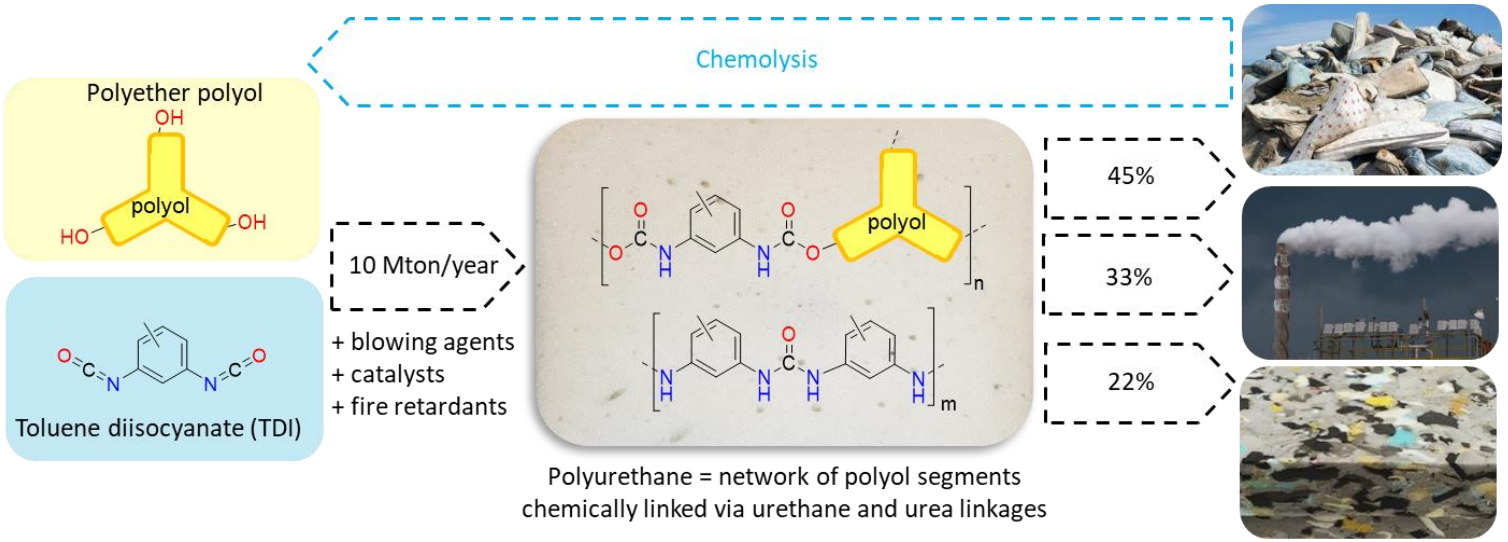
methylene diphenyl diisocyanate (MDI)



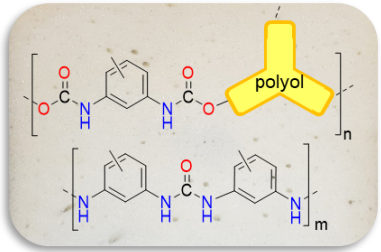


polyester polyol

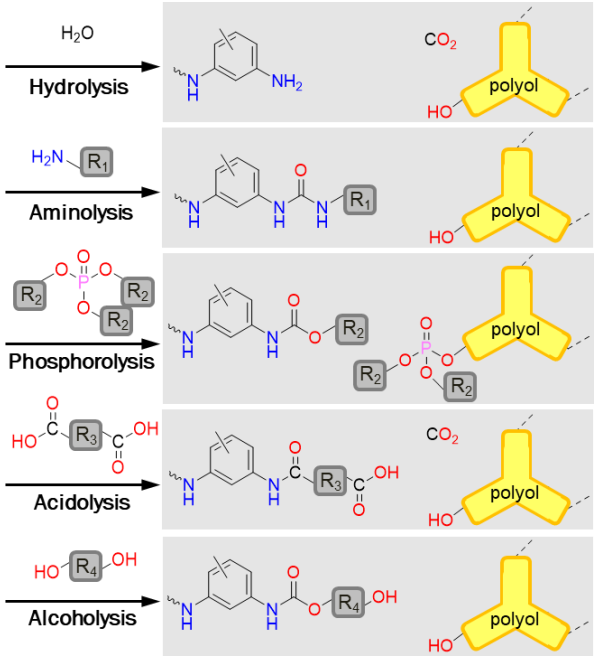
Flexible polyurethane foam



State-of-the-art polyurethane chemolysis



PU foams



+ Recovery of amines and polyether polyols
- Energy intensive
- Extensive purification

+ Less stringent reaction conditions
- Complex reaction mixtures

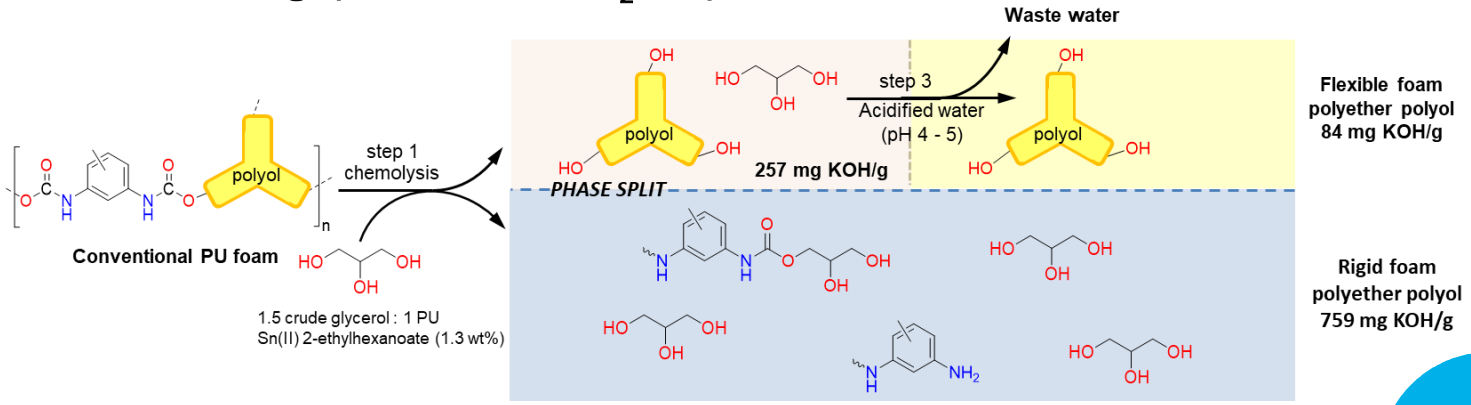
+ Less stringent reaction conditions
+ Flame retardant polyols
- Complex reaction mixtures

+ Low hydroxyl values
- Low reactivity
- Clean PU feed required

+ Split-phase option
+ PU compatibility
- Extensive purification

State-of-the-art polyurethane alcoholysis

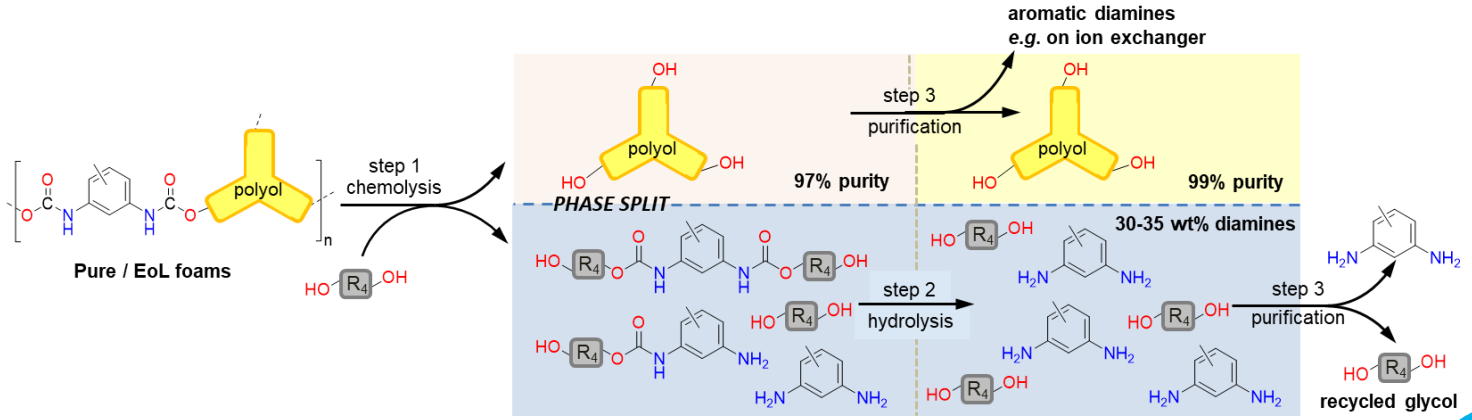
- Excess input of alcoholyzing agent *e.g.* glycerol
- Extensive upper phase (UP) purification
- Inadequate lower phase (LP) valorization
  - → unfavorable mass balance
  - → high process cost + CO_2 footprint



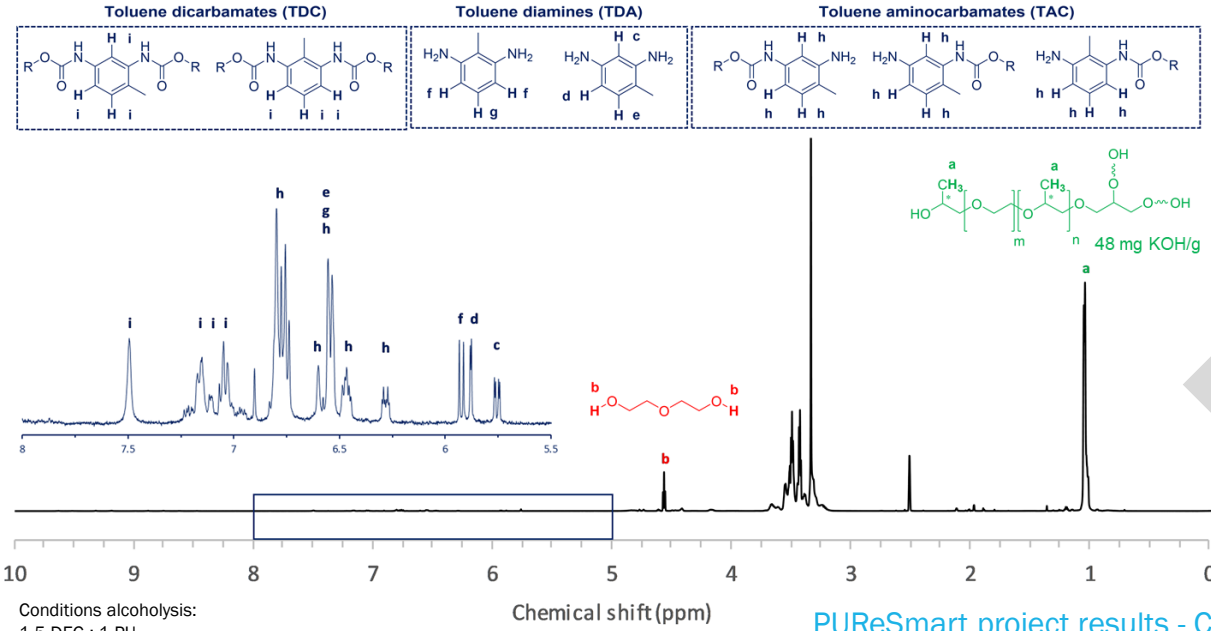
D. Simón et al., Polymer Degradation and Stability 121 (2015) 126-136

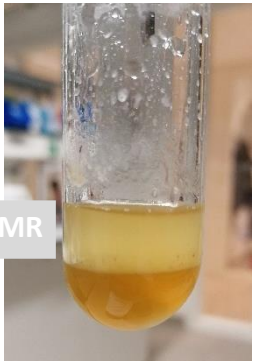
PUReSmart strategy

- Catalysts + additives → higher reaction rate
- Alcoholyzing agents → higher purity and yields of polyether polyol
- Valorization of aromatic compounds in lower phase



Polyurethane foam alcoholysis in diethylene glycol



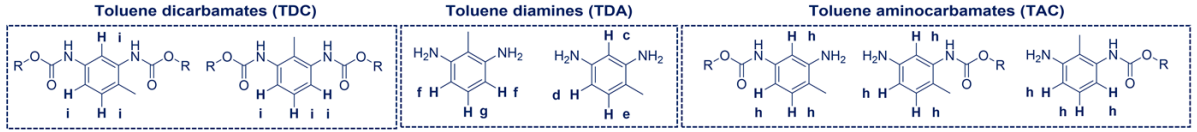


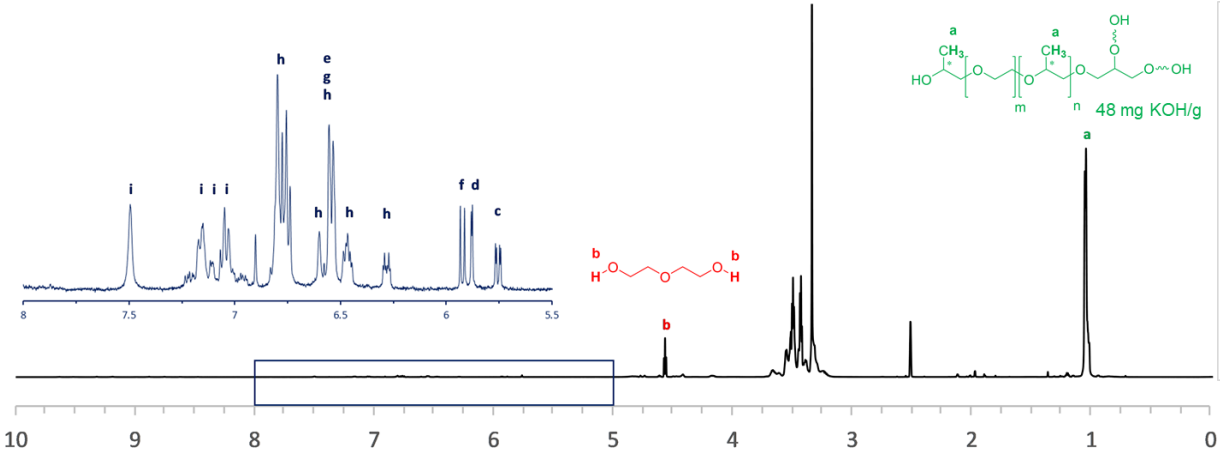
¹H NMR

Conditions alcoholysis:
1.5 DEG : 1 PU
0.01 Bi(III) neodecanoate : 1 PU
200°C, 180 min depolymerization

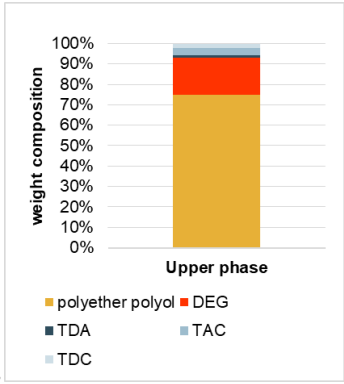
Vanbergen et al., ChemSusChem 2020, 13, 3835 – 3843

Polyurethane foam alcoholysis in diethylene glycol





Yield polyether polyol (%)	81
Theor. IOH (mg KOH/g)	248



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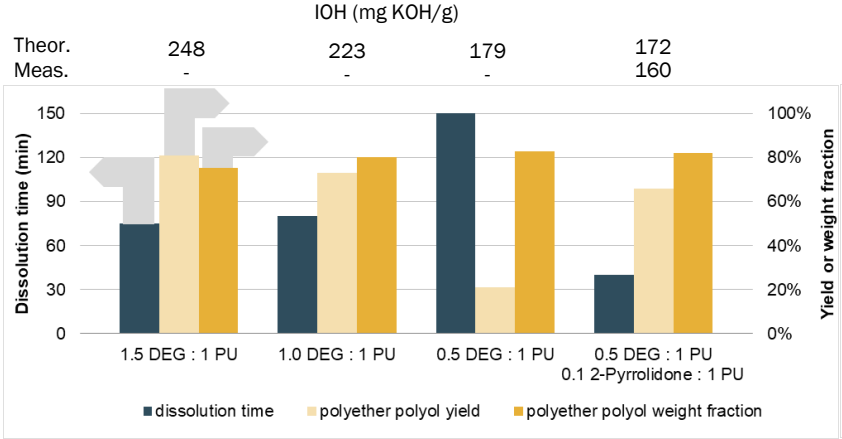
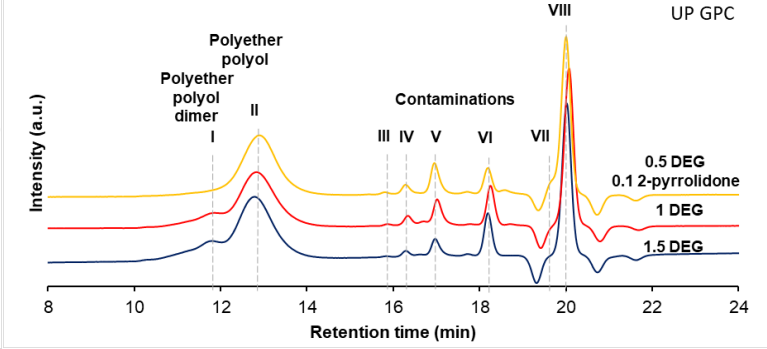
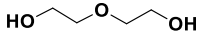






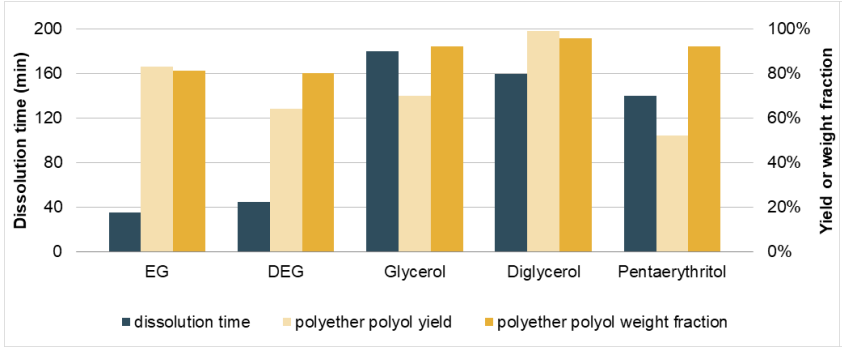
(**I**) polyether polyol dimer
(**II**) polyether polyol
(**III-IV**) aromatic products
(**V**) diethylene glycol
(**VI**) 2,4- and 2,6-toluenediamine
(**VII**) 2-pyrrolidone
(**VIII**) toluene (internal standard)

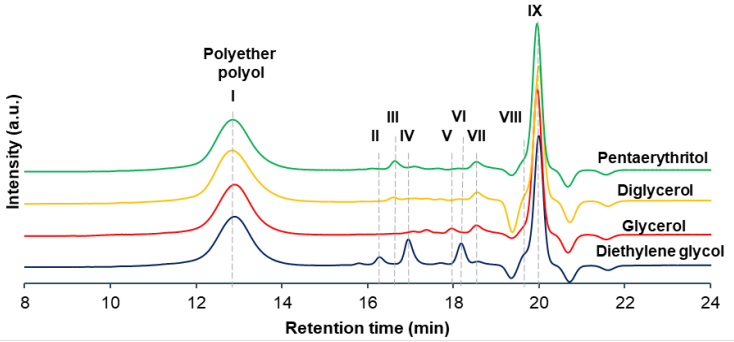
Conditions alcoholysis:
4 g PU foam
0.01 Bi(III) neodecanoate : 1 PU
200°C , 180 min depolymerization

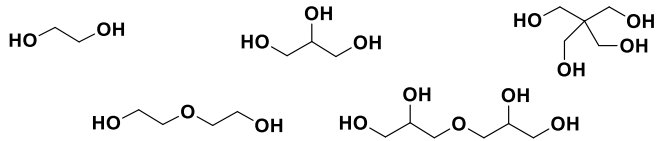
Vanbergen et al., ChemSusChem 2020, 13, 3835 – 3843

Polyurethane foam alcoholysis in various alcohols

	IOH (mg KOH/g)				
Theor.	234	172	133	74	89
Meas.	-	160	124	80	81







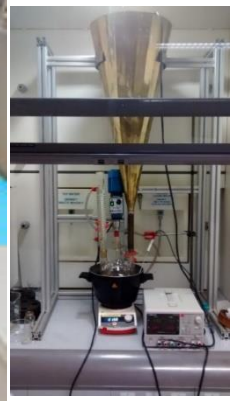
(**I**) polyether polyol
(**II-IV**) aromatic products
(**V-VI**) alcoholyzing agent
(**VII**) 2,4- and 2,6-TDA
(**VIII**) 2-pyrrolidone
(**IX**) toluene (internal standard)

Conditions alcoholysis:
4 g PU foam
0.5 alcoholyzing agent : 1 PU,
0.1 2-pyrrolidone : 1 PU
0.01 Bi(III) neodecanoate : 1 PU
200 °C
180 min depolymerization

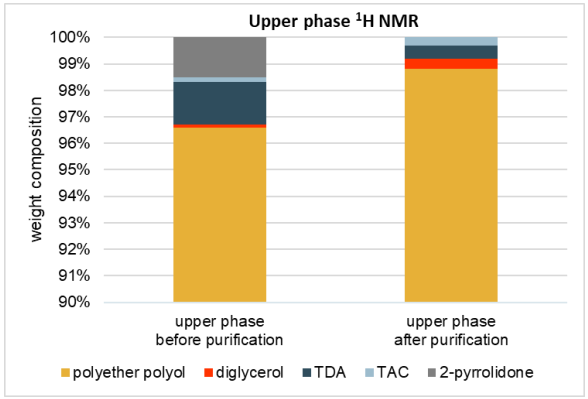
Vanbergen et al., ChemSusChem 2020, 13, 3835 – 3843f

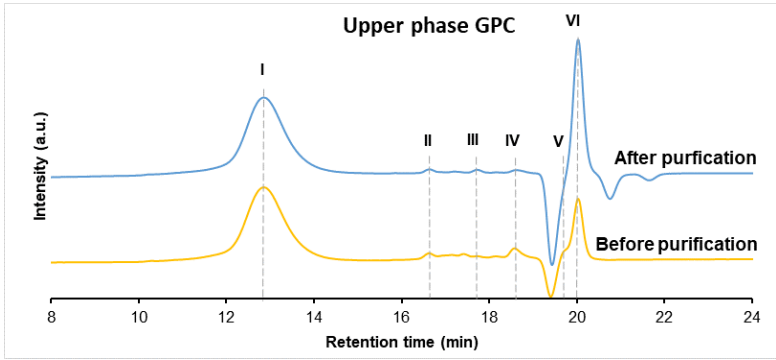
Upscale polyurethane foam alcoholysis with diglycerol

- 90 min dissolution, 300 min depolymerization
- High yield (98%) and purity (97%) of polyether polyol
- Purification step with diglycerol → improved purity (99%)



Meas. IOH (mg KOH/g) 80 61





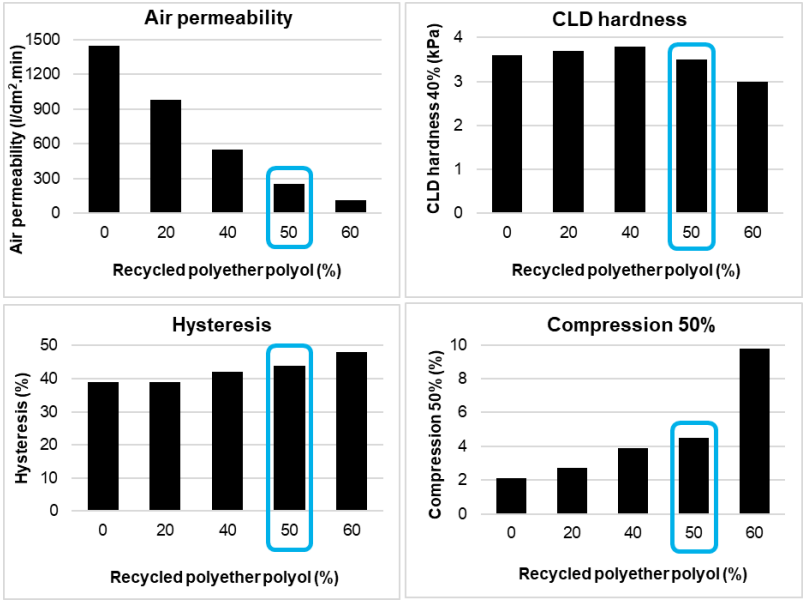
(**I**) polyether polyol
(**II**) aromatic products
(**III**) diglycerol
(**IV**) 2,4- and 2,6-TDA
(**V**) 2-pyrrolidone
(**VI**) toluene (internal standard)

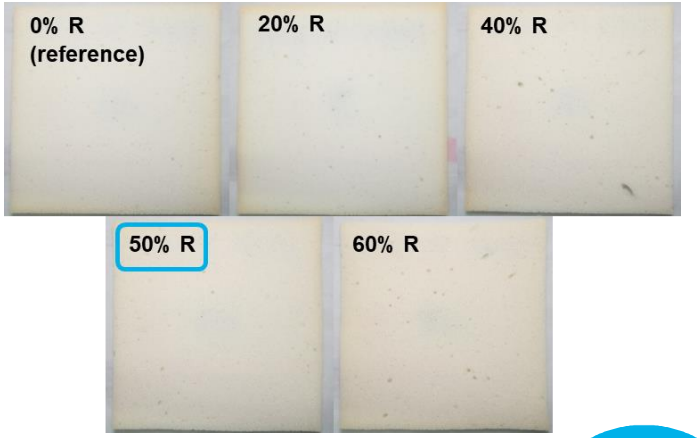
Conditions alcoholysis (400 g PU foam)
0.5 diglycerol : 1 PU
0.1 2-pyrrolidone : 1 PU
0.01 Bi(III) neodecanoate : 1 PU
200°C, 300 min depolymerization

Conditions purification:
1 diglycerol : 1 upper phase
150°C
30 min mixing

Vanbergen et al., ChemSusChem 2020, 13, 3835 – 3843

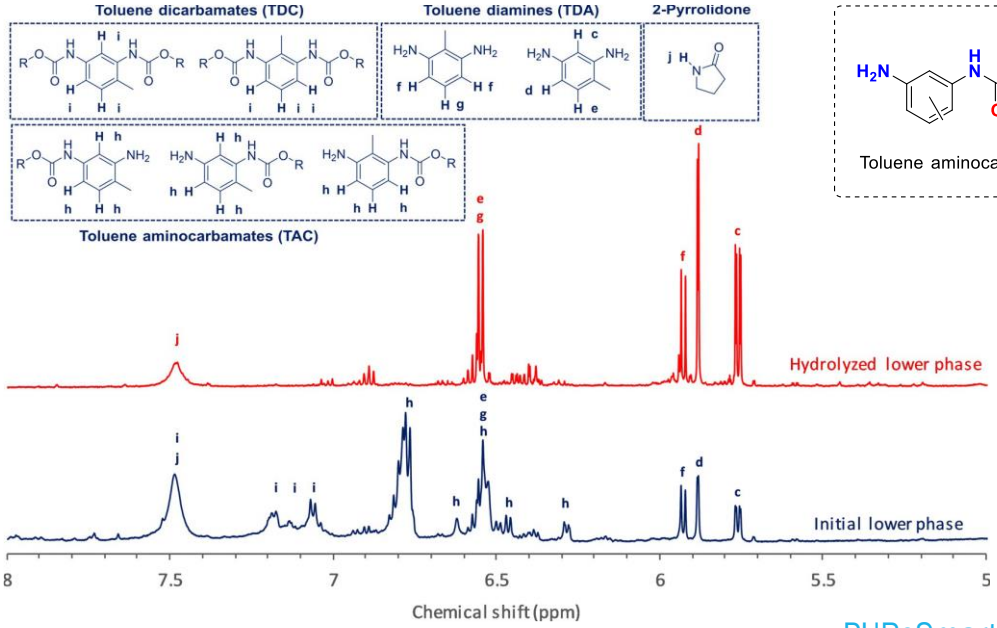
Synthesis of flexible polyurethane foam with recycled polyether polyol

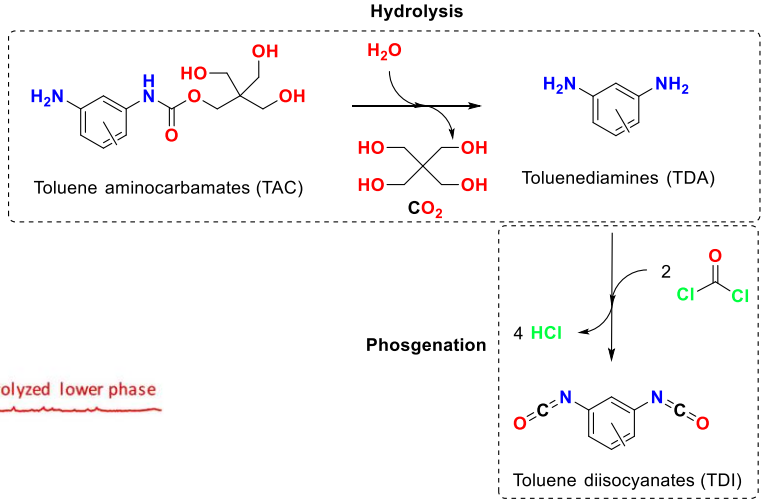




Vanbergen et al., ChemSusChem 2020, 13, 3835 – 3843

Valorization of the lower phase





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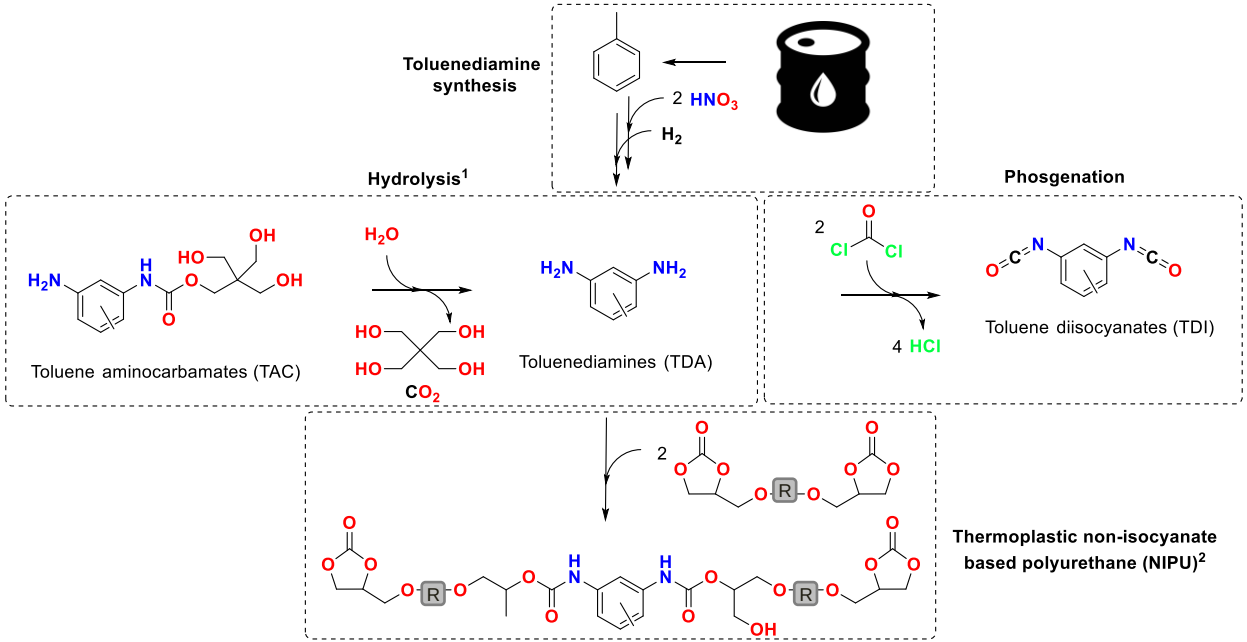

[1] Vanbergen et al., ChemSusChem 2020, 13, 3835 – 3843

[2] C. Carré et al., European Polymer Journal, 2016, 84, 759 – 769

Conclusion

Catalyst: Bi(III) neodecanoate Additive: 2-pyrrolidone	Alcohol : PU ratio from 1.5 : 1 to 0.5 : 1 no loss of polyether polyol yield or purity
Upscale alcoholysis + purification with diglycerol	Recovery of polyether polyol in high yield and purity 50% replacement of virgin polyol with limited effect on foam properties
Hydrolysis of lower phase	Recovery of aromatic compounds as toluene diamines (TDA) and alcoholyzing agent

Thank you

Any question?

PUReSmart