Insight into solventless production of Hydrophobically-Modified Ethoxylated Urethanes (HEURs): the role of moisture concentration, reaction temperature and mixing efficiency

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A. Sampling of the produced polymers

The sampling procedure was based on GPC analysis data. More specifically, sampling directly in dry chloroform (GPC solvent) showed lower values of M_n/M_w compared to the analysis performed by diluting the samples after solidification in the same solvent. As an example, data from the mixing study are presented in the current paragraph. The details of the formulation follow in Table S1 below:

Table S1. Reaction conditions for the sampling experiments from the mixing study.

Moisture (ppm)	Reaction Temperature (°C)	Mixing Speed (rpm)	Catalyst (%)	HMDI/ PEG	PEG/ Oct	Sampling Time (min)
700-800	80	30/100/300/750	0.035	1.5	1	3/15

The results from the GPC analysis are shown in Figure S1 and Figure S2 below for 3 and 15 minutes of reaction respectively:
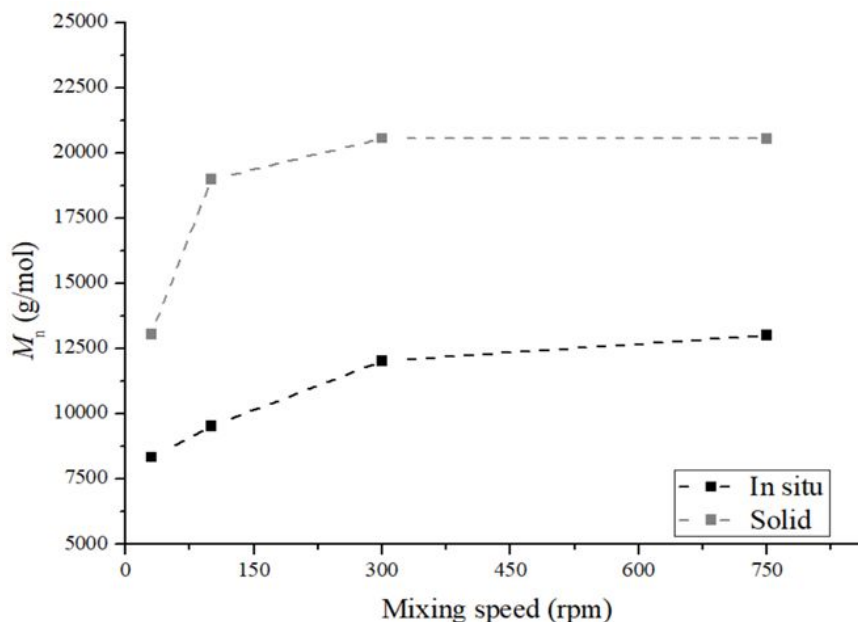

Figure S1. Results from GPC analysis for solid samples (grey data points) compared to sampling directly in dry chloroform (black data points). The experimental operating conditions are those

applied for the mixing speed parametric study, and the samples were collected at 3 minutes after the start of the reaction. The dashed lines have been added to guide the eye.
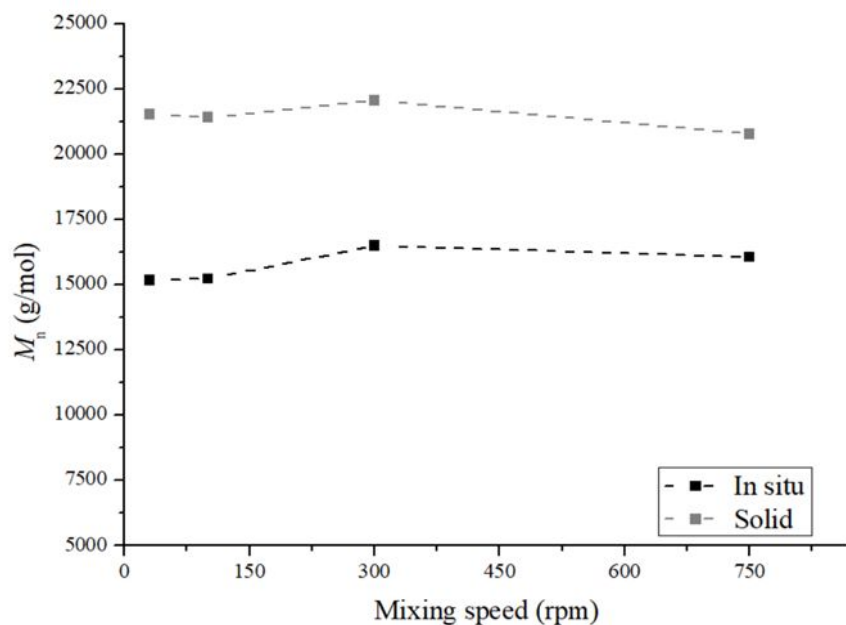

Figure S2. Results from GPC analysis for solid samples (grey data points) compared to sampling directly in dry chloroform (black data points). The experimental operating conditions are those applied for the mixing speed parametric study, and the samples were collected at 15 minutes after the start of the reaction. The dashed lines have been added to guide the eye.

In the work of Arnould et al.[1], excess of dry methanol was added to the solvent to ensure the end capping of $N=C=O$ terminated polymers in the system. Specifically, in case the produced polymers are terminated with $N=C=O$ groups, side reactions can occur during GPC analysis resulting in different M_n/M_w values. In order to evaluate whether this effect occurs in our system, selected HEUR samples were ''in situ'' dissolved in the GPC solvent (dry chloroform) containing excess of dry MeOH.

The obtained GPC results of ''in situ'' sampling in both chloroform and chloroform/MeOH were directly compared. Samples from the moisture and the mixing study were analyzed and are presented below as examples. The details of the formulation follow in Table S2 (moisture parametric study) and Table S3 (mixing parametric study) below:

Table S2. Reaction conditions for the sampling (chloroform / chloroform $MeOH$) experiments based on the moisture parametric study.

Moisture (ppm)	Reaction Temperature (°C)	Mixing Speed (rpm)	Catalyst (%)	HMDI/ PEG	PEG/ Oct	Sampling Time (min)
various	80	100	0.035	1.5	1	45

Table S3. Reaction conditions for the sampling (chloroform / chloroform $MeOH$) experiments based on the mixing speed parametric study.

Moisture (ppm)	Reaction Temperature (°C)	Mixing Speed (rpm)	Catalyst (%)	HMDI/ PEG	PEG/ Oct	Sampling Time (min)
800	110	100	0.035	1.5	1	5

The results presented in Figure S3 indicate that the two methods result in very similar M_n values. It was decided that quenching with dry MeOH is not necessary for the produced polymers of the current study.
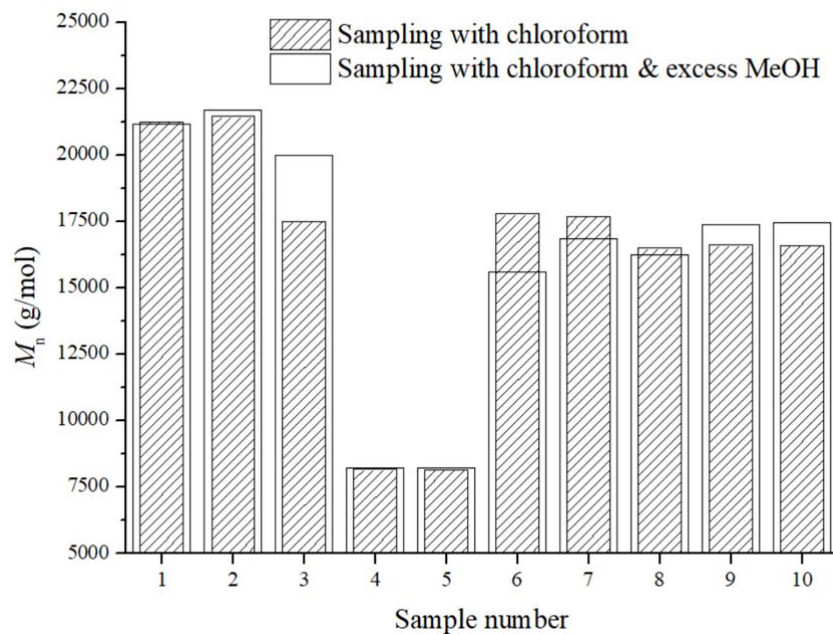
Figure S3. Results from GPC analysis for sampling directly in dry chloroform (dashed columns) compared to sampling in dry chloroform with methanol excess (solid columns). Examples 1 to 5: samples from the moisture parametric study and 6 to 10: samples from the mixing speed parametric study.

B. Homogeneity of the bulk polymers

In order to evaluate the homogeneity of the polymeric bulk, various samples from the same reaction product were analysed. More specifically, for two different cases from the reaction temperature parametric study, samples from five different spots (perpendicular and along to the agitator axis) were collected from the bulk at the same reaction times (5 and 15 minutes of reaction). The stoichiometric ratios and other details are presented in Table S4 for both cases:

Table S4. Reaction conditions for the homogeneity experiments based on the temperature parametric study.

	Moisture (ppm)	Reaction Temperature (°C)	Mixing Speed (rpm)	Catalyst (%)	HMDI/P EG	PEG/ Oct	Sampling Time (min)
Case 1	780	110	100	0.035	1.5	1	5
Case 2	760	80	100	0.035	1	1	15

The GPC analysis of the samples from both cases shows that a deviation of up to $\approx 9\%$ (in terms of M_n/M_w values) exists in the bulk mixture. More specifically, in case 1, the M_n range (maximum-minimum M_n) was 1287 g/mol, while the average M_n was 17029 g/mol. In case 2, the corresponding M_n range was 1233 g/mol, while the average M_n was 13995 g/mol. The results are presented in Figure S4 and Table S5.
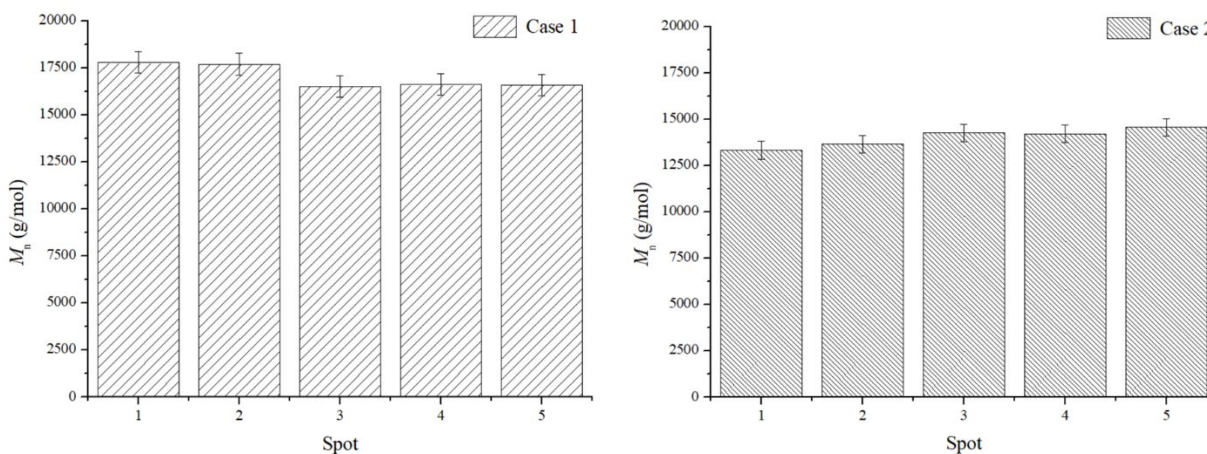
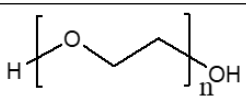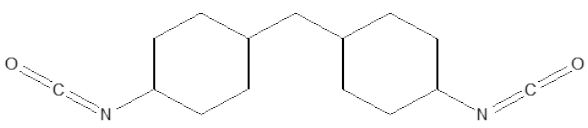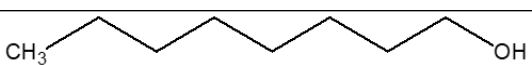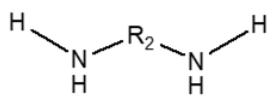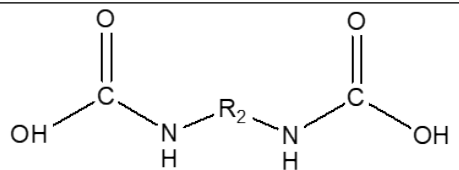**Figure S4.** Results from GPC analysis for the evaluation of the bulk homogeneity.

Table S5. Results from GPC analysis for the evaluation of the bulk homogeneity: average, STD, min and max values.

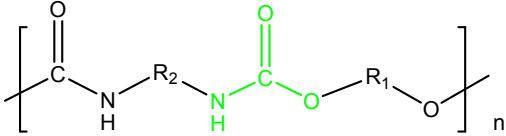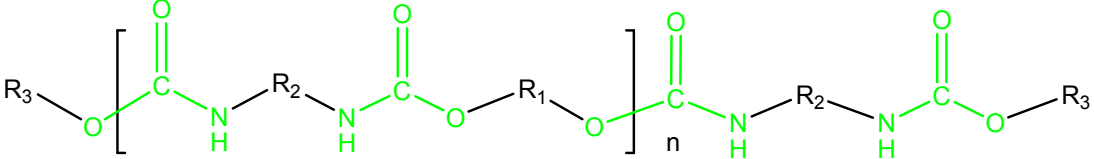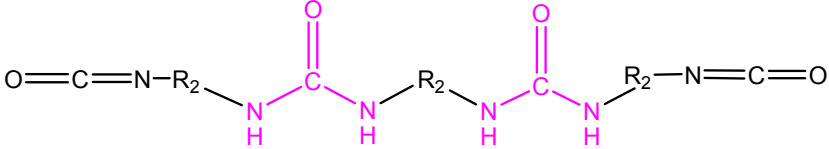|	Case 1	Case 2
Average (g/mol)	17029	13995
STD (g/mol)	577	447
Max M_n	17778	14551
Min M_n	16491	13318
Range=max-min	1287	1233

C. Chemical structures and basic chemical reactions

In Table S6 the chemical structures of the main reactants and (by)products can be found.

Table S6. List of chemical reactants and major (by)products related to the HEURs production.

Reactant/ (by)product	Simplified structure	Chemical structure
Polyethylene glycol	HO——R₁——OH	
4,4-dicyclohexyl methane diisocyanate	O=C=N–R₂–N=C=O	
Octanol	R₃——OH	
Amine	H——N(H)——R₂——N(H)——H	
Carbamic acid	HOOC——N(H)——R₂——N(H)——COOH	
Carbon dioxide		O=C=O
Water		H——OH

Polyurethane (PU)	
HEUR	
Polyurea	

The main possible reactions in the HEUR/ Prepolymer system evaluated in the current work can be summarized in the following five reactions:

- Main polyurethane (PU) reaction: PEG + H_{12}MDI
- Hydrophobic modification of polyurethane (HEUR synthesis): PU + 1-Octanol
- Diisocyanate and hydrophobe reaction: H_{12}MDI + 1-Octanol
- Diisocyanate and water reaction: H_{12}MDI + H_2O
- Diisocyanate and amine reaction: H_{12}MDI + Amine

A simplified representation of this chemistry is presented in the following section. It should be noted that other possible primary (e.g urea with H_{12}MDI) or secondary reactions (e.g., PU or polyurea with H_{12}MDI) have not been considered. For further reactions and details reference to the literature is made. [2, 3]

Main polyurethane (PU) reaction: PEG + H_{12}MDI

Step A
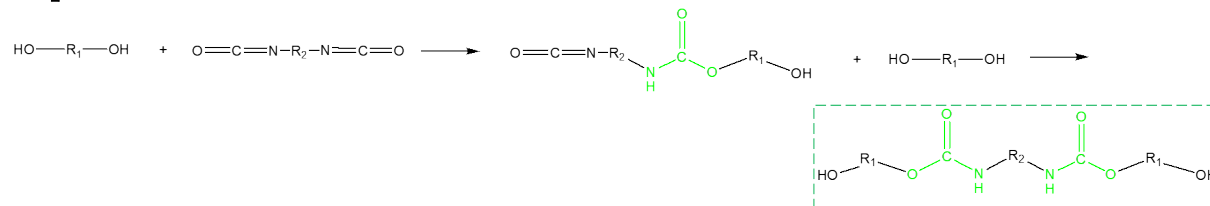
Step B
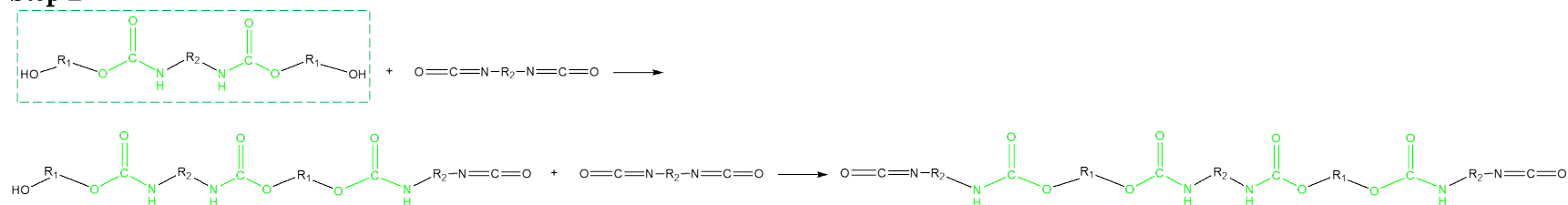
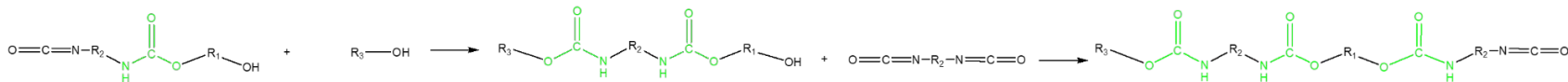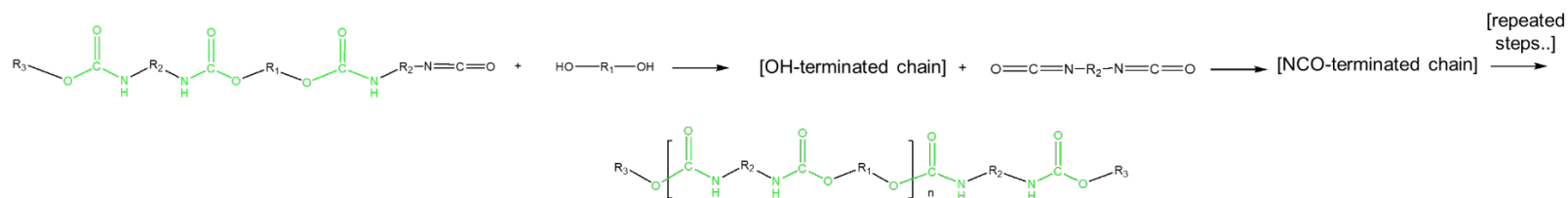### Repeated step A followed by step B for chain build up: polyurethane production
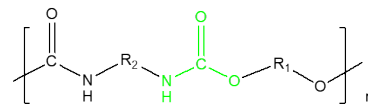
Figure S5. Mechanism of main polyurethane (PU) reaction between polyol (PEG) and diisocyanate (H_{12}MDI).

Hydrophobic modification of polyurethane (HEUR synthesis): PU + Octanol

PU: octanol attachment in step A followed by step B

Hydrophobical modification step

PU: octanol attachment in the developed chain (Hydrophobical modification step)
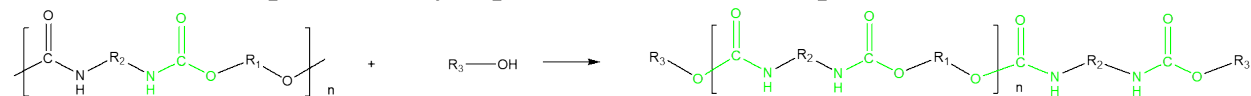
Figure S6. Mechanism of the reaction between 1-Octanol and PU during step A or directly at the PU formed polymer.

Diisocyanate and hydrophobe reaction: H$_{12}$MDI + 1-Octanol
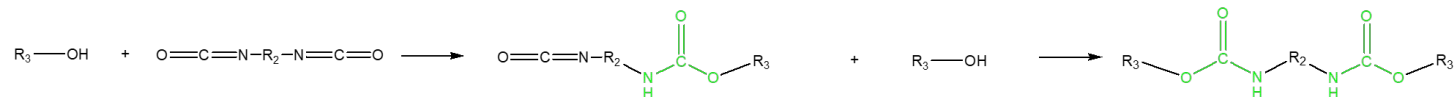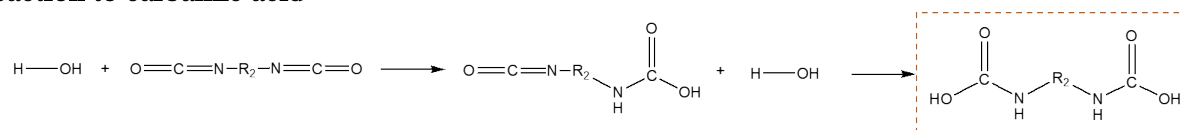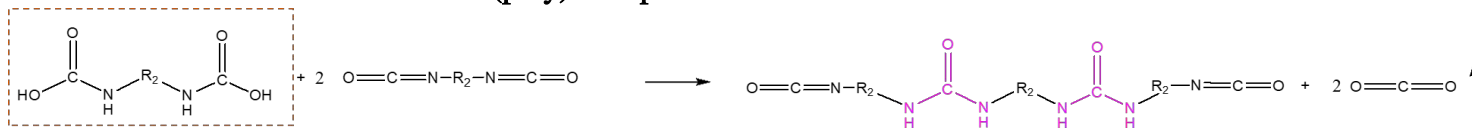
Blocking of HMDI by octanol

Figure S7. Mechanism of the reaction between octanol and diisocyanate.

Diisocyanate and water reaction: $H_{12}MDI + H_2O$

HMDI and water reaction to carbamic acid

Carbamic acid reaction with 2 mol of HMDI: (poly)Urea production

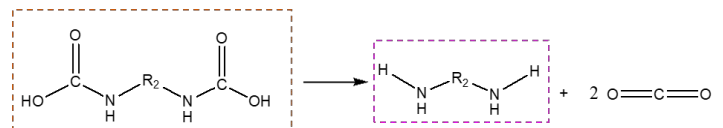Carbamic acid to amine and CO_2

Figure S8. Mechanism of the reaction between water and diisocyanate.

It should be noted that carbamic acid is reported to be unstable, therefore its participation in the reaction with diisocyanate is unlikely.[3] On the contrary, the most probable route is its decomposition to amine and CO_2. Further on, the amine produced will fast react with isocyanate as described next.

Diisocyanate and amine reaction: $H_{12}MDI + Amine$

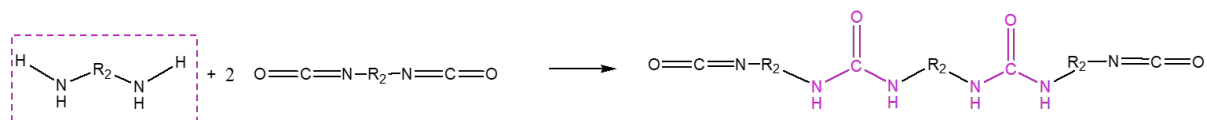Amine reaction with 2 mol of HMDI: (poly)Urea production

Figure S9. Mechanism of the reaction between amine and diisocyanate.

The urea bond containing molecules from Figure S8 and Figure S9 are $N = C = O$ terminated and could futher react with $-OH$ containing molecules. The reaction of these molecules with PEG, water (for the higher moisture concentration PEGs) and octanol would result in the following $-OH$ or $-CH_3$ end capped polymers:

(poly)urea reaction with PEG
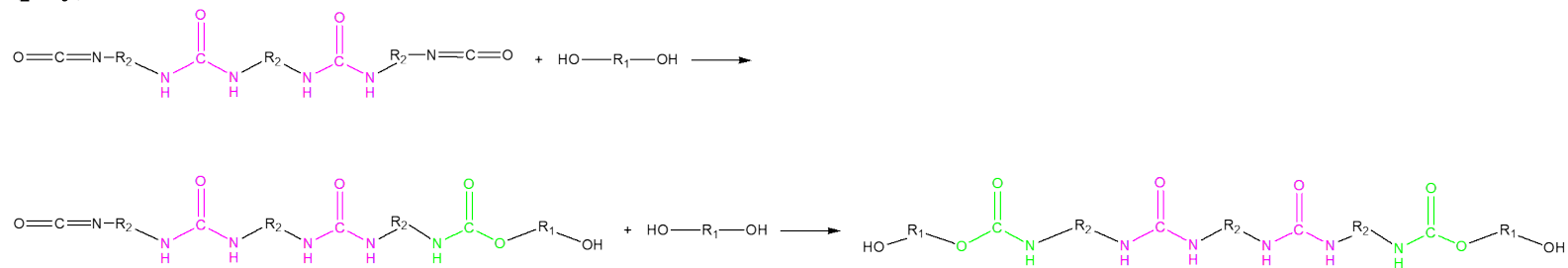
(poly)urea reaction with water

S13
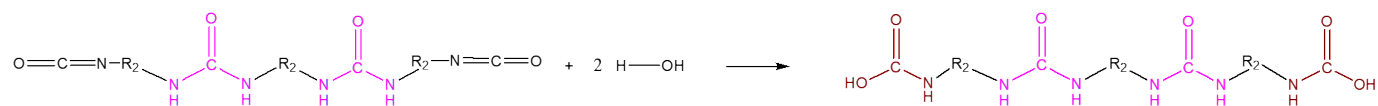
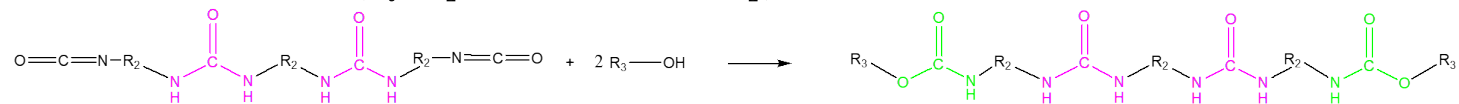**(poly)urea reaction with 1- Octanol (Hydrophobic modification step)**

Figure S10. Mechanisms of reaction of the urea containing polymer with PEG, water and 1-Octanol.
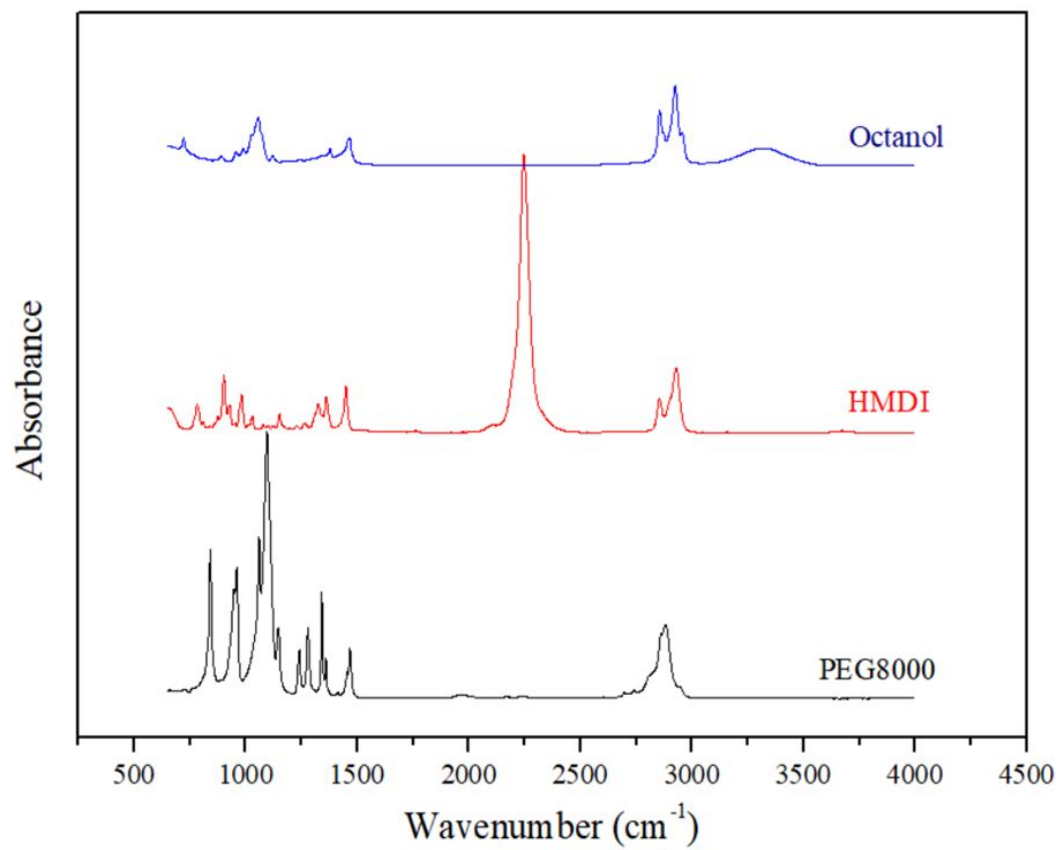
D. Analysis results

FTIR spectra

Figure S11. FTIR spectra of pure reactants (1-Octanol, H_{12}MDI and PEG8000 as received).
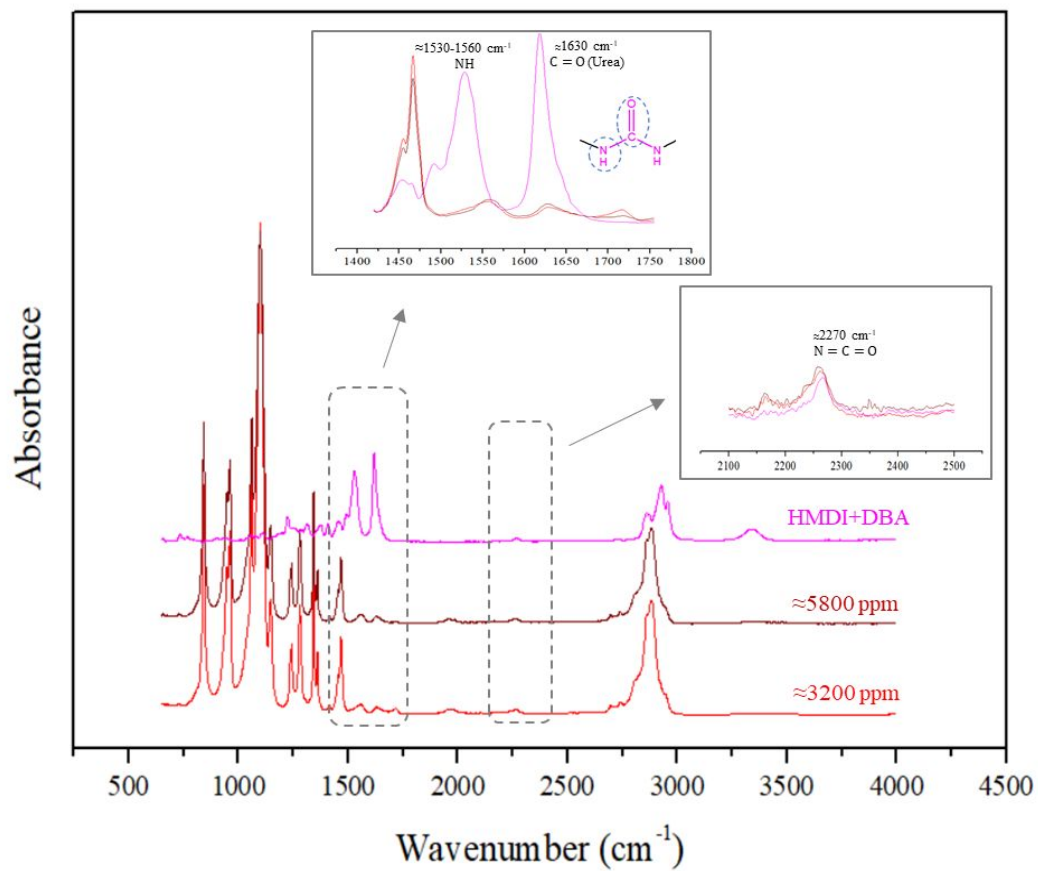
Figure S12. FTIR spectra of high moisture concentration PEG products compared to the reaction product of H$_{12}$MDI with dibutylamine (DBA); the peak at 1630 cm^{-1} confirms the type of the $C = O$ bond.
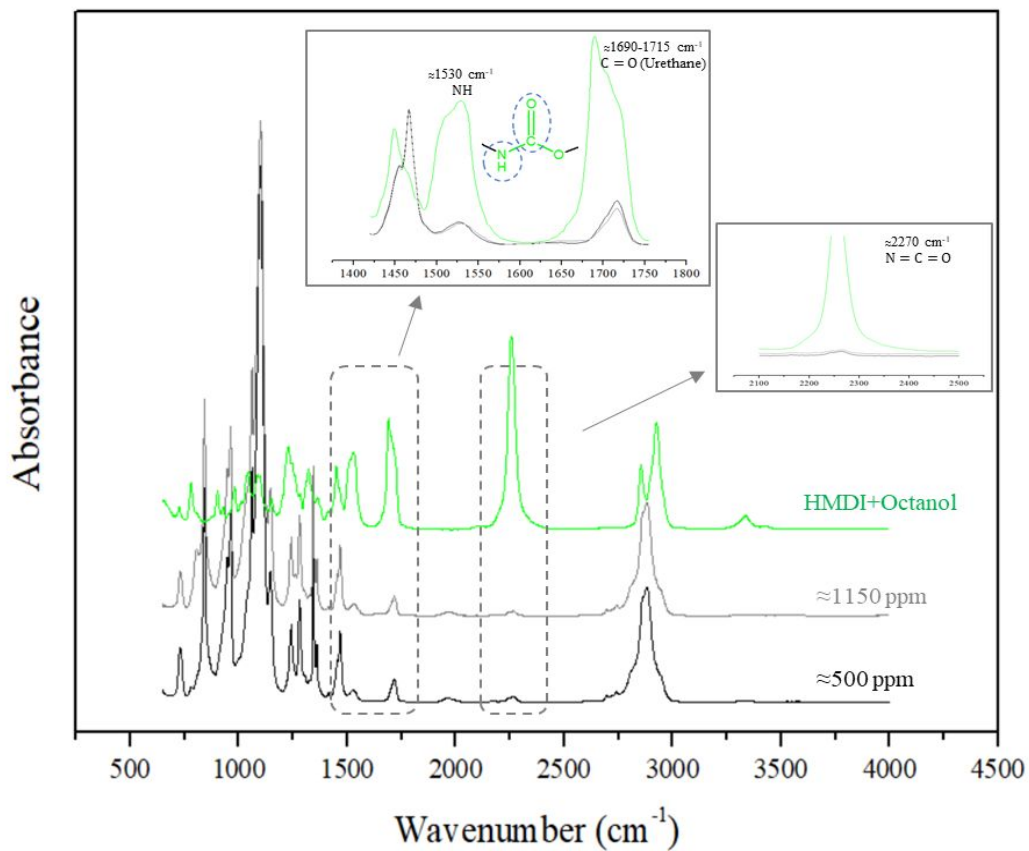
Figure S13. FTIR spectra of low moisture concentration PEG products compared to the reaction product of H$_{12}$MDI with 1-octanol; the peak at 1690-1715 cm^{-1} confirms the type of the $C = O$ bond.
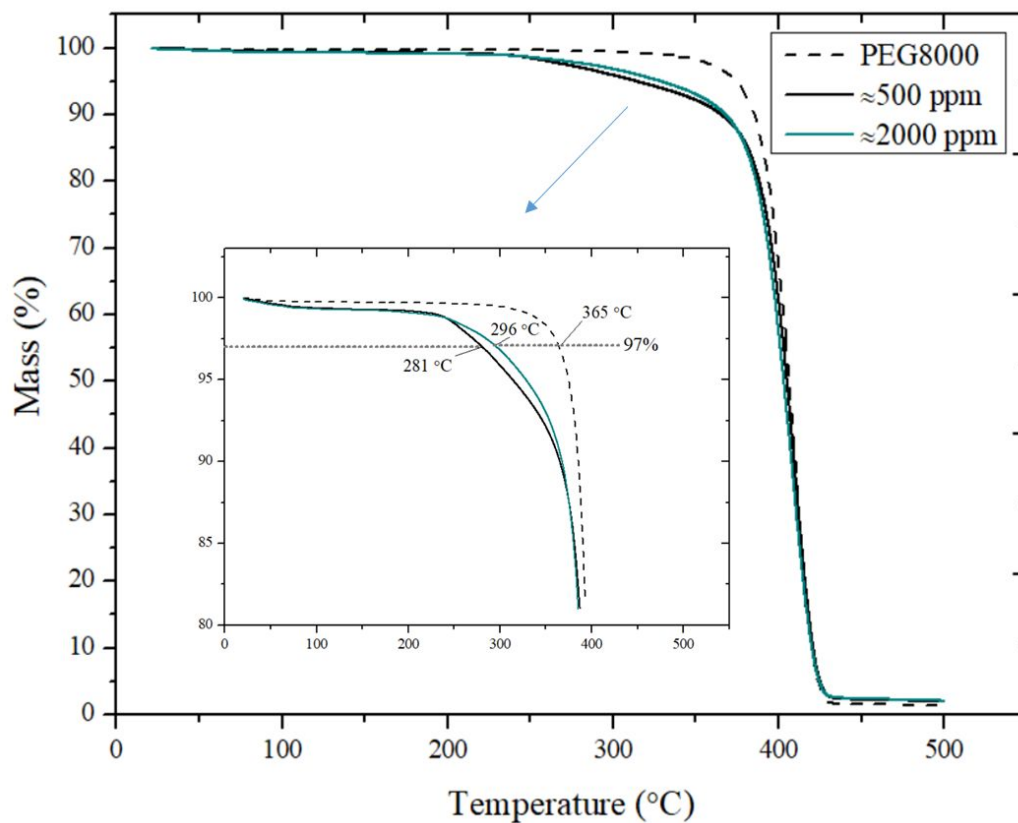
Figure S14. TGA curves of two selected HEUR samples from the moisture study (500 and 2000 ppm initial moisture concentration of the polyol). The HEUR produced from higher moisture concentration PEG requires higher temperature for mass reduction of 3% compared to the HEUR produced from low moisture concentration PEG. The curve of PEG8000 as received has also been added for reference.
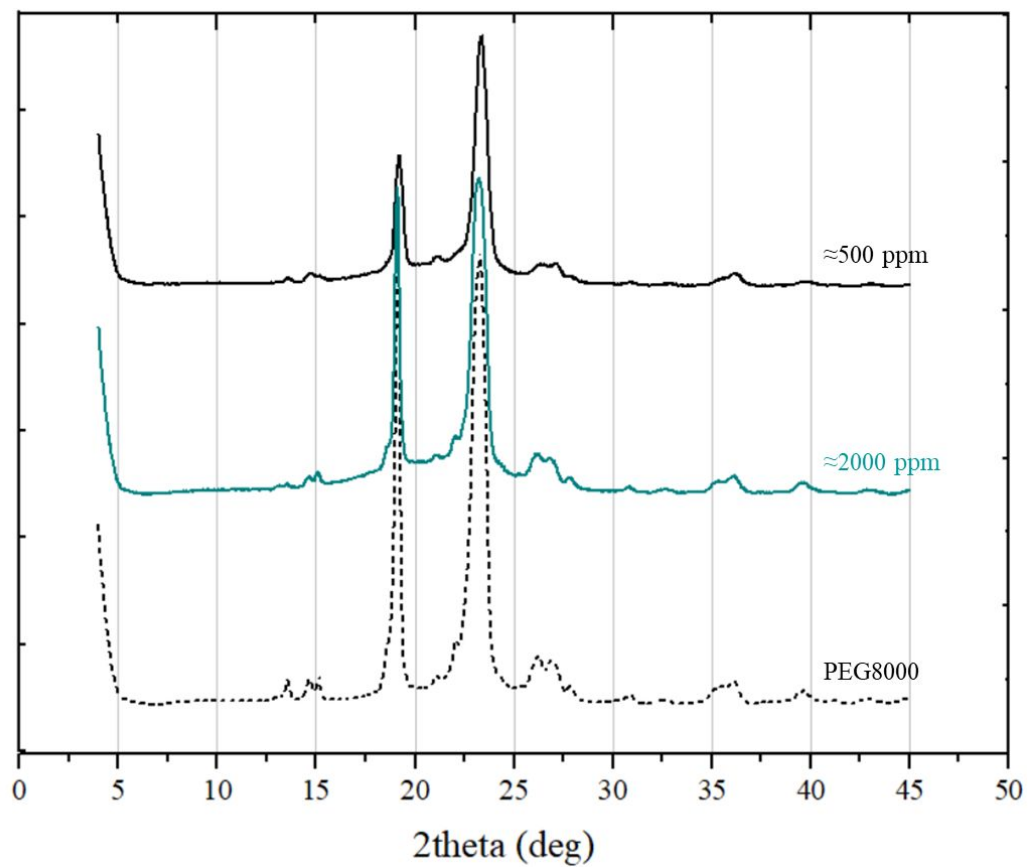
XRD results

≈500 ppm

≈2000 ppm

PEG8000

2theta (deg)

Figure S15. XRD patterns from PEG8000 and selected HEUR samples from the moisture study.
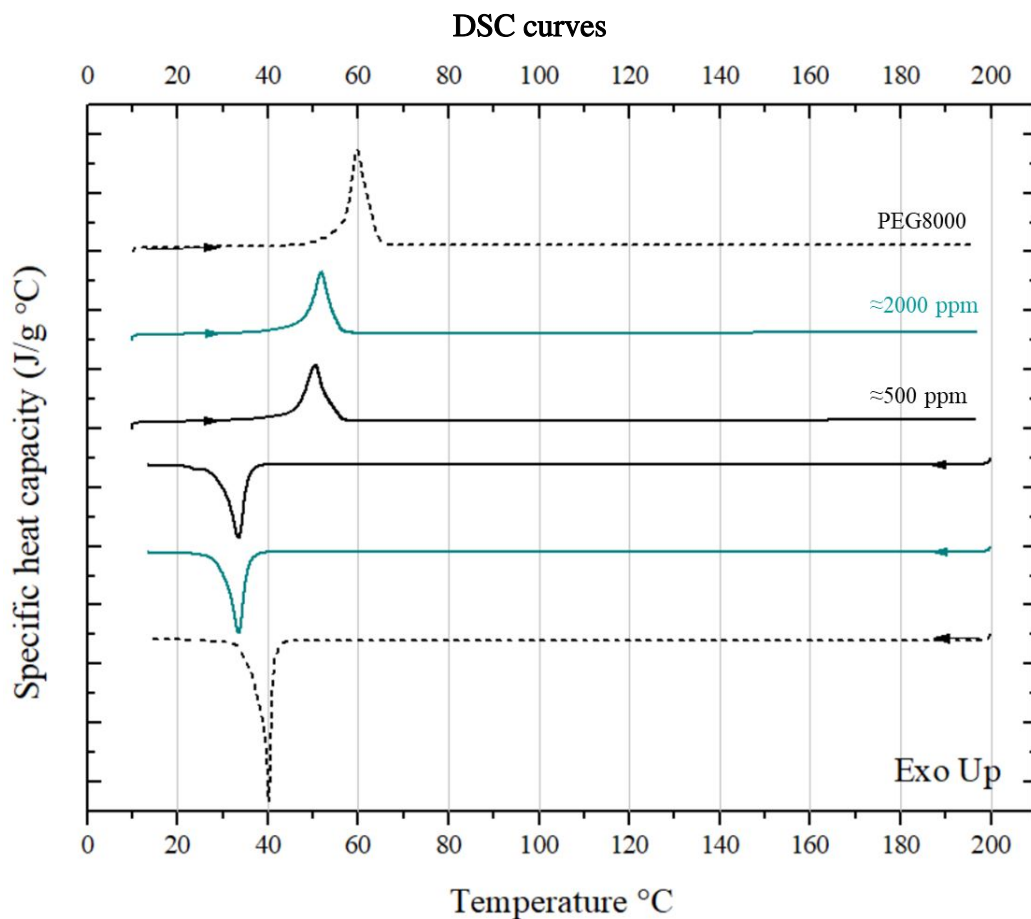
Figure S16. DSC heating (top) and cooling (bottom) runs at 10 ˚C/min for PEG8000 and two selected samples from the moisture parametric study (500 and 2000 ppm initial moisture concentration of the polyol). Arrows show the direction of the heating and cooling. The cooling curves have been shifted for clarity. The data are based on the third and fourth cycle in order to compare the materials after being exposed to the exact same thermal history.

References

(1)　Arnould, P.; Bosco, L.; Sanz, F.; Simon, F. N.; Fouquay, S.; Michaud, G.; Raynaud, J.; Monteil, V. Identifying Competitive Tin-or Metal-Free Catalyst Combinations to Tailor Polyurethane Prepolymer and Network Properties. *Polym. Chem.* **2020**, *11* (36), 5725–5734. https://doi.org/10.1039/d0py00864h.

(2)　Sharmin, E.; Zafar, F. *Polyurethane: An Introduction*; Sharmin, E., Zafar, F., Eds.; IntechOpen: London, United Kingdom, 2012. https://doi.org/10.5772/51663.

(3)　Szycher, M. *Szycher's Handbook of Polyurethanes*, Second edi.; Szycher, M., Ed.; CRC Press, 2013.