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Supporting information

Synthesis of 2-(2-methoxyethoxy)ethyl-4-methylphenyl carbamate

A Schlenk flask (50 mL) equipped with a water-cooled condenser was charged under an atmosphere of argon with *p*-tolyl isocyanate (5 mL, 5.26 g, 0.039 mol). Diethylene glycol methyl ether was added in excess (28.46 g, 0.237 mol). The mixture was stirred and heated to 120°C for two hours. The mixture was then cooled to room temperature and the organic phase extracted with 40 mL of dry chloroform. The remaining alcohol was removed from the chloroform phase by extraction with distilled water (3 x 20 mL). The chloroform was then removed in a partial vacuum using a rotary evaporator to afford 9.50 g (95% yield) of pure 2-(2-methoxy-ethoxy)ethyl *p*-tolyl carbamate as viscous colourless liquid.



Scheme S1. Synthesis of 2-(2-methoxyethoxy)ethyl-4-methylphenyl carbamate.

¹H-NMR (400 MHz, CDCl₃): δ (ppm) 2.23 (s, 3H, *CH*₃-C₆H₄-N-), 3.32 (s, 3H, *CH*₃-O-), 3.50 (m, 2H, CH₃-O-*CH*₂-), 3.60 (m, 2H, CH₃-O-CH₂-*CH*₂-), 3.67 (m, 2H, -N-C(=O)-O-CH₂-*CH*₂-), 4.26 (t, 2H, -N-C(=O)-O-*CH*₂-CH₂-), 6.62 (s, 1H, -C₆H₄-*NH*-C(=O)-O-), 7.03 (d, 2H, -NH-*C*₆H^{a,a'}₂*H*^{b,b'}₂-CH₃), 7.18 (d, 2H, -NH-*C*₆*H*^{a,a'}₂*H*^{b,b'}₂-CH₃). ¹³C-NMR (100 MHz, CDCl₃): δ (ppm) 21.3, 59.3, 62.1, 69.0, 69.8, 71.6, 121.5, 129.2, 135.0, 136.8, 153.8.

Elemental analysis calc. (%) for $C_{13}H_{19}NO_4$: C 61.64, H 7.56, N 5.53; exptl. (%): C 61.33, H 7.52, N 5.88.

Isolation of 2-(2-methoxyethoxy) ethyl *p*-tolyl (*p*-tolylcarbamoyl) carbamate (APH) by preparative HPLC and characterization by ¹H-NMR and COSY

Samples of the reaction of *p*-tolyl isocyanate and diethylene glycol methyl ether (3.5:1) in the presence of potassium trifluoroacetate were taken at different reaction times. The samples were analysed by LC-MS to detect and identify also trace chemicals in the complex mixtures.¹⁻⁴ The MS spectra revealed ion masses at m/z 205, 241, 254, 387 and 400 that were assigned to isocyanate quenched by pyrrolidine, urea, carbamate, allophanate and isocyanurate, respectively. As a UV detector was used for LC, diethylene glycol methyl ether was not detected. A larger fraction of the allophanate (2-(2-methoxyethoxy) ethyl *p*-tolyl (*p*-tolyl-carbamoyl) carbamate) was collected by preparative HPLC using the same mobile phase (methanol) and the same method as used for LC-MS analyses. The collected fraction was concentrated under reduced pressure and analysed by ¹H-NMR spectroscopy and COSY.^{5, 6} The results obtained by LC-MS, ¹H-NMR spectroscopy and COSY are given in Figure S1 and Figure S2. The structure of the allophanate was verified and the proton signals were assigned, integrated and correlated.

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Figure S2. ¹H-NMR spectrum (top) and COSY (bottom) of the methanolic solution of allophanate collected by preparative HPLC.

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 $^1\mbox{H-NMR}$ spectrum of a typical reaction mixture confirming the presence of intermediate I_1



Figure S3. ¹H-NMR spectrum of the reaction mixture of *p*-tolyl isocyanate and diethylene glycol methyl ether in the presence of potassium trifluoroacetate recorded at 1170 min (19.5 h). The signals marked with symbols are assigned to intermediate I_1 . The assignment of the protons is confirmed by the corresponding integrals.

Table S1. High abundance signals obtained from the negative-ionmode of ESI-MS analysis.

m/z	Relative abundance [%]	Assignment
202.05	38	p-Tol ~ N CF3
264.18	60	$\begin{pmatrix} \rho \cdot T_0 & \vec{N} & O & CF_3 \\ O & O & O \end{pmatrix} H_2 O$
264.93	100	(CF ₃ COOK) CF ₃ COO
416.88	35	(Isocyanurate-H) H ₂ O
568.83	64	(СҒ ₃ СООК) ₃ СҒ ₃ СОО
720.94	19	(СF ₃ СООК) ₄ СF ₃ СОО
872.98	8	(СF ₃ СООК) ₅ СF ₃ СОО

Calculation of the molar ratio

For the reaction profiles, the molar ratio x_i of every component in the reaction mixture was calculated according to the following equation:

$$\mathcal{L}_{i} = \frac{\frac{I_{i}}{n_{i}}}{\sum_{j} \left(\frac{I_{j}}{n_{j}}\right)} \times 100 \text{ (mol\%)}$$

where I is the integral of the area of the characteristic signal of components i and j, and n is the number of the protons that correspond to the signal. The nominator in the equation calculates the normalized integral of component i, while the denominator calculates the sum of the normalized integrals of all components j in the reaction mixture.

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Assignment of a typical ¹H-NMR spectrum indicating the signals used for quantification



Figure S4. Selected ¹H-NMR spectrum of the reaction mixture of *p*-tolyl isocyanate, 2-(2-methoxyethoxy)ethyl-4-metyhlphenyl carbamate (molar ratio of 1:1) and the catalyst potassium trifluoroacetate. The reaction was performed at 25 °C. The spectrum was recorded at 12 min. The characteristic signals of all species in the reaction mixture were identified and labelled in the following colours: isocyanate (*p*TI) dark red, alcohol (DEME) orange, carbamate (CRB) dark blue, allophanate (APH) light blue and isocyanurate (ISR) green.



Figure S5. ¹H-NMR spectra of the reaction mixture of pTI and KOAc^F (molar ratio of 1:1). The reaction was performed at 25 °C. Spectra were recorded after 2, 4, 8, 24, and 120 min.

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Figure S6. ¹H-NMR spectra of the reaction mixture of *p*TI and DEME in the presence of the catalyst KOAc^F. Spectra were recorded at 2, 37, 78, 118 min and 18.3 h.

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Figure S7. 1H-NMR spectra of the reaction mixture of pTI and CRB in the presence of the catalyst KOAc^f. Spectra were recorded at 1, 3, 6, 12 min and 20 h.

Catalyst test in a PU/PIR rigid foam formulation

To confirm the catalyst activity in a PU/PIR foam formulation, a typical rigid PU/PIR foam was obtained with KOAc as catalyst. MDI (Baymer 30HB05K) was reacted with polyol (Desmodur 44V70L) in the presence of KOAc (molar ratio 3.5:1:0.002) and pentane as blowing agent. After cooling overnight, a sample was taken from the core and surface of the rigid foam and analysed with IR spectroscopy.

FTIR spectra of the sample taken from the core and the surface of the foam are shown in Figure S8 as red and blue traces, respectively. The signals at 2200-2350 cm⁻¹ were attributed to unreacted NCO groups of MDI (NCO), the signals at 1380-1450 cm⁻¹ to isocyanurate moieties (ISR). The ratio of the signal intensities NCO/ISR was 0.53 for the sample taken from the core of the foam and 0.77 for the sample taken from the surface of the foam. Signals amenable to reaction intermediates were not identified.



Figure S8. FTIR spectra of samples taken from the core (blue line) and the surface (redline) of a typical rigid PU/PIR foam obtained with KOAc as catalyst.

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Notes and references

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