Supporting information

Turning down the heat: catalyst-free, low-temperature chemical degradation of thermoplastic polyurethanes

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Materials

N,N-dimethyl-1,6-diaminohexane (>97%), 4-methylpiperidine (>98.0%), p-tolyl isocyanate (> 98.0%), butyl isocyanate (>98.0%), hexyl isocyanate (>98.0%), ethyl glycolate (>98.0%) hexamethylene diisocyanate (>98.0%, HDI), tolylene diisocyanate mixture of 80% 2,4- and 20% 2,6 (>98.0%, TDI) and dibutyltin dilaurate (>95.0%, DBTDL) were purchased from TCI chemicals. 2-Hydroxyethyl acrylate (96%), tetratethylene glycol (99%, TEG) and activated aluminum oxide (AlOx) were obtained from Sigma Aldrich while 1-pentanol (99%) was purchased from Acros Organics. Dichloromethane (≥99.8%, DCM), chloroform (>99.8%, $CHCl_3$) and tetrahydrofuran (≥99.8%, THF) were obtained from Fisher Chemical. Deuterated solvents, $CDCl_3$ (99.8%D), DMSO-d_6 (99.8%D) and DMF-d_7 (99.8%D) were purchased from Eurisotop. Dimethyl acetamide (99.8%, HPLC grade, DMAc) and acetonitrile (99.8%, HPLC grade, ACN) were obtained from ChemLab. All chemicals were used without further purification except TEG that was dried in a vacuum oven at 80 °C prior to use.

Instrumentation

Size Exclusion Chromatography (SEC)

SEC analyses were performed on a Waters instrument, with a RI detector (2414 Waters), equipped with 3 Polymer Standards Services SEC serial columns (1 GRAM Analytical 30 A, 10 ˚ mm and 2 GRAM Analytical 1000 A, 10 ˚ mm) at 35 °C. PMMA standards were used for calibration and DMAc containing LiBr (5 $g \cdot L^{-1}$) was used as a solvent at a flow rate of 1 $mL \cdot min^{-1}$. Molar mass (M_n, M_w) and dispersity (Đ) values were determined based on the calibration curve each time, using the Water's Empower Pro software.

Nuclear Magnetic Resonance (NMR)

NMR spectra were recorded on a Bruker Advance Ultrashield 400 MHz spectrometer. Deuterated chloroform ($CDCl_3$) and deuterated dimethylformamide (DMF-d_7) were used as solvents. Chemical shifts (δ) are given in parts per million (ppm) relative to the deuterated solvent used as the internal reference.

Fourier Transform Infrared Spectroscopy (FTIR)

IR spectra were recorded on a Perkin-Elmer Spectrum 1000 FTIR spectrometer equipped with a diamond ATR probe.

Differential Scanning Calorimetry (DSC)

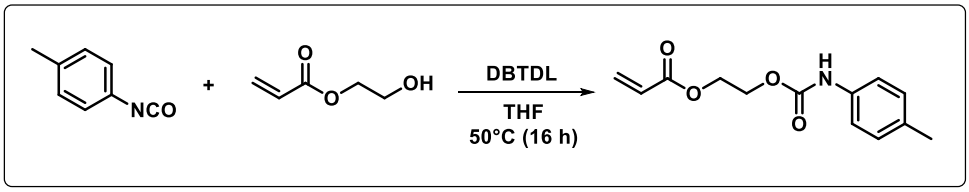
DSC analyses were measured on a Mettler Toledo 1/700 instrument. The measurements were performed under a nitrogen atmosphere with heating and cooling rates of 10 $°C \cdot min^{-1}$ from -50 °C to 150 °C.

Thermogravimetric Analysis (TGA)

TGA were performed on a Mettler-Toledo TGA/SDTA 851. The dynamic thermogravimetric measurements were recorded in nitrogen atmosphere from 30 to 800 °C with a heating rate of 10 $°C \cdot min^{-1}$.

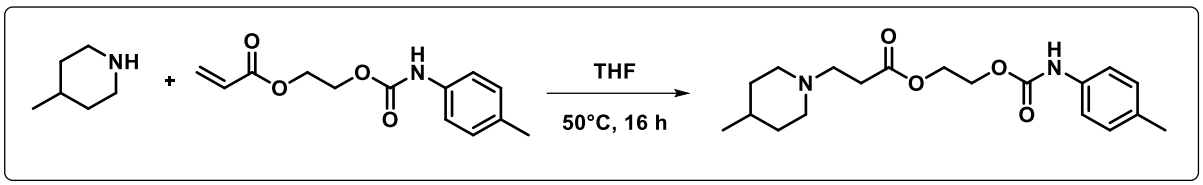
Synthesis procedures

Synthesis of acrylate tolyl carbamate



In a 100 mL one-necked round bottom flask, 2-hydroxyethyl acrylate (4 g, 34.45 mmol, 1 eq.) and DBTDL (271.6 mg, 1 mol% to NCO) were dissolved in 50 mL of THF and kept under a N_2 atmosphere. Then, *p*-tolyl isocyanate (4.59 g, 34.45 mmol, 1 eq.) was added dropwise and the reaction was heated to 50 °C and left to react overnight. Afterwards, the reaction mixture was filtered through AlOx, dried with anhydrous Na_2SO_4 and concentrated in the rotary evaporator to yield a colorless transparent viscous oil. Yield = quantitative. ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 7.26 (d, 2H), 7.10 (d, 2H), 6.81 (s, 1H), 6.44 (dd, 1H), 6.15 (dd, 1H), 5.86 (dd, 1H), 4.40 (s, 4H), 2.30 ppm (s, 3H) (Figure S1). ^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm): 166.06, 153.28, 135.14, 133.26, 131.57, 129.63, 128.03, 118.94, 62.87, 62.69, 20.82 (Figure S2).

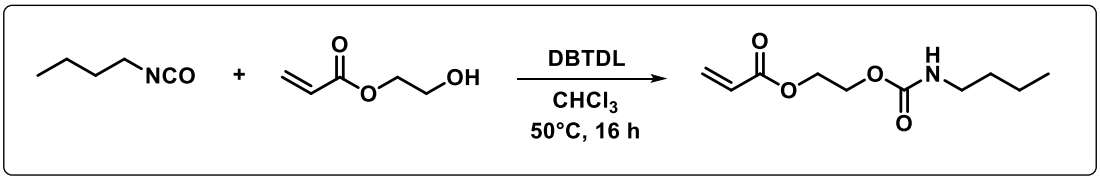
Synthesis of BAE-containing p-tolyl carbamate model compound (M1)



In a 100 mL one-necked round bottom flask, 4-methylpiperidine (1.99 g, 20.06 mmol, 1 eq.) was dissolved in 50 mL of THF. Then, the acrylate *p*-tolyl carbamate (5 g, 20.06 mmol, 1 eq.) was added dropwise and the reaction was kept at room temperature for 30 min and then heated to 50 °C overnight. Afterwards, the reaction mixture was concentrated in the rotary evaporator to yield a slightly yellowish solid. Yield = quantitative. ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 7.25 (d, 2H), 7.10 (d, 2H), 6.78 (s, 1H), 4.33 (m, 4H), 2.84 (dt, 2H), 2.68 (m, 2H), 2.54 (m, 2H), 2.30 (s, 3H), 1.95 (dt, 2H), 1.59 (m, 2H),

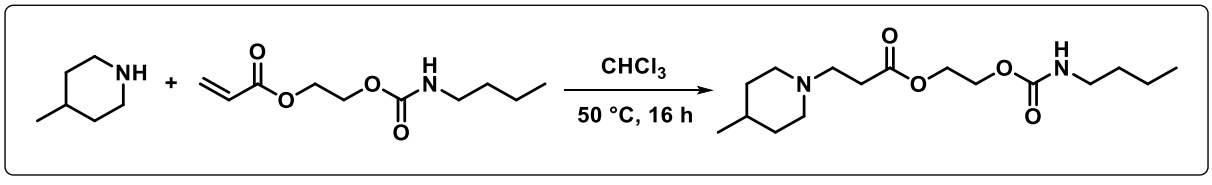
1.32 (m, 1H), 1.19 (m, 2H), 0.89 (d, 3H) (Figure S3). ^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm): 172.61, 153.27, 135.26, 133.21, 129.60, 118.94, 62.89, 62.51, 53.90, 53.82, 34.31, 32.30, 30.72, 21.92, 20.82 (Figure S4).

Synthesis of acrylate butyl carbamate



In a 100 mL one-necked round bottom flask, 2-hydroxyethyl acrylate (4 g, 34.45 mmol, 1 eq.) and DBTDL (217.6 mg, 1 mol% to NCO) were dissolved in 50 mL of $CHCl_3$ and kept under a N_2 atmosphere. Then, butyl isocyanate (3.41 g, 34.45 mmol, 1 eq.) was added dropwise and the reaction was heated to 50 °C and left to react overnight. Afterwards, the reaction mixture was filtered through AlOx, dried with anhydrous Na_2SO_4 and concentrated in the rotary evaporator to yield a colorless transparent viscous oil. Yield = quantitative. ^{1}H NMR (400 MHz, DMSO-d_6, δ in ppm): 7.21 (t, 1H), 6.34 (dd, 1H), 6.18 (dd, 1H), 5.96 (dd, 1H), 4.22 (m, 4H), 2.96 (q, 2H), 1.36 (m, 2H), 1.25 (m, 2H), 0.85 (t, 3H) (Figure S5). ^{13}C NMR (100 MHz, DMSO-d_6, δ in ppm): 165.33, 155.90, 131.86, 128.06, 62.89, 61.58, 39.88, 31.43, 19.37, 13.61 (Figure S6).

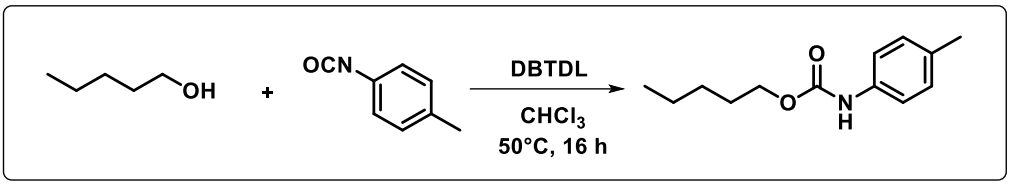
Synthesis of BAE-containing butyl carbamate model compound (M2)



In a 100 mL one-necked round bottom flask, 4-methylpiperidine (2.3 g, 23.23 mmol, 1 eq.) was dissolved in 50 mL of $CHCl_3$. Then, the acrylate butyl carbamate (5 g, 23.23 mmol, 1 eq.) was added dropwise and the reaction was kept at room temperature for 30 min and then heated to 50 °C overnight. Afterwards, the reaction mixture was concentrated in the rotary evaporator to yield a colourless transparent viscous oil. Yield = quantitative. ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 4.85 (t, 1H), 4.22

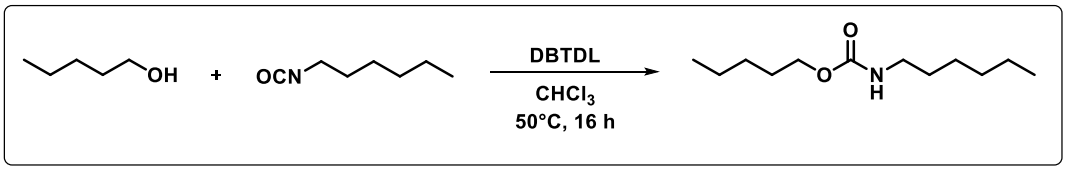
(s, 4H), 3.13 (m, 2H), 2.81 (dt, 2H), 2.63 (m, 2H), 2.49 (m, 2H), 1.92 (dt, 2H), 1.57 (m, 2h), 1.45 (m, 2H), 1.30 (m, 3H), 1.18 (m, 2H), 0.88 (dt, 6H) (Figure S7). ^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm): 172.57, 156.19, 62.70, 62.54, 53.89, 53.74, 40.85, 34.31, 32.31, 32.03, 30.70, 21.91, 19.95, 13.77 (Figure S8).

Synthesis of reference aromatic carbamate model compound (R1)



In a 100 mL one-necked round bottom flask, 1-pentanol (3.31 g, 37.55 mmol, 1 eq.) and DBTDL (237.2 mg, 1 mol% to NCO) were dissolved in 50 mL of $CHCl_3$ and kept under a N_2 atmosphere. Then, *p*-tolyl isocyanate (5 g, 37.55 mmol, 1 eq.) was added dropwise and the reaction was heated to 50 °C and left to react overnight. Afterwards, the reaction mixture was filtered through AlOx, dried with anhydrous Na_2SO_4 and concentrated in the rotary evaporator to yield a colorless transparent solid. Yield = quantitative. ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 7.26 (d, 2H), 7.10 (d, 2H), 6.58 (s, 1H), 4.15 (t, 2H), 2.30 (s, 3H), 1.67 (m, 2H), 1.36 (m, 2H), 0.92 (t, 3H) (Figure S9). ^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm): 154.00, 135.52, 133.00, 129.64, 118.89, 65.38, 28.78, 28.14, 22.48, 20.85, 14.10 (Figure S10).

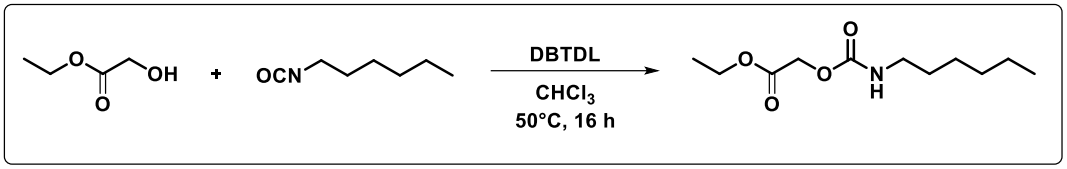
Synthesis of reference aliphatic carbamate model compound (R2)



In a 100 mL one-necked round bottom flask, 1-pentanol (3.47 g, 39.31 mmol, 1 eq.) and DBTDL (248.2 mg, 1 mol% to NCO) were dissolved in 50 mL of $CHCl_3$ and kept under a N_2 atmosphere. Then, hexyl isocyanate (5 g, 39.31 mmol, 1 eq.) was added dropwise and the reaction was heated to 50 °C and left to react overnight. Afterwards, the reaction mixture was filtered through AlOx, dried with anhydrous Na_2SO_4 and concentrated in the rotary evaporator to yield a colorless transparent oil. Yield =

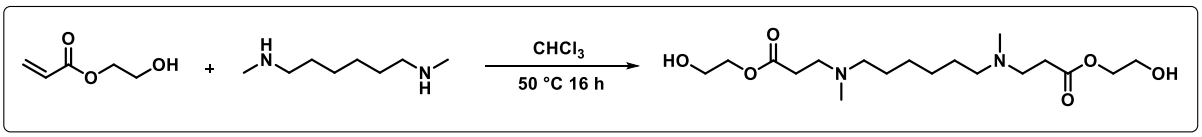
quantitative. ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 4.69 (s, 1H), 4.01 (t, 2H), 3.12 (m, 2H), 1.58 (m, 2H), 1.45 (m, 2H), 1.29 (m, 10H), 0.87 (dt, 6H) (Figure S11). ^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm): 156.92, 64.93, 41.09, 31.58, 30.08, 28.87, 28.14, 26.51, 22.65, 22.46, 14.08, 14.06 (Figure S12).

Synthesis of reference aliphatic ester-containing carbamate model compound (E2)



In a 100 mL one-necked round bottom flask, ethyl glycolate (2.86 g, 27.52 mmol, 1 eq.) and DBTDL (175 mg, 1 mol% to NCO) were dissolved in 50 mL of $CHCl_3$ and kept under a N_2 atmosphere. Then, hexyl isocyanate (3.5 g, 27.52 mmol, 1 eq.) was added dropwise and the reaction was heated to 50 °C and left to react overnight. Afterwards, the reaction mixture was filtered through AlOx, dried with anhydrous Na_2SO_4 and concentrated in the rotary evaporator to yield a colorless transparent oil. Yield = quantitative. ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 4.94 (s, 1H), 4.56 (s, 2H), 4.21 (q, 2H), 3.18 (q, 2H), 1.50 (m, 2H), 1.28 (m, 9H), 0.87 (t, 3H) (Figure S13). ^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm): 168.97, 155.61, 61.37, 61.16, 41.35, 31.55, 29.91, 26.46, 22.65, 22.46, 14.23, 14.11 (Figure S14).

Synthesis of BAE-containing diol (BAEOH)



In a 100 mL one-necked round bottom flask, N,N-dimethyl-1,6-diaminohexane (6 g, 41.6 mmol, 1 eq.) was dissolved in 50 mL of $CHCl_3$. Then, the 2-hydroxyethyl acrylate (9.66 g, 83.2 mmol, 2 eq.) was added dropwise and the reaction was kept at room temperature for 30 min and then heated to 50 °C overnight. Afterwards, the reaction mixture was concentrated in the rotary evaporator to yield a yellowish transparent viscous oil. Yield = quantitative. ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 4.28 (m, 4H), 3.73 (m, 4H), 2.67 (t, 4H), 2.53 (t, 4H), 2.33 (m, 4H), 2.23 (s, 6H), 1.46 (m, 4H), 1.27 (m, 4H)

(Figure S14). ^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm): 172.67, 65.84, 60.69, 57.68, 53.49, 41.96, 33.22, 27.45, 26.66 (Figure S15).

Preparation of thermoplastic-like polyurethane (TPU-like) polymers

First, a specific amount of BAEOH (1-100 mol% of the total alcohol groups) and the total amount of diisocyanates (HDI or TDI) were weighed in a 20 mL polypropylene cup and mixed for 1 min using a DAC 150.1 FVZ speed mixer at a speed of 2500 rpm. Then, the corresponding amount of TEG to react with the excess of NCO groups was weighed and the whole mixture, mixed again in the speed mixer for 1 min at 2500 rpm. The polypropylene cup was then flushed with N_2, closed and put in a conventional oven at 80 °C for 24 h to conduct the polymerization. For the reference material (no BAE moieties), the same protocol was used but adding 0.05 mol% to NCO groups of DBTDL before the second mixing step. Table S1 depicts the compositions of each formulation.

Table S1. Composition of all the TPU-like polymers.

Sample	HDI	TDI	BAEOH	TEG	DBTDL
HDI-ref	3.24 g	-	-	3.75 gr	12.2 mg
HDI-1%BAE	3.35 g	-	0.075 g	3.83 g	-
HDI-2.5%BAE	2.68 g	-	0.15 g	3.0 g	-
HDI-5%BAE	3.85 g	-	0.375 g	3.68 g	-
HDI-10%BAE	3.35 g	-	0.75 g	3.48 g	-
HDI-25%BAE	2.68 g	-	1.5 g	2.32 g	-
HDI-100%BAE	1.34 g	-	3.0 g	-	-
TDI-1%BAE	-	3.47 g	0.075 g	3.83 g	-
TDI-2.5%BAE	-	2.78 g	0.15 g	3.0 g	-
TDI-5%BAE	-	3.47 g	0.375 g	3.68 g	-
TDI-10%BAE	-	3.47 g	0.75 g	3.48 g	-
TDI-25%BAE	-	2.78 g	1.5 g	2.32 g	-
TDI-100%BAE	-	1.39 g	3.0 g	-	-

Degradability studies with model compounds

In a 25 mL two-necked round bottom flask equipped with a magnetic stirrer, model compound M1, M2, R1 or R2 (4 mmol, 1 eq.) were weighed and dissolved in MeOH (400 mmol, 100 eq.). Then, an air condenser was connected, and the reaction was heated to 70 °C. Aliquots of 2 mL were taken at different times and concentrated. The degradability was then monitored via ^{1}H NMR by following the disappearance of the signal corresponding to the protons of the methylene unit next to the ester and next to the urethane groups (Figures S15-S18).

Degradability of the TPU-like polymers

In a 40 mL glass vial, 0.5 g of TPU was added together with 20 mL of MeOH. The vial was then heated up to 70 °C and kept for 24 h. Aliquots were taken at 5 and 24h, concentrated in the rotary evaporator and the remaining solid was dissolved in DMAc for SEC analysis (Figures S24-S25).

NMR spectra

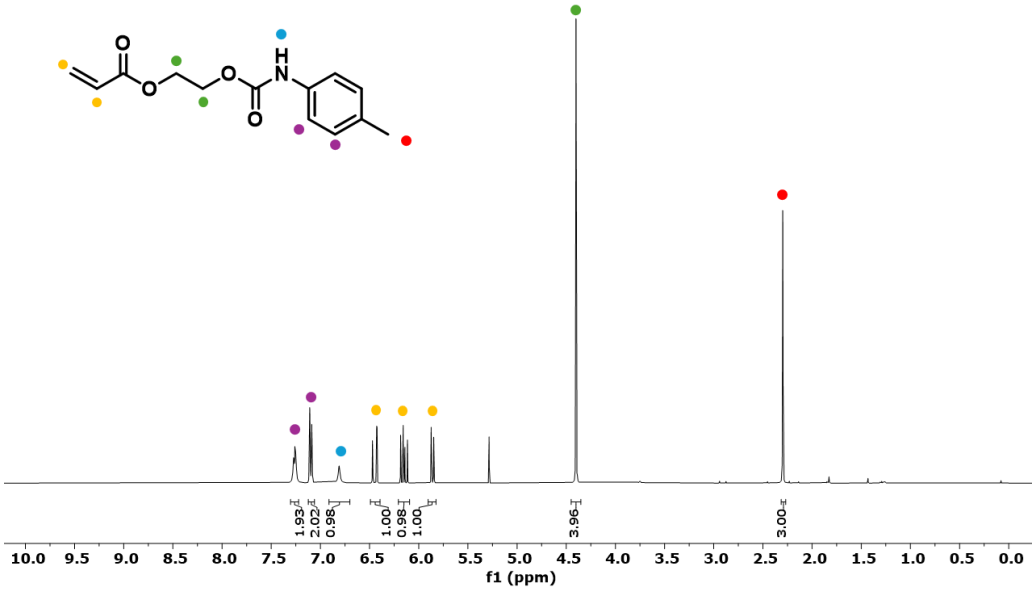


Figure S1. ^{1}H NMR spectrum of acrylate *p*-tolyl carbamate in $CDCl_3$.

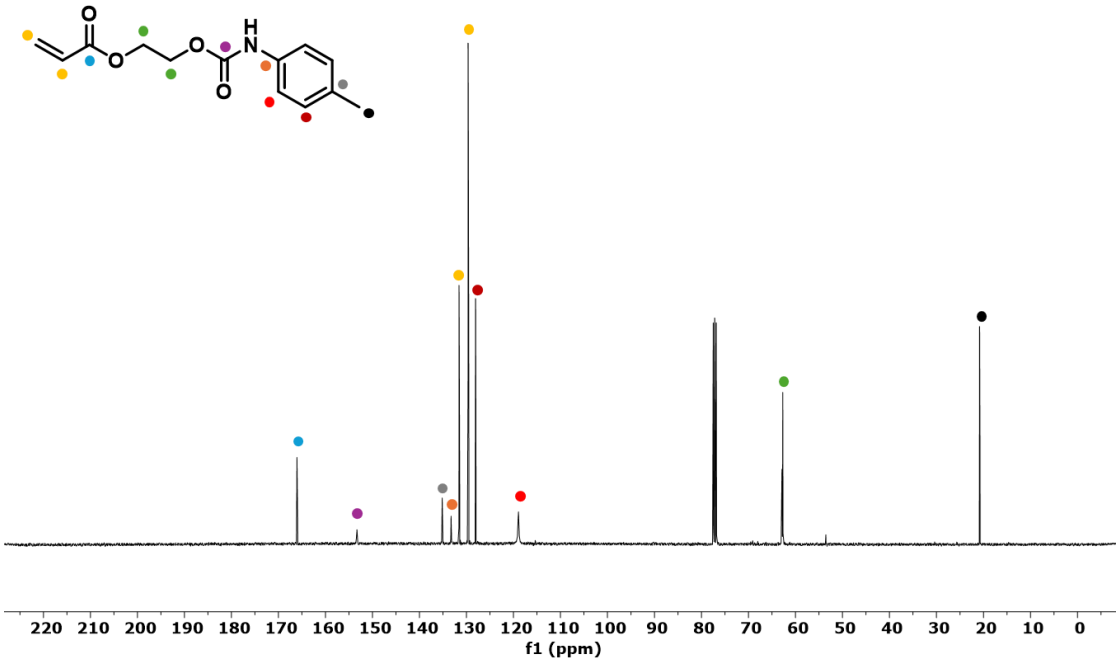


Figure S2. ^{13}C NMR spectrum of acrylate *p*-tolyl carbamate in $CDCl_3$.

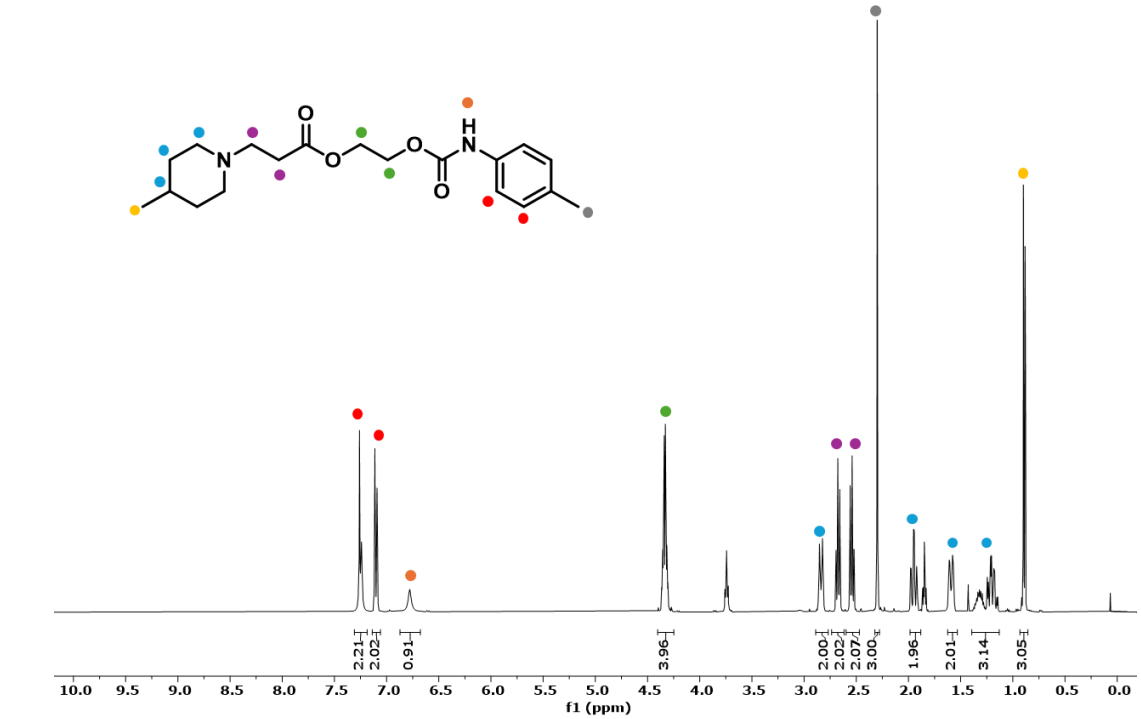


Figure S3. ^{1}H NMR spectrum of BAE-containing *p*-tolyl carbamate (M1) in $CDCl_3$.

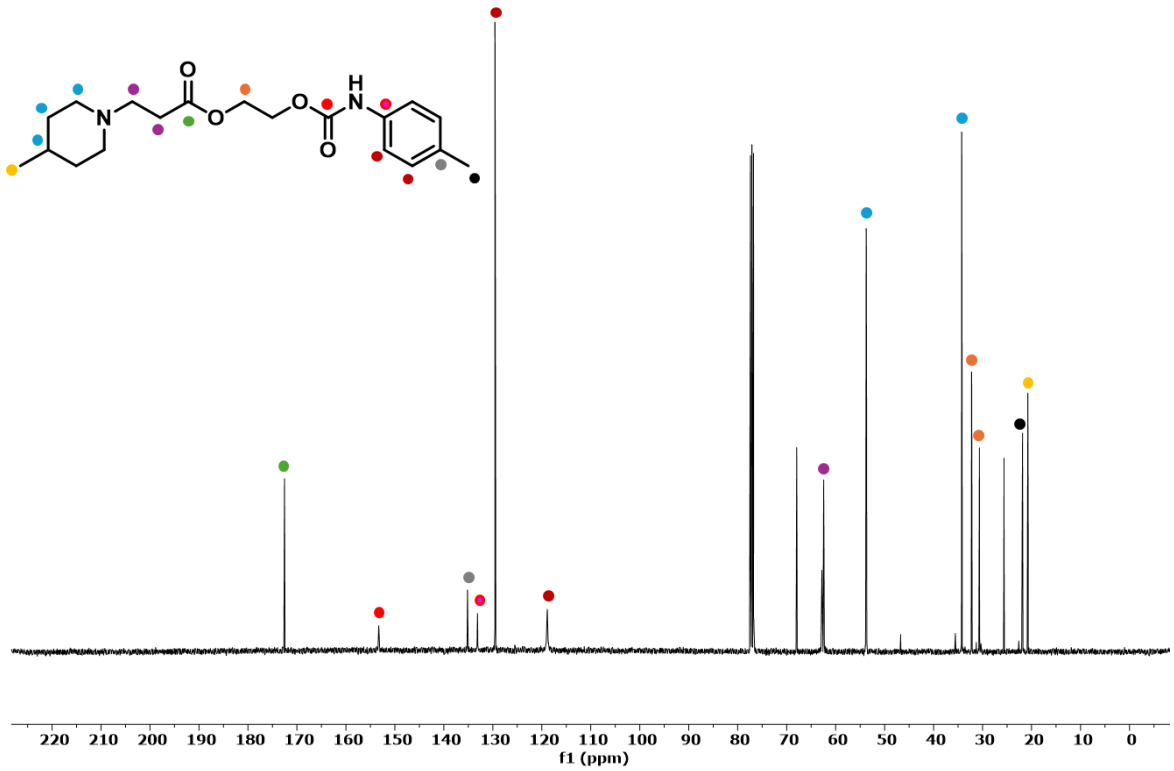


Figure S4. ^{13}C NMR spectrum of BAE-containing *p*-tolyl carbamate (M1) in $CDCl_3$.

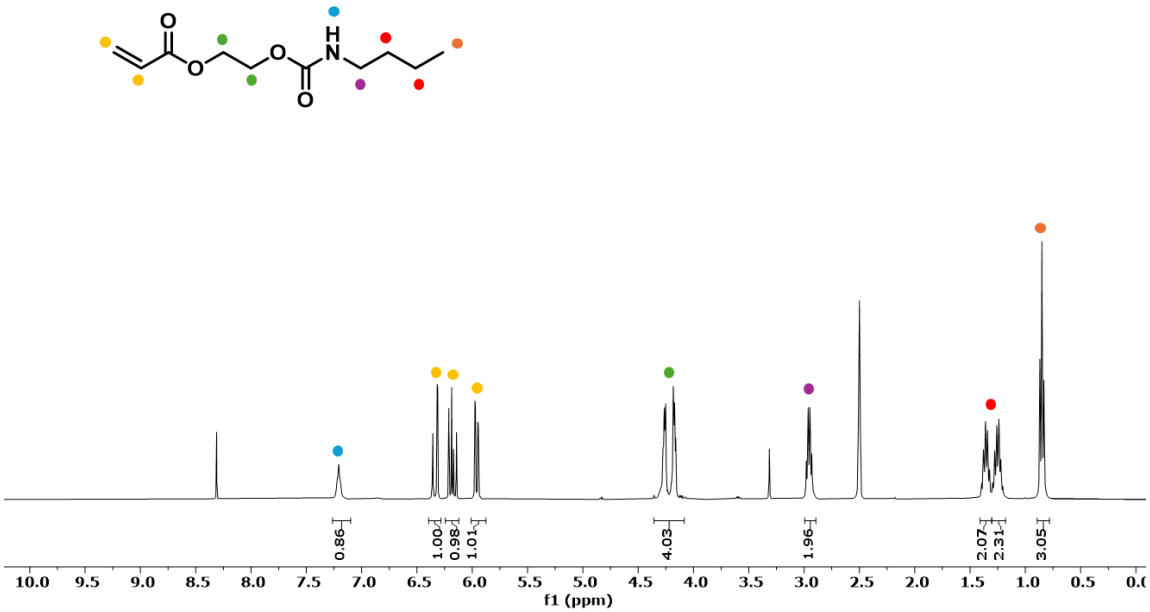


Figure S5. ^{1}H NMR spectrum of acrylate butyl carbamate in DMSO-d_6.

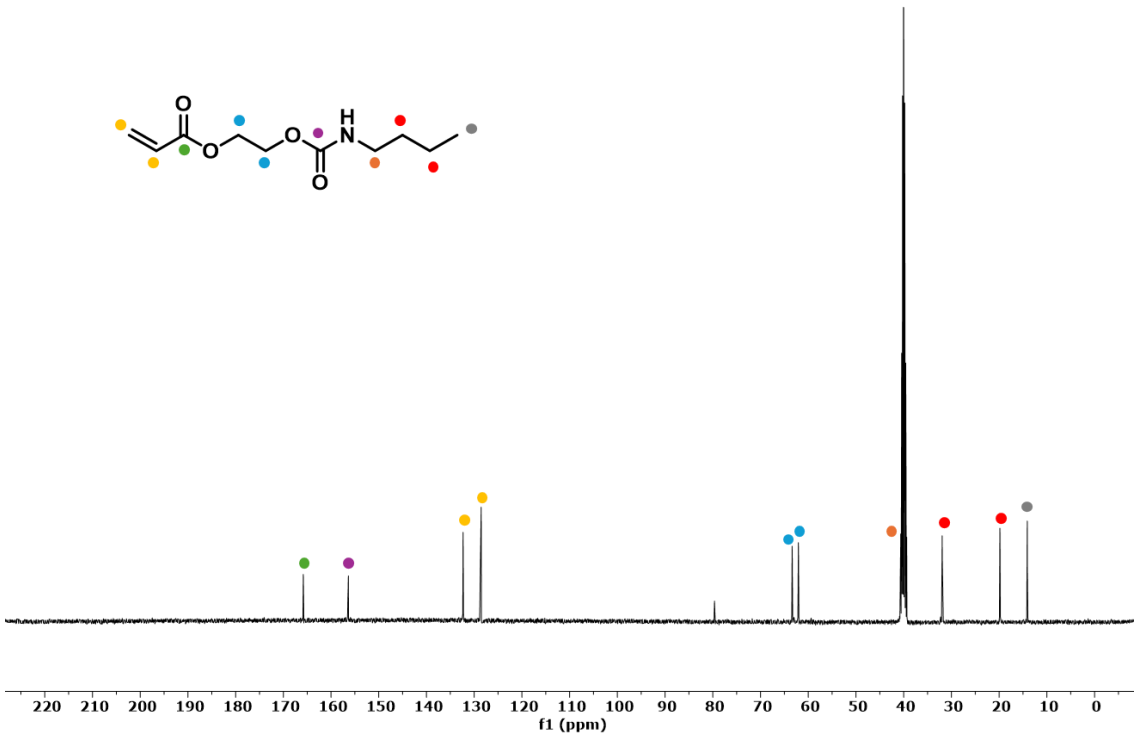


Figure S6. ^{13}C NMR spectrum of acrylate butyl carbamate in DMSO-d_6.

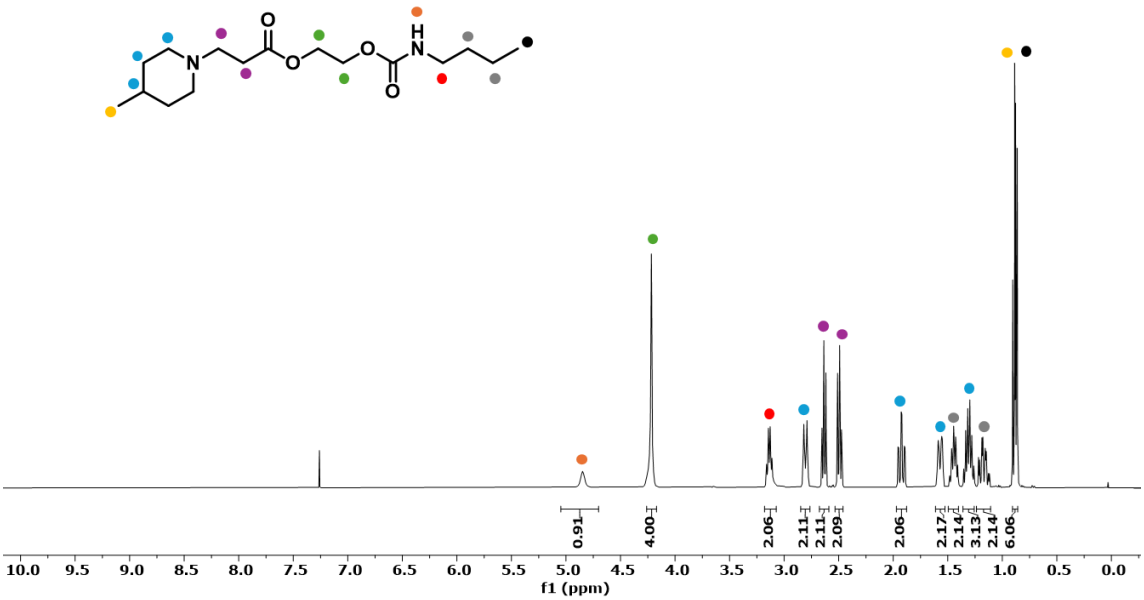


Figure S7. ^{1}H NMR spectrum of BAE-containing butyl carbamate (M2) in $CDCl_3$.

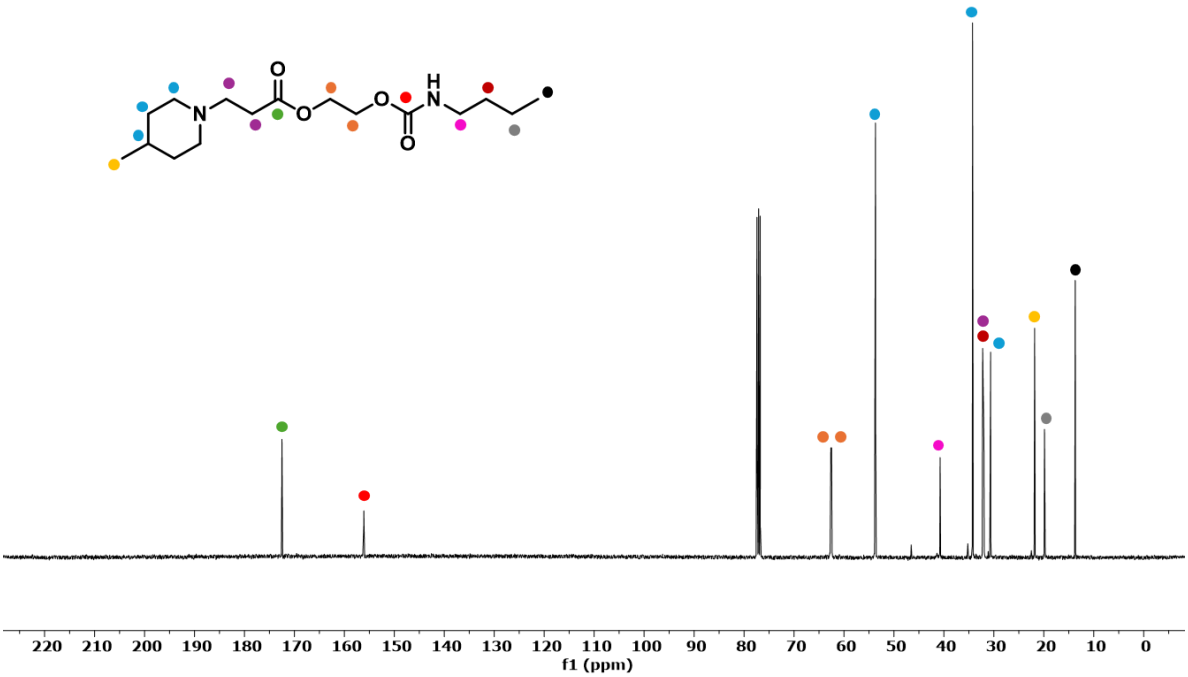


Figure S8. ^{13}C NMR spectrum of BAE-containing butyl carbamate (M2) in $CDCl_3$.

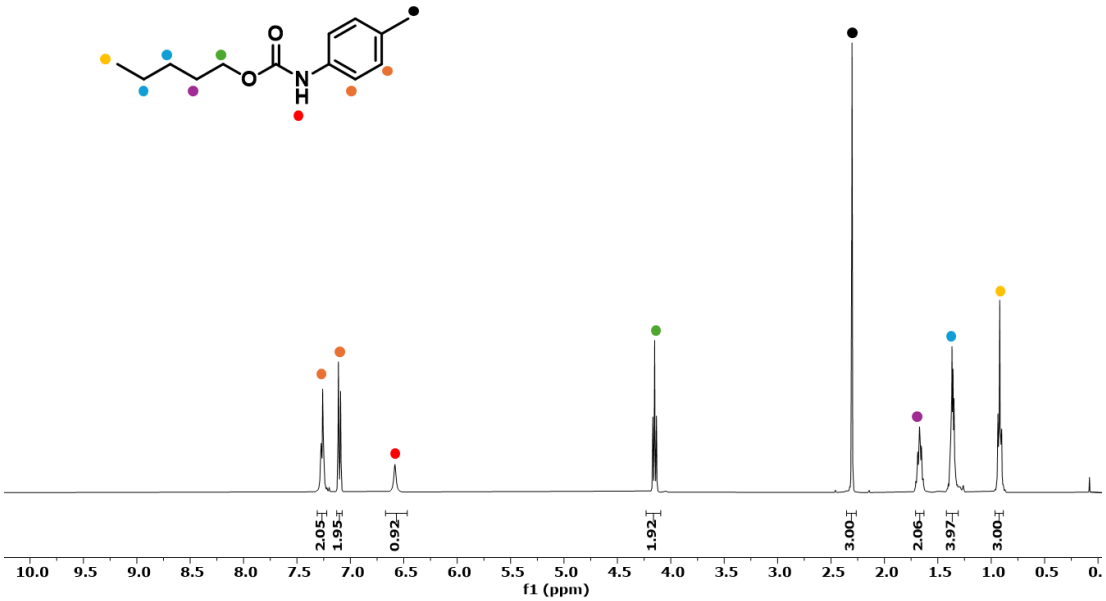


Figure S9. ^{1}H NMR spectrum of reference aromatic model compound (R1) in $CDCl_3$.

Figure S10. ^{13}C NMR spectrum of reference aromatic model compound (R1) in $CDCl_3$.

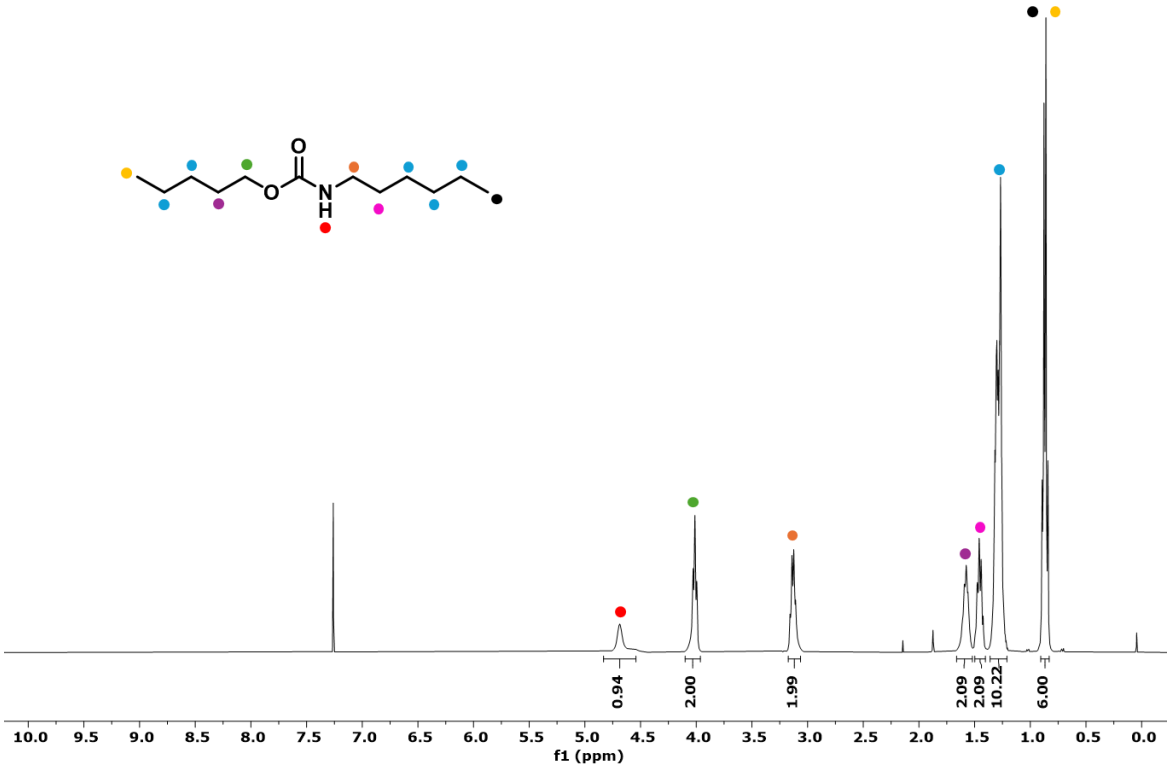


Figure S11. ^{1}H NMR spectrum of reference aliphatic model compound (R2) in $CDCl_3$.

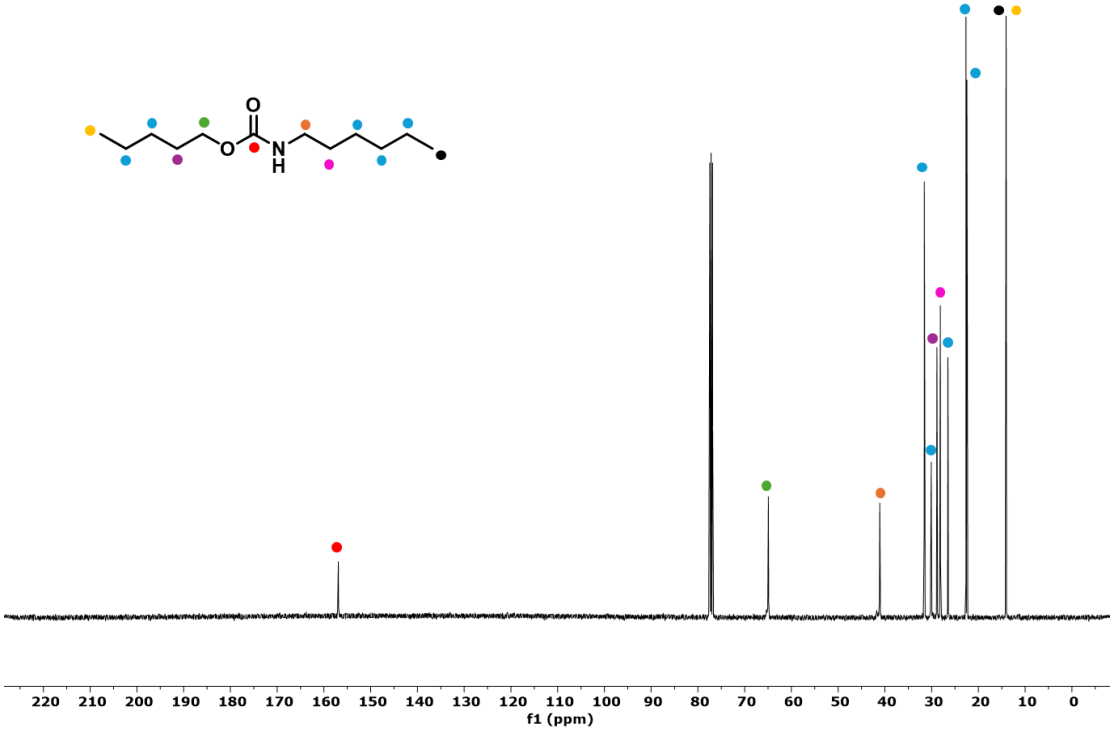


Figure S12. ^{13}C NMR spectrum of reference aliphatic model compound (R2) in $CDCl_3$.

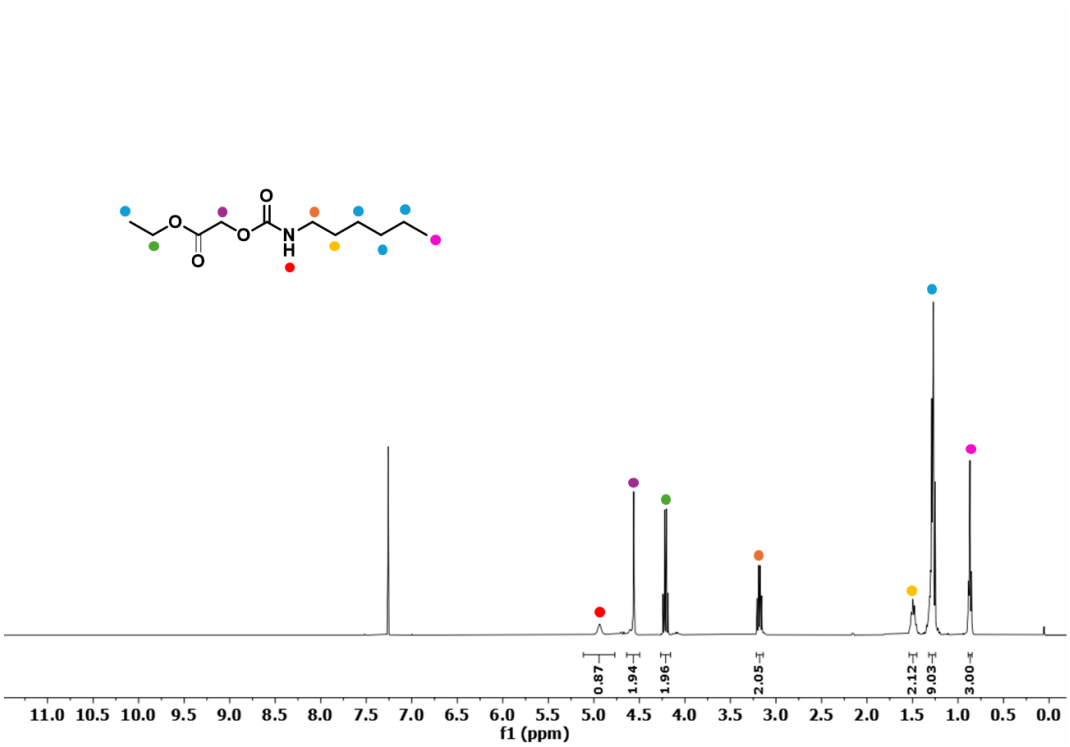


Figure S13. ^{1}H NMR spectrum of reference aliphatic ester-containing model compound (E2) in $CDCl_3$

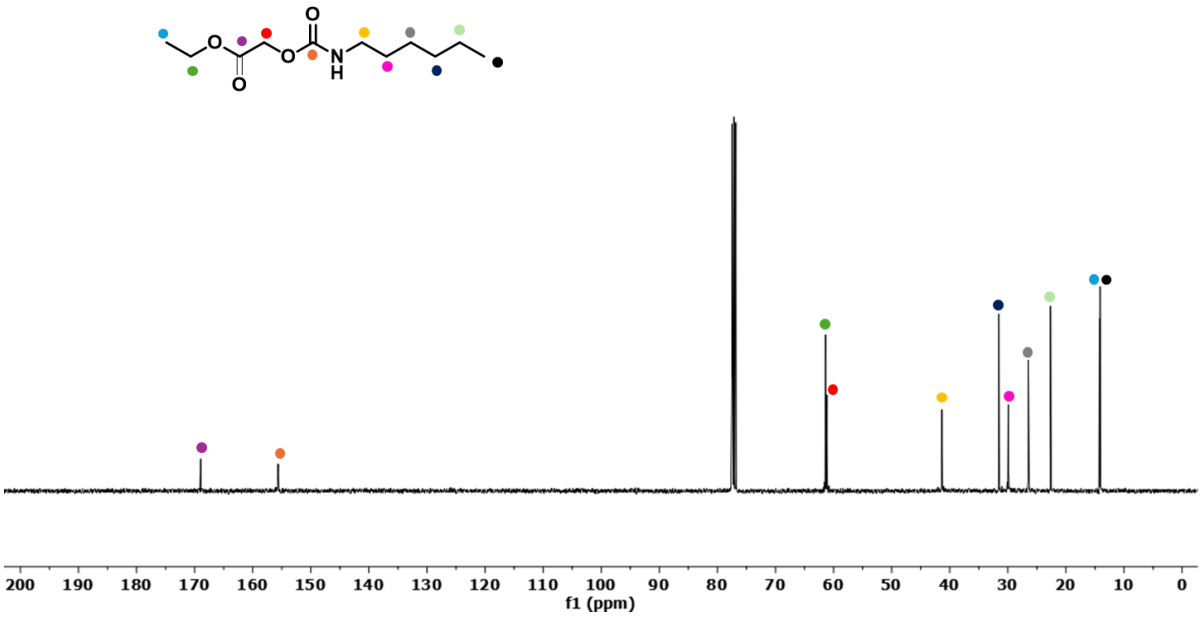


Figure S14. ^{13}C NMR spectrum of reference aliphatic ester-containing model compound (E2) in $CDCl_3$.

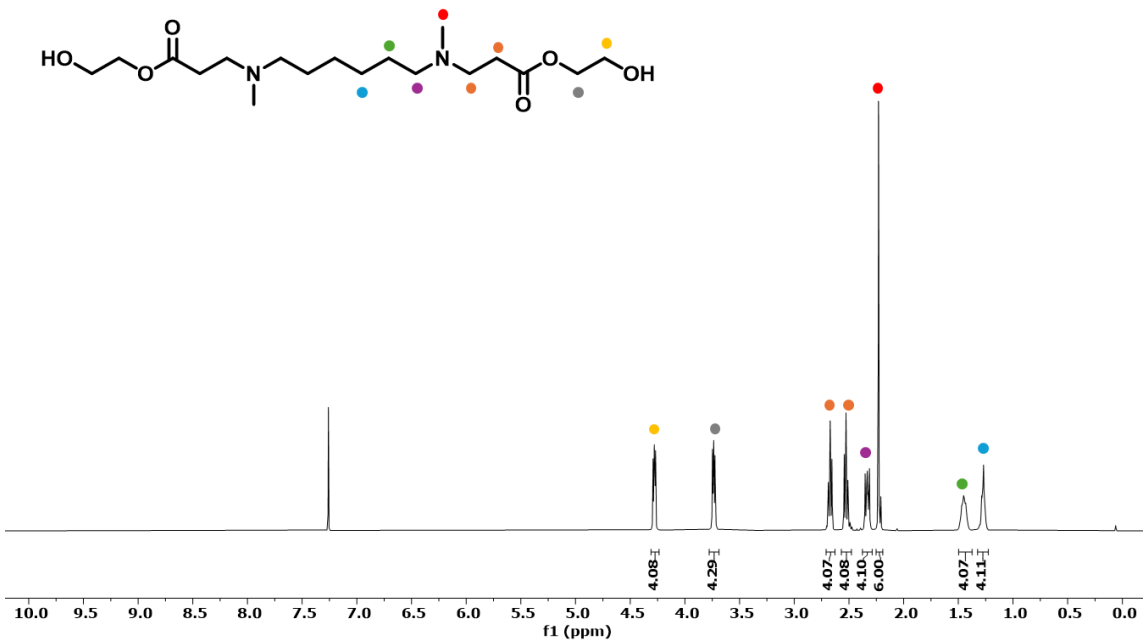


Figure S15. ^{1}H NMR spectrum of BAE-containing diol (BAEOH) in $CDCl_3$.

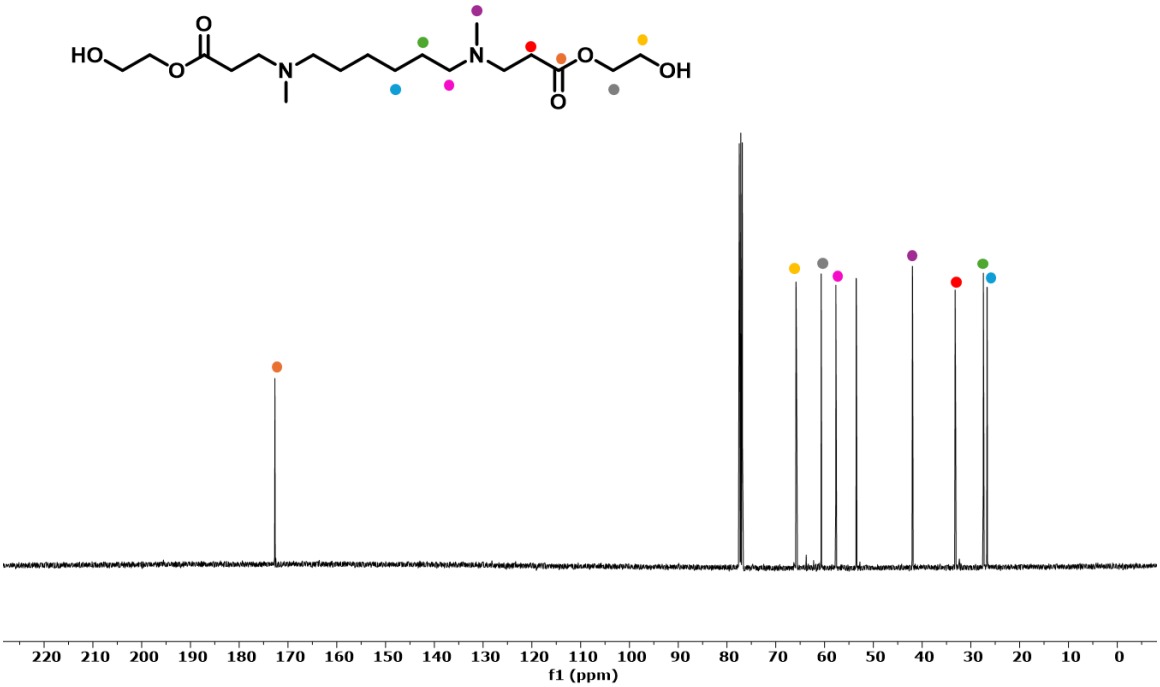


Figure S16. ^{13}C NMR spectrum of BAE-containing diol (BAEOH) in $CDCl_3$.

NMR spectra degradability kinetic studies

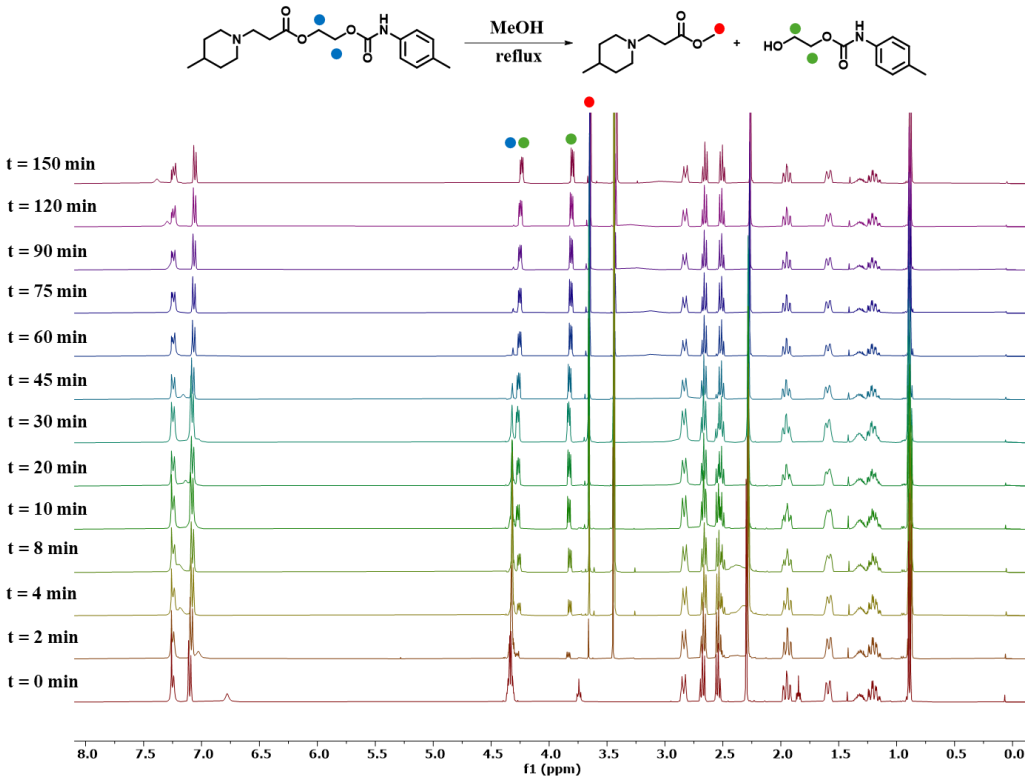


Figure S17. Stacked ^{1}H NMR spectra obtained from the degradability tests of BAE-containing *p*-tolyl carbamate (M1) at different times.

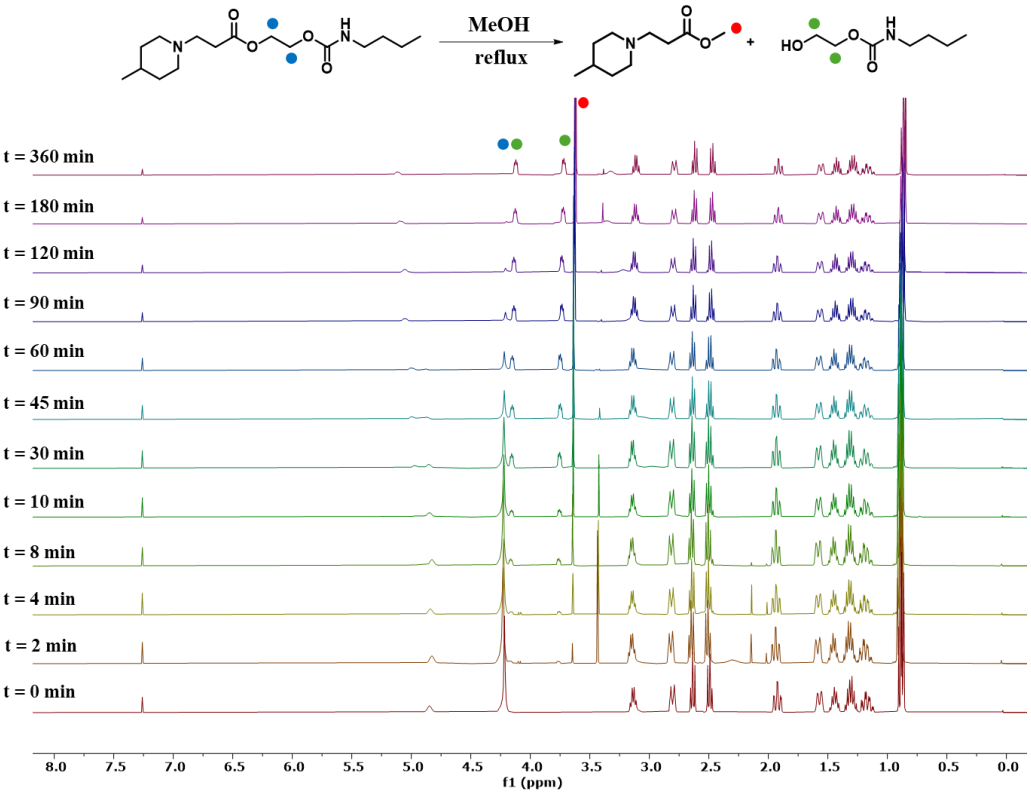


Figure S18. Stacked ^{1}H NMR spectra obtained from the degradability tests of BAE-containing butyl carbamate (M2) at different times.

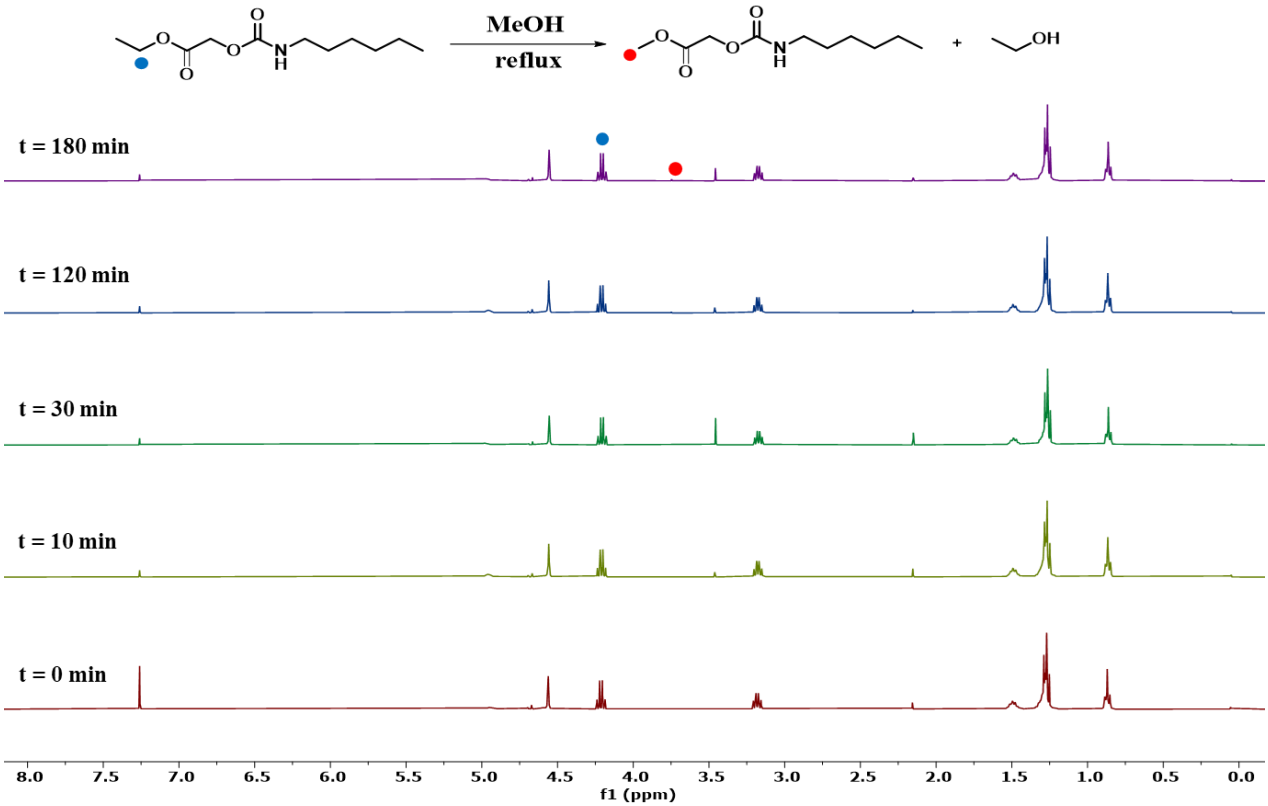


Figure S19. Stacked ^{1}H NMR spectra obtained from the degradability tests of the reference aliphatic ester-containing carbamate (E2) at different times, showing that only 2% degradation is taking place.

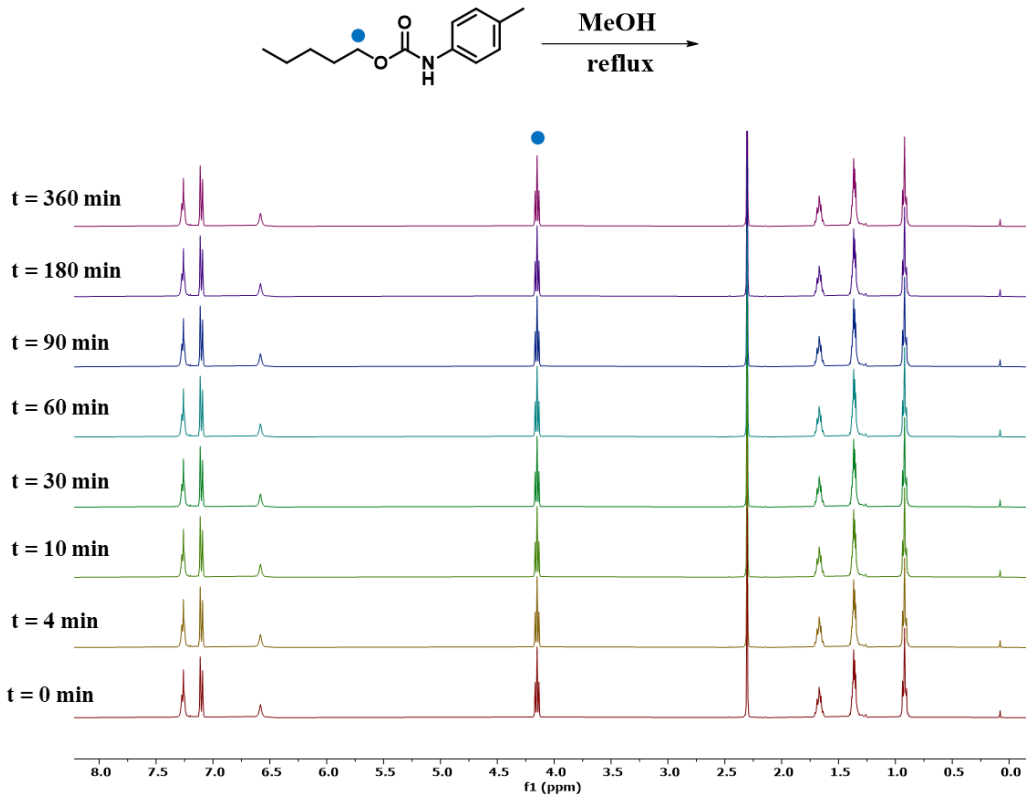


Figure S20. Stacked ^{1}H NMR spectra obtained from the degradability tests of the reference aromatic carbamate (R1) at different times showing that no degradation is taking place.

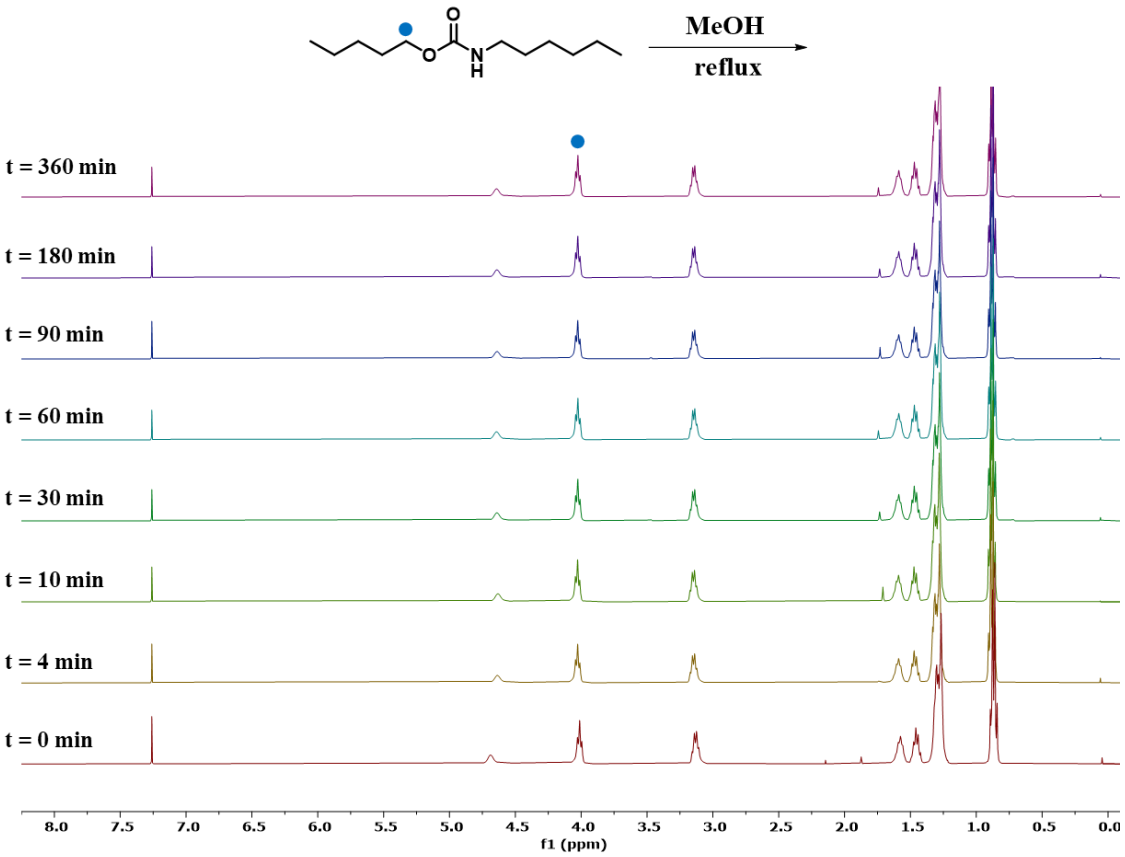


Figure S21. Stacked ^{1}H NMR spectra obtained from the degradability tests of the reference aliphatic carbamate (R2) at different times showing that no degradation is taking place.

FTIR spectra

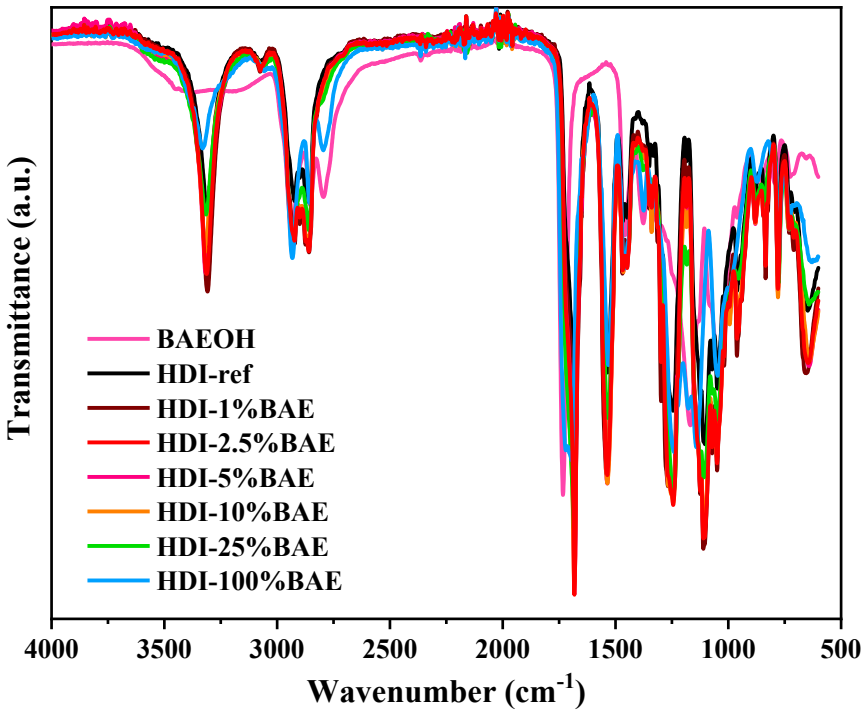


Figure S22. Overlayed FTIR spectra of the BAE-containing diol (BAEOH, pink) and the different HDI-derived TPU polymers prepared.

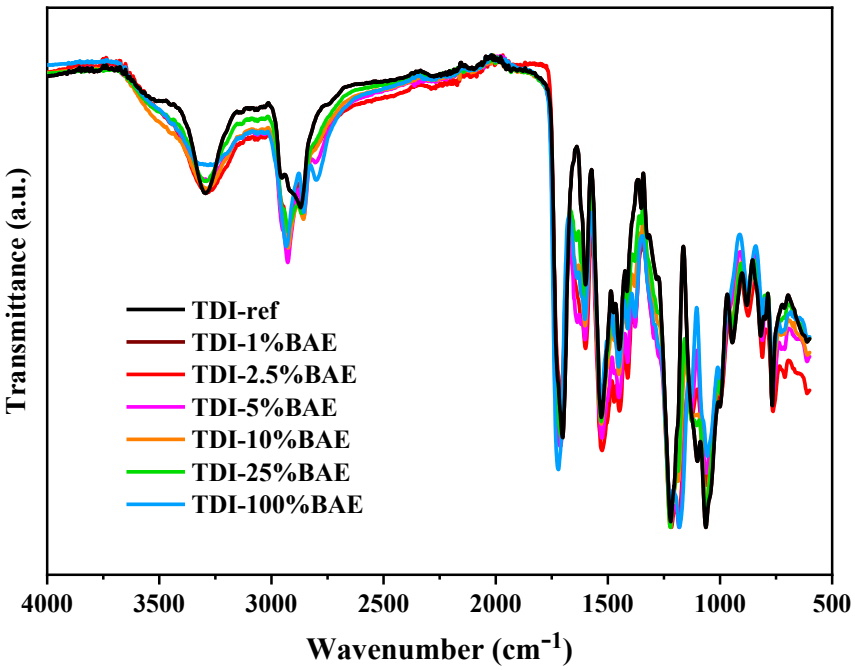


Figure S23. Overlayed FTIR spectra of the different TDI-derived TPU polymers prepared.

NMR spectra of the TPU polymers

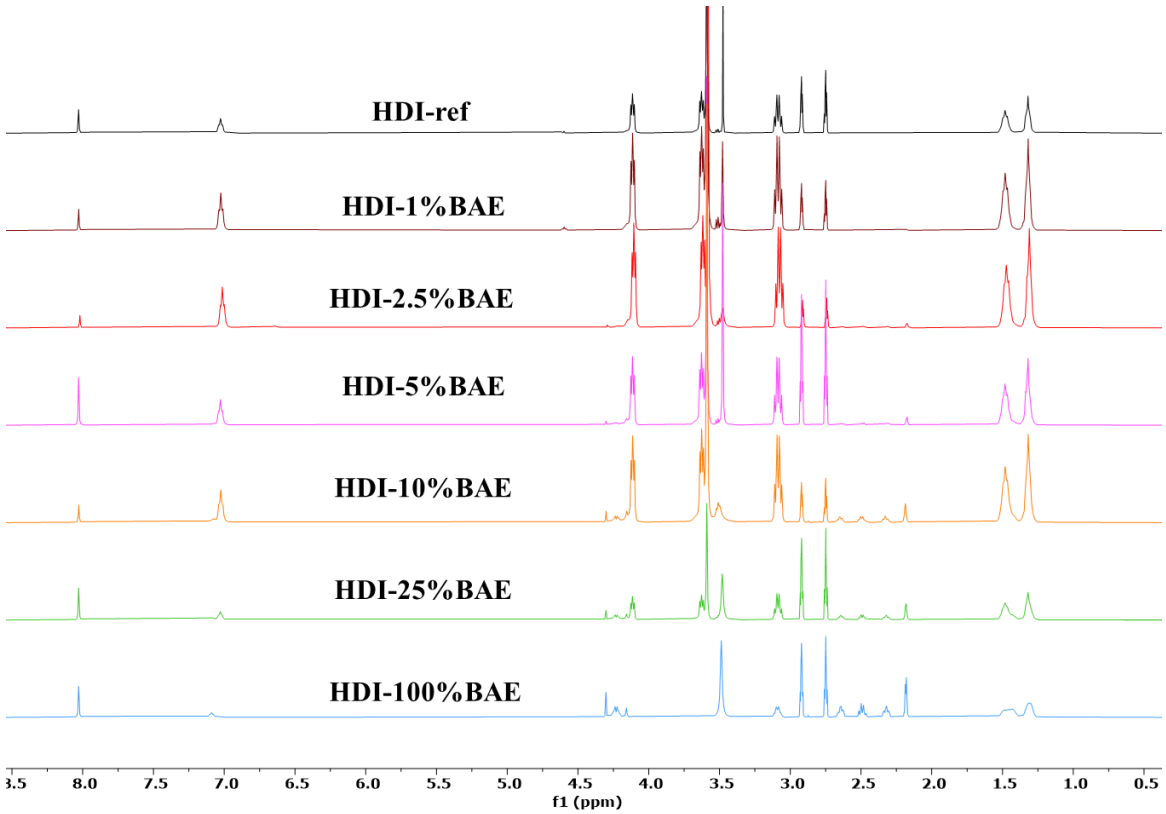


Figure S24. Stacked ^{1}H NMR spectra of the different HDI-derived TPU polymers prepared in DMF-d_7.

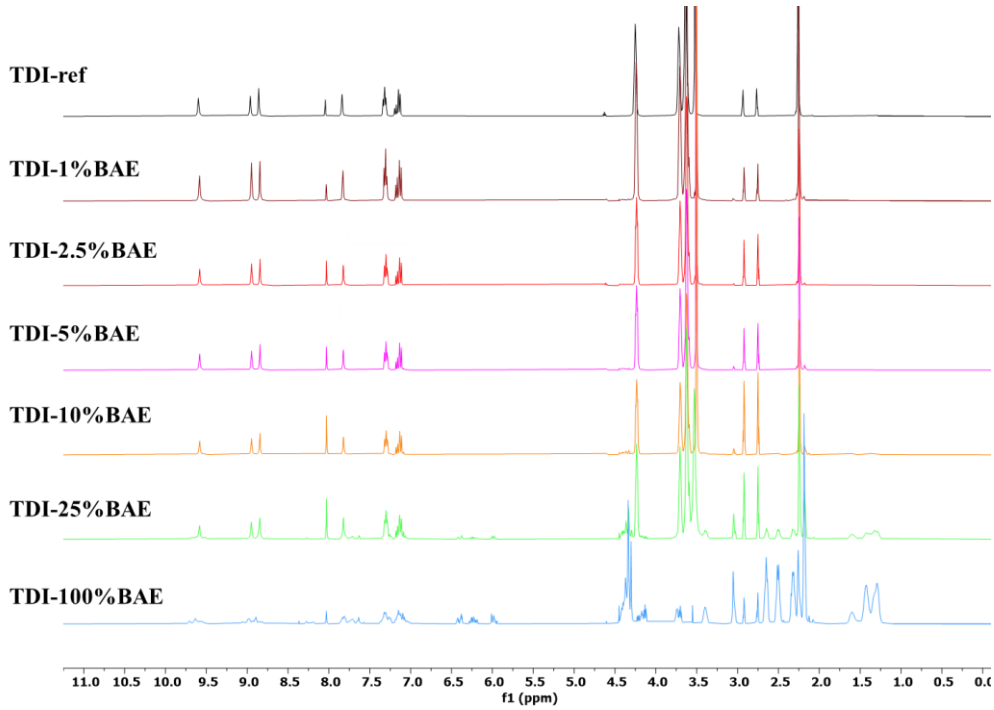


Figure S25. Stacked ^{1}H NMR spectra of the different TDI-derived TPU polymers prepared with THF.

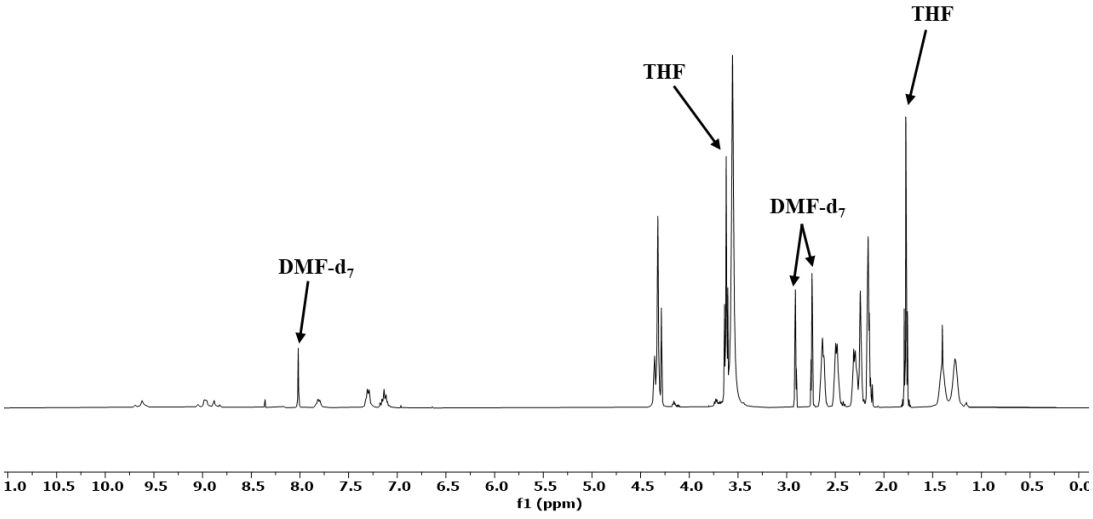


Figure S26. ^{1}H NMR spectrum (in DMF-d_7) of TDI-100%BAE prepared with THF.

TGA analysis of the TPUs

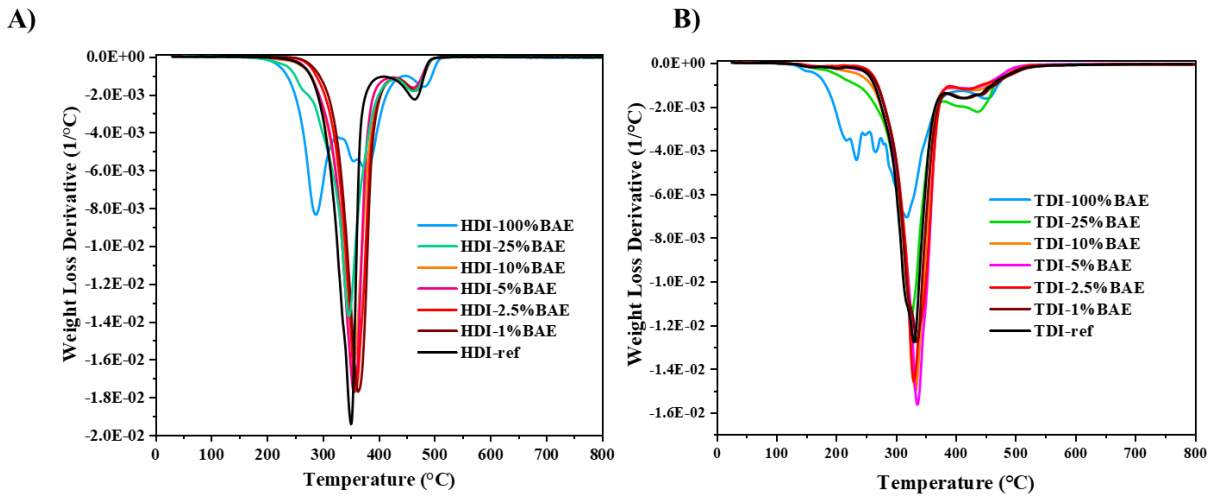


Figure S27. DTGA curves of A) HDI-derived TPU polymers and B) TDI-derived TPU polymers.

Degradation and stability of TPUs determined via SEC

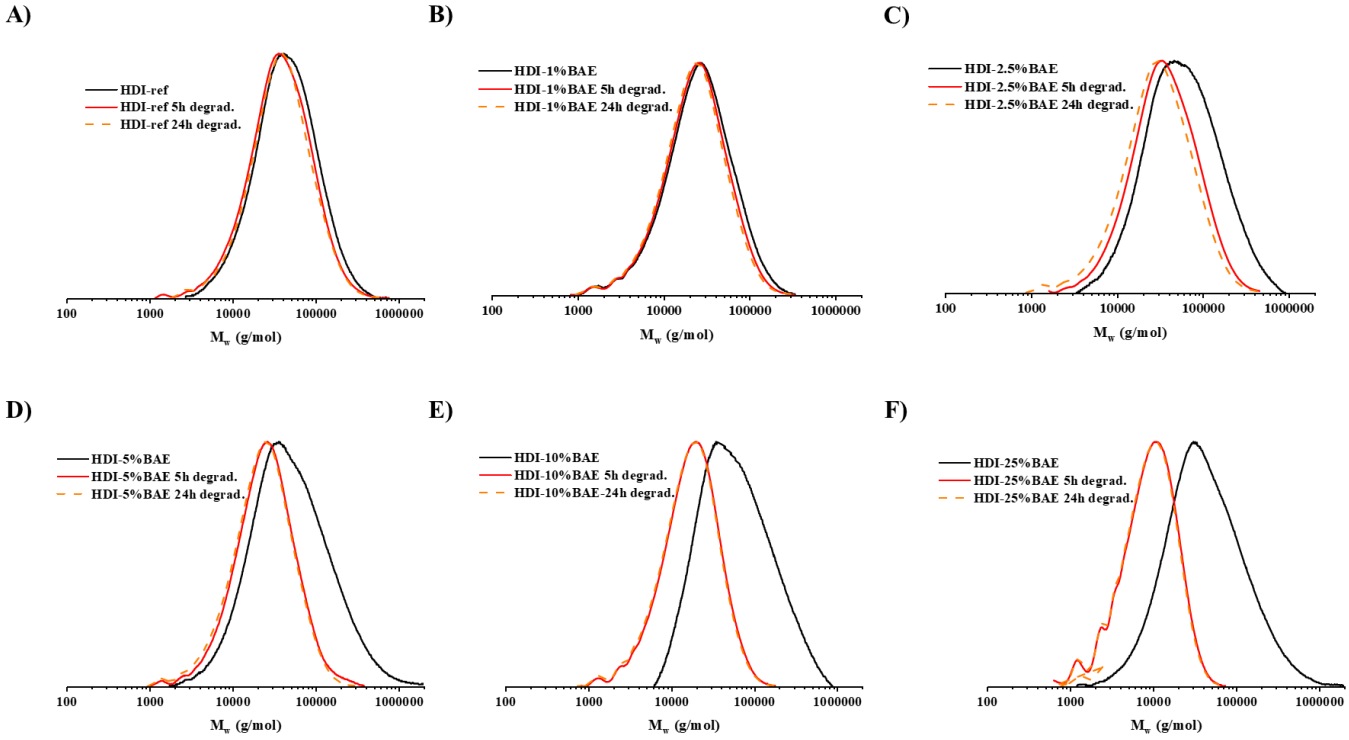


Figure S28. SEC traces of the original TDI-derived TPUs (black solid lines), after the degradation with MeOH for 5h (red solid lines) and after the degradation with MeOH for 24h (dashed orange lines).

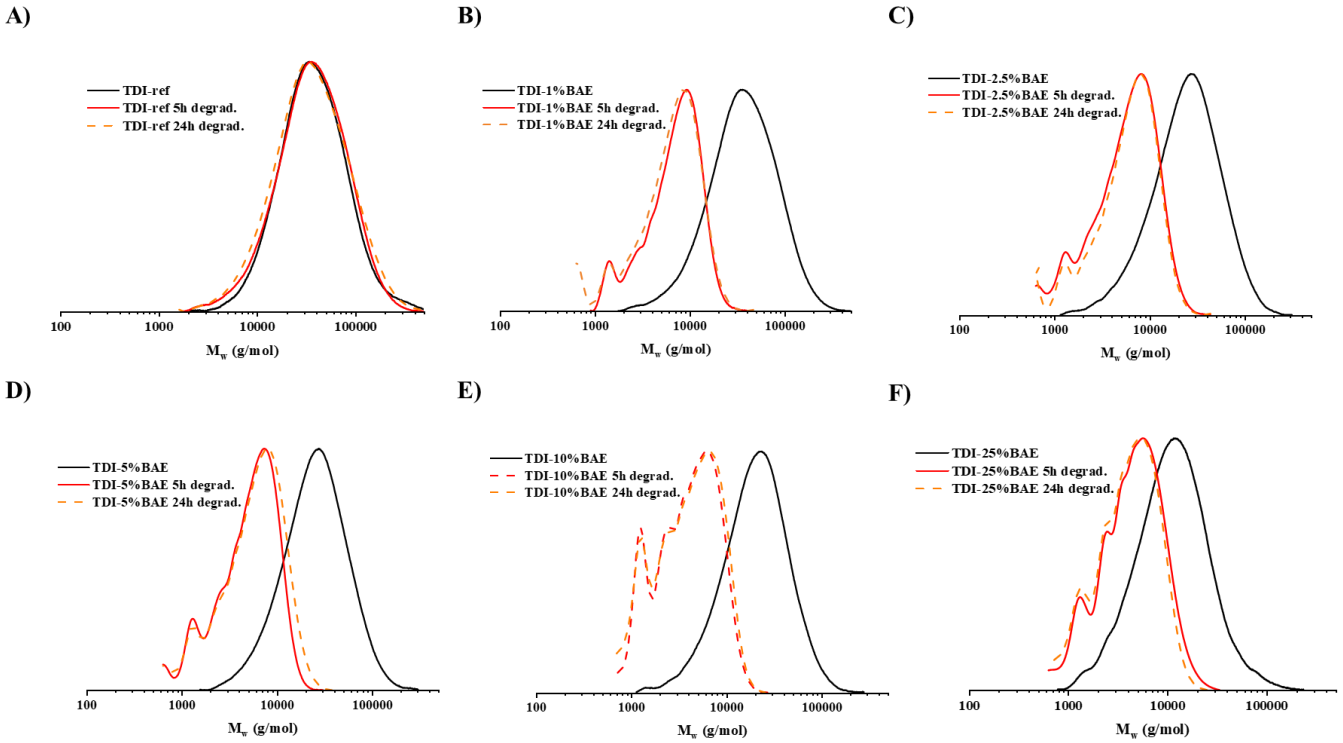


Figure S29. SEC traces of the original TDI-derived TPUs (black solid lines), after degradation with MeOH for 5 h (red solid lines) and 24 h (dashed orange lines).

Table S2. SEC data of all TPUs before and after 5 h in MeOH at 70 °C.

Sample	Original TPU		Degradation after 5 h	
	M_n (kDa)	M_w (kDa)	M_n (kDa)	M_w (kDa)
HDI-ref	25.8	52.1	24.8	51.6
HDI-1%BAE	40.3	90.6	39.3	87.4
HDI-2.5%BAE	37.1	82.6	24.5	49.9
HDI-5%BAE	39.0	87.9	12.0	22.3
HDI-10%BAE	39.3	93.8	6.4	11.0
HDI-25%BAE	34.9	74.2	2.1	2.8
TDI-ref	27.8	50.5	27.0	50.2
TDI-1%BAE	25.1	48.9	5.2	9.1
TDI-2.5%BAE	16.6	32.7	3.7	6.1
TDI-5%BAE	16.0	31.9	3.3	5.4
TDI-10%BAE	13.8	26.4	2.9	4.8
TDI-25%BAE	8.0	15.7	1.6	2.1

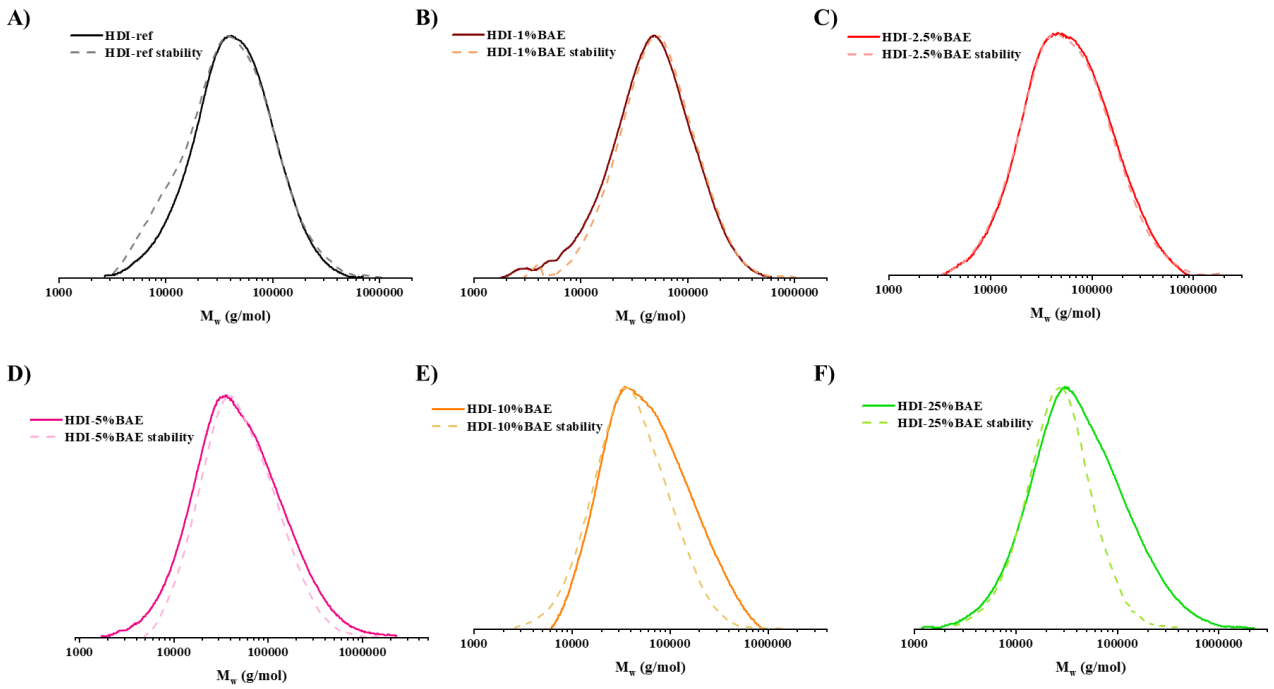


Figure S30. SEC traces of the original HDI-derived TPUs (solid lines) and after being in MeOH at room temperature for 24 h (dashed lines) for A) HDI-ref, B) HDI-1%BAE, C) HDI-2.5%BAE, D) HDI-5%BAE, E) HDI-10%BAE and F) HDI-25%BAE.