Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Dynamic polyurethane thermosets: tuning associative/dissociative behavior by catalyst selection

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1. FT-IR characterization and representative images

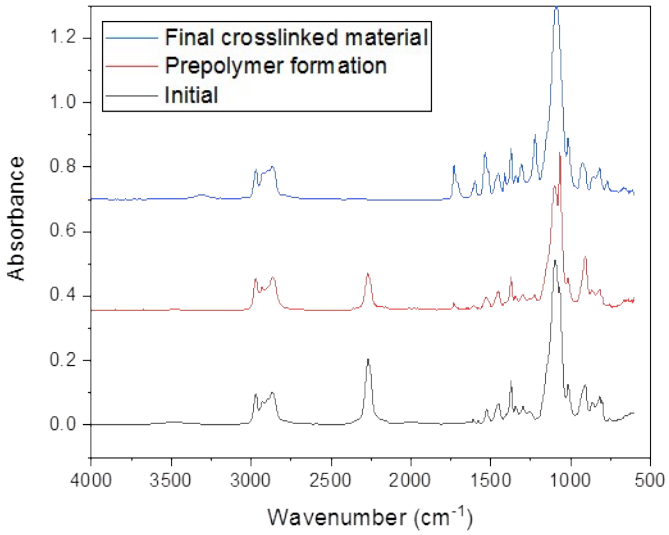

Figure S1. Representative FTIR spectra of the reaction of PPG triol (Mn=3740 g/mol) with MDI at t=0min (black trace) and t=300 min (pre-polymer formation, red trace). Blue trace corresponds to the final polyurethane film cross-linked for 24h at 70°C with 1,6-Hexanediol.

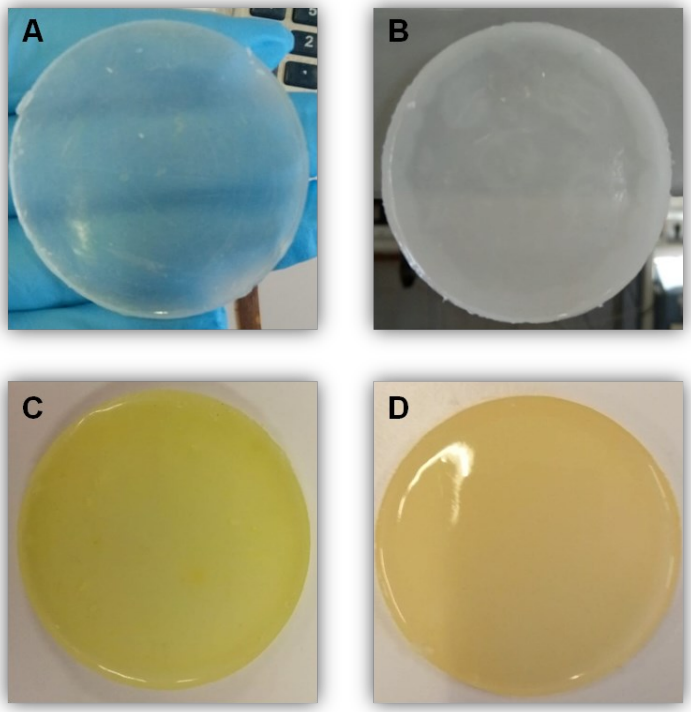

Figure S2. A) Aromatic polyurethane film cross-linked without catalyst. B) Aromatic polyurethane film cross-linked with DBTDL. C) Aromatic polyurethane film cross-linked with PTSA D) Aromatic polyurethane film cross-linked with TBD.

2. Stress-relaxation measurements

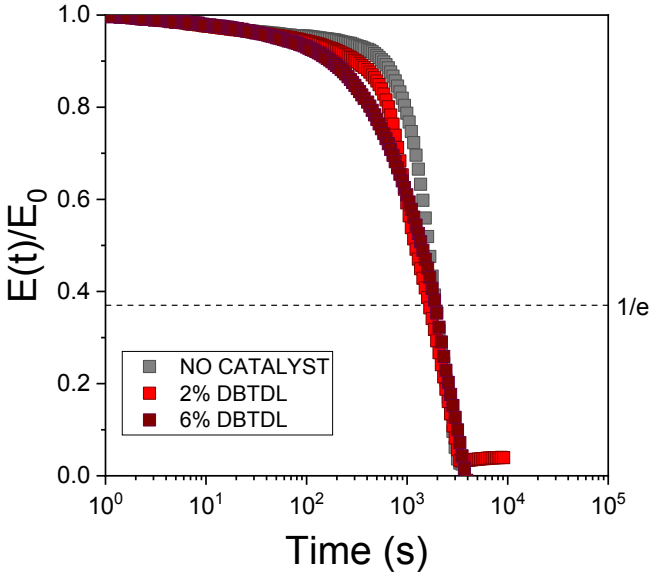

Figure S3. Stress-relaxation measurements for aliphatic (HDI) polyurethanes cross-linked with 2% and 6% of DBTDL performed at 120°C.

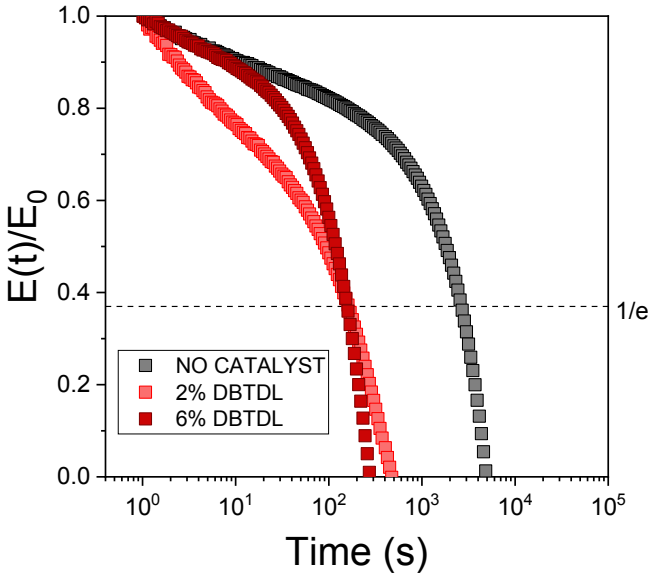

Figure S4. Stress-relaxation measurements for aromatic (MDI) polyurethanes cross-linked with 2% and 6% of DBTDL performed at 120°C.

3. DMTA measurements

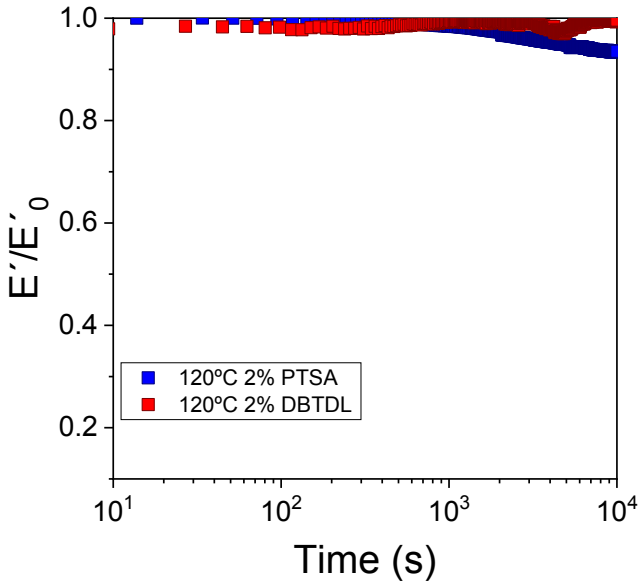

Figure S5. DMTA measurements for aromatic (MDI) polyurethanes cross-linked with 2% of DBTDL (red) and 2% of PTSA (blue) performed at 120°C.

4. ^{1}H-NMR for alcohol mediated transcarbamoylation aromatic model reactions

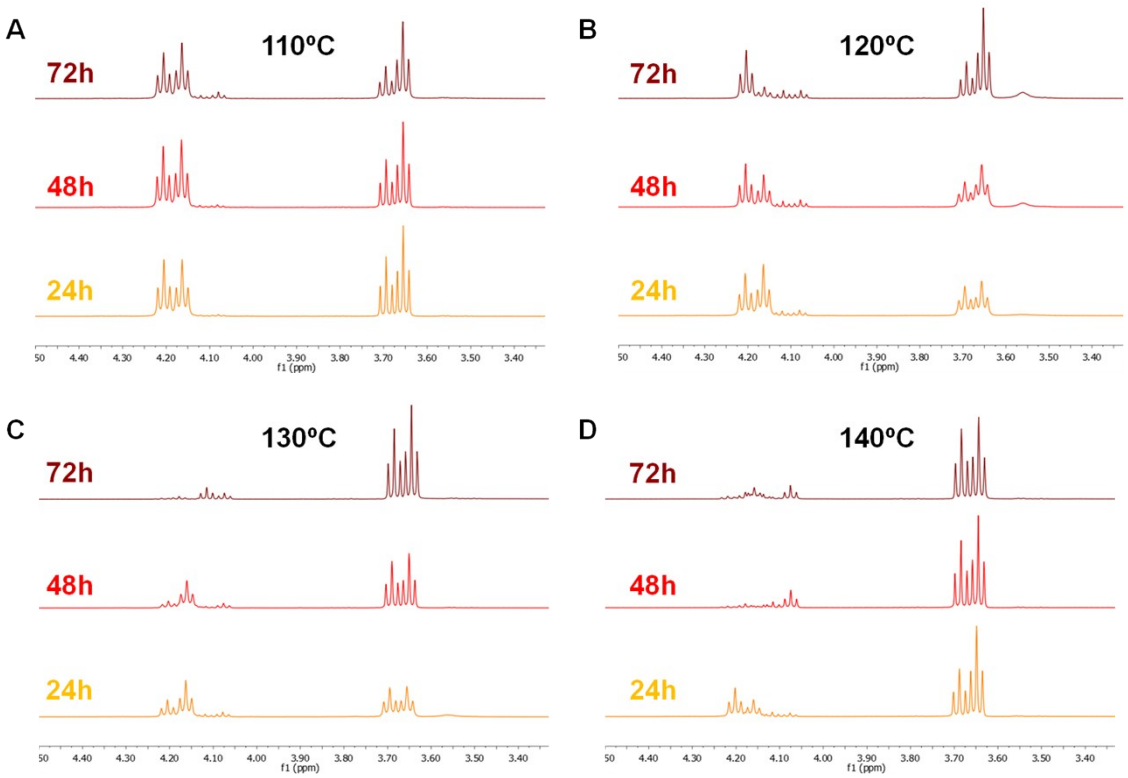

Figure S6. ^{1}H-NMR measurements for aromatic polyurethane model reactions catalyzed with 2% of DBTDL performed at 110ºC (A), 120°C (B), 130ºC (C) and 140ºC (D).

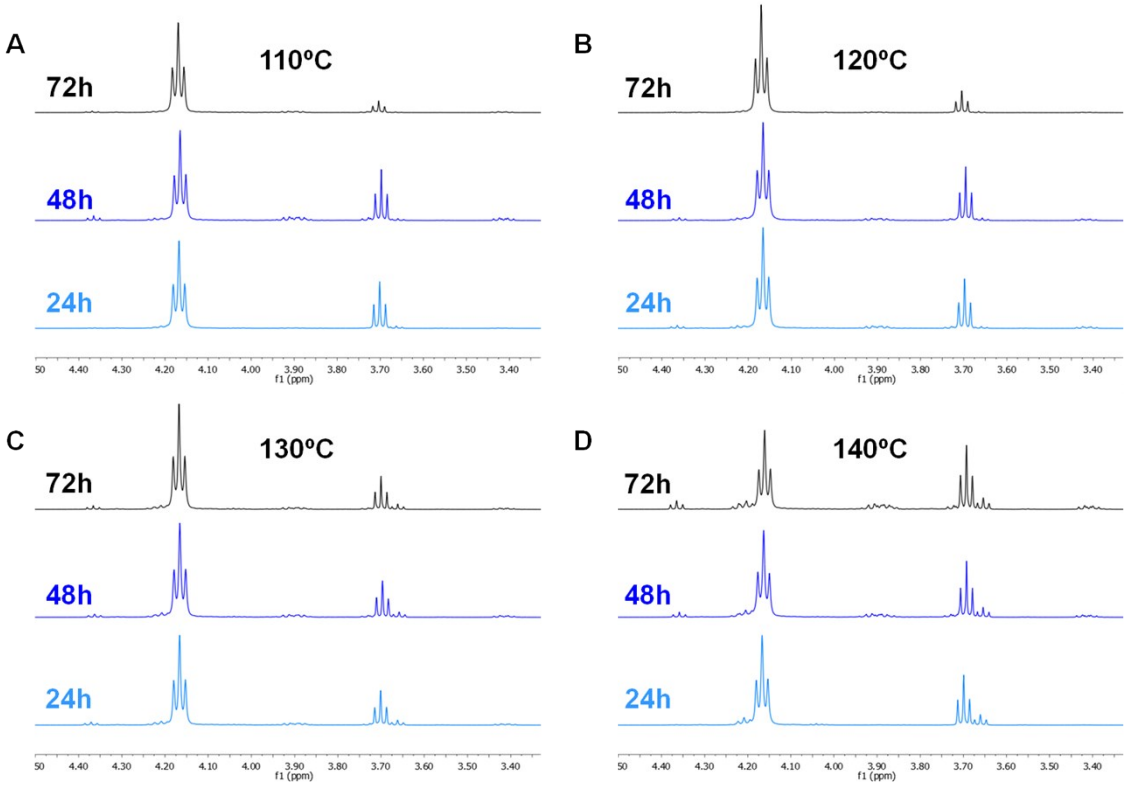

Figure S7. ^{1}H-NMR measurements for aromatic polyurethane model reactions catalyzed with 2% of p-TSA performed at 110ºC (A), 120°C (B), 130ºC (C) and 140ºC (D).

5. MALDI-TOF characterization

In this part, the MALDI-TOG characterization of every synthesized model diurethane compound employed for the study of the dissociative transcarbamoylation exchange is shown. The MALDI-TOF spectrum of the employed DCTB matrix is shown also.

DCTB Matrix

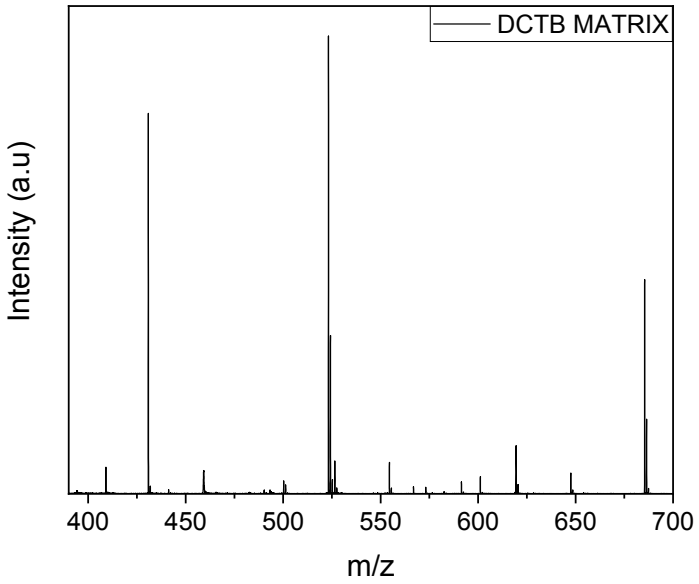

Figure S8. Characterization by MALDI-TOF of the employed DCTB matrix.

Most relevant signals corresponding to DCTB Matrix: 409.056, 430.589, 459.233, 500.253, 523.248, 526.483, 554.514, 619.496 and 685.403.

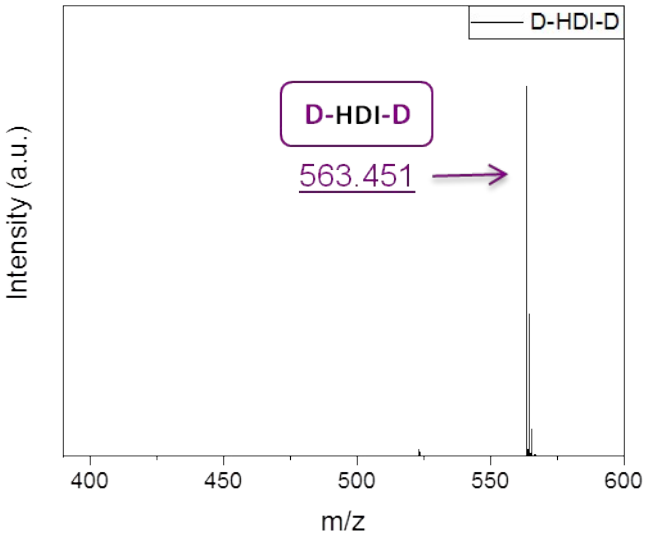

Figure S9. Characterization by MALDI-TOF of *Didodecyl hexane-1,6- diyldicarbamate* (D-HDI-D).

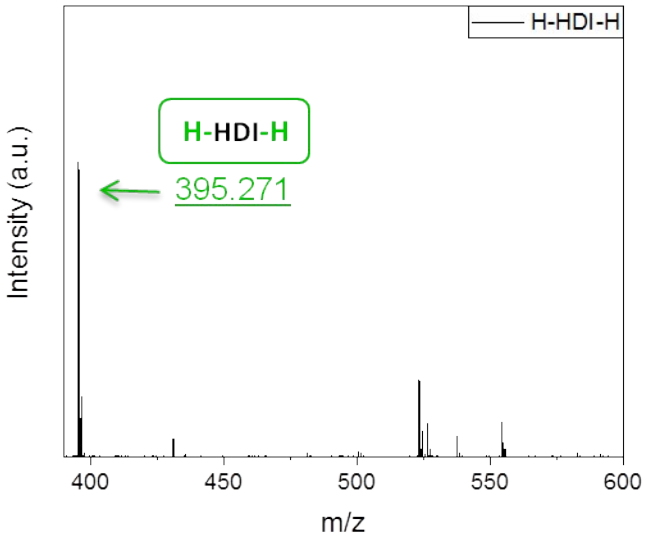

Figure S10. Characterization by MALDI-TOF of *Dihexyl hexane-1,6- diyldicarbamate* (H-HDI-H).

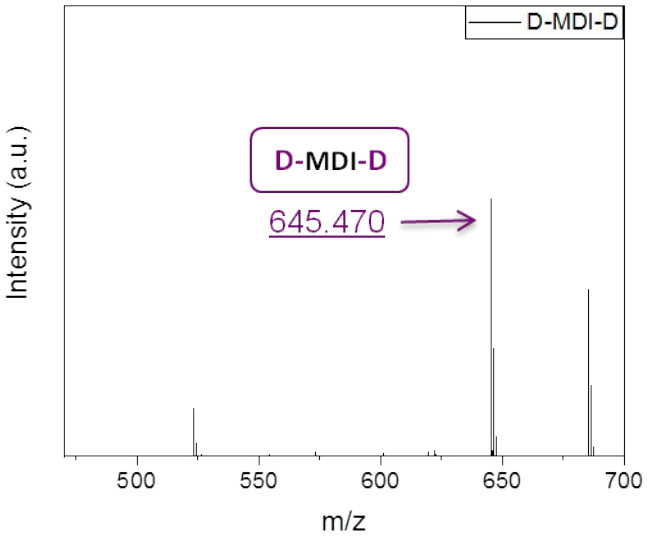

Figure S11. Characterization by MALDI-TOF of *Didodecyl (methylenebis(4,1-phenylene))dicarbamate* (D-MDI-D).

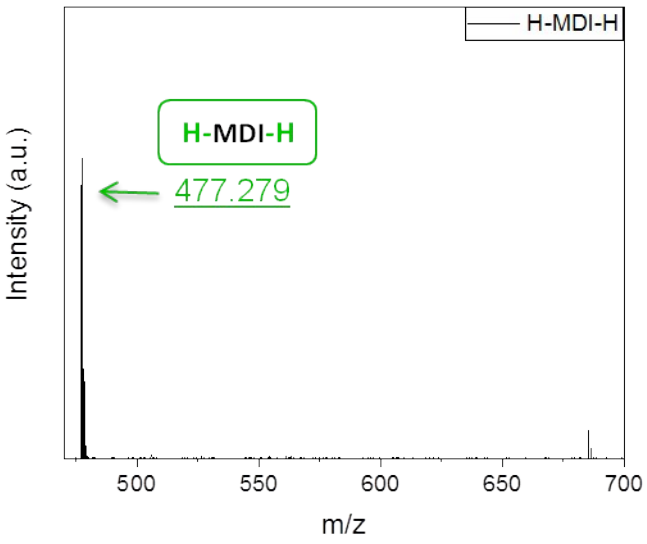

Figure S12. Characterization by MALDI-TOF of *Dihexyl (methylenebis(4,1-phenylene))dicarbamate* (H-MDI-H).

6. Model Urethane Compounds: ^{1}H-NMR characterization

Dodecyl hexyl carbamate

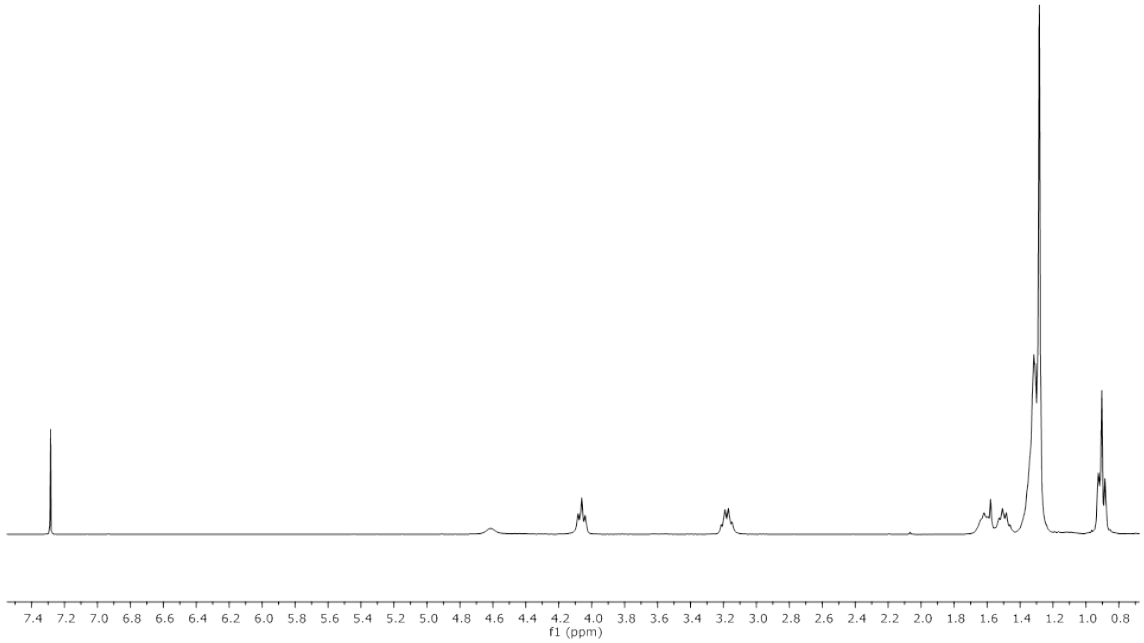

Figure S13. ^{1}H-NMR spectra of dodecyl hexyl carbamate.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 4.61 (s, 1H), 4.06 (td, *J* = 6.7, 0.0 Hz, 2H), 3.18 (q, *J* = 6.7 Hz, 2H), 1.71 – 1.58 (m, 4H), 1.49 (q, *J* = 7.0 Hz, 2H), 1.31 (dd, *J* = 8.3, 0.0 Hz, 22H), 1.02 – 0.77 (m, 6H).

Dodecyl p-tolyl carbamate

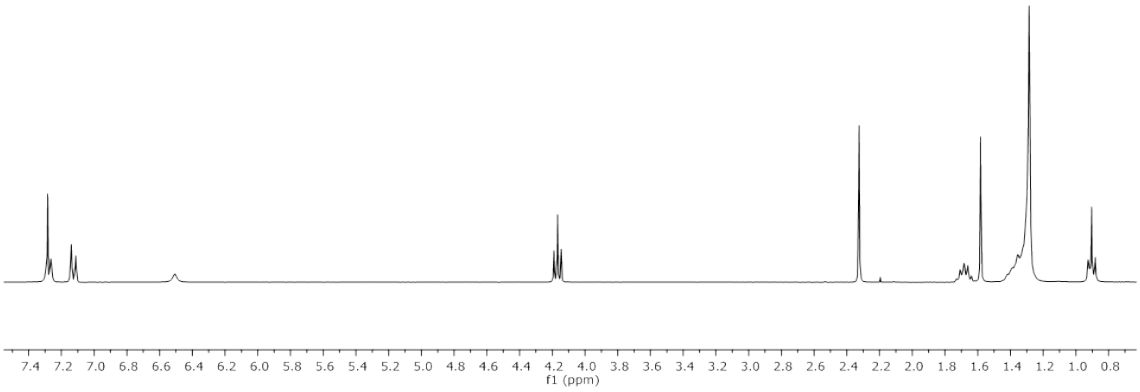

Figure S14. ^{1}H-NMR spectra of dodecyl p-tolyl carbamate.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.37 – 7.19 (m, 2H), 7.13 (d, *J* = 8.3 Hz, 2H), 6.51 (s, 1H), 4.17 (t, *J* = 6.7 Hz, 2H), 2.33 (s, 3H), 1.76 – 1.62 (m, 2H), 1.29 (m, *J* = 5.2 Hz, 18H), 0.98 – 0.83 (m, 3H).

7. Model diurethane compounds: ^{1}H-NMR characterization

Didodecyl hexane -1,6- diyldicarbamate

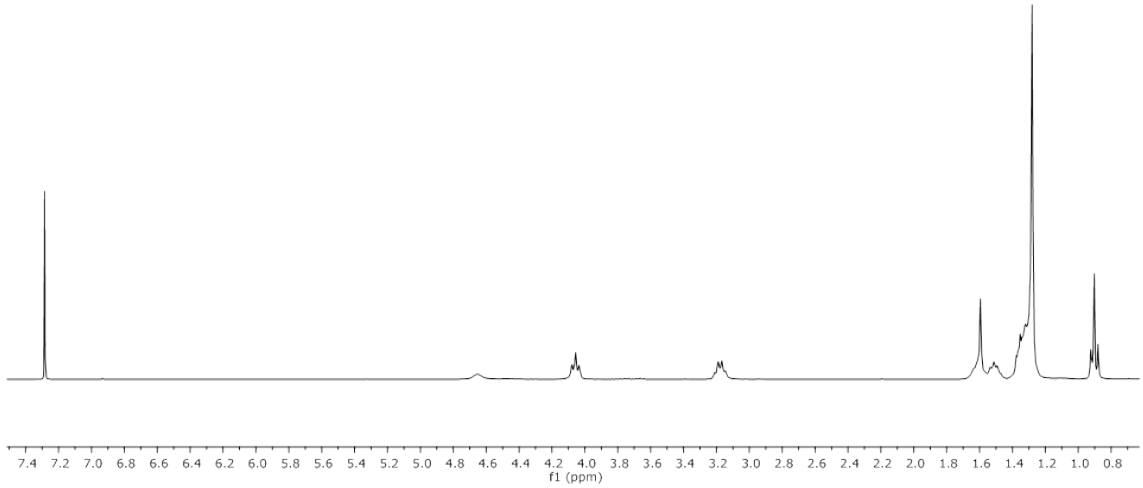

Figure S15. ^{1}H-NMR spectra of didodecyl hexane -1,6- diyldicarbamate.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 4.65 (s, 2H), 4.06 (t, *J* = 6.7 Hz, 4H), 3.18 (q, *J* = 6.6 Hz, 4H), 1.61 (d, *J* = 6.0 Hz, 8H), 1.51 (t, *J* = 6.6 Hz, 2H), 1.42 – 1.16 (m, 38H), 0.97 – 0.81 (m, 6H).

Dihexyl hexane -1,6- diyldicarbamate

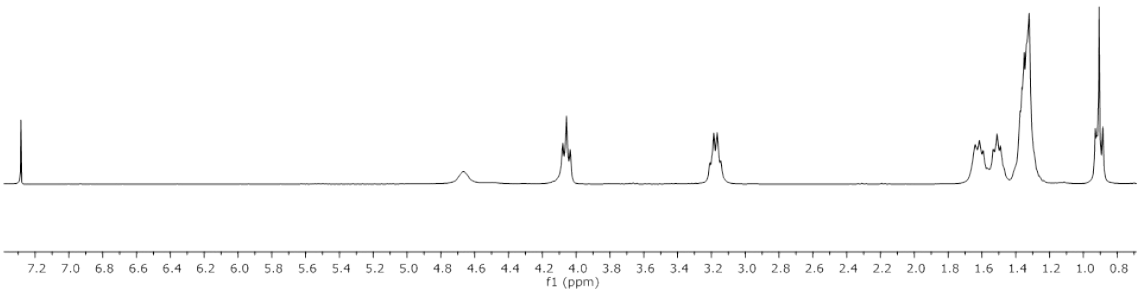

Figure S16. ^{1}H-NMR spectra of dihexyl hexane -1,6- diyldicarbamate.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 4.67 (s, 2H), 4.06 (t, *J* = 6.7 Hz, 4H), 3.18 (q, *J* = 6.6 Hz, 4H), 1.72 – 1.55 (m, 4H), 1.51 (t, *J* = 6.6 Hz, 4H), 1.43 – 1.22 (m, 16H), 0.98 – 0.81 (m, 6H).

Didodecyl (methylenebis(4,1-phenylene)) dicarbamate

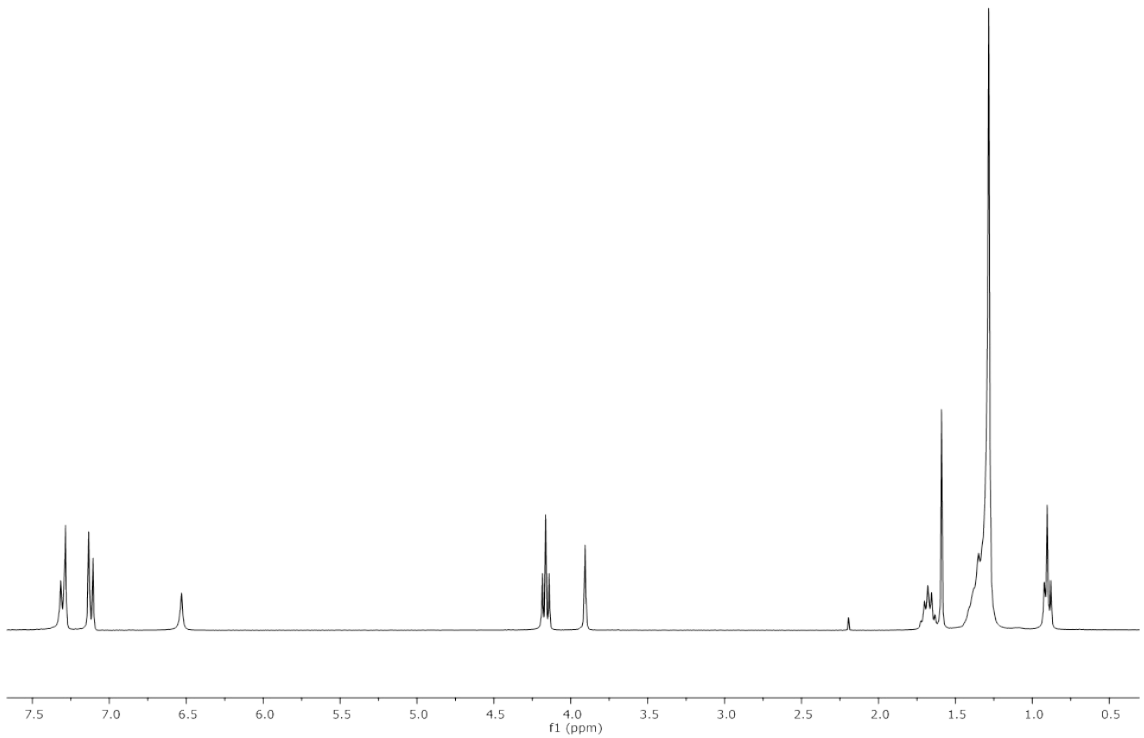

Figure S17. ^{1}H-NMR spectra of didodecyl (methylenebis(4,1-phenylene)) dicarbamate.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.38 – 7.25 (m, 4H), 7.12 (d, *J* = 8.4 Hz, 4H), 6.53 (s, 2H), 4.16 (t, *J* = 6.7 Hz, 4H), 3.91 (s, 2H), 1.67 (q, *J* = 7.0 Hz, 4H), 1.29 (m, *J* = 4.6 Hz, 36H), 0.99 – 0.82 (m, 6H).

Dihexyl (methylenebis(4,1-phenylene)) dicarbamate

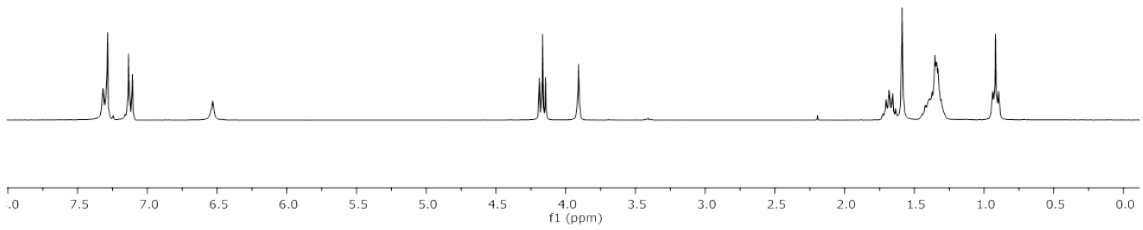

Figure S18. ^{1}H-NMR spectra of dihexyl (methylenebis(4,1-phenylene))dicarbamate.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.39 – 7.27 (m, 4H), 7.20 – 7.01 (m, 4H), 6.53 (s, 2H), 4.17 (t, *J* = 6.7 Hz, 4H), 3.91 (s, 2H), 1.67 (dt, *J* = 8.0, 6.5 Hz, 4H), 1.48 – 1.18 (m, 12H), 0.92 (td, *J* = 6.9, 5.7, 2.9 Hz, 6H).