

Supporting Information

Thermoset Shape-Memory Polyurethane with Intrinsic Plasticity Enabled by Transcarbamylation

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Section S1. Materials:

Poly(ethylene glycol)diol (PEG, $M_n=2,000$, Sigma-Aldrich), hexamethylene diisocyanate (HDI, J&K Scientific LTD), 4,4'-methylenebis(phenyl isocyanate) (MDI, J&K Scientific LTD), glycerine (GLY, J&K Scientific LTD), and dibutyltin dilaurate (DBTDL, J&K Scientific LTD), 4,4'-Bis(α,α -dimethylbenzyl)diphenylamine (TCI, antioxidant) were all used as received unless otherwise noted.

Section S2. Polymer network synthesis:

PEG was dried with a vacuum freeze dryer for 24 hours immediately prior to use. In a typical experiment, 1.5 g of PEG was weighted into a glass bottle and melted by heating in an oven at 60 °C. Afterwards, PEG, GLY (weight ratio: PEG:GLY=1.5:0.05) and the antioxidant (0.5 wt%) were dissolved in 1g of THF (tetrahydrofuran) and stirred for several minutes. After the mixing, a stoichiometric amount of HDI and a predetermined amount of DBTDL were added into the bottle. The mixture was poured into an aluminum pan and curing was conducted thermally at 60 °C for 2 h. Finally, the cured sample was vacuum dried (100 °C) overnight and demolded.

Section S3. Thermal and thermo-mechanical characterization:

Differential scanning calorimetry (DSC) analyses were carried out using DSC Q200 (TA instruments) with a cooling and heating rate of 10 °C/min. Dynamic mechanical analyses (DMA) were conducted using a DMA Q800 machine (TA

instruments) under the following conditions: tensile, 1 Hz, 0.2% strain, and a heating rate of 3 °C /min. All the quantitative shape memory and plasticity experiments were conducted with the same DMA machine under stress controlled and strain controlled conditions, respectively.

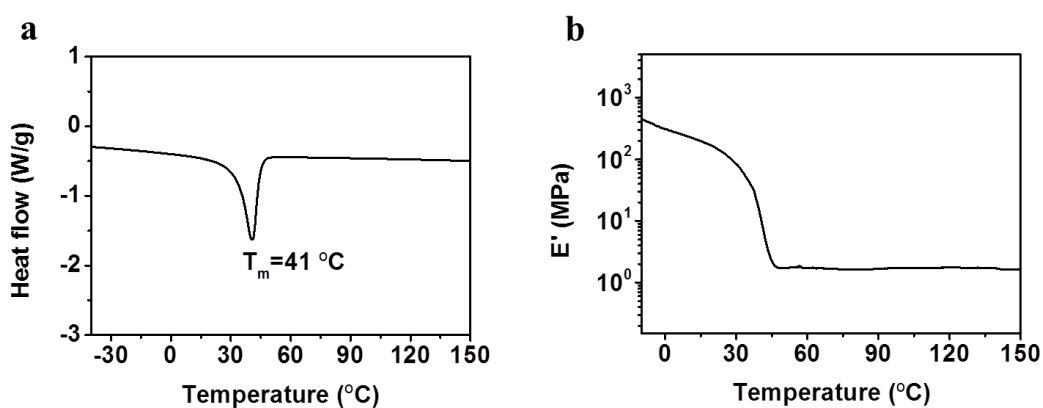


Figure S1. Thermo-mechanical characterization of the thermoset polyurethanes.

a, DSC curve. b, DMA curve.

Section S4. Rheological Characterization:

The sample was stretched by applying a tensile stress and allowed to creep (Figure S2). The strain rate ($\dot{\gamma}$) was calculated as the slope corresponding to the initial linear portion of the creep curve. The true stress (τ) was corrected from the constant apparent stress by taking into account the strain change immediately prior to the creep. The viscosity can be calculated according to the following equation.

$$\tau = \eta \frac{d\varepsilon}{dt} = \eta \dot{\gamma}$$

The rheological curve was obtained by varying the apparent constant stress in a set of experiments.

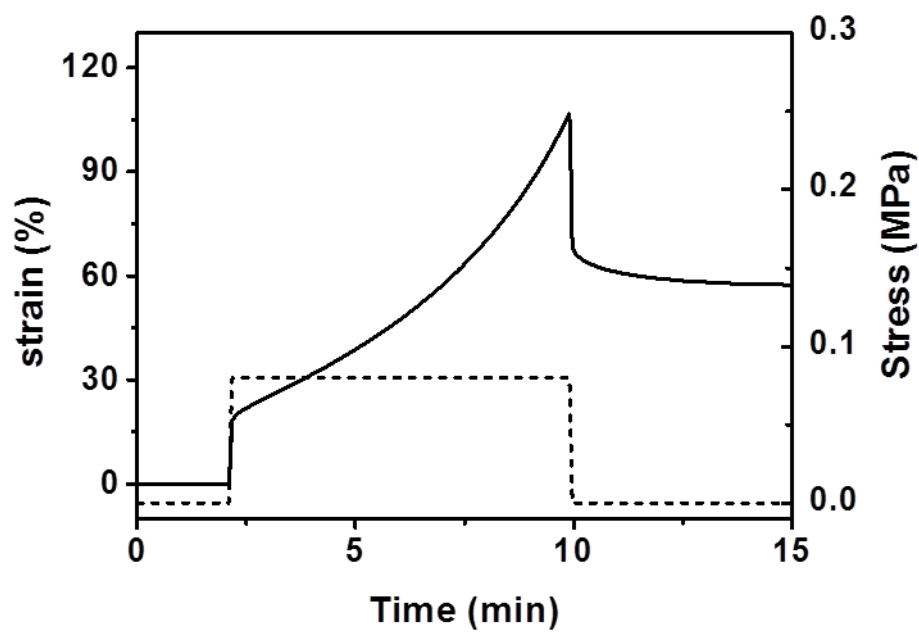


Figure S2. A representative creep curve.

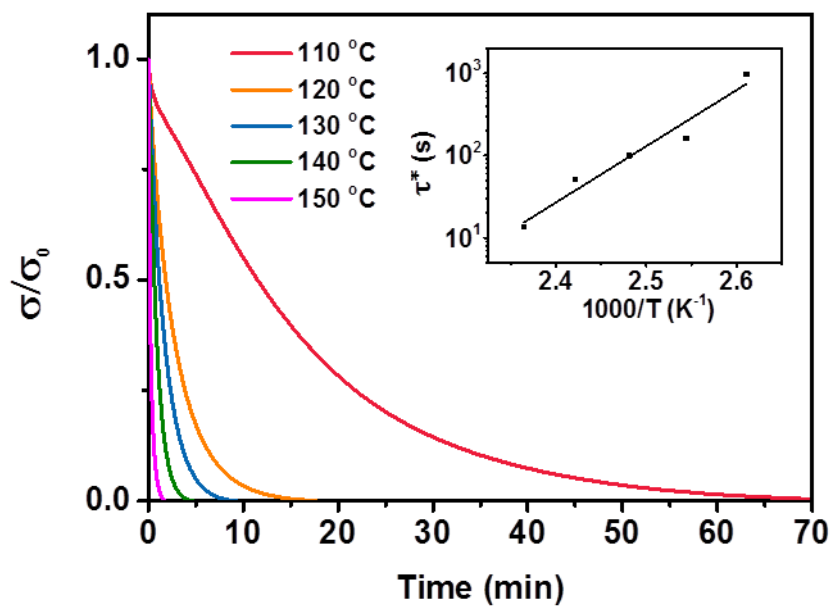


Figure S3. Stress relaxation and Arrhenius analysis of polyurethane from aromatic diisocyanate.

Section S5. Characterization of elasticity and plasticity:

Shape retention (R_{ret}) is calculated by $R_{ret} = \epsilon_f / \epsilon_{dload} \times 100\%$ is 100%, where ϵ_{dload} and ϵ_f are the maximum strain under load and the fixed strain after the stress is completely relaxed.

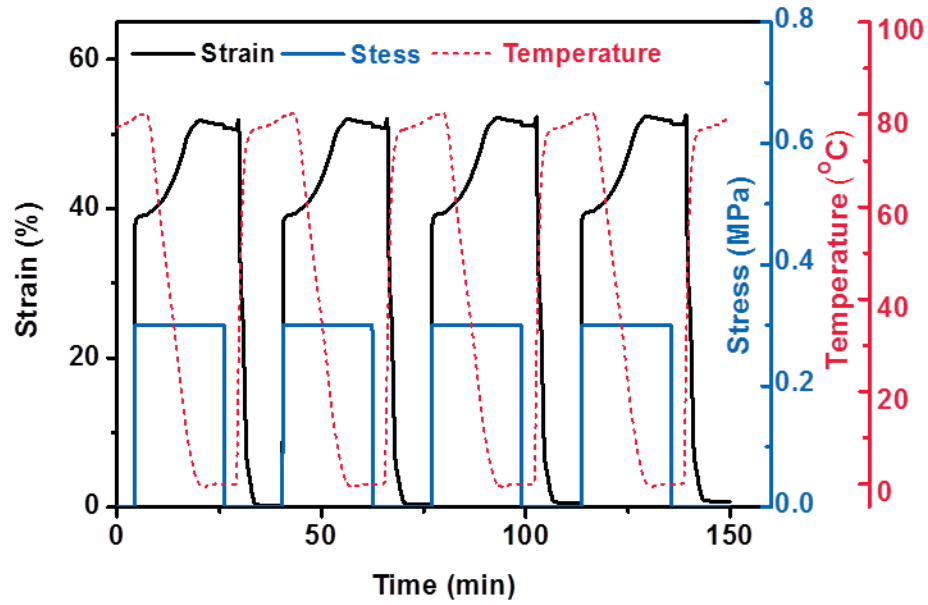


Figure S4. Consecutive shape memory cycles.

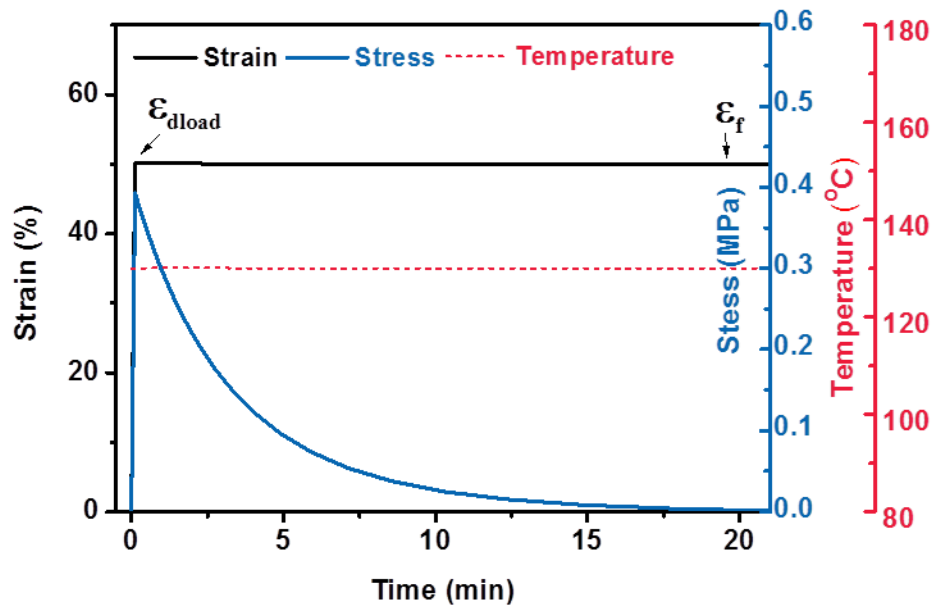


Figure S5. A representative plasticity cycle.

Section S6. Demonstration of shape manipulation:

The through-lines on a square film were created with a laser cutter. In the first plasticity step, the film was stretched by hanging a weight in the middle and thermally annealed (130 °C, ~30 min). After the permanent shape was created, the sample was cooled to room temperature. The second plasticity step was accomplished by placing the sample between two glass slides and thermally annealed under compression (130 °C, ~30 min). In a typical shape memory experiment, the sample was heated with an infrared lamp for about 10 s. After turning off the light, it was immediately deformed into a temporary shape and cooled at room temperature with the deformation force maintained. Releasing the deformation force after cooling completed the temporary shape fixing. Shape recovery was accomplished by infrared heating under a stress free condition.

Section S7. Gel content tests:

Weighted PU polymer (~0.5 g) was soaked in THF (10 mL) for three days with the THF refreshed each day. Afterwards, the undissolved polymer sample was dried at 100 °C in vacuum oven until the weight reached its plateau. The gel content was calculated as the weight ratio of the polymer sample after and before the solvent extraction. Each gel content value represents an average over three repeat tests.

Section S8. Additional results and discussion on the dominant role of trans-carbamoylation on the stress relaxation:

Figure 1 illustrates the trans-carbamoylation reaction generically applicable to all polyurethanes. In principle, a less generic trans-carbamoylation mechanism involving residual hydroxyl groups^[1] in the network is also possible. Residual hydroxyl groups are indeed very likely to be present in the network given the fact that it is difficult to achieve perfectly quantitative reaction between the isocyanates and hydroxyl groups. To investigate the potential impact of residual hydroxyl groups, we synthesized three network samples with the only variation lying in the HDI/PEG ratio (100%, 105%, and 110%, respectively). While the exact concentration of the residual hydroxyl groups (if present) for each sample is difficult to characterize directly, the slight increase of HDI in the formulation should undoubtedly lead to significantly lowered residual hydroxyl contents. However, the stress relaxation kinetics of these three network samples (Figure S6) are quantitatively quite similar, which proves that the role of residual hydroxyl groups is negligible (if any) for the current system.

The formation of a carbamate bond through isocyanate and hydroxyl group is known as an equilibrium reaction^[1] which means the dissociation of carbamate back to the isocyanate and hydroxyl group coexists with the association reaction. Typically, this equilibrium reaction occurs at relative high temperatures.^[1] In our system, however, the relatively large amount of catalyst (1 wt%) played an important role in reducing the temperature required for the exchange (Figure 2a). One possible reaction mechanism is that the hydroxyl group from the dissociated carbamates may act as the nucleophile for trans-carbamoylation reaction. The other possibility is that the trans-carbamoylation occurs directly between the dissociated species (i.e. an

isocyanate group reacting with the non-original hydrogel group). Neither of these two mechanisms requires residual hydroxyl groups and is consistent with the exchange reaction in Figure 1.

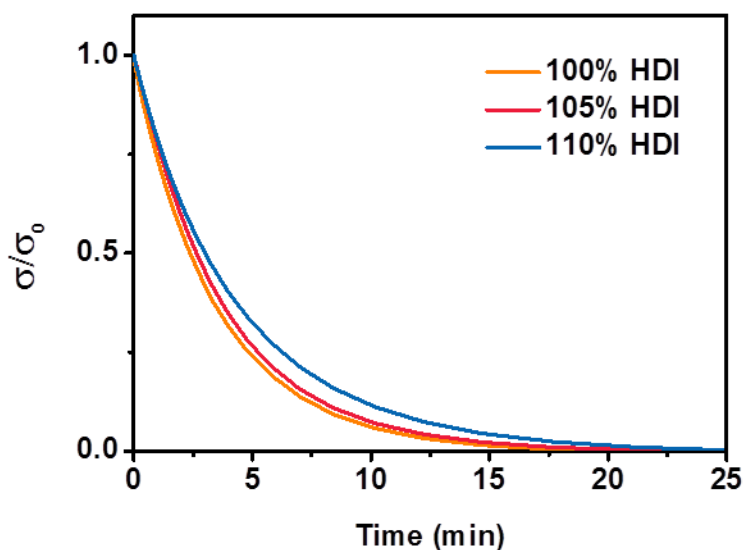


Figure S6. Stress relaxation behaviors.

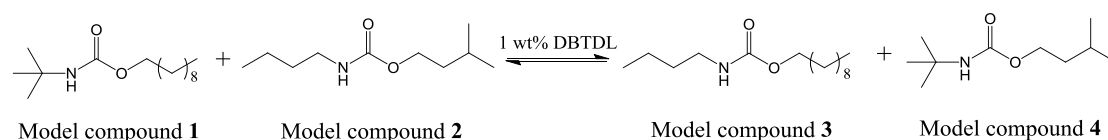


Figure S7. Model compound exchange.

While the evidence in Figure S6 shows the non-hydroxyl promoted trans-carbamoylation as the dominant mechanism for the plasticity, additional model compound study below provides additional direct proof of such a trans-carbamoylation. In this model compound study (Figure S7), an equimolar mixture of the model compounds **1** and **2** (with 1 wt% DBTDL) was heated in an oil bath preset to a desired temperature (110-150 °C) for a certain period of time. The

reacted mixture (50 mg dissolved in 1 g of THF) was then analyzed via GC analysis (Figure S8) with 50 mg of di-*tert*-butylbiphenyl as the internal standard. Product **3** was detected in all reaction conditions, confirming directly the trans-carbamoylation reaction. Quantitatively, the trans-carbamoylation based on the model compound study fit to an Arrhenius relationship to determine an activation energy of 157.9 kJ/mole (Figure S9). This activation energy is significantly higher than that of the network relaxation, which is 113.6 kJ/mole. We believe this discrepancy arises from the significant difference in the contribution of diffusion on the reactions as the former involves only small molecules and the latter are reactions within a solid network. We further note that similar discrepancy has been reported in the literature.^[1]

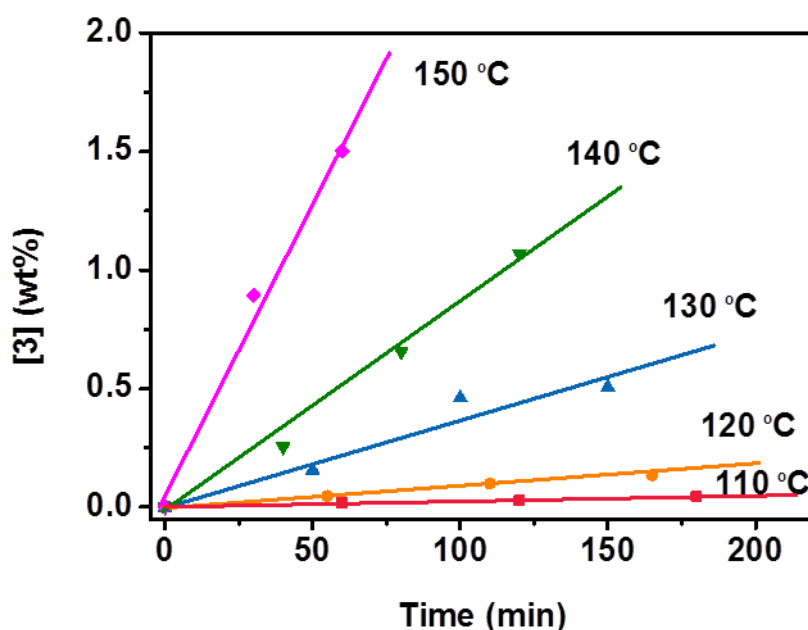


Figure S8. Concentrations of trans-carbamoylation product **3** versus time. Linear fits are shown for initial rates under condition.

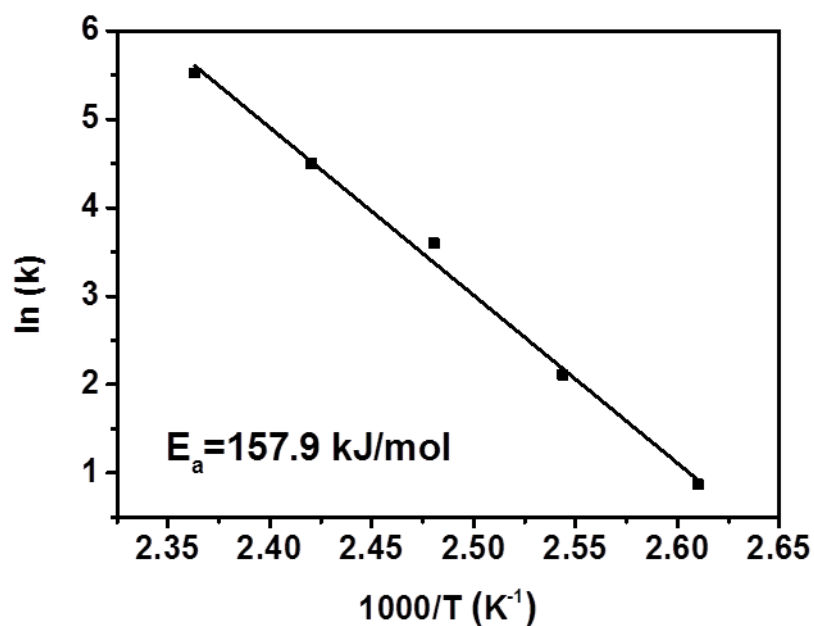
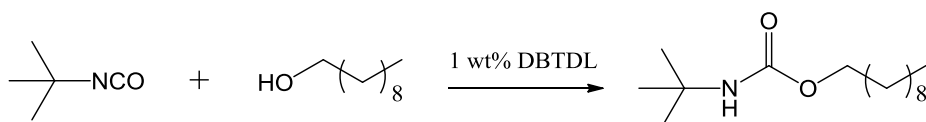


Figure S9. Arrhenius analysis of the small molecules trans-carbamoylation reactions.

In the above model compound study, all model compounds were synthesized by reacting the corresponding isocyanates and alcohols in the presence of 1 wt% DBTDL. The reaction conditions were 60 °C for 10 h. ¹H-NMR analyses confirm the identity of the model compound **1~4**.

Model compound 1.



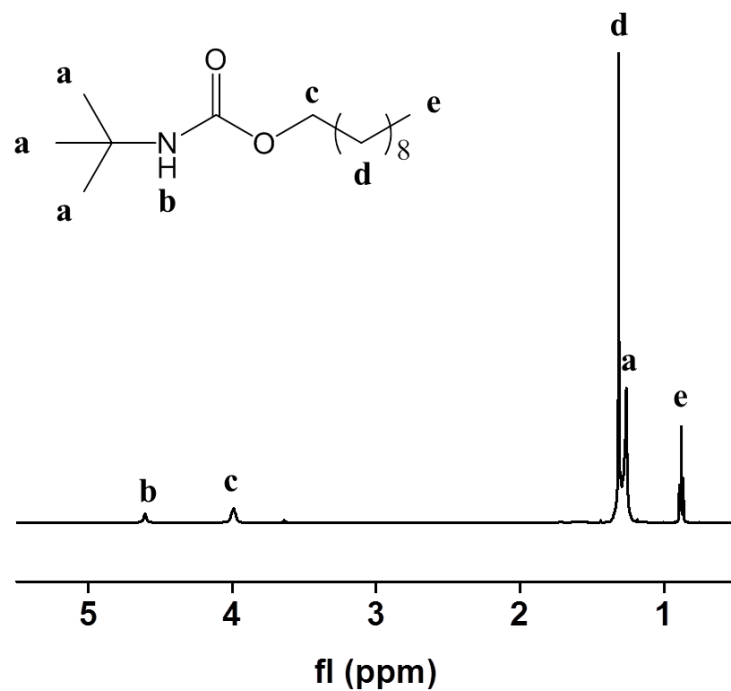


Figure S10. $^1\text{H-NMR}$ (CDCl_3 , 500 MHz, 298K) of model compound **1**.

Model compound 2.

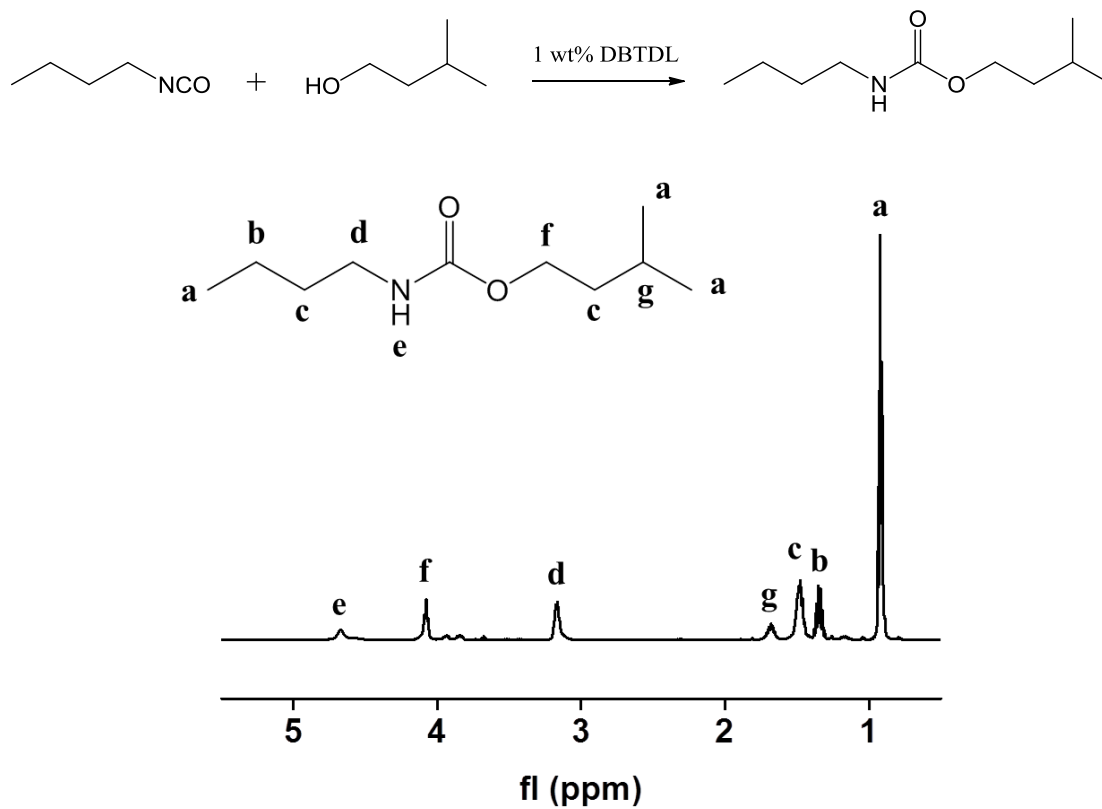


Figure S11. $^1\text{H-NMR}$ (CDCl_3 , 500 MHz, 298K) of model compound **2**.

Model compound 3.

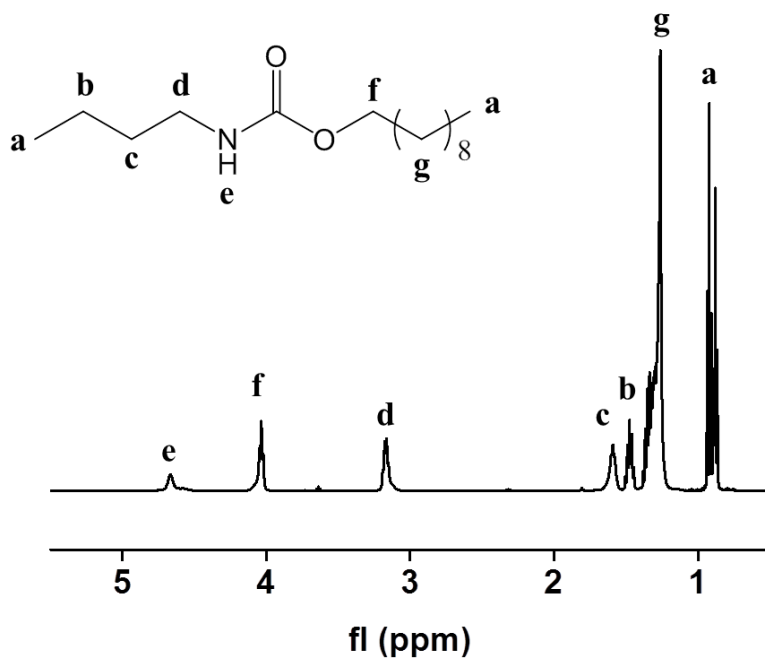
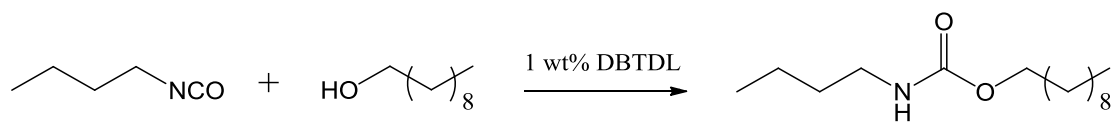
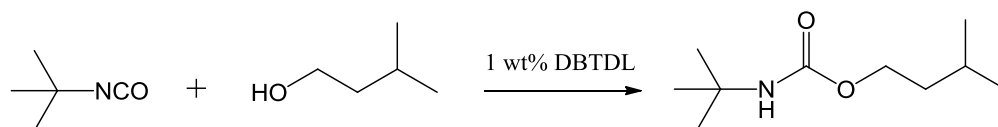


Figure S12. ¹H-NMR (CDCl₃, 500 MHz, 298K) of model compound 3.

Model compound 4.



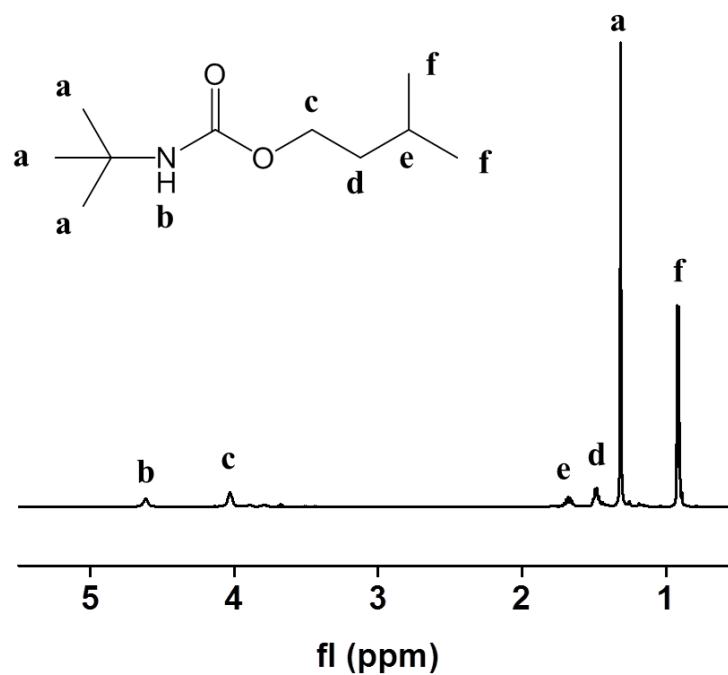


Figure S13. ¹H-NMR (CDCl₃, 500 MHz, 298K) of model compound 4.

Section S9. Videos:

Video S1: recovery from a flat film into a pop-up pyramid as triggered by infrared radiation (accelerated by a factor of 5).

Video S2: recovery from a flat film into an elongated three dimensional shape as triggered by infrared radiation (accelerated by a factor of 5).

Video S3: recovery from a kirigami pyramid into a flat film as triggered by infrared radiation (accelerated by a factor of 5).

References:

- [1] D. J. Fortman, J. P. Brutman, C. J. Cramer, M. A. Hillmyer, W. R. Dichtel, *J. Am. Chem. Soc.* **2015**, 137, 14019-14022.
- [2] B. Jousseau, C. Laporte, T. Toupance, J. Bernard, *Tetrahedron Lett.* **2002**, 43, 6305-6307.
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- [4] W. Denissen, G. Rivero, R. Nicolaÿ, L. Leibler, J. M. Winne, F. E. D. Prez, *Adv. Funct. Mater.* **2015**, 25, 2451–2457.