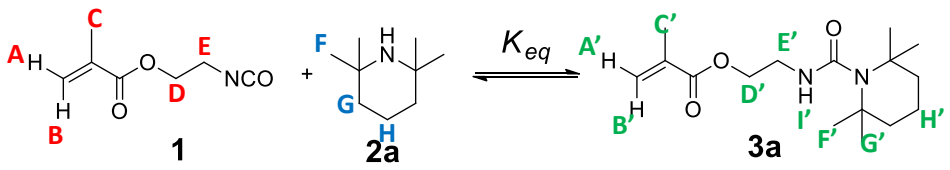
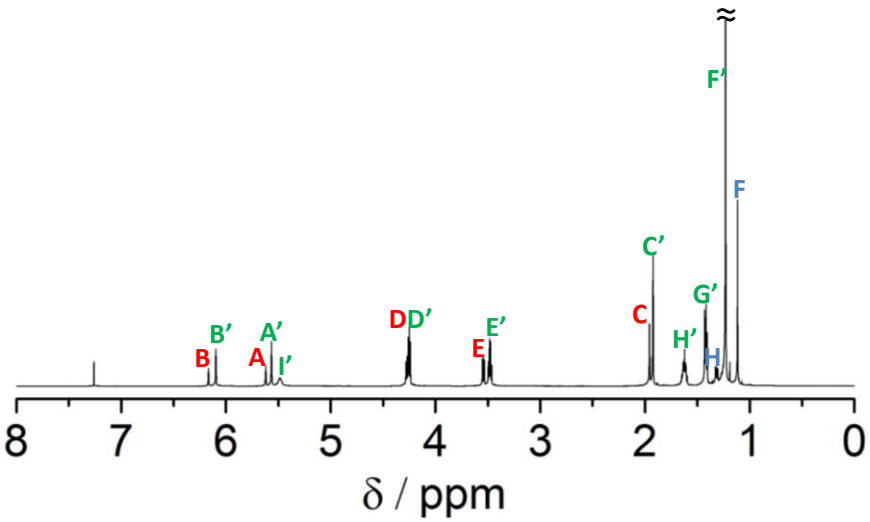
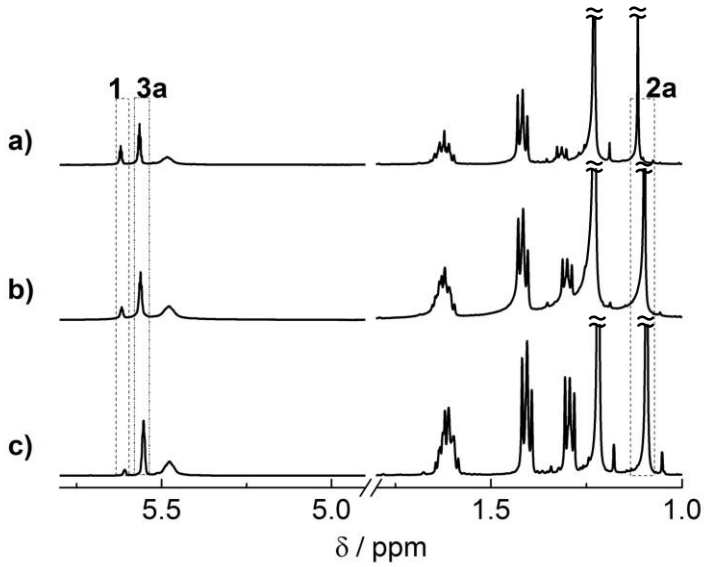
a





b

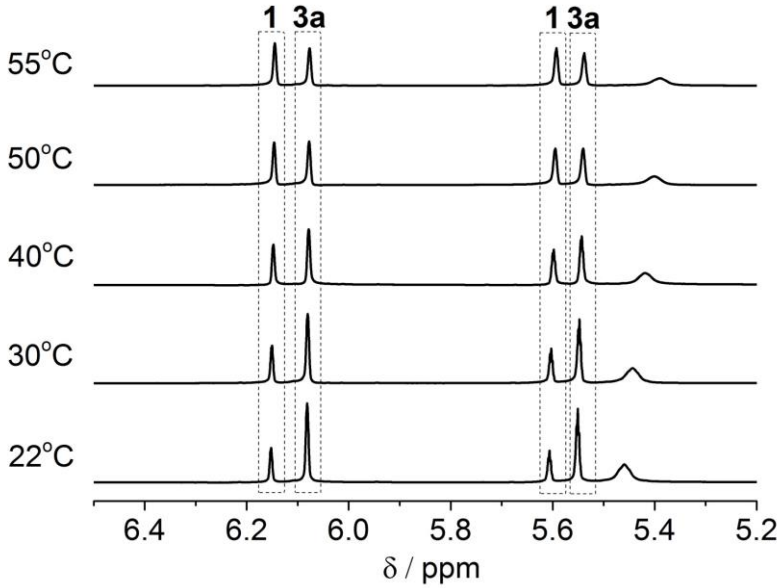


c

	$[\mathbf{1}]_0$ (M)	$[\mathbf{2a}]_0$ (M)	$[\mathbf{1}]_{eq}$ (M)	$[\mathbf{2a}]_{eq}$ (M)	$[\mathbf{3a}]_{eq}$ (M)	K_{eq} (M^{-1})
a)	0.160	0.139	0.049	0.028	0.111	81
b)	0.147	0.180	0.025	0.058	0.122	84
c)	0.157	0.270	0.013	0.126	0.144	88

Supplementary Figure 1 | Thermodynamic equilibrium of the TMPCA bond at different initial ratios of 1:2a. (**a**) ^{1}H NMR spectrum of the mixture of compound **1** and **2a** at initial ratio of 1.15:1 and the produced compound **3a** in $CDCl_3$. The spectrum was taken 30 min after **1** and **2a** were mixed. (**b**) ^{1}H NMR spectra of **1** and **2a** mixture with different initial concentrations at room temperature (see Supplementary Fig. 1c for the initial concentrations of **1** and **2a**). All spectra showed coexistence of compound **1**, **2a** and **3a** when the equilibrium was reached. (**c**) Concentrations of **1**, **2a** and **3a** with calculated equilibrium constants from each experiment with different initial ratios of **1**:**2a** at room temperature. Different initial ratios of **1**:**2a** gave identical K_{eq} values, demonstrating that the mixture is in thermodynamic equilibrium. The equilibrium concentrations of **1** and **2a** and the calculated equilibrium constants did not change once the equilibrium was reached.

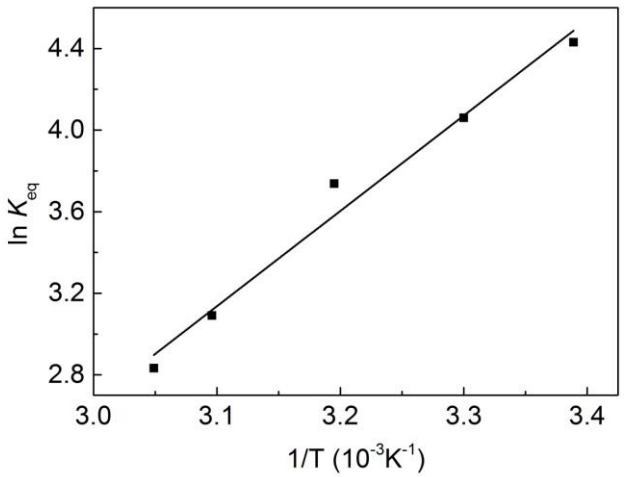
a



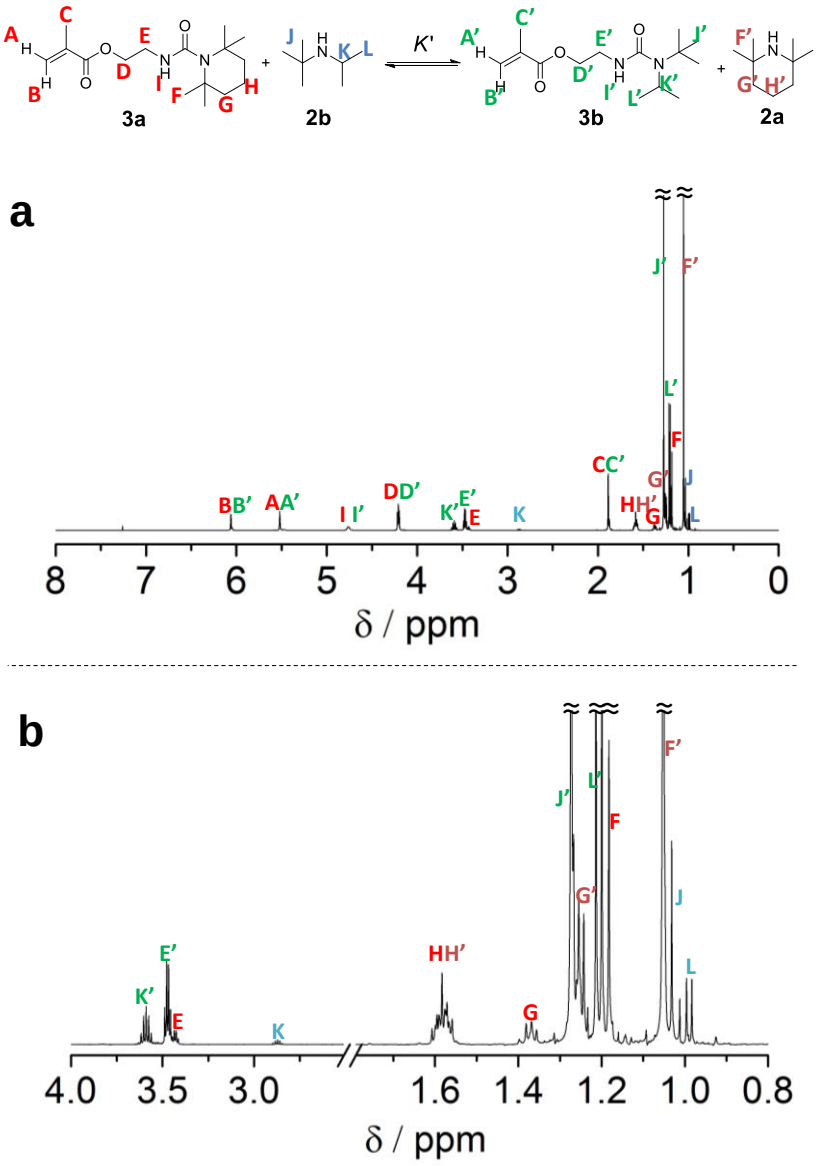
b

T(°C)	[**1**]$_0$ (M)	[**2a**]$_0$ (M)	[**1**]$_{eq}$ (M)	[**2a**]$_{eq}$ (M)	[**3a**]$_{eq}$ (M)	K_{eq} (M^{-1})
22	0.110	0.107	0.032	0.029	0.078	84
30	0.110	0.107	0.037	0.034	0.073	58
40	0.110	0.107	0.042	0.039	0.068	42
50	0.110	0.107	0.053	0.050	0.057	22
55	0.110	0.107	0.057	0.054	0.053	17

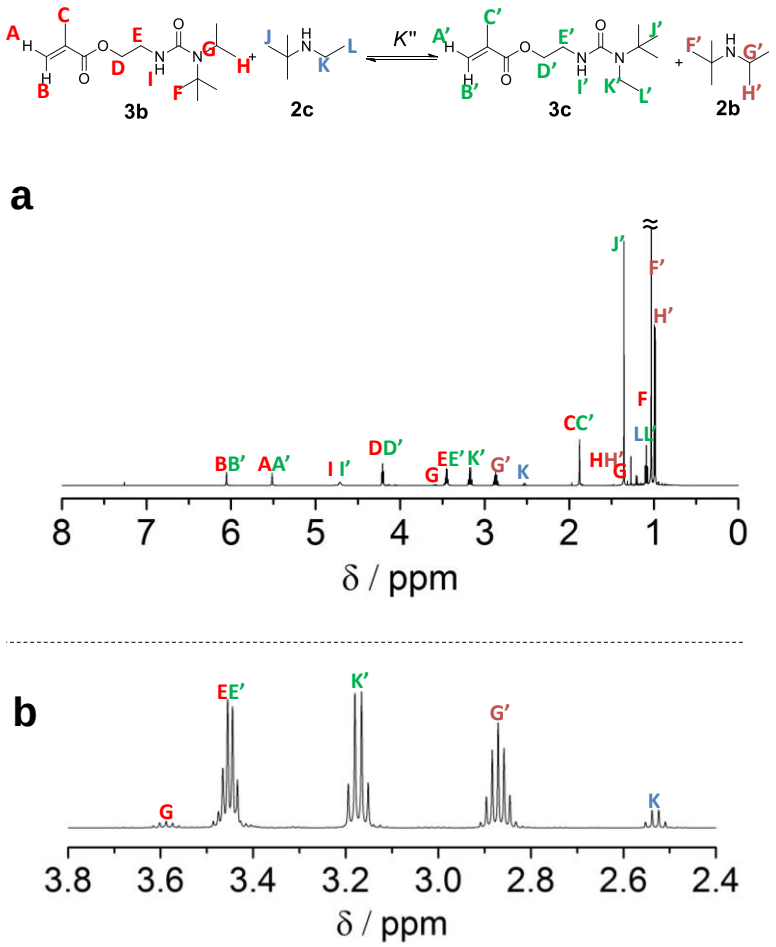
c



Supplementary Figure 2 | Thermodynamic equilibrium of the TMPCA bond at different temperatures. (**a**) ^{1}H NMR spectra of the mixture of compound **1** and **2a** at initial concentration of 0.110 M and 0.107 M, respectively, at different temperatures (see Supplementary Fig. 1a for complete assignments of peaks). Dissociation is more favoured at higher temperature. (**b**) Concentrations of **1**, **2a** and **3a** with calculated equilibrium constants at different temperatures. Equilibrium constants decrease with the increase of solution temperature. (**c**) Plot of linear regression of the logarithm of equilibrium constant $\ln K_{eq}$ vs. reciprocal of temperature 1/T. The equilibrium reaction follows Arrhenius' relationship with thermodynamic constant calculated as follows: $\Delta H = -39$ kJ mol^{-1}; $\Delta S = -94$ J mol^{-1} K^{-1}

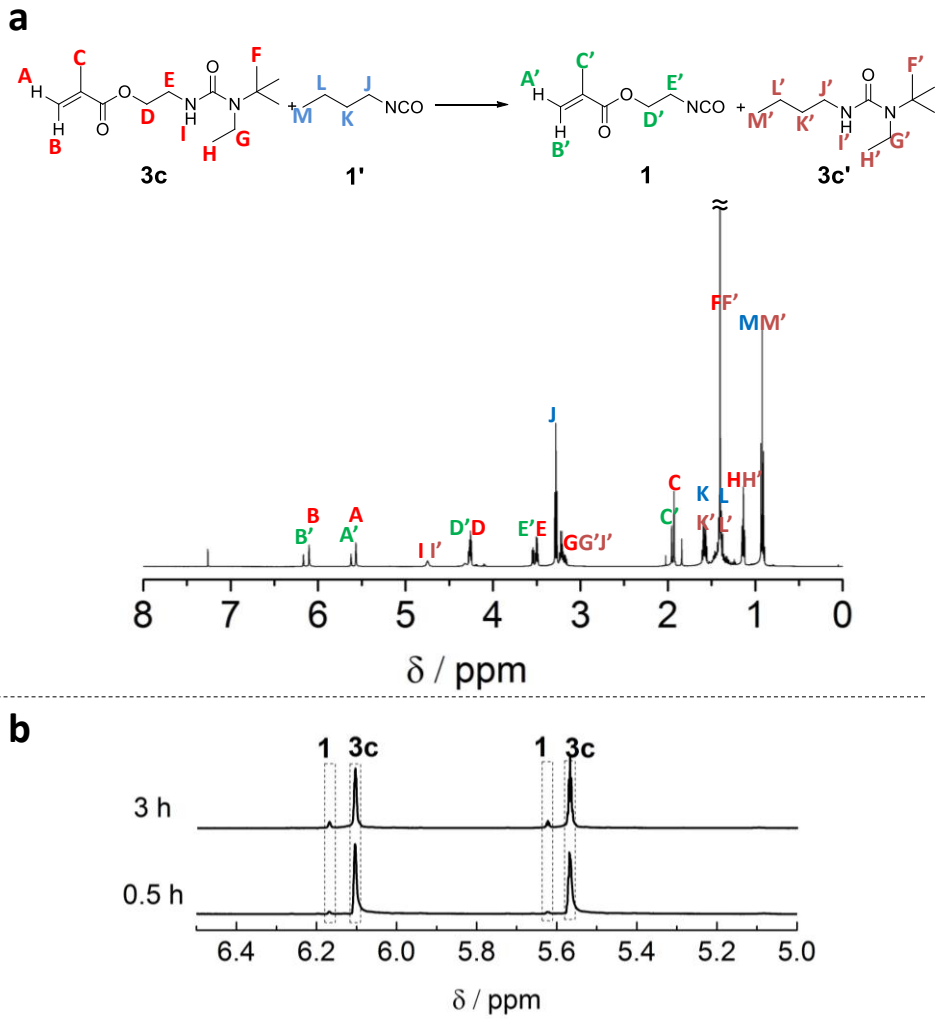


Supplementary Figure 3 | Determination of equilibrium constant of the TBIPU bond. (**a**) ^{1}H NMR spectrum of the mixture of compound **1**, **2a**, **2b** (and the produced compound **3a**, **3b**) in $CDCl_3$. Peaks were assigned to each compound. The spectrum was taken 12 h after mixing. (**b**) The peaks K', K, F and F' of the NMR spectrum in the Supplementary Fig. 3a were integrated and used for the calculation of the concentration of each species. $K' = ([\mathbf{3b}]_{eq} \bullet [\mathbf{2a}]_{eq} / ([\mathbf{3a}]_{eq} \bullet [\mathbf{2b}]_{eq}) = 63$, $K_{eq,TBIPU} = K' \bullet K_{eq,TMPCA} = 88 \times 63 = 5.6 \times 10^{3}\ M^{-1}$.



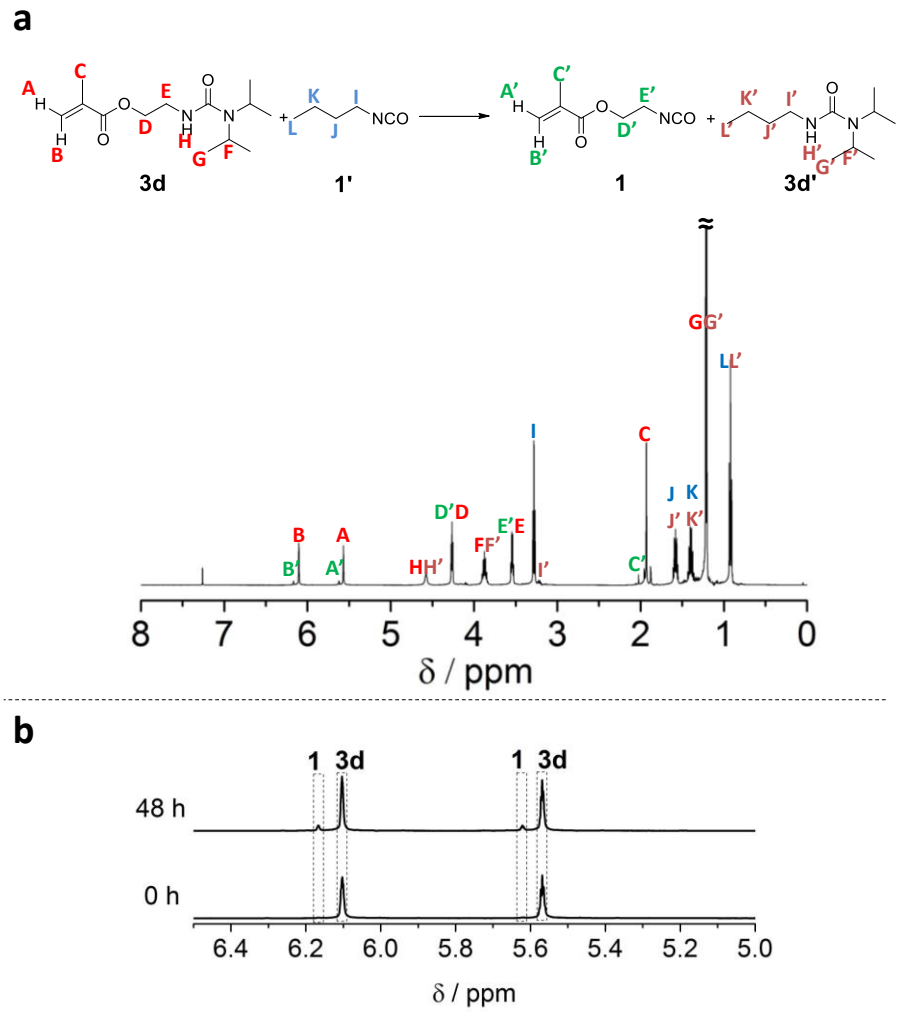
Supplementary Figure 4 | Determination of the equilibrium constant of the TBEU bond. (**a**) ^{1}H NMR spectrum of the mixture of compound **1**, **2b** and **2c** (and the produced compound **3b** and **3c**) in $CDCl_3$. The spectrum was taken 24 h after mixing. (**b**) The peaks G, K', G' and K of the NMR spectrum in the Supplementary Fig. 4a were integrated and used for the calculation of the concentration of each species. $K' = ([\mathbf{3c}]_{eq} \bullet [\mathbf{2b}]_{eq} / ([\mathbf{3b}]_{eq} \bullet [\mathbf{2c}]_{eq}) = 141$**,**

$K_{eq,TBEU} = K' \bullet K_{eq,TBIPU} = 5.6 \times 10^{3}\ M^{-1} \times 141 = 7.9 \times 10^{5}\ M^{-1}$



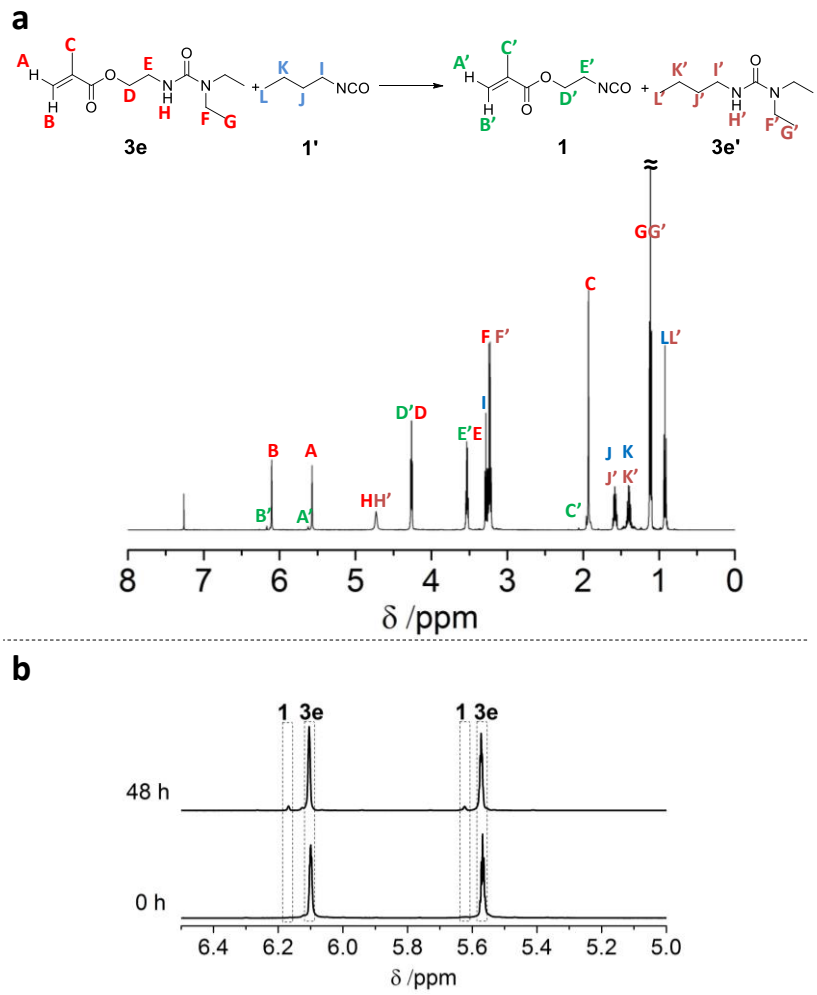
Supplementary Figure 5 | The dissociation kinetics of the TBEU bond. (**a**) ^{1}H NMR spectrum of the mixture of **1'** (10.4 mg, 0.105 mmol), **3c** (12.2 mg, 0.048 mmol) and the produced compound **1** and **3c'** in $CDCl_3$ (500 μL). The spectrum was taken 48 h after **1'** and **3c** were mixed. (**b**) ^{1}H NMR spectra showing exchange reaction between **3c** and **1'** at room temperature for different reaction time. The consumption rate of **3c** was used to calculate the dissociation rate of the TBEU bond with the following equation:

$$k_{-1} = -\frac{\ln \frac{[\mathbf{3c}]}{[\mathbf{3c}]_0}}{\mathrm{T}} = -\frac{\ln 0.88}{3.0\,\mathrm{h}} = 0.042\ \mathrm{h}^{-1}\ (\mathrm{T}\text{: reaction time}) \qquad (1)$$



Supplementary Figure 6 | The dissociation kinetics of the DIPU bond. (**a**) ^{1}H NMR spectrum of the mixture of compound **1'** (9.9 mg, 0.100 mmol) and **3d** (14.0 mg, 0.055 mmol), and the produced compound **1** and **3d'** in $CDCl_3$ (500 μL). The spectrum was taken 48 h after **1'** and **3d** were mixed. (**b**) ^{1}H NMR spectra showing exchange reaction between **3d** and **1'** at 37°C. The consumption rate of **3d** was used to calculate the dissociation rate of the DIPU bond with the following equation:

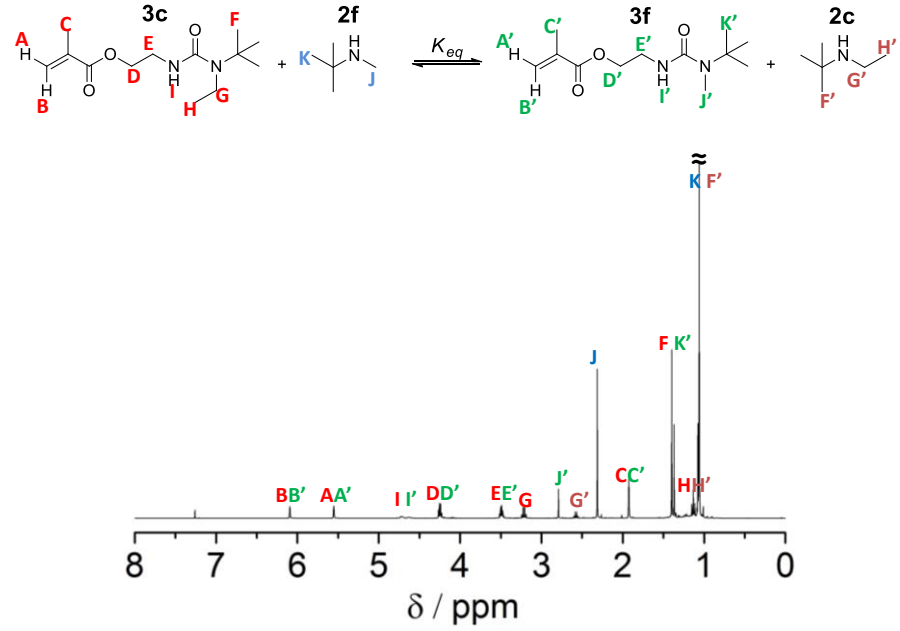
$$k_{-1} = -\frac{\ln \frac{[\mathbf{3d}]}{[\mathbf{3d}]_0}}{T} = -\frac{\ln 0.93}{48.0\,\mathrm{h}} = 0.0015\ \mathrm{h}^{-1} \qquad (2)$$



Supplementary Figure 7 | The Dissociation kinetics of the DEU bond. (**a**) ^{1}H NMR spectrum of the mixture of **1'** (6.7 mg, 0.067 mmol) and **3e** (16.0 mg, 0.070 mmol), and the produced compounds **1** and **3e'** in $CDCl_3$ (500 μL). The spectrum was taken 48 h after **1'** and **3e** were mixed. (**b**) ^{1}H NMR spectra showing exchange reaction between **3e** and **1'** at 37°C. The consumption rate of **3e** was used to calculate the dissociation rate of DEU bond with the following equation:

$$k_{-1} = \frac{\ln \frac{[\mathbf{3e}]}{[\mathbf{3e}]_0}}{\mathrm{T}} - \frac{\ln 0.95}{48.0\,\mathrm{h}} = 0.0011\ \mathrm{h}^{-1} \qquad (3)$$

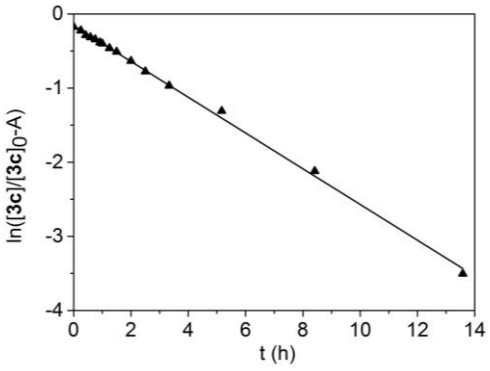
a



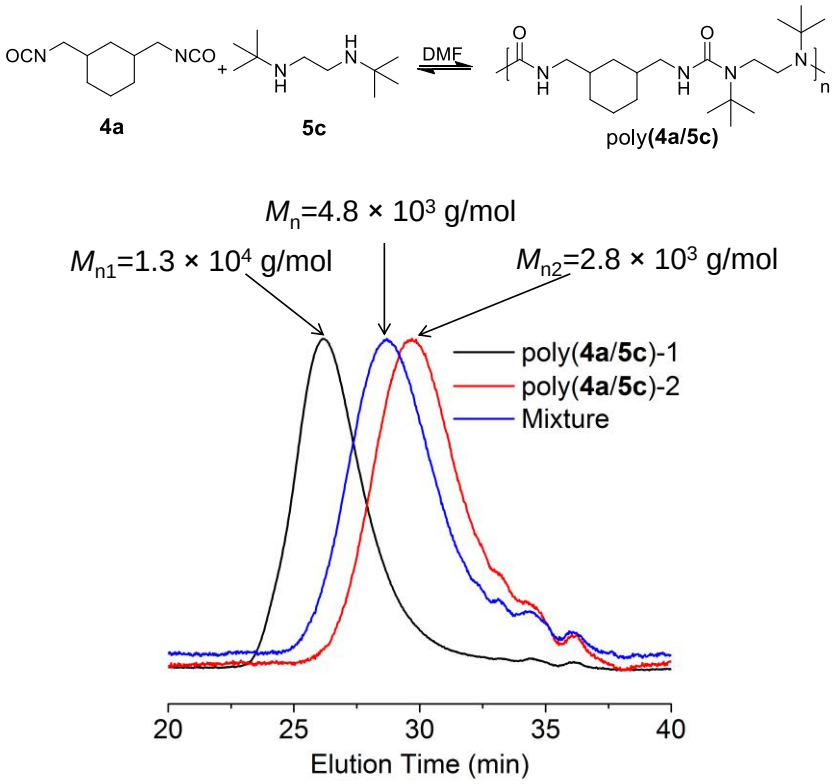
b

t(h)	$[3c]/[3c]_0$	$[2c]/[3c]_0$	$\ln([3c]/[3c]_0\text{-A})$
0.00	0.97	0.03	-0.17
0.25	0.93	0.07	-0.22
0.42	0.88	0.12	-0.29
0.58	0.86	0.14	-0.31
0.75	0.84	0.16	-0.34
0.92	0.81	0.19	-0.39
1.00	0.80	0.20	-0.40
1.25	0.76	0.24	-0.46
1.50	0.73	0.27	-0.51
2.00	0.66	0.34	-0.63
2.50	0.59	0.41	-0.78
3.33	0.51	0.49	-0.97
5.17	0.40	0.60	-1.31
8.42	0.25	0.75	-2.12
13.58	0.16	0.84	-3.51
14.08	0.16	0.84	-3.51
18.67	0.13	0.87	/
44.50	0.13	0.87	/

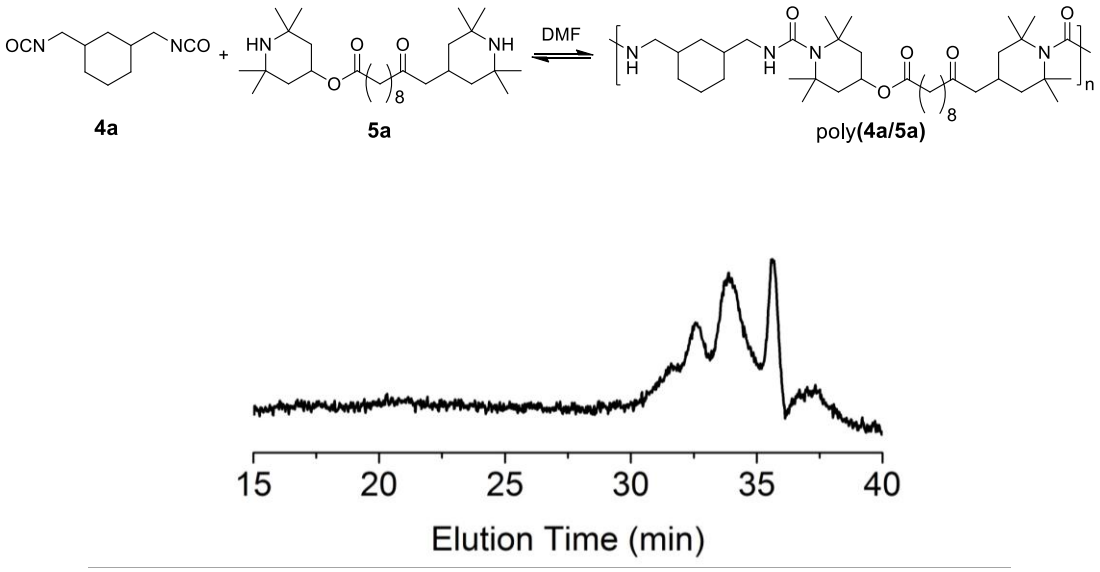
c



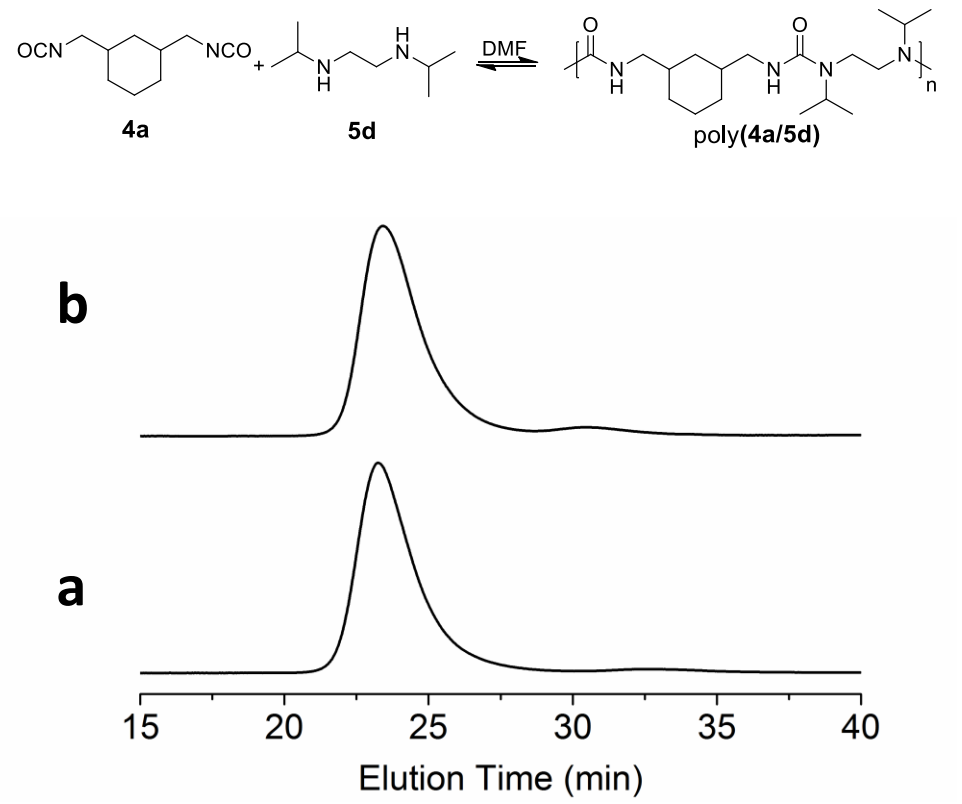
Supplementary Figure 8 | Dynamic exchange between compounds 3c and 2f. (**a**) ^{1}H NMR spectrum of the mixture of **3c** and **2f**, and the produced compound **3f** and **2c** in $CDCl_3$ (500 μL). The spectrum was taken 2 h after **3c** and **2f** were mixed. (**b**) Change of the concentrations of compound **3c** and **2c** over time showing the progress of exchange reaction. ($\mathbf{A}=\frac{[\mathbf{3c}]_{eq}}{[\mathbf{3c}]_{eq}+[\mathbf{2c}]_{eq}}=0.13$). (**c**) Linear regression of $\ln(\frac{[\mathbf{3c}]}{[\mathbf{3c}]_0}-\mathrm{A})\sim \mathrm{t}$.



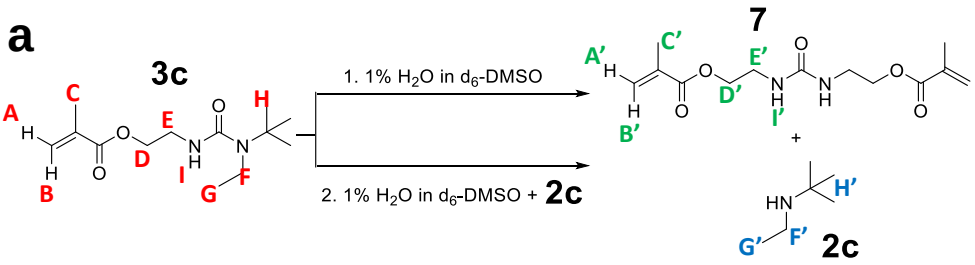
Supplementary Figure 9 | Chain reshuffling of two TBEU-based polymers with different molecular weights. GPC curves (light scattering signal) showing two poly(**4a**/**5c**)s with different molecular weights, the black curve for poly(**4a**/**5c**)-1 (M_{n1} = 1.3 × 10^4 g/mol) and the red curve for poly(**4a**/**5c**)-2 ($M_{n\,2}$= 2.8 × 10^3 g/mol). After they were mixed and stirred for 12 h at 37 °C, the original GPC curves of poly(**4a**/**5c**)-1 and poly(**4a**/**5c**)-2 disappeared and a new monomodal GPC curve was observed (blue curve, M_n = 4.8 × 10^3 g/mol) with a retention time between the two original peaks.



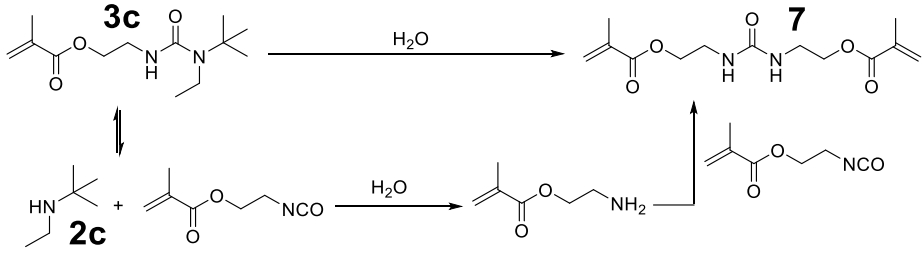
Supplementary Figure 10 | Dynamic property of TMPCA-based poly(4a/5a). GPC curves (light scattering signal) of poly(**4a**/**5a**) prepared with equal molar **4a** and **5a** at room temperature for 12 h. Only oligomers were obtained because of the low binding constant of the TMPCA bond.

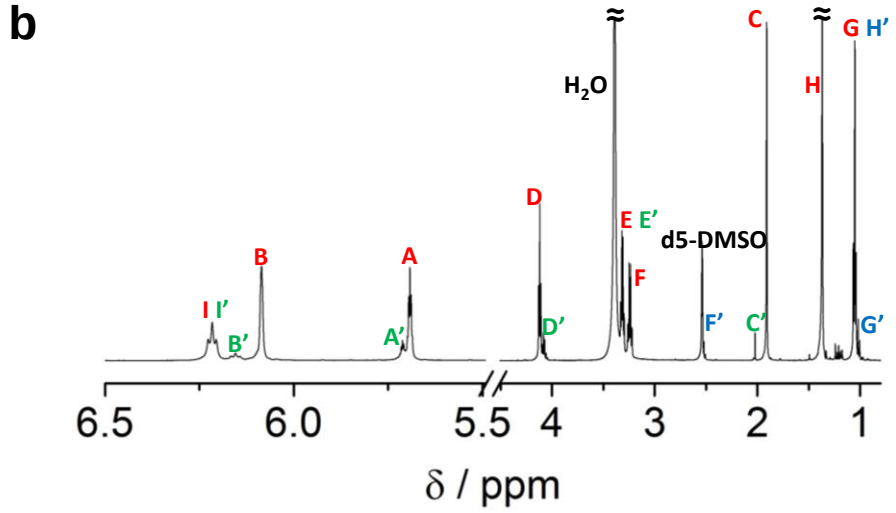


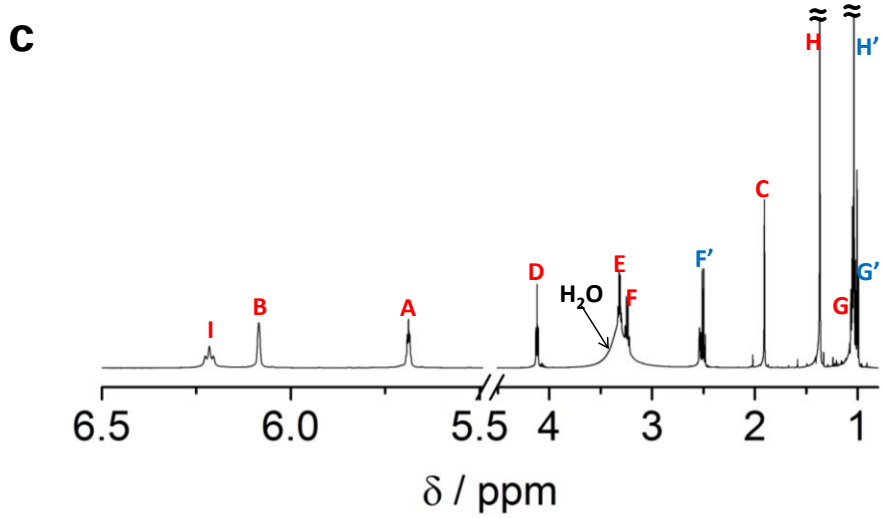
Supplementary Figure 11| Dynamic property of DIPU-based poly(4a/5d). GPC curves from the light scattering detector of poly(**4a**/**5d**) prepared with **4a** and **5d**. (**a**) $[\mathbf{4a}]_0$:$[\mathbf{5d}]_0$ = 1:1 in DMF. (**b**) One equiv of **5d** was added to (**a**) to make $[\mathbf{4a}]_0$:$[\mathbf{5d}]_0$ = 1:2. No significant change of GPC peak was observed with the addition of **5d** after the solution was stirred for 12 h at 37 ^{o}C, substantiating that DIPU is very stable, shows nearly no dynamic property, and is subject to limited dissociation and bond exchange reactions.

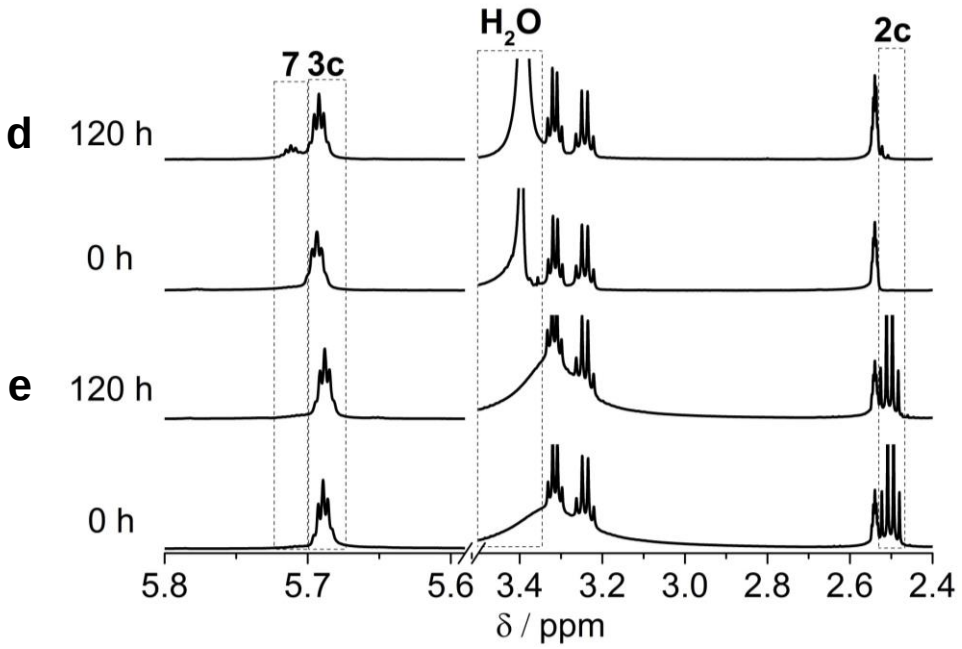


How **3c** hydrolyses:

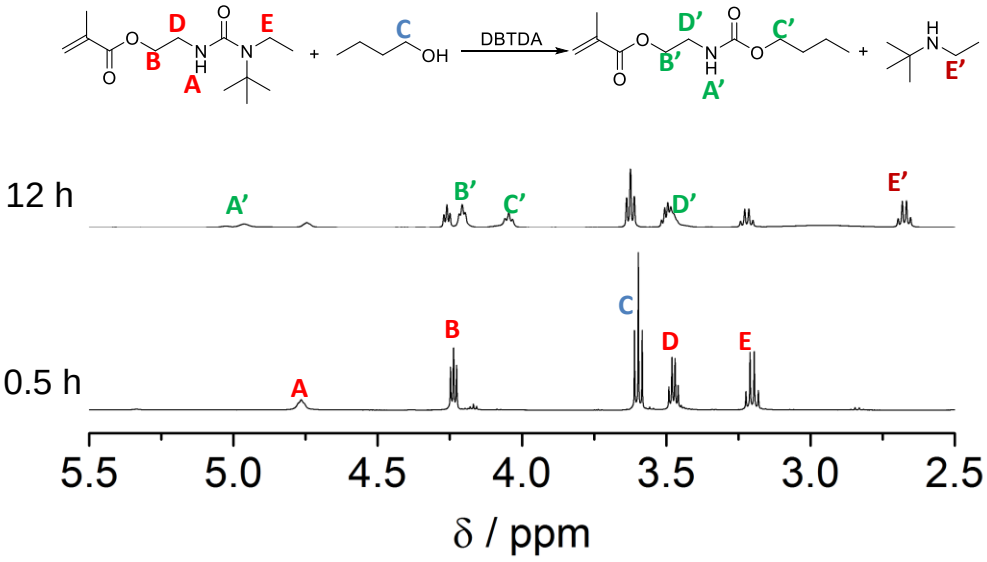




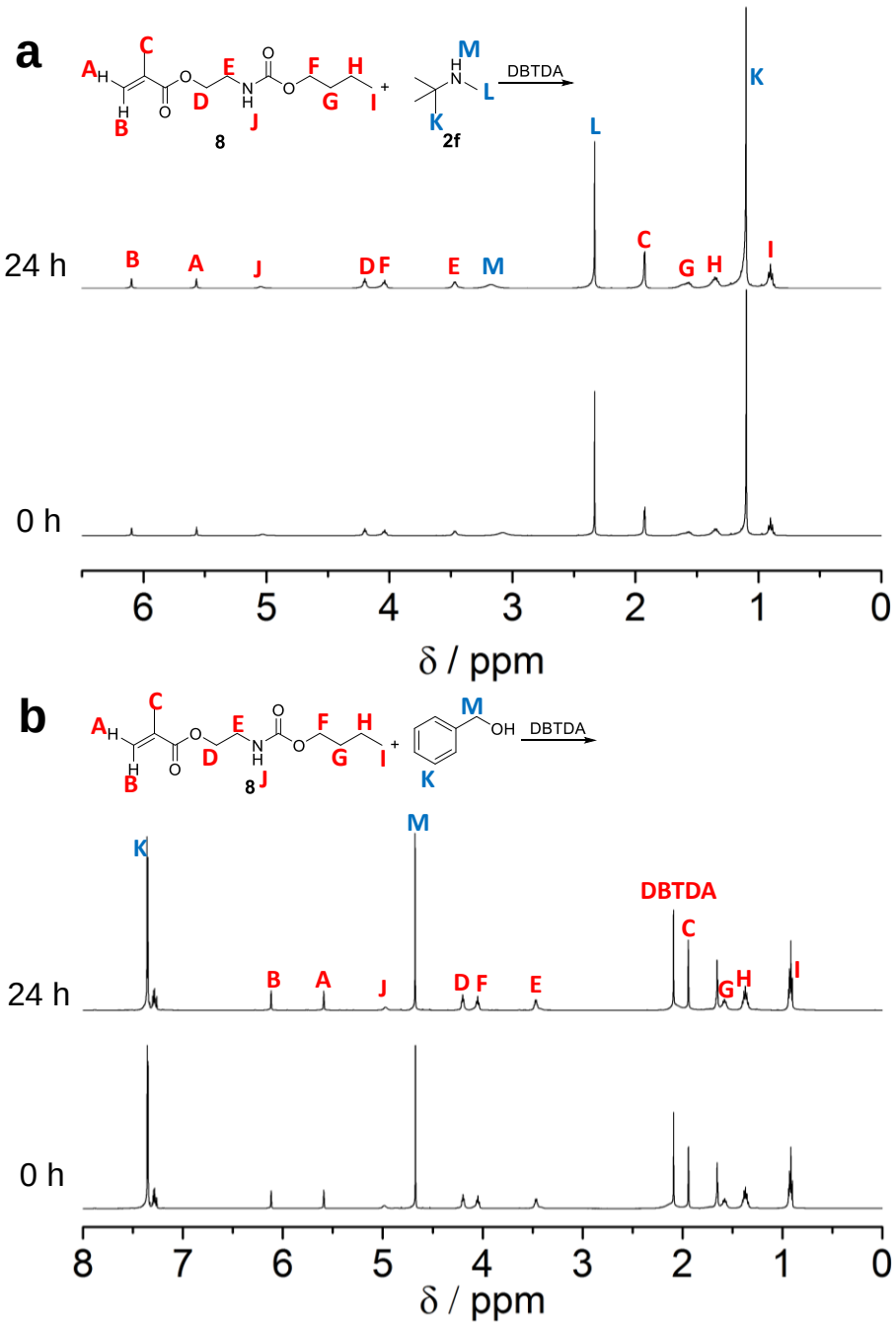




Supplementary Figure 12 | Stability of TBEU-containing compound 3c in water. (**a**) Hydrolysis of TBEU-containing compound **3c**. (**b**) The NMR spectrum of the freshly prepared **3c** (11.5 mg) solution in d_6-DMSO (0.5 mL) containing H_2O (5 mg, 1% in DMSO) (taken at t = 120 h). (**c**) The NMR spectrum of the freshly prepared solution of the mixture of **3c** (11.5 mg) and **2c** (8.6 mg) in d_6-DMSO (0.5 mL) containing H_2O (5 mg, 1% in DMSO) (taken at t = 120 h). (**d**) The overlay of the NMR spectra of (**b**) taken at t = 0 and the same solution retaken 120 h later at room temperature. (**e**) The overlay of the NMR spectra of (**c**) taken at t = 0 and the same solution retaken 120 h later at room temperature. After 120 h, partial hydrolysis (production of **7**) of the TBEU bond was observed for the solution without compound **2c** (**d**), while the hydrolysis of TBEU bond was negligible for the solution containing compound **2c** (**e**).

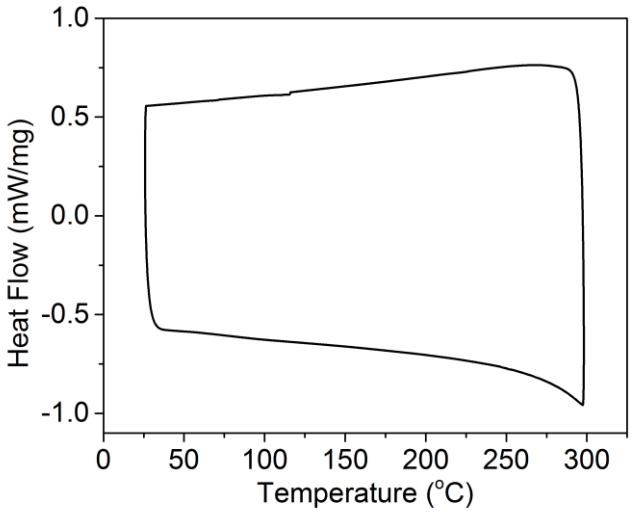


Supplementary Figure 13 | Reaction between a TBEU-containing hindered urea and 1-butanol. ^{1}H NMR analysis showed that about 60% of the amine was replaced from the reaction of alcohol with hindered urea at 60^{o}C for 12 h in the presence of DBTDA.

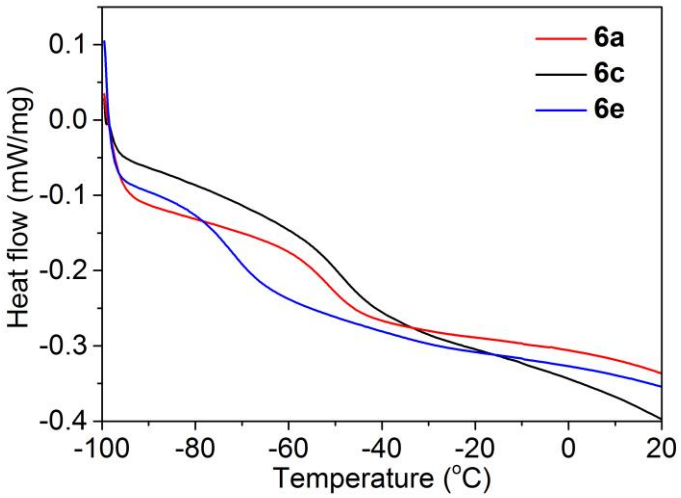


Supplementary Figure 14 | Dynamic exchange property of urethane bond. To evaluate whether the dynamic property of **6c** is exclusively due to the hindered urea bond or due to both the hindered urea bond and the urethane bond in this network polymer, we designed this experiment to analyse the stability of the urethane bond against an amine (**2f**, **a**) or an alcohol

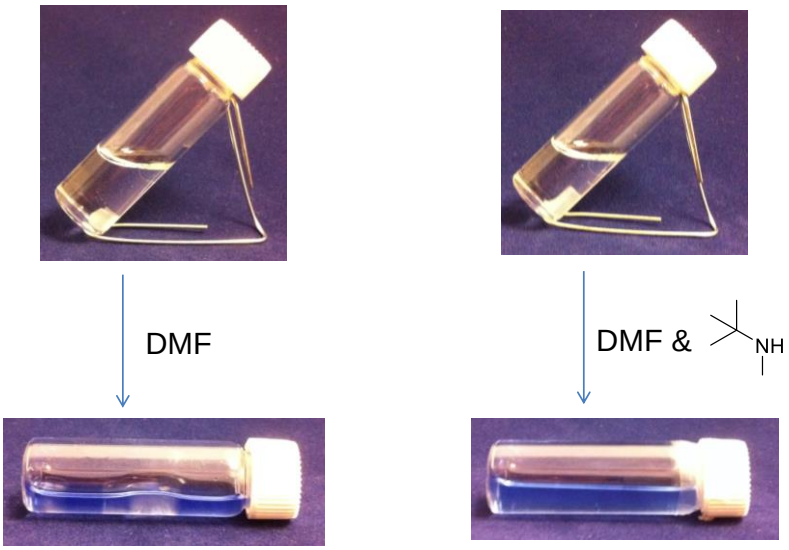
(benzyl alcohol, **b**) under the self-healing condition (37^{o}C in the presence of the tin catalyst). (**a**) The overlay of the NMR spectra of the mixture of 2-((butoxycarbonyl)amino)ethyl methacrylate (compound **8**, 10.0 mg, 0.044 mmol), **2f** (10.0 mg, 0.115 mmol) and dibutyl tin diacetate (1.0 mg, 0.003 mmol) in $CDCl_3$ (550 µL) at t = 0 and after incubation at 37^{o}C for 24 h. (**b**) The overlay of the NMR spectra of the mixture of 2-((butoxycarbonyl)amino)ethyl methacrylate (compound **8**, 10.0 mg, 0.044 mmol), benzyl alcohol (11.5 mg, 0.106 mmol) and dibutyl tin diacetate (27.9 mg, 0.080 mmol) in $CDCl_3$ (550 µL) at t = 0 and after incubation at 37^{o}C for 24 h. No obvious changes were observed in ^{1}H-NMR spectra in both (**a**) and (**b**), which demonstrated that urethane bond is stable under the self-healing condition.



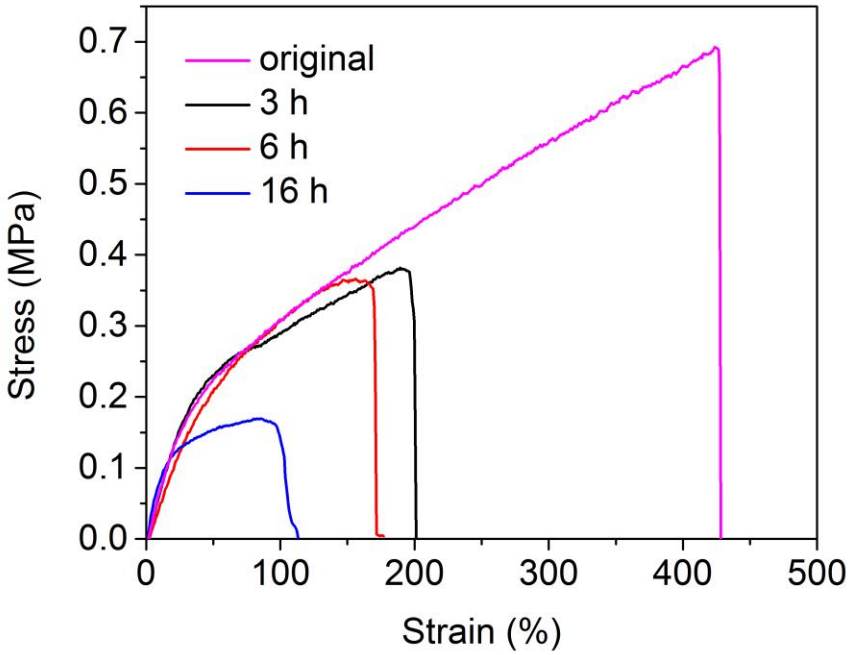
Supplementary Figure 15 | Thermal stability of 6c. No decomposition or phase transition was observed for **6c** according to DSC after it was heated to 300 °C, demonstrating the thermal stability of TBEU based material. DMF was removed in the first cycle.



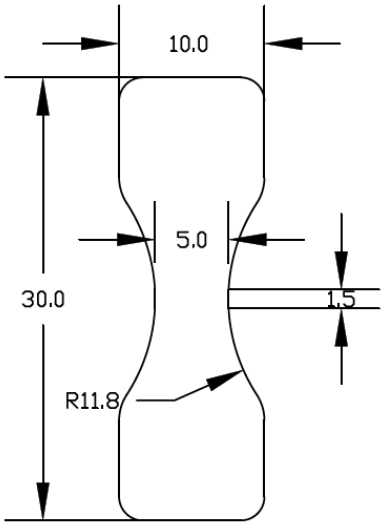
Supplementary Figure 16 | Characterization of T_g of 6a, 6c and 6e. DSC curves of cross-linked poly(urea-urethane) **6a**, **6c** and **6e**. See Table 2 for detailed T_g data.



Supplementary Figure 17 | Swelling and amine-induced degradation of 6c. When **6c** was put in DMF, it swelled (570% of its initial weight, 24 h incubation at 37 ^{o}C) rather than being dissolved in DMF (left). This experiment demonstrated that **6c** is a cross-linked network polymer. When **2f** (2 equiv relative to TBEU bonds) was added to DMF containing **6c**, degradation of **6c** network structure was observed (right) after 24 h incubation at 37 ^{o}C, demonstrating the dynamic property of TBEU bonds capable of exchange reaction with the added amine **2f**. Trypan blue dye was added after 24 h incubation in order to enhance the contrast of solution/gel interface in the photographs.



Supplementary Figure 18 | Self-healing efficiencies of 6a after healing for 3, 6 and 16h. Good breaking strain recovery was observed after **6a** was healed for 3 h. However, the breaking strain decreased with prolonged healing because of the irreversible hydrolysis of the isocyanate at the cut site.



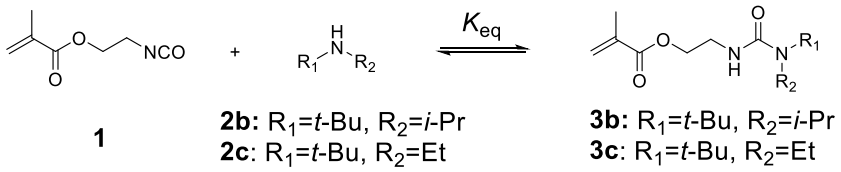
Supplementary Figure 19 | The dimension of the dog-shaped specimen used in the study (unit: mm, thickness: 2.0 mm).

Supplementary Table 1 | The binding constants and dissociation kinetics of urea compounds prepared with two isocyanates (1 and 1'' cyclohexanemethyl isocyanate) with different substituent bulkiness and three amines (2a-c).[a]

	$K_{eq,TMPCA}$ (M^{-1})	$K_{eq,TBIPU}$ (M^{-1})	$K_{eq,TBEU}$ (M^{-1})	$k_{-1,TBEU}$ (37 °C) (h^{-1})
1	88	5.6×10^{3}	7.9×10^{5}	0.21
1''	24	6.0×10^{2}	7.1×10^{4}	0.19

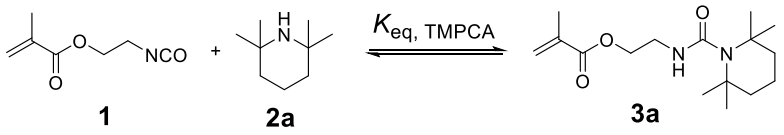
[a] See the Methods section and the Supplementary Note 1 for methods used for the determination of the binding constants and exchange kinetics. Experiments were performed at room temperature unless otherwise noted**.** These two different isocyanates led to HUBs with similar dynamic properties (especially nearly identical k_{-1}).

Supplementary Note 1 | The equilibrium constants of TBIPU and TBEU bond



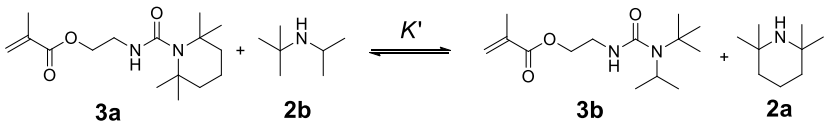
Because the binding constants of TBIPU and TBEU are fairly large, it is difficult to determine the equilibrium concentrations of the isocyanate, amine and urea species. Only in a very dilute solution, we were able to observe the coexistence of all three species. To accurately determine the binding constants, we used an 'indirect' method through equilibrium reaction between different urea species.

Since we already got the binding constant of TMPCA bond $K_{eq,\ TMPCA}$,



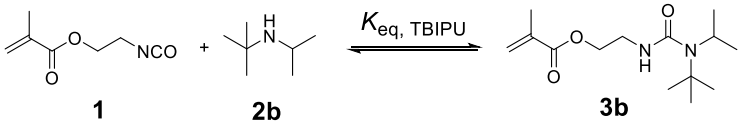
(4)

we reasoned that if we let TMPCA and TBIPU reach equilibrium and calculate the constant *K*' between them,



(5)

by combining the two equations above, we would have the following equation (Equation 6).



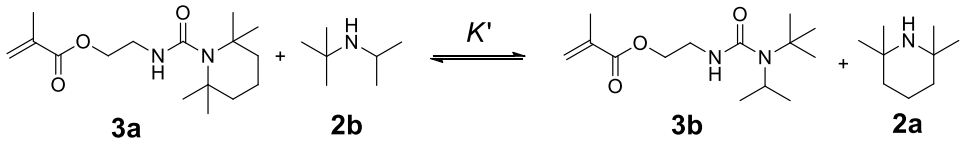
(6)

We can get the $K_{eq,\ TBIPU}$ through the equation 7.

$$K_{eq,\,TBIPU} = K' \bullet K_{eq,\,TMPCA} \tag{7}$$

Similar method can be used to determine the binding constant of TBEU with the known $K_{eq,\ TBIPU}$.

Determination of the equilibrium constants of TBIPU bond.

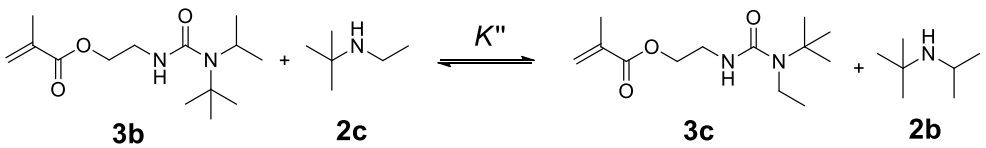


2-Isocyanatoethyl methacrylate (**1**, 24.4 mg, 0.157 mmol), 2,2,6,6-tetramethylpiperidine (**2a**, 21.9 mg, 0.155 mmol) and *N*-tertbutyl-*N*-isopropyl amine (**2b**, 17.4 mg, 0.151 mmol) were dissolved in $CDCl_3$ (0.55 mL) and added to a NMR tube. ^{1}H NMR spectra were collected 12 h after mixing at room temperature after equilibrium was reached (Supplementary Fig. 3). The equilibrium constant of the reaction *K*' was calculated according to the ratio of the concentration of each species:

$$K' = ([\mathbf{3b}]_{eq} \bullet [\mathbf{2a}]_{eq} / ([\mathbf{3a}]_{eq} \bullet [\mathbf{2b}]_{eq}) \tag{8}$$

The equilibrium constant of TBIPU was calculated based on Equation 7.

Determination of the equilibrium constants of TBEU bond.



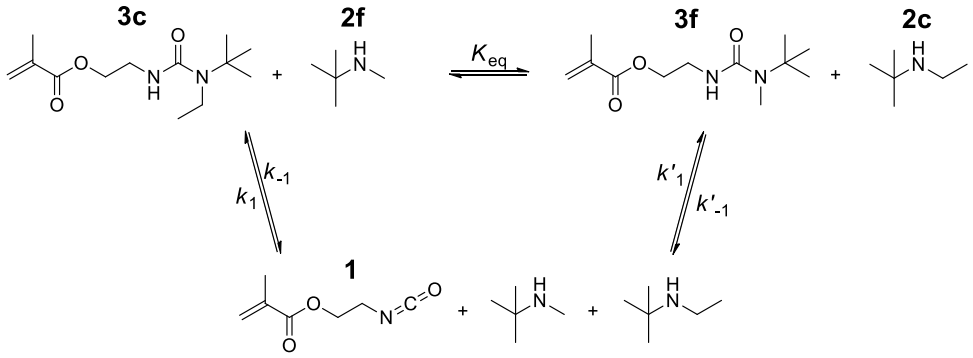
2-Isocyanatoethyl methacrylate (**1**, 18.8 mg, 0.121 mmol), *N*-tertbutyl-*N*-isopropyl amine (**2b**, 24.4 mg, 0.212 mmol) and *N*-tertbutyl-*N*-ethyl amine (**2c**, 12.2 mg, 0.121 mmol) were dissolved in $CDCl_3$ (0.55 mL) and added to NMR tubes. ^{1}H NMR spectra were collected 24 h after mixing at room temperature after equilibrium was reached (Supplementary Fig. 4). The equilibrium constant of the reaction *K*" was calculated according to the ratio of the concentration of each species.

$$K'' = ([3c]_{eq} \bullet [2b]_{eq} / ([3b]_{eq} \bullet [2c]_{eq}) \quad (9)$$

The equilibrium constant of TBEU was calculated based on the equilibrium constant of TBIPU and *K*":

$$K_{eq,TBEU} = K'' \bullet K_{eq,TBIPU} \quad (10)$$

Supplementary Note 2 | Kinetic study of the dynamic exchange of amine in the TBEU bond



Urea **3c** (11.3 mg, 0.044 mmol) that has a TBEU moiety and *tert*-butylmethylamine **2f** (8.8 mg, 0.102 mmol) were mixed in $CDCl_3$ (0.5 mL), quickly transferred to a NMR tube, and heated to 37°C. ^{1}H NMR spectra were collected at selected time intervals until equilibrium was reached (Supplementary Fig. 8). Kinetic analysis was conducted to validate the proposed mechanism: ($[M]_0$: initial concentration, $[M]_{eq}$: equilibrium concentration)

Kinetic analysis to prove the proposed equilibrium mechanism. If the exchange reaction works through the proposed mechanism, we have:

$$-\frac{d[\mathbf{3c}]}{dt} = -\frac{d[\mathbf{2f}]}{dt} = k_{-1}[\mathbf{3c}] - k_1[\mathbf{1}][\mathbf{2c}] \tag{11}$$

Here, the concentration of isocyanate intermediate **1** can be regarded as a constant, so we have:

$$[\mathbf{1}] = [\mathbf{1}]_{eq} = \frac{k_{-1}}{k_1} \times \frac{[\mathbf{3c}]_{eq}}{[\mathbf{2c}]_{eq}} \tag{12}$$

After combining Equation 12 and 11, we can get Equation 13.

$$-\frac{d[\mathbf{3c}]}{dt} = k_{-1}[\mathbf{3c}] - k_{-1} \times \frac{[\mathbf{3c}]_{eq}}{[\mathbf{2c}]_{eq}} \times [\mathbf{2c}] \quad (13)$$

Because $[\mathbf{2c}] = [\mathbf{3c}]_0 - [\mathbf{3c}]$, we will have the following equation (Equation 14).

$$-\frac{d[\mathbf{3c}]}{dt} = k_{-1}[\mathbf{3c}] - k_{-1} \times \frac{[\mathbf{3c}]_{eq}}{[\mathbf{2c}]_{eq}} \times ([\mathbf{3c}]_0 - [\mathbf{3c}]) = k_{-1} \times (1 + \frac{[\mathbf{3c}]_{eq}}{[\mathbf{2c}]_{eq}}) \times [\mathbf{3c}] - k_{-1} \times \frac{[\mathbf{3c}]_{eq}}{[\mathbf{2c}]_{eq}} \times [\mathbf{3c}]_0 \quad (14)$$

By solving the differential equation, we can have Equation 15 and then Equation 16.

$$[\mathbf{3c}] = [\mathbf{3c}]_0 \times \frac{[\mathbf{2c}]_{eq}}{[\mathbf{3c}]_{eq} + [\mathbf{2c}]_{eq}} e^{-k_{-1}\frac{[\mathbf{3c}]_{eq} + [\mathbf{2c}]_{eq}}{[\mathbf{2c}]_{eq}} \times t} + [\mathbf{3c}]_0 \times \frac{[\mathbf{3c}]_{eq}}{[\mathbf{3c}]_{eq} + [\mathbf{2c}]_{eq}} \quad (15)$$

$$\ln(\frac{[\mathbf{3c}]}{[\mathbf{3c}]_0} - A) = -\frac{1}{1 - A} k_{-1} t + \ln A \quad (16)$$

Here, $A = \frac{[\mathbf{3c}]_{eq}}{[\mathbf{3c}]_{eq} + [\mathbf{2c}]_{eq}}$. We obtained linear regression of $\ln(\frac{[\mathbf{3c}]}{[\mathbf{3c}]_0} - A) \sim t$ (R^2 = 0.998) (Supplementary Fig. 8c). From the slope of the curve, we determined the dissociation rate of TBEU bond (k_{-1} = 0.21 h^{-1}).

Supplementary Note 3 | Stability of the TBEU bond against hydrolysis and strategy to improve TBEU moisture stability.

One possible issue of using HUB in preparing dynamic or self-healing polymers is its potential instability to moisture since the isocyanate intermediate produced by HUB dissociation might slowly react with water (Supplementary Fig. 12a). Since TBEU has a large binding constant for the formation of urea, the concentration of the free isocyanate should be very low, which reduces the kinetics of degradation in moisture. In addition, the presence of free hindered amine should be able to further reduce the concentration of free isocyanate according to the equilibrium equation:

$$[\text{isocyanate}] = [\text{urea}]/(K_{eq}\cdot[\text{amine}]) \quad (17)$$

thus further reduce the TBEU hydrolysis kinetics. Here, we demonstrated the hydrolysis reduction strategy by comparing the hydrolysis of TBEU compound **3c** in 1% water/DMSO solution in the presence versus in the absence of free amine **2c**. As we expected, after the solution was incubated for 5 days at room temperature, a small shoulder peak (for compound **7**, ~δ = 5.7 ppm) was observed in the solution without **2c,** depicting partial hydrolysis of the TBEU bond (Supplementary Fig. 12d). On the contrary, negligible hydrolysis was observed for sample with free amine **2c** contained (Supplementary Fig. 12e).

Existence of free amine groups in the materials. To make sure there were free amine groups presence in the materials, the hydroxyl and amine groups were included in larger excess relative to the isocyanate groups (3[TEA]+2[TEG]+2[**5**] > 2[**4b**]) for the synthesis of the self-healing materials (2[**4b**]>[TEA]+[TEG]+[**5**]+[**4b**] is required to ensure gel point to be reached). Since the amine reacts with isocyanate much faster than the hydroxyl, all of the amine groups should

be consumed and some hydroxyl groups should stay intact. However, since HUB is dynamic but urethane group is inert (Supplementary Fig. 14), the excess hydroxyl groups should slowly react with HUBs to form urethane in the presence of tin catalyst (DBTDA) at high temperature and release free amine groups to the materials that can increase the stability of HUBs against hydrolysis. To demonstrate this process, we used ^{1}H NMR to monitor the reaction of model small molecules under the condition same as that for the synthesis of cross-linked polymer. Compound **3c** (10.0 mg, 0.039 mmol) was dissolved in $CDCl_3$ (550 µL), then butanol (4.5 mg, 0.061 mmol) and dibutyl tin diacetate (3.0 mg, 0.008 mmol) were added. The solution was incubated at 60^{o}C for 12 h and characterized by ^{1}H NMR (Supplementary Fig. 13). ^{1}H NMR analysis showed that about 60% of the amine was replaced from the reaction of alcohol with hindered urea at 60^{o}C for 12 h in the presence of DBTDA.