Supporting Information

New Strategy in Efficient Chemical Degradation and Recycle of Polyurethane Materials: Multi-Stage Degradation Method

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Material and methods

Materials

PUFs waste (supplied by Sinomax (Zhejiang) Polyurethane Technology Limited.) uses diethanolamine (supplied by Shanghai Aladdin Biochemical Technology Co., Ltd.) and succinic acid (supplied by Shanghai Aladdin Biochemical Technology Co., Ltd.) as degradation agent for multi-stage degradation. The model molecules 1,3-diphenylurea (DPU, supplied by Shanghai Aladdin Biochemical Technology Co., Ltd.).In the production of regenerated foam, traditional petroleum-based polyol (PPG5623, supplied by Zhejiang Hengfeng New Material Co., Ltd.), 2,4-toluene diisocyanate (TDI, supplied by Shanghai Aladdin Biochemical Technology Co., Ltd.), surfactant (silicone oil, supplied by Shanghai Aladdin Biochemical Technology Co., Ltd.), foaming agent (distilled water) Catalysts (triethylamine and stanous octanoate, Shanghai Aladdin Biochemical Technology Co., Ltd.), ethanolamine, diethylenetriamine, ethylene glycol, diethylene glycol (EA, DETA, EG, DEG, supplied by Shanghai Aladdin Biochemical Technology Co., Ltd.), glutaric acid, adipic acid, sebacic acid (supplied by Shanghai Aladdin Biochemical Technology Co., Ltd.).

Recycling of polyurethane foams.

500 g DEA and 2500 g VP (PPG) are mixed and added into a 20 L glass reactor equipped with a decompression device, a heating device, a condensation reflux device and a mechanical stirring device. Firstly, the temperature is raised to 160 ^{o}C, and 5000 g PUFs fragments and 2500 g VP (PPG) are continuously injected into the reactor at a rate of about 70-120 g/min, which takes about 60-100 min. After 1 hours of continuous reaction, the temperature is raised to 180 ^{o}C and 1000 g SA are continuously injected into the reactor at a rate of about 30-50 g/min. After continuous reaction for 1.5 hours, the reaction can be stopped and discharged to obtain recovered polyol (without post-treatment such as separation and purification). DEA/PUFs weight ratio of 0.1, SA/PUFs weight ratio of 0.2.

Characterization methods for polyols

The acid value (AV) was determined in accordance with the ASTM D4662-08 standard. Approximately 2 g of polyol was dispersed in 50 mL of ethanol in a 100 mL Erlenmeyer flask. Titrations were conducted using 0.1 N NaOH solution and the end point determined using a digital pH meter (HI 2211 pH/ORP−Hanna Instruments), equipped with a HI 1043B probe. The AV was calculated using equation 1.

$$AV=(A-B)\times 56.1\times N/W \qquad (1)$$

where A is the volume of NaOH solution required for the titration of the sample (mL); B is the volume of NaOH solution required for the titration of the blank (mL); N is the normality of the NaOH solution; and W is the weight of the sample (g).

The hydroxyl number (HV) was determined in accordance with the ASTM D4274-05 standard in which the esterification process is catalyzed by imidazole. Titrations were conducted using 0.5 N NaOH solution. The HV was corrected taking into account the AV and calculated according to equation 2.

$$HV=((A-B)\times 56.1\times N)/W+AV \qquad (2)$$

Where A is the volume of NaOH solution required for the titration of the sample (mL); B is the volume of NaOH solution required for the titration of the blank (mL); N is the normality of the NaOH solution; W is the weight of the sample (g); and AV is the acid value of the sample (mg KOH/g).

Preparation of regenerated flexible polyurethane foam (RPUF).

Take X g of recovered polyol (RP), (100-X) g of virgin polyol (VP), 3.2 g of H_2O, 0.8 g of silicone oil, 0.05 g of triethylamine, 0.2 g of diethanolamine, and 0.14 g of stannous octanoate and place them in a plastic beaker. Use a high-speed stirring plate to stir at 2000 rpm for 20 s until a uniform dispersion is formed; Take 46 g TDI and add it to the dispersion solution. Continue to use the high-speed stirring plate to stir at 2000 rpm for 10 seconds, and then quickly pour the mixture into the mold for molding. After the foaming height no longer changes, move it into an oven at 70 ^oC and take it out after curing for 22 hours to obtain RPUF. X represents the replacement amount of RP.

Characterization methods for RPUF

PUF specimens (100 cm x 100 cm) were cut. Mechanical properties of RPUFs by GB/T 10802-2006, GB/T 6344-2008, GB/T 6342-1996, GB/T 6669-2008, GB/T 6670-2008, GB/T 10807-2006. The data given in the Results and Discussion part represent mean values.

Nuclear magnetic resonance (NMR).

^1H NMR spectra were recorded using a Bruker AVANCE NEO 600 MHz instrument (Bruker Corporation, USA) at room temperature in DMSO-d_6. Chemical shifts are given in ppm relative to a DMSO-d6 residual peak.

Gas chromatography-Mass spectrometry (GC-MS)

The instrument model is GCMS-QP2010 Plus (chromatographic columnmodel: DB-17MS; chromatographic column size: 60 m × 250 µm × 0.25 µm).

Results and discussion

Screening of degradation agents for MSD

Table S1 Effects of different glycolysis agents and ammonolysis agents on RP.

entry	degradation agent	X[a]/PUFs(wt/wt)	time[b] (h)	η (mPa·s)	remark
1	Diethanolamine (DEA)	0.1	90	9.7k	
2	Ethanolamine (EA)	0.1	110	12.3k	
3	Diethylenetriamine (DETA)	0.1	80	9.0k	The obtained RP has a strong amine odor
4	Ethylene glycol (EG)	0.1	/	/	
5	Ethylene glycol (EG)	0.5	110	8.9k	
6	Diethylene glycol (DEG)	0.1	/	/	
7	Diethylene glycol (DEG)	0.5	120	10.4k	

[a] X: degradation agent

[b] Time required to put all foam into a 20L reactor.

Table S2 Effects of different acidolysis agents on RP.

entry	degradation agent	HV (mgKOH·g^{-1})	AV (mgKOH·g^{-1})	η (mPa·s)
1	Succinic acid	37.9	1.73	8.7k
2	Glutaric acid	21.6	3.57	16.7k
3	Adipic acid	4.6	8.72	/
4	Sebacic acid	8.2	6.58	/
5	Compound acid[c]	28.4	2.61	12.4k

[c] The compound acid is a mixture of succinic acid and glutaric acid in a molar ratio of 1: 1.

Table S3 Effects of different MSD agents on RP.

entry	primary degradation agent	secondary degradation agent	HV (mgKOH·g^{-1})	AV (mgKOH·g^{-1})	η (mPa·s)	remark
1	DEA	Succinic acid	57	0.72	2.9k	
2	DEA	Glutaric acid	36	6.09	3.5k	
3	DEA	Adipic acid	12	29.89	4.6k	
4	DEA	Sebacic acid	9	35.43	20k	
5	EA	Succinic acid	53	0.92	4.6k	
6	DETA	Succinic acid	77	0.57	2.6k	The obtained RP has a strong amine odor

Synthesis and characterization of DMPC and DPU.

In order to better simulate the reaction of polyurethane foam in the process of multi-stage degradation, diethyl (4-methyl-1,3-phenylene) dicarbamate (DMPC) and 1,3-diphenylurea (DPU), which has a similar chemical environment with polyurethane foam, was selected as the small molecule model compound of urethane bond in this study. DMPC synthesized under the reaction conditions of low -temperature ultrasound and no catalyst, which avoids the influence of catalyst on the reaction of small molecule model compounds in later research. The synthetic method is show in Fig. S1a) The synthesis steps are as follows: First, 250 mL absolute ethanol is weighed and transferred to a 500 mL round bottom flask equipped with a constant pressure drop funnel, and 25 g TDI is weighed and transferred to a constant pressure drop funnel, and placed in an ultrasonic cell containing an ice water bath. The reaction temperature is kept at 0 ^{o}C -5 ^{o}C, and the reaction lasts for 2 hours. Then, the obtained reactant was subjected to spin evaporation at 55 ^{o}C to obtain a white viscous solution, which was then transferred to a 100 ^{o}C blast oven for drying treatment to finally obtain a white powder, namely DMPC. The characterization results of ^{1}H NMR (in DMSO-d_6) is shown in Fig. S1b. DPU, provided by Shanghai Aladdin Biochemical Technology Co., Ltd., its ^{1}H NMR (in DMSO-d_6) characterization results are shown in Fig. S1c.[1]

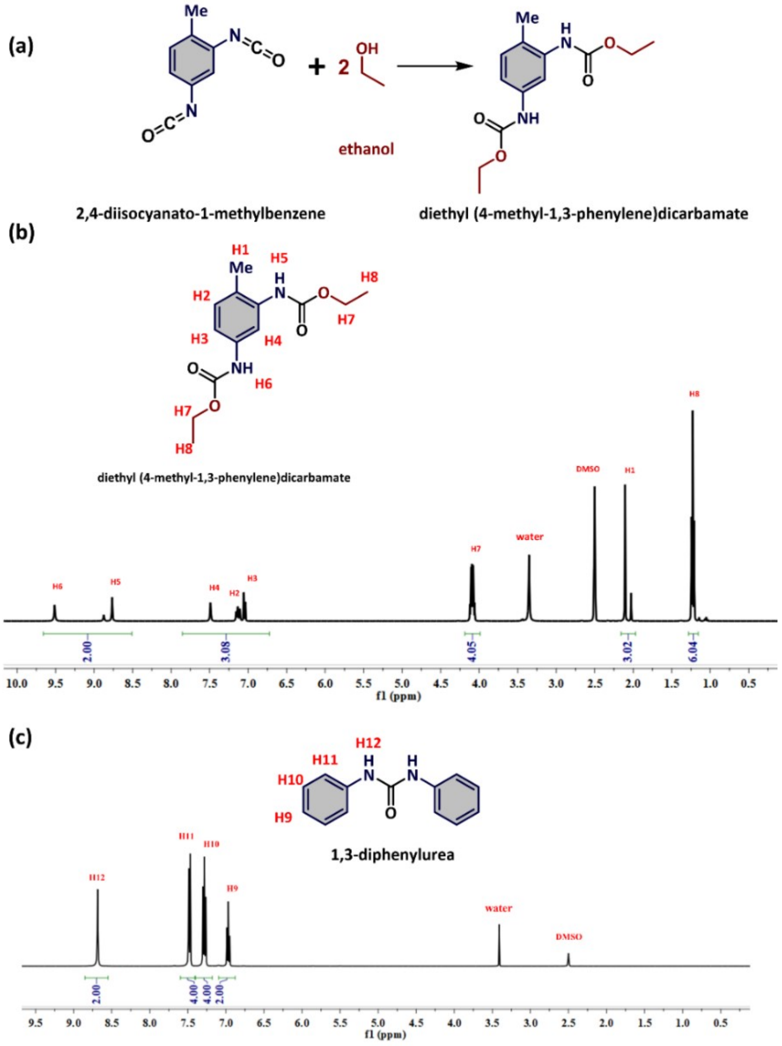


Fig. S1 (a) reaction equation of DMPC synthesis, (b) ^{1}H NMR (in DMSO-d_6) spectra of DMPC, (c) ^{1}H NMR (in DMSO-d_6) spectra of DPU.

Multi-stage degradation of carbamate bonds in model molecule DMPC

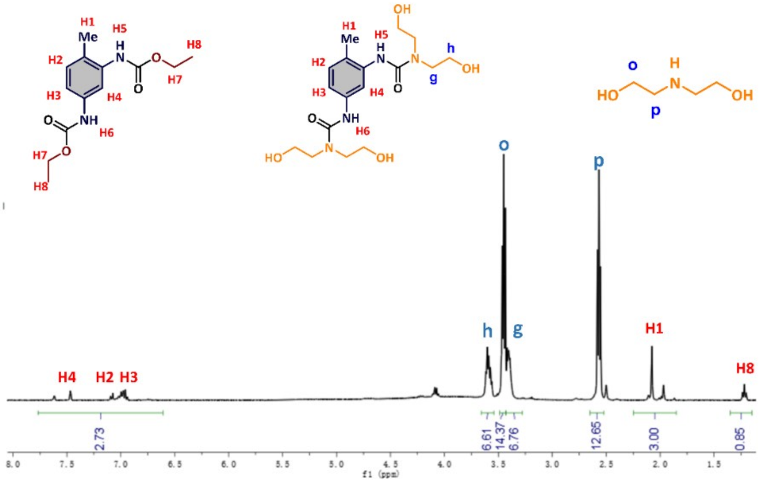
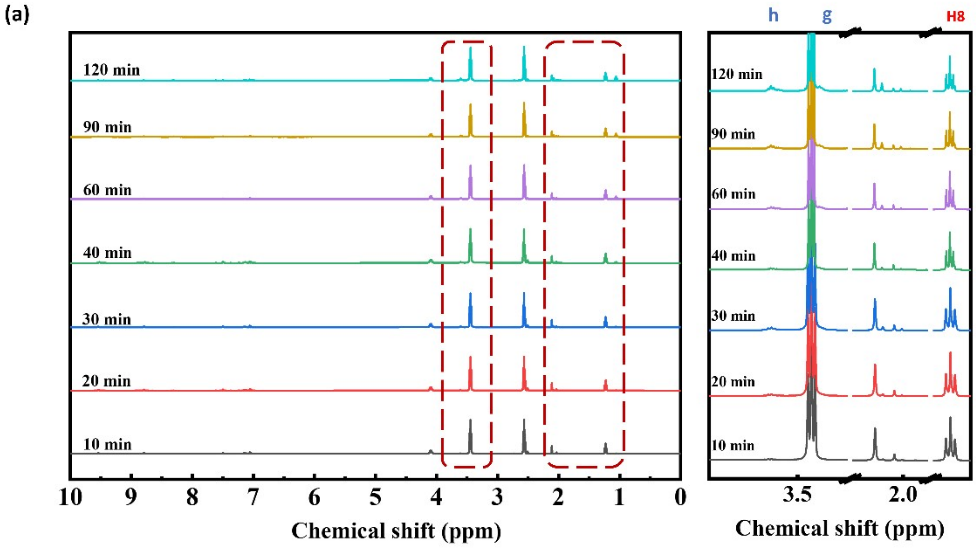
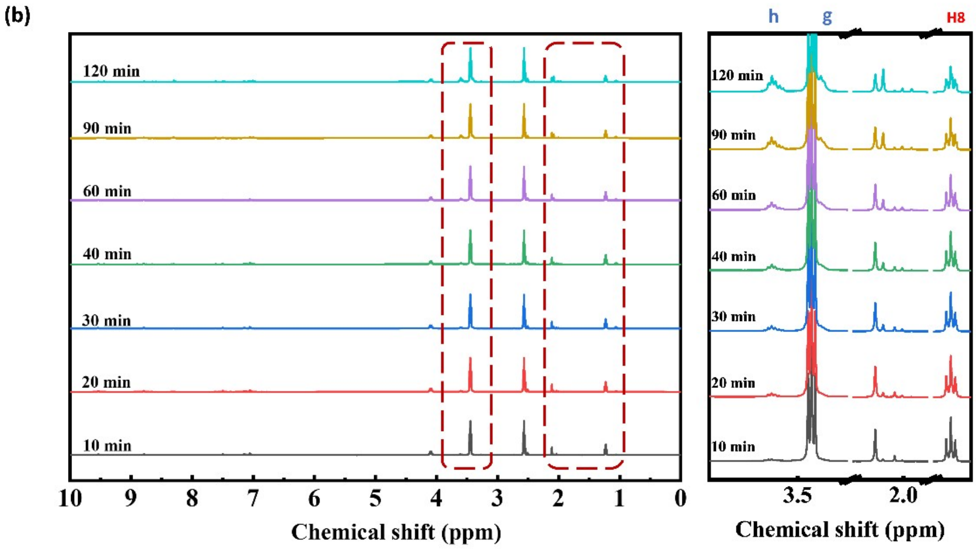


Fig. S2 ^{1}H NMR (in DMSO-d_6) spectrum of **DMPC** after reaction at 120minutes and 160 ^{o}C.





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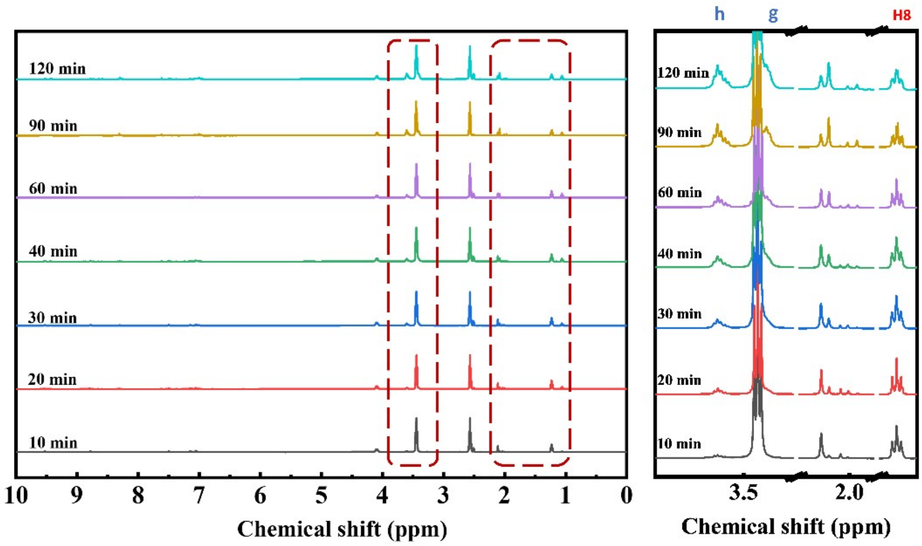
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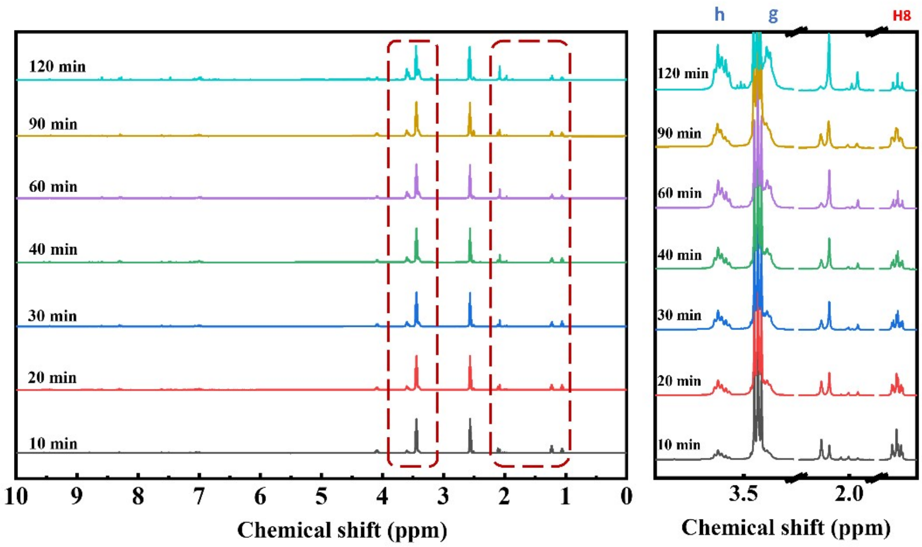
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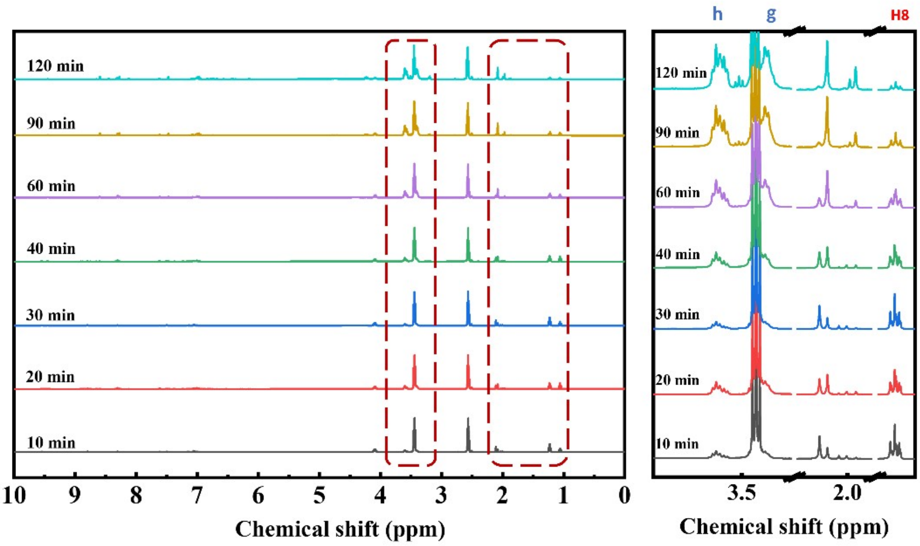
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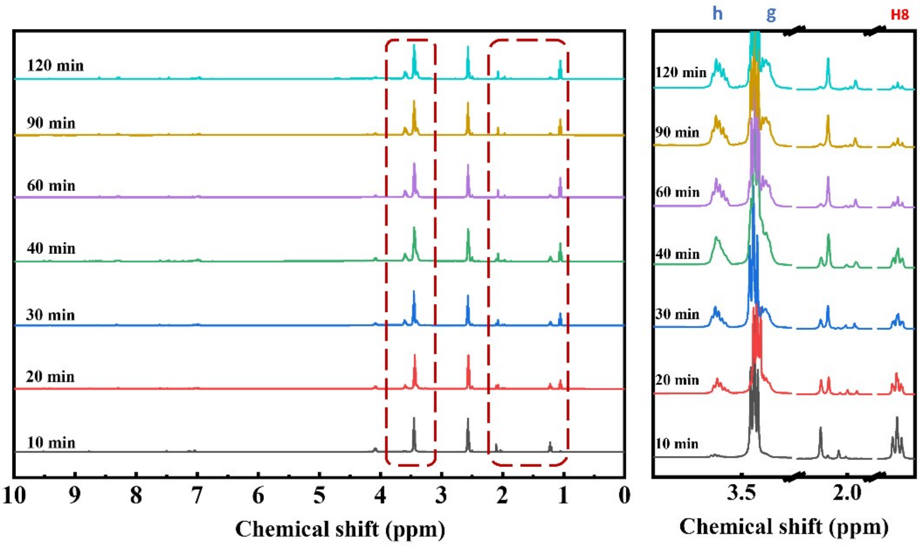
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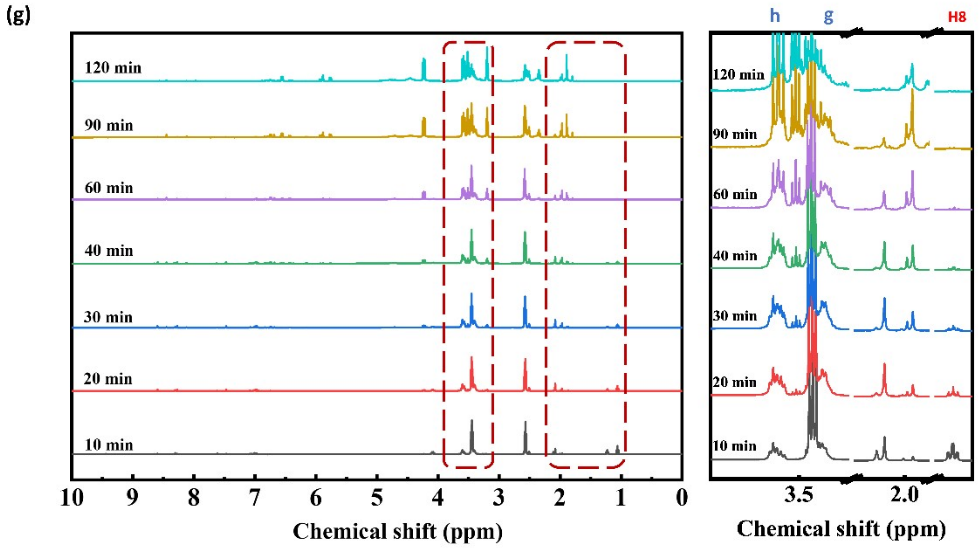


Fig. S3 ^{1}H NMR (in DMSO-d_6) spectrum of **DMPC** after reaction at different times and temperatures (a)120 ^{o}C, (b)130 ^{o}C, (c)140 ^{o}C, (d)150 ^{o}C, (e) 160 ^{o}C, (f) 170 ^{o}C, (g) 180 ^{o}C.

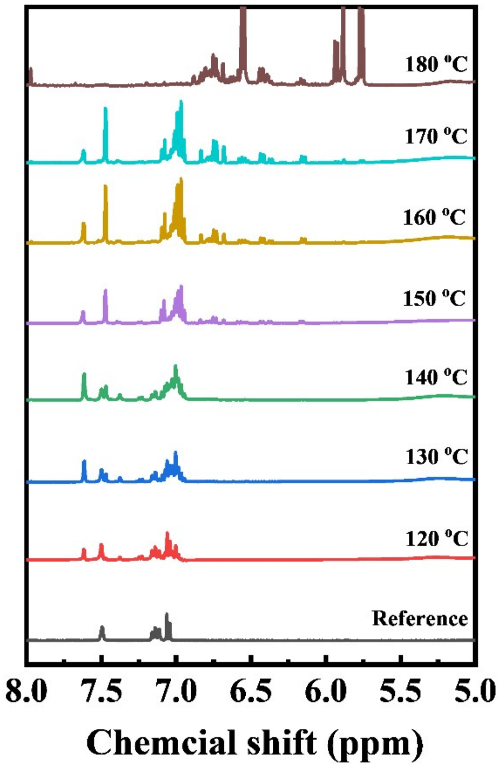
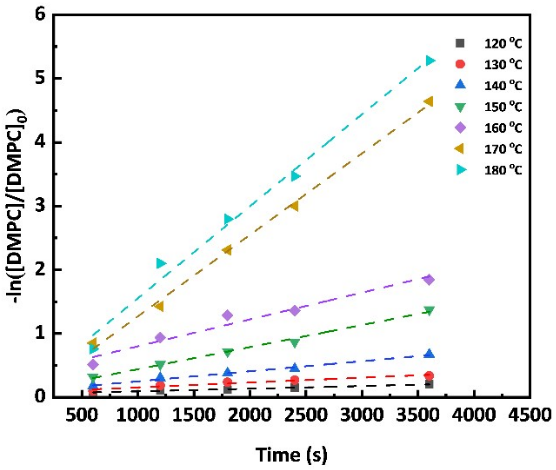


Fig. S4 ^{1}H NMR (in DMSO-d_6) spectrum of **DMPC** after reaction at different temperatures for 120min.



180 °C $y = 1.44 \times 10^{-3} x - 0.111$ $R^2 = 0.988$

170 °C $y = 1.28 \times 10^{-3} x - 0.001$ $R^2 = 0.997$

160 °C $y = 4.21 \times 10^{-4} x - 0.380$ $R^2 = 0.957$

150 °C $y = 3.47 \times 10^{-4} x - 0.094$ $R^2 = 0.993$

140 °C $y = 1.58 \times 10^{-4} x - 0.092$ $R^2 = 0.990$

130 °C $y = 7.55 \times 10^{-5} x - 0.081$ $R^2 = 0.945$

120 °C $y = 4.15 \times 10^{-5} x - 0.053$ $R^2 = 0.980$

Fig. S5 Plots of –ln ([DMPC]/[DMPC]$_0$) versus time (t) at different temperatures from 120 °C to 180 °C.

k at each temperature was determined by its slope value. This reaction can be described in terms of pseudo-first kinetics (supplementary equation 3).

$$\frac{d[DMPC]}{dt} = -k[DMPC] \qquad (3)$$

If the initial concentration of DMPC is described as [DMPC]$_0$, supplementary equation 1 can be transformed to supplementary equation 4.

$$ln\frac{[DMPC]}{[DMPC]_0} = -kt \qquad (4)$$

To calculate the activation energy for each reaction, the Arrhenius plots were made using *kexp*. $k = -A\exp(-E_a/RT)$ (*A*: pre-exponential factor, E_a: activation energy, *R*: universal gas constant) $R = 8.314$ J K^{-1} mol^{-1} was used to calculate the activation energies from the slope values. [2-4]

Multi-stage degradation of urea bonds in model molecule DPU.

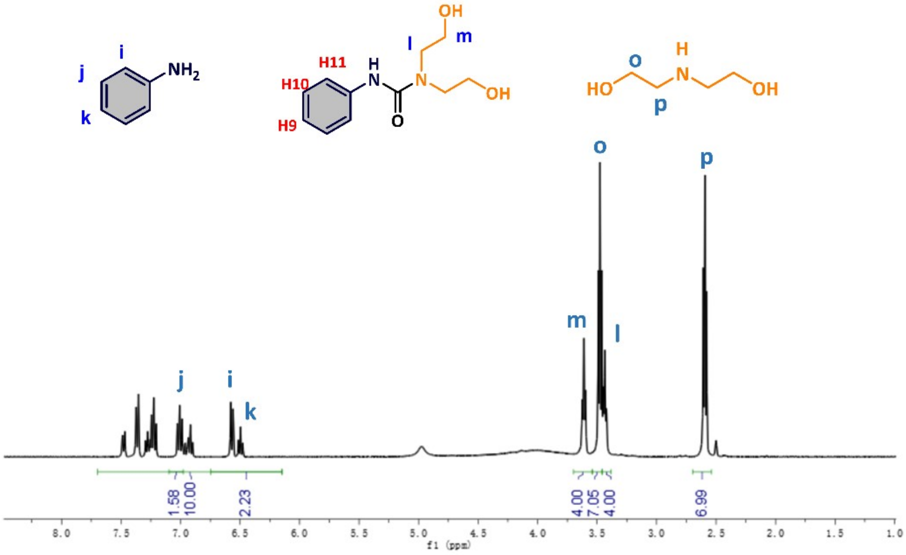


Fig. S6 ^{1}H NMR (in DMSO-d_6) spectrum of ***DPU** after reaction at 120minutes and 130 ^{o}C.

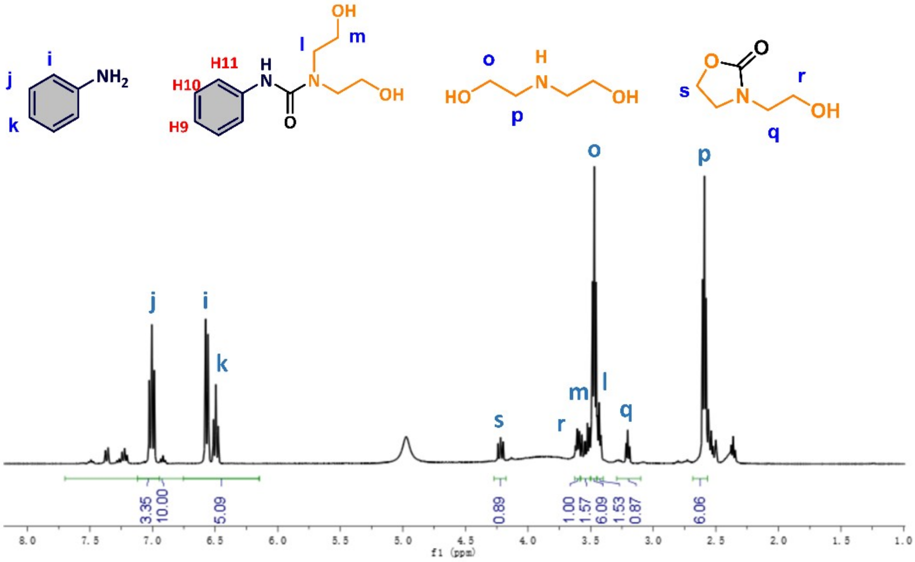


Fig. S7 ^{1}H NMR (in DMSO-d_6) spectrum of ***DPU** after reaction at 120minutes and 180 ^{o}C.

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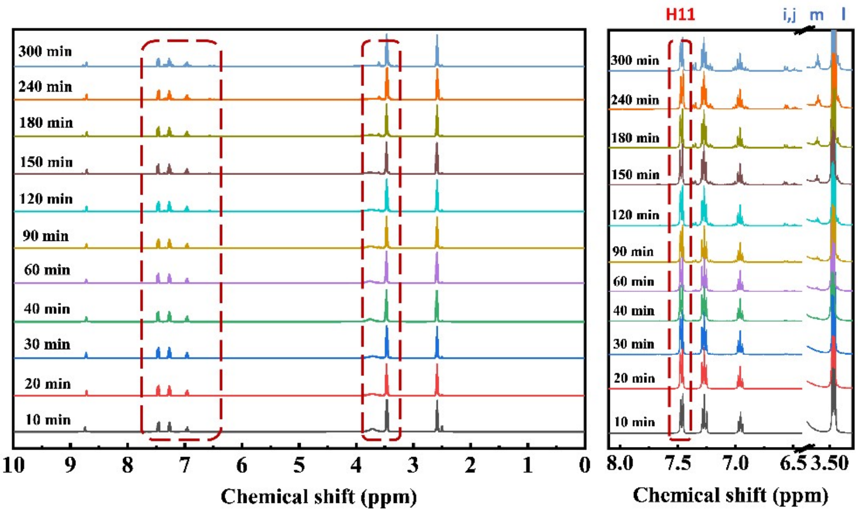
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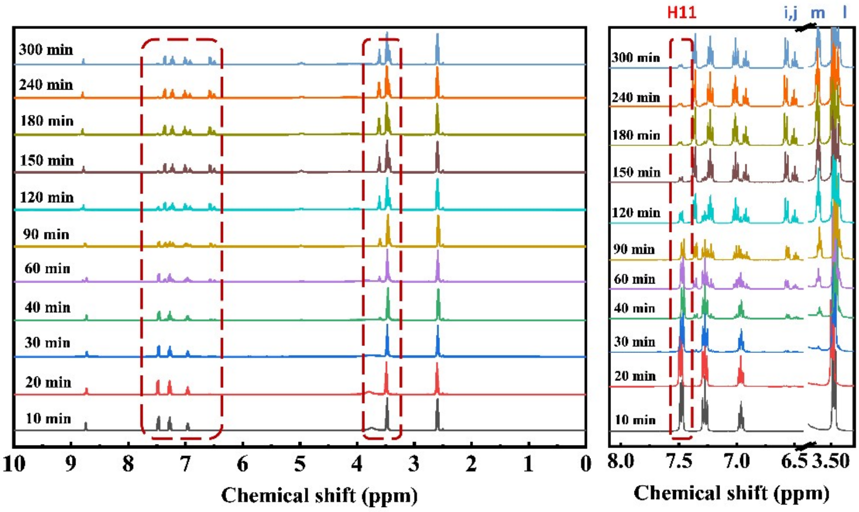
(b)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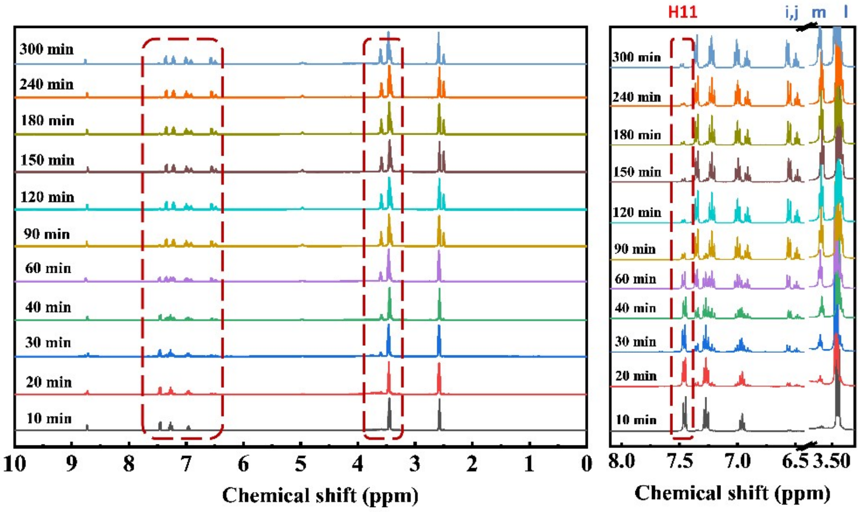
(c)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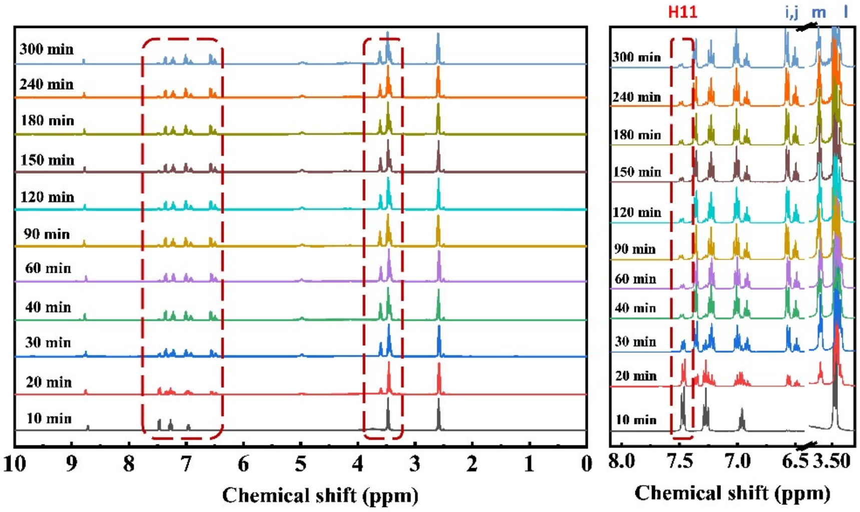
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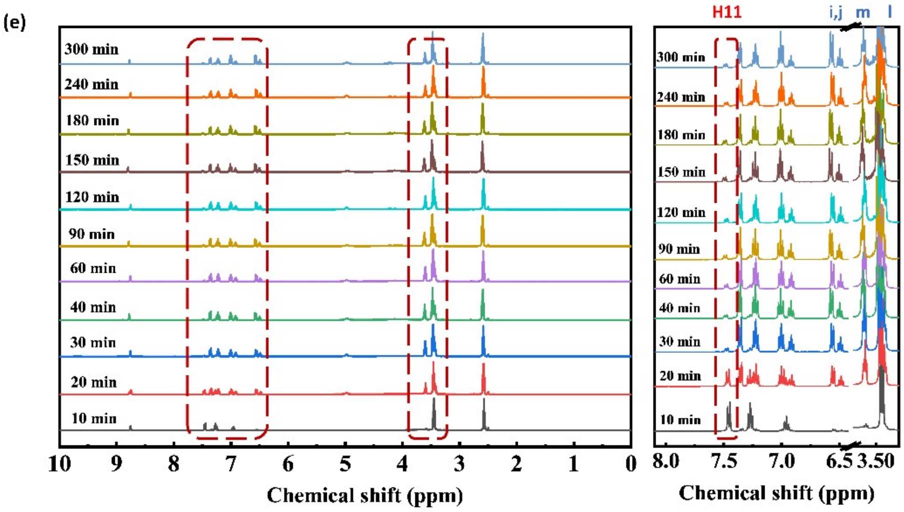
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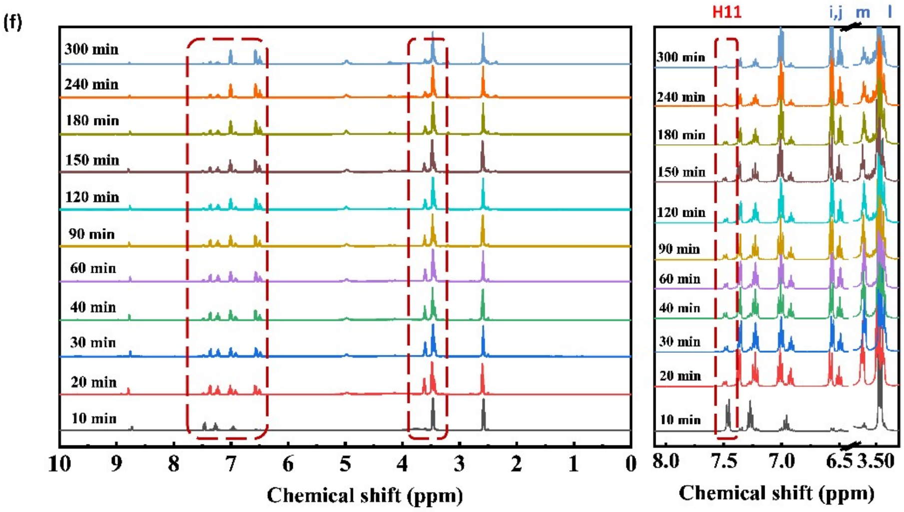
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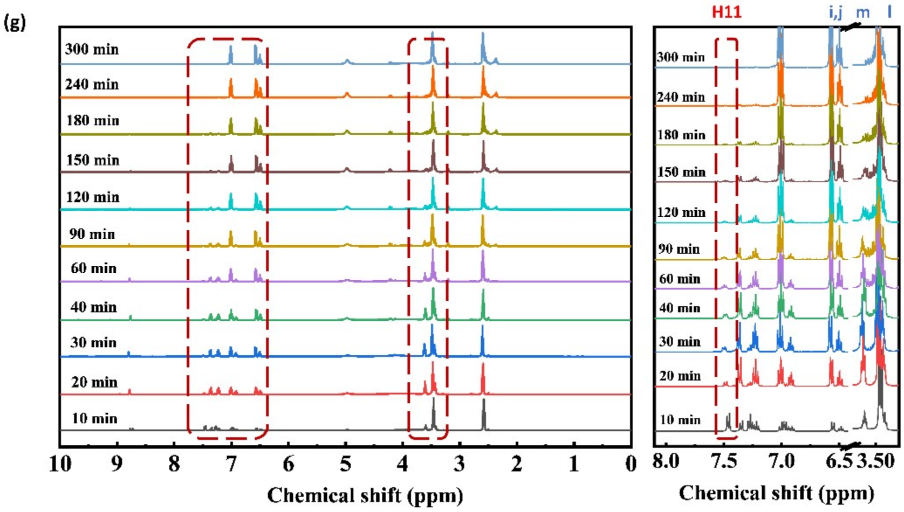
Chemical shift (ppm)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8.0 7.5 7.0 6.5 3.50
Chemical shift (ppm)

Fig. S8 ^{1}H NMR (in DMSO-d_6) spectrum of ***DPU** after reaction at different times and temperatures (a)120 ^{o}C, (b)130 ^{o}C, (c)140 ^{o}C, (d)150 ^{o}C, (e) 160 ^{o}C, (f) 170 ^{o}C, (g) 180 ^{o}C.

note: *DPU represents benzene ring content in DPU.

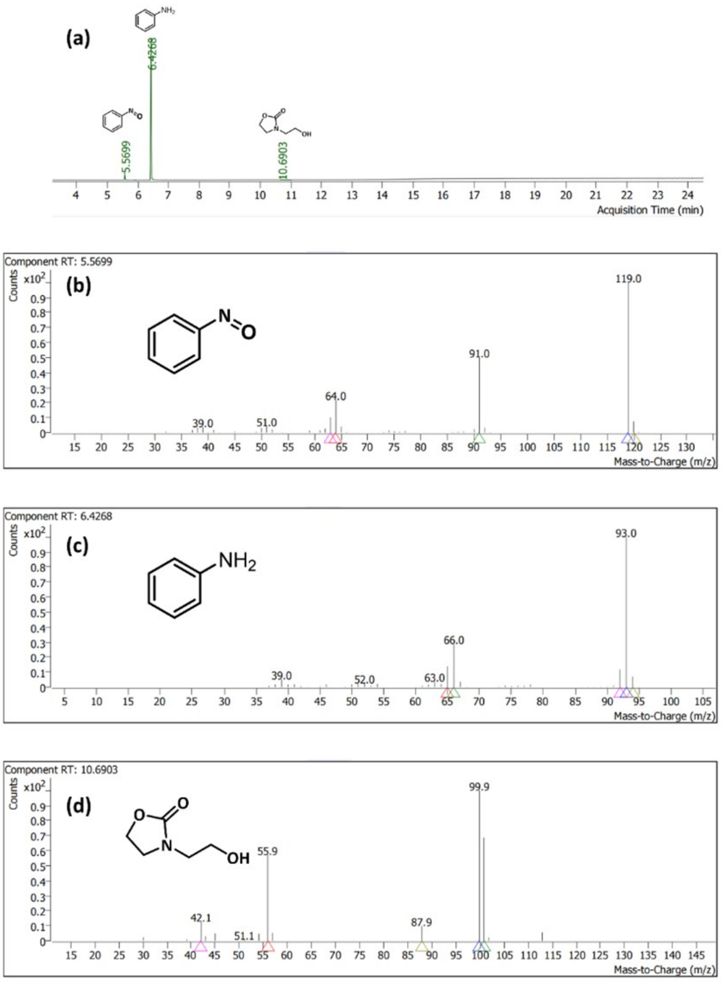


Fig. S9 (a)GC-MS chromatogram of DPU at 160 ℃ and 300 minutes, (b-d) Mass spectrum of the peaks.

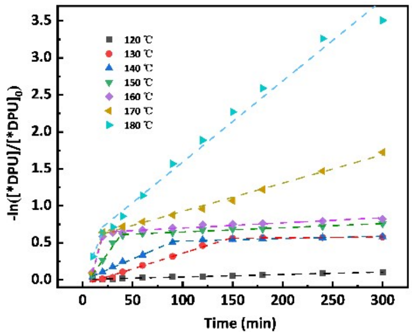


Fig. S10 Plots of –ln ([*DPU]/[*DPU]$_0$) versus time (t) at different temperatures from 120 ℃ to 180 ℃.

180 °C $y = 3.20 \times 10^{-2}x - 0.005 \quad R^2 = 1$

170 °C $y = 5.52 \times 10^{-2}x - 0.464 \quad R^2 = 1$

160 °C $y = 4.82 \times 10^{-2}x - 0.137 \quad R^2 = 1$

150 °C $y = 1.88 \times 10^{-2}x - 0.115 \quad R^2 = 0.961$

140 °C $y = 5.78 \times 10^{-3}x - 0.008 \quad R^2 = 0.992$

130 °C $y = 4.23 \times 10^{-3}x - 0.064 \quad R^2 = 0.991$

120 °C $y = 3.31 \times 10^{-4}x + 0.006 \quad R^2 = 0.991$

180 °C $y = 1.10 \times 10^{-2}x + 0.495 \quad R^2 = 0.981$

170 °C $y = 3.82 \times 10^{-3}x + 0.544 \quad R^2 = 0.993$

160 °C $y = 6.95 \times 10^{-4}x + 0.518 \quad R^2 = 0.991$

150 °C $y = 5.39 \times 10^{-4}x + 0.596 \quad R^2 = 0.972$

140 °C $y = 2.33 \times 10^{-4}x + 0.514 \quad R^2 = 0.995$

Fig. S11 Plots of –ln ([*DPU]/[*DPU]$_0$) versus time (t) (a) the first step reaction, (b) the second step reaction.

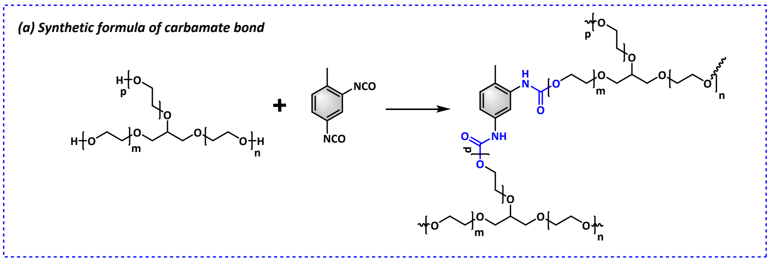
k at each temperature was determined by its slope value. This reaction can be described in terms of pseudo-first kinetics (supplementary equation 5).

$$\frac{d[*DPU]}{dt} = -k[*DPU] \qquad (5)$$

If the initial concentration of *DPU is described as [*DPU]$_0$, supplementary equation 1 can be transformed to supplementary equation 6.

$$ln\frac{[*DPU]}{[*DPU]_0} = -kt \qquad (6)$$

To calculate the activation energy for each reaction, the Arrhenius plots were made using *kexp*. *k* = -*A*exp (-E_a/RT) (*A*: pre-exponential factor, E_a: activation energy, *R*: universal gas constant) *R* = 8.314 J K^{-1} mol^{-1} was used to calculate the activation energies from the slope values.[2-4]



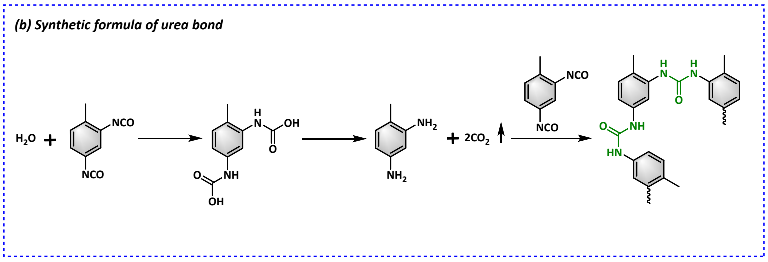


Fig. S12 Reaction formula of polyurethane foam synthesis (a) Synthetic formula of carbamate bond, (b) Synthetic formula of urea bond.

Table S4 Dissociation degree of DMPC-DEA-120/130/140/150/160/170/180 °C-60 min and DMPC-DEA-120/130/140/150/160 °C-120 min.

Temperature/ °C	dissociation degree of DMPC/% (60min)	dissociation degree of DMPC/% (120min)
120	18.55	26.95
130	28.62	49.26
140	48.94	68.91
150	74.73	86.24
160	84.2	99.17
170	99.04	/
180	99.49	/

Table S5 Dissociation degree of *DPU-DEA-120/130/140/150/160/170/180 °C-60 min and *DPU-DEA-120/130/140/150/160 °C-120 min.

Temperature/ °C	dissociation degree of *DPU/% (30min)	dissociation degree of *DPU/% (120min)
120	1.33	4.50
130	3.17	37.17
140	16.00	41.83
150	39.50	49.00
160	42.83	46.33
170	48.83	61.67
180	51.00	84.83

Notes and references

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