

Supporting information

Synthesis of Polyurea Thermoplastics through a Nonisocyanate Route Using CO₂ and Aliphatic Diamines

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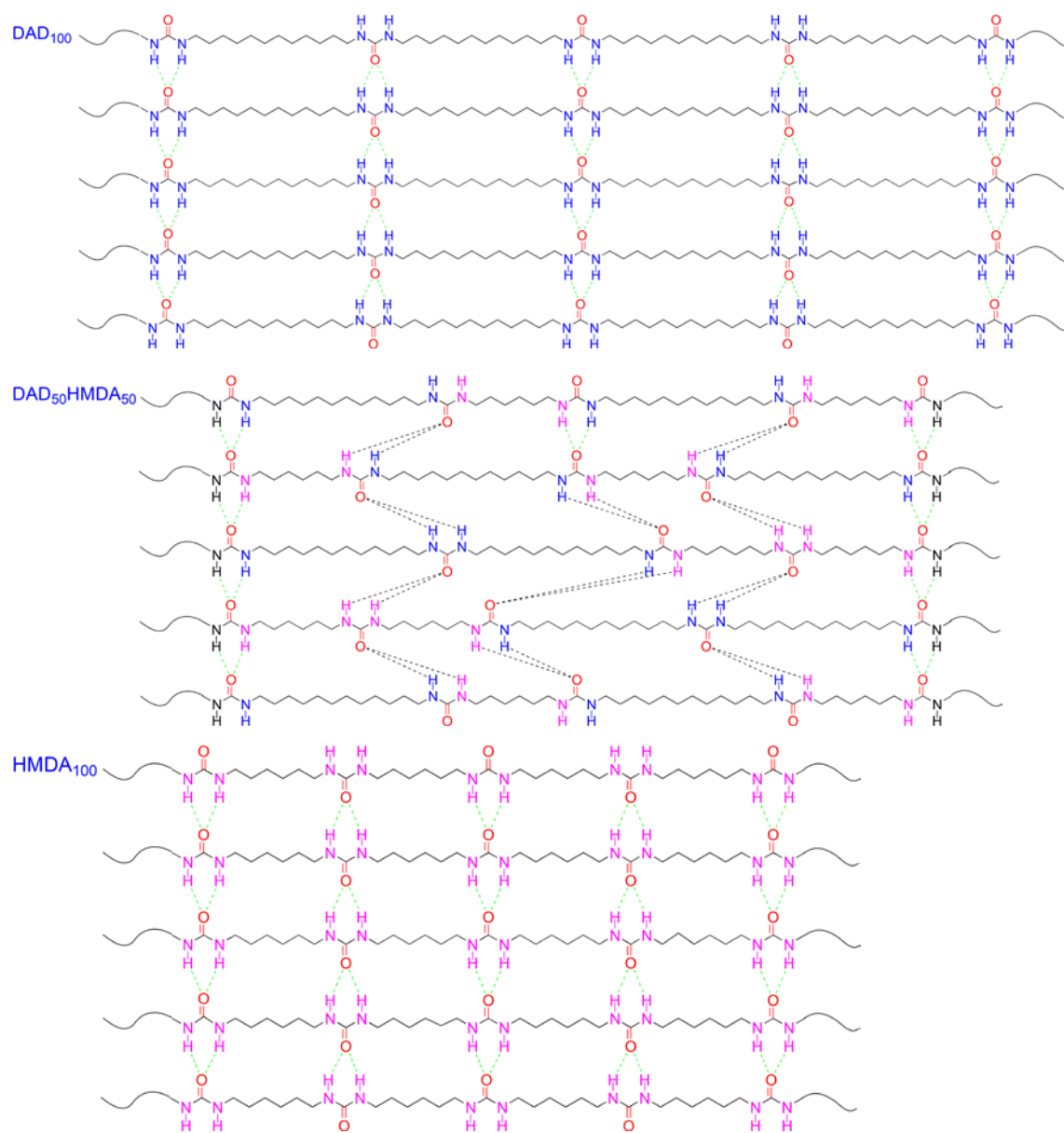
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Materials. 1,12-Diaminododecane (DAD) was purchased from TCI. 1,10-Diaminodecane (DA10), 1,8-octanediamine (DA8), 1,6-hexamethylene diamine (HMDA) and 1,4-butanediamine (DA4) were purchased from Sanbang Pharmaceutical Technology. Cyclohexane, tetrahydrofuran (THF), dimethylformamide (DMF), *N*-methyl-2-pyrrolidinone (NMP), dimethyl sulfoxide (DMSO), acetone, dichloromethane (CH₂Cl₂), methanol (CH₃OH), acetic acid (CH₃COOH), and formic acid (HCOOH) were purchased from Beijing Chemical Reagent. Trifluoroethanol (TFE), trifluoroacetic acid (TFA) and hexafluoroisopropanol (HFIP) were purchased from Aladdin Reagent. Hexafluoroisopropanol-D₂ (HFIP-D₂) was purchased from J&K. All those chemicals were used as received without further purification. Carbon dioxide (CO₂) and nitrogen (N₂) with purity of >99.999% were purchased from Changchun JuYang Gas Company. Deionized water (H₂O) was used.

Characterization. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet iS50 FTIR spectrometer using KBr pellet pressing method in a range of 400 to 4000 cm⁻¹. ¹H and ¹³C NMR were examined on a Bruker AV-400 and HFIP-D₂ was selected as a solvent to dissolve samples for analysis. X-ray diffraction (XRD) was investigated on a Bruker D8 ADVANCE instrument using CuK α radiation from 2 θ = 10° to 70°. Differential scanning calorimeter (DSC) curves were collected with a PerkinElmer apparatus at a heating/cooling/heating rate of 10 °C/min from -50 to 250 °C or -50 to 300 °C in a continuous N₂ flow. Thermogravimetric analysis (TGA) was performed on the PerkinElmer Thermal instrument at a heating rate of 10 °C/min from 50 to 500 °C under continuous N₂ flow conditions. Mechanical properties, such as tensile strength and Young's modulus, were investigated by a tensile test using an Instron-1121 machine at 25 °C with a crosshead speed of 5 mm/min. Polymer specimens were prepared in a dumbbell shape with a dimension of 30 mm \times 4 mm \times 1.6 mm by the melt-press method according to GB/T 1040-2006 Type 5A standard. For each PUa sample, the data are reported with the average value of at least five different specimens. The solubility was examined according to the same method described previously.⁵⁴ Swelling test was performed by immersing the dumbbell shape sample (30 mm \times 4 mm \times 1.6 mm) in CH₂Cl₂ or H₂O at 25 °C for 96 h. The swelling capacity in CH₂Cl₂ or H₂O was determined by a change in weight before and after the swelling. Matrix-assisted laser desorption and ionization time-of-flight (MALDI-TOF) mass spectra were collected on Bruker Autoflex III mass spectrometer equipped with a 355 nm Nd : YAG laser with a 5 ns pulse duration in positive ion mode and 2,5-dihydroxybenzoic acid (2,5-DHB) was selected as the matrix. The solid powder of DAD₃₇HMDA₆₃ was dispersed in ethanol, ultrasound for 2 h and then kept with no ultrasound for 24 h. The resulting sample dissolved in ethanol was examined by MALDI-TOF.



Scheme S1. Intermolecular hydrogen bonds formed in PUAs of DAD₁₀₀, DAD₅₀HMDA₅₀, HMDA₁₀₀.

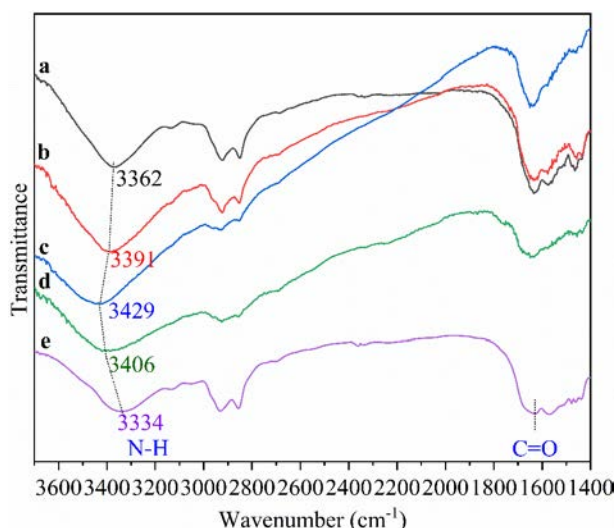
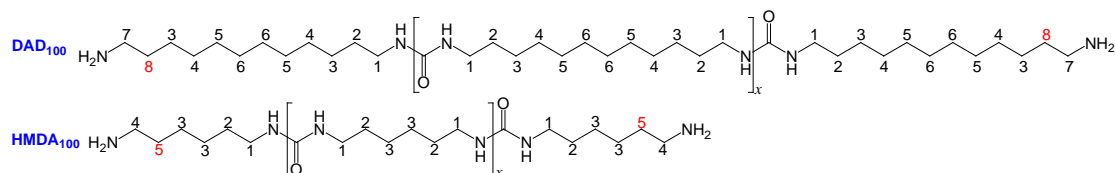


Figure S1. FTIR spectra of (a) DAD₁₀₀, (b) DAD₆₃HMDA₃₇, (c) DAD₅₀HMDA₅₀, (d) DAD₃₇HMDA₆₃, (e) HMDA₁₀₀.

Determination of molecular weight of PUas samples

The number average molecular weight (M_n) of DAD₁₀₀ and HMDA₁₀₀ were calculated from the ¹H NMR data with the following equations according to the literature ^{1,2}. The NMR data used and the calculation results are presented later (Figure 2, Table S1). The hydrogen in the α C-position to the terminal amino group is overlapped with that in the α C-position to the nitrogen of the urea linkage, so the hydrogen in the β C-position to the terminal amino group and the β C-position to the nitrogen of the urea linkage were used as below scheme and equations S1, S2.



$$(4x + 4) / 4 = I_{CH_2CH_2NH} / I_{CH_2CH_2NH_2 \text{ (chain-ends)}} \quad \text{Eq. S1}$$

$$M_n = M_{\text{repeating-unit}} \times x + M_{\text{chain-ends-1}} + M_{\text{chain-ends-2}} \quad \text{Eq. S2}$$

where:

x is the number of repeating unit. $4x + 4$ is the number of hydrogen in the β C-position to the nitrogen of the urea linkage. 4 is the number of hydrogen in β C-position to the terminal amino group.

$I_{CH_2CH_2NH}$ is the relative integration of the peaks arising from protons in β C-position to the nitrogen of the urea linkage for peak 2 in Figure 2a (DAD₁₀₀) and for peak 2 in Figure 2c (HMDA₁₀₀).

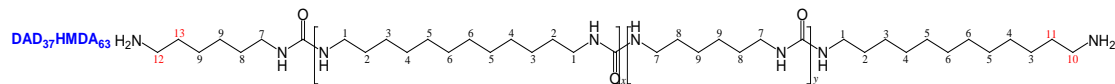
$I_{CH_2CH_2NH_2 \text{ (chain-ends)}}$ is the relative integration of the peaks arising from protons in β C-position to the terminal amino group for peak 8 in Figure 2a (DAD₁₀₀) and for peak 5 in Figure 2c (HMDA₁₀₀).

$M_{\text{repeating-unit}}$ is the molecular weight of the repeating unit (226.4 g/mol for DAD₁₀₀; 142.2 g/mol for HMDA₁₀₀).

$M_{\text{chain-ends-1}}$ is one of the molecular weight of the chain-ends (199.4 g/mol for DAD₁₀₀; 115.2 g/mol for HMDA₁₀₀).

$M_{chain-ends-2}$ is the other of the molecular weight of the chain-ends (227.4 g/mol for DAD₁₀₀; 143.2 g/mol for HMDA₁₀₀).

We assume that one end of the chain is the DAD segment and the other end of the chain is the HMDA segment as below described.



The number average molecular weight (M_n) of DAD₃₇HMDA₆₃ was calculated from the ¹H NMR data with the following equations S3-5:

$$(4x + 4y + 4)/4 = (I_{CH_2CH_2NH-DAD} + I_{CH_2CH_2NH-HMDA}) / (I_{CH_2CH_2NH_2 (chain-ends)-DAD} + I_{CH_2CH_2NH_2 (chain-ends)-HMDA}) \quad \text{Eq. S3}$$

$$x / y = 37 / 63 \quad \text{Eq. S4}$$

$$M_n = M_{repeating-unit-DAD} \times x + M_{repeating-unit-HMDA} \times y + M_{chain-ends-1} + M_{chain-ends-2} \quad \text{Eq. S5}$$

where:

x and y are the numbers of repeating unit in DAD and HMDA segment, respectively. $4x + 4y + 4$ is the number of hydrogen in β C-position to the nitrogen of the urea linkage in DAD and HMDA segments. 4 is the number of hydrogen in β C-position to the terminal amino groups.

$I_{CH_2CH_2NH-DAD}$ and $I_{CH_2CH_2NH-HMDA}$ are the relative integrations of the peaks arising from protons in β C-position to the nitrogen of the urea linkage in the DAD and HMDA segments (peak 2 and peak 8 in Figure 2b), respectively.

$I_{CH_2CH_2NH_2 (chain-ends)-DAD}$ and $I_{CH_2CH_2NH_2 (chain-ends)-HMDA}$ are the relative integrations of the peaks arising from protons in β C-position to the terminal amino group in the DAD and HMDA segments (peak 11 and peak 13 in Figure 2b), respectively.

$M_{repeating-unit-DAD}$ and $M_{repeating-unit-HMDA}$ are the molecular weights of the repeating unit in DAD (226.4 g/mol) and HMDA (142.2 g/mol) segments, respectively.

$M_{chain-ends-1}$ and $M_{chain-ends-2}$ are the molecular weights of the chain-ends, one end of the chain is the DAD segment and the other end of the chain is the HMDA segment as illustrated in the above Scheme, the molecular weight of the chain-ends are 199.4 and 143.2 g/mol, respectively.

The number average molecular weights (M_n) so calculated are listed in Table S1.

Table S1. Calculated number average molecular weight (M_n) of PUas and OUas

Entry	Sample	M_n (g/mol)
1	DAD ₁₀₀	3553
2	DAD ₃₇ HMDA ₆₃	4534
3	HMDA ₁₀₀	1656
4	OUa-DAD ₁₀₀	823
5	OUa-DAD ₃₇ HMDA ₆₃	726
6	OUa-HMDA ₁₀₀	325

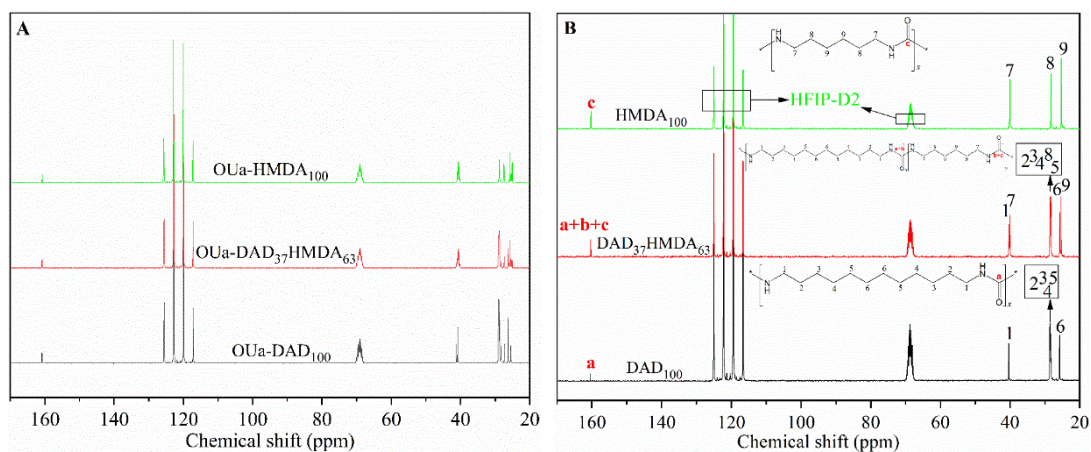


Figure S2. (A) ^{13}C NMR spectra of OUas of OUa-DAD₁₀₀ (bottom), OUa-DAD₃₇HMDA₆₃ (medium) and OUa-HMDA₁₀₀ (top). (B) ^{13}C NMR spectra of PUas of DAD₁₀₀ (bottom), DAD₃₇HMDA₆₃ (medium) and HMDA₁₀₀ (top).

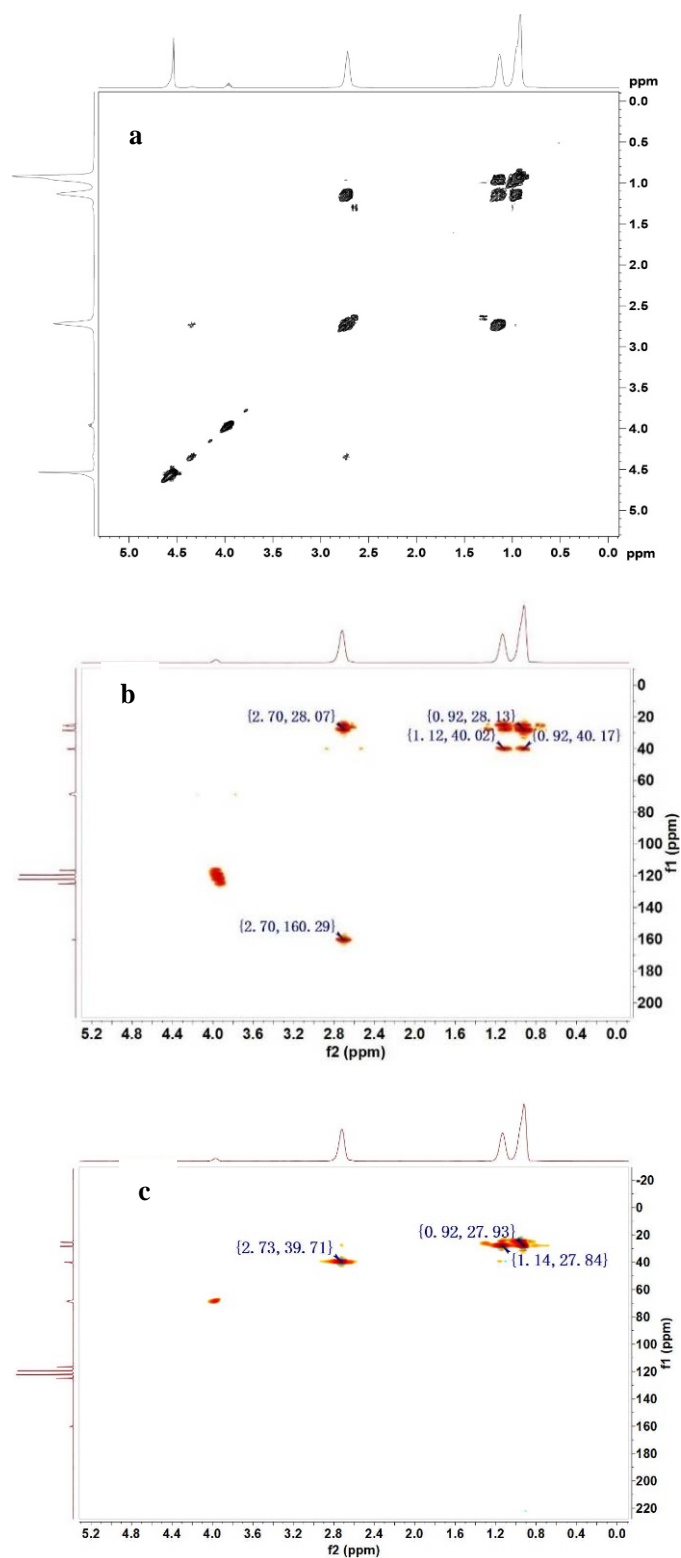


Figure S3. Two-dimensional NMR spectra of DAD₃₇HMDA₆₃. (a) ¹H-¹H correlation spectroscopy (COSY), (b) ¹H-¹³C heteronuclear multiple bond correlation (HMBC) and (c) ¹H-¹³C heteronuclear single quantum correlation (HSQC).

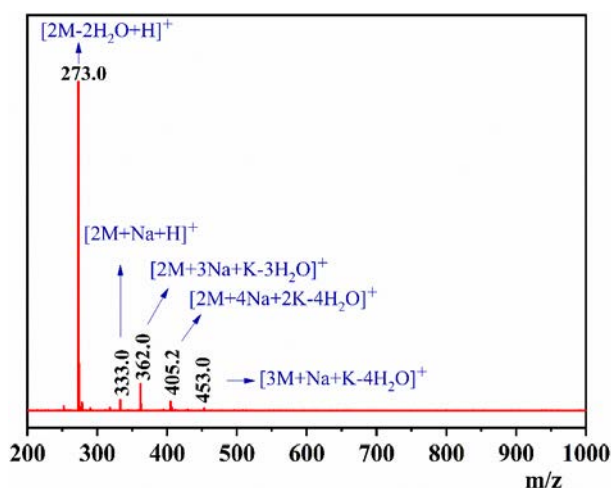


Figure S4. MALDI-TOF spectra of DAD₃₇HMDA₆₃ soluble in ethanol. “M” is MALDI matrix of 2,5-dihydroxybenzoic acid.

Matrix-assisted laser desorption and ionization time-of-flight (MALDI-TOF) mass spectra were collected on Bruker Autoflex III mass spectrometer equipped with a 355 nm Nd : YAG laser with a 5 ns pulse duration in positive ion mode and 2,5-dihydroxybenzoic acid (2,5-DHB) was selected as the matrix. The solid powder of DAD₃₇HMDA₆₃ was dispersed in ethanol, kept in a bath sonicator for 2 h, and then kept with no sonication for 24 h at room temperature. After centrifugation, a solid sample was obtained and dried at 120 °C, the mass of solid sample changed slightly before and after dissolving in ethanol. The sample dissolved in ethanol was examined by MALDI-TOF in the reflection mode with an acceleration voltage of 20 kV over the m/z 200-3000. There were neither monomers of DAD nor oligomers of DAD₃₇HMDA₆₃, and a series of ion peaks of MALDI matrix were observed (**Figure S4**), indicating that DAD and HMDA were completely polymerized into DAD₃₇HMDA₆₃.

Table S2. Solubility of PUAs in several solvents

Solvent	α ^a	Sample ^b				
		DAD ₁₀₀	DAD ₆₃ HMDA ₃₇	DAD ₅₀ HMDA ₅₀	DAD ₃₇ HMDA ₆₃	HMDA ₁₀₀
Cyclohexane	0	--	--	--	--	--
THF	0	--	--	--	--	--
DMF	0	--	--	--	--	--
NMP	0	--	--	--	--	--
DMSO	0	--	--	--	--	--
Acetone	0.08	--	--	--	--	--
CH ₂ Cl ₂	0.13	--	--	--	--	--
CH ₃ OH	0.98	--	--	--	--	--
CH ₃ COOH	1.12	--	--	--	--	--
H ₂ O	1.17	--	--	--	--	--
HCOOH	1.23	--	--	--	--	--
TFE	1.51	--	--	--	--	--
TFA	-- ^c	-- ^d	-- ^d	-- ^d	-- ^d	-- ^d
HFIP	1.96	+	+	+	+	+

^a α is the hydrogen bond donation (HBD) ability of solvent³. ^b “+”: soluble (> 1 g polyurea/100 g solvent), “--”: insoluble (< 1 g polyurea/100 g solvent). ^c The α value of TFA is unknown, but should be a little larger than that of TFE. ^d insoluble but melted. THF: tetrahydrofuran, DMF: dimethylformamide, NMP: *N*-methyl-2-pyrrolidinone, DMSO: dimethyl sulfoxide, TFE: trifluoroethanol, TFA: trifluoroacetic acid, HFIP: hexafluoroisopropanol.

Table S3. Swelling test of PUAs in CH₂Cl₂ and H₂O

Sample	Mass increase (%) ^a	
	CH ₂ Cl ₂	H ₂ O
DAD ₅₀ TTD ₅₀	26%	7.4%
DAD ₅₀ HMDA ₅₀	24%	0.6%
DAD ₃₇ HMDA ₆₃	24%	0.6%

^a The mass increase was measured in 96 h on the immersion of PUAs dumbbell shape sample in the solvents.

Table S4. Mechanical properties of PUAs

Sample	Modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
DAD ₁₀₀	1170 ± 46	53.3 ± 5.0	13 ± 6
DAD ₆₃ HMDA ₃₇	780 ± 14	55.2 ± 1.5	260 ± 10
DAD ₅₀ HMDA ₅₀	918 ± 36	62.1 ± 6.2	267 ± 42
DAD ₃₇ HMDA ₆₃	1247 ± 147	63.2 ± 1.5	54 ± 12
HMDA ₁₀₀	1194 ± 45	18.3 ± 0.4	1.6 ± 0.7
DAD ₅₀ DA10 ₅₀	951 ± 8	42.3 ± 0.2	60 ± 13
DAD ₅₀ DA8 ₅₀	718 ± 98	38.8 ± 1.4	167 ± 35
DAD ₅₀ DA4 ₅₀	1163 ± 68	42.4 ± 0.6	5.5 ± 0.6

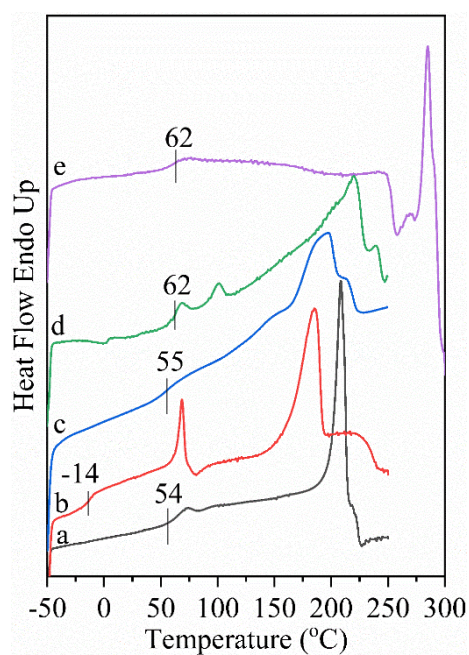
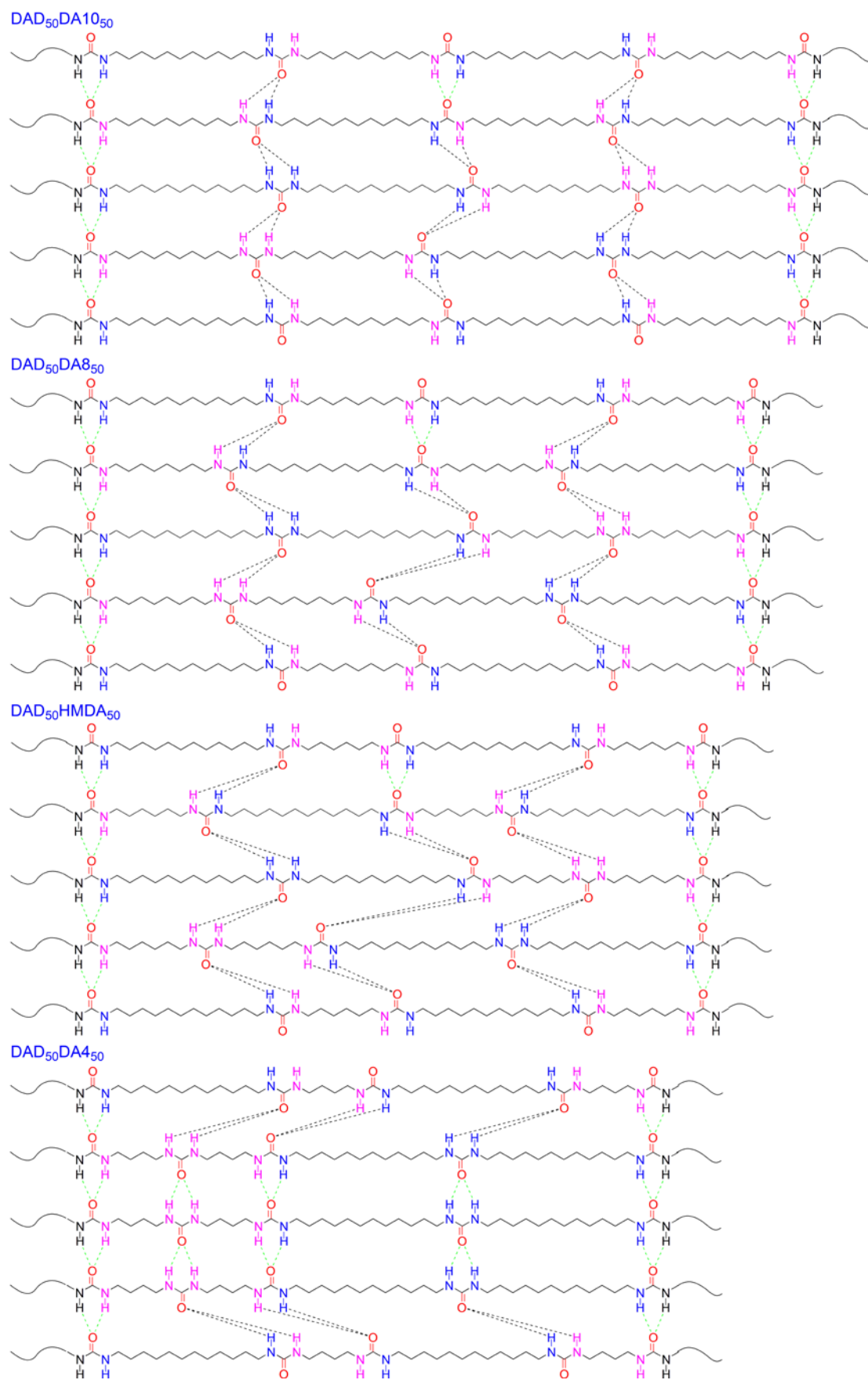


Figure S5. First heating DSC scans of PUAs. T_g determined is given on the graph. (a) DAD₁₀₀, (b) DAD₆₃HMDA₃₇, (c) DAD₅₀HMDA₅₀, (d) DAD₃₇HMDA₆₃ and (e) HMDA₁₀₀.



Scheme S2. Intermolecular hydrogen bonding formed in the PUAs of DAD₅₀DA4₅₀, DAD₅₀HMDA₅₀, DAD₅₀DA8₅₀ and DAD₅₀DA10₅₀.

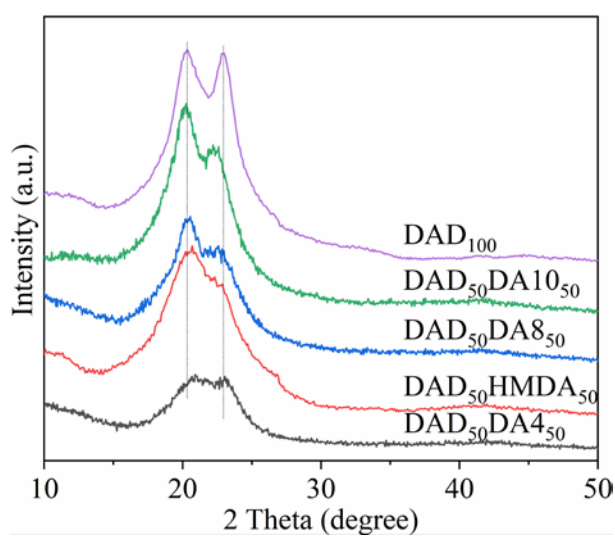


Figure S6. X-ray diffraction patterns of DAD₁₀₀, DAD₅₀DA₁₀₅₀, DAD₅₀DA₈₅₀, DAD₅₀HMDA₅₀ and DAD₅₀DA₄₅₀.

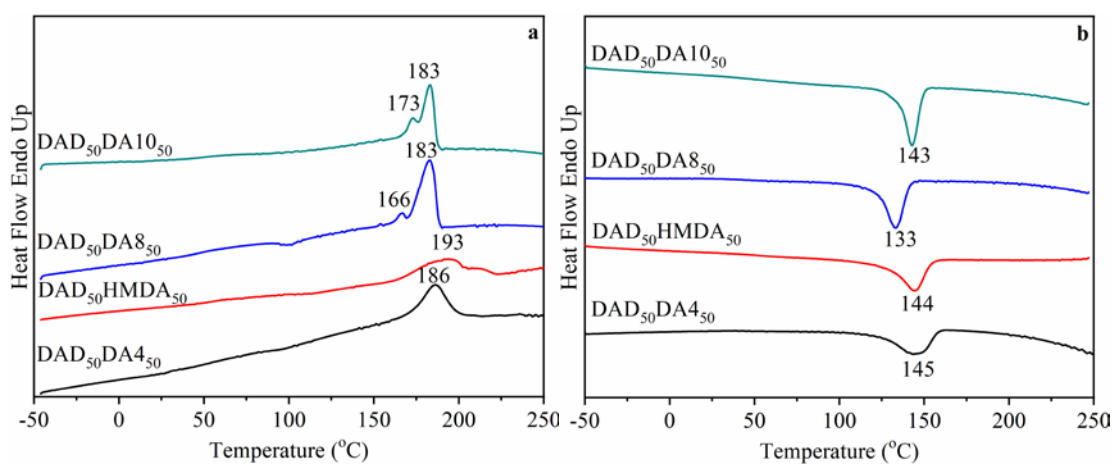


Figure S7. (a) Second heating and (b) cooling DSC scans of DAD₅₀DA₄₅₀, DAD₅₀HMDA₅₀, DAD₅₀DA₈₅₀ and DAD₅₀DA₁₀₅₀.

Table S5. Thermal properties of PUAs determined by DSC and TGA

Entry	Sample	DSC ^a	DSC ^b					$\Delta H_{m,100\%}$ (J/g) ^f	X_c (%) ^g	TGA
		T_g (°C)	T_{m1} (°C) ^c	T_{m2} (°C) ^c	T_c (°C) ^c	$T_{d,5\%}$ (°C)	ΔH_c (J/g) ^e			$T_{d,5\%}$ (°C)
1	DAD ₁₀₀	54	207	--	181	79	69	230	34	327
2	DAD ₅₀ DA10 ₅₀	57	173	183	143	57	48	225	25	298
3	DAD ₅₀ DA8 ₅₀	43	166	183	133	43	46	221	20	328
4	DAD ₅₀ HMDA ₅₀	55	193	--	144	39	44	217	18	324
5	DAD ₅₀ DA4 ₅₀	58	186	--	145	59	38	212	28	292

^a Heating/cooling/heating thermal cycles of 10 °C/min, values determined from the first heating scans. ^b values determined from cooling and second heating scans. ^c T_{m1} , T_{m2} and T_c are measured as the peak temperature in the endotherm and exotherm, respectively. ^d ΔH_m determined as area under the endothermic event. ^e ΔH_c determined as area under the exothermic event. ^f $\Delta H_{m,100\%}$ is the fusion enthalpy of a 100% crystalline sample estimated by group contribution theory,⁴ which could be estimated according to the group contribution in proportion to their relative amounts.^{5,6} ^g The degree of crystallinity (X_c), $X_c = [(\Delta H_m - \Delta H_{cc})/\Delta H_{m,100\%}]$; where $(\Delta H_m - \Delta H_{cc})$ is the melting enthalpy of the component under consideration. ΔH_{cc} determined as area under the exothermic event during heating sweep (cold crystallization), the value is 0.

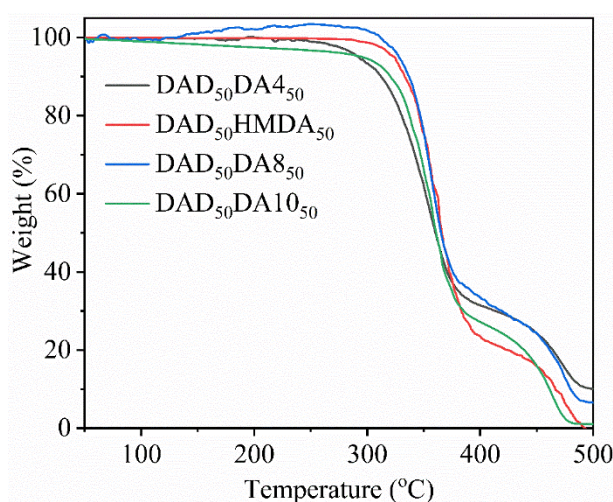
**Figure S8.** TGA curves of DAD₅₀DA4₅₀, DAD₅₀HMDA₅₀, DAD₅₀DA8₅₀ and DAD₅₀DA10₅₀.

Table S6. Mechanical properties of the present DAD₃₇HMDA₆₃ and DAD₅₀HMDA₅₀ materials compared with those of the reported CO₂-based PUAs, isocyanate-free polyhydroxyurethanes, CO₂-based polycarbonates, polyamide 6 and PUAs from isocyanate of MDI

Polymers	Sample	Young's modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)	Ref.
CO ₂ -based PUAs	DAD ₃₇ HMDA ₆₃	1247±147	63.2±1.5	54±12	This work ⁶
	DAD ₅₀ HMDA ₅₀	918±36	62.1±6.2	267±42	
	DAD ₅₀ TTD ₅₀	406±11	42.9±2.8	330±40	
	DAD ₉₀ EDR-104 ₁₀	1190±50	57.4±0.6	71±6	
Non-isocyanate polyhydroxyurethane	NIPU-DETA-3	124.1±5.5	16.0±0.8	98.3±8.6	7
	GGC/POSS-GC/HMDA	639±8	26.6±1.3	32±9	8
	PA ₁₂ HU-PTMO25	94.2±24.5	5.7±0.4	25±8	9
	BDC/DFS-1,6-AA_IPDA_2	300±40	--	40±40	10
CO ₂ -based polycarbonate	PLimC	950	55	15	11
	PPC	1122±55	43±2	13.5±1.5	12
Polyamide 6	--	580	22	12	13
Traditional PUAs from diisocyanate and diamine	MDI/m-PDA	1389	74.1	13.9	14
	MDI/HDA	371	12.0	2.9	

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