

## Supplementary Information

### High-Performance Thermoplastic Polyurethane Elastomers with Enhanced Mechanical Properties Prepared with Chain Extenders Containing Urea and Carbamate Moieties

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Figure S1. Left: Dissolution of ethanolamine in dimethyl carbonate.

Right: Dissolution of *N, N*-bis(2-hydroxyethyl) urea (MEA-DMC) in dimethyl carbonate.

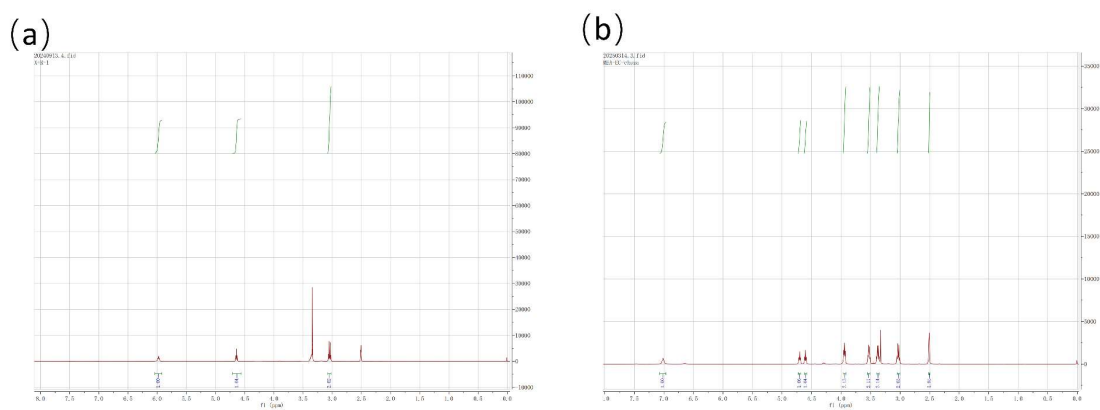


Figure S2. <sup>1</sup>H NMR spectra of TPUs synthesized with different chain extenders.

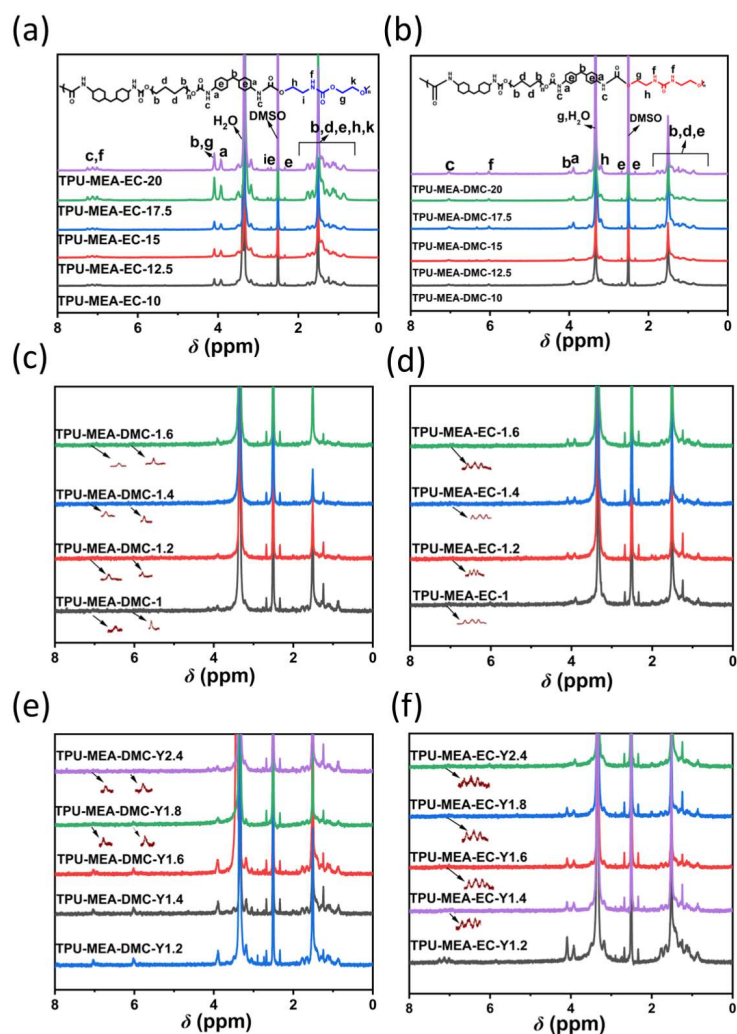


Figure S3.  $^1\text{H}$  NMR spectra of TPUs with varying mass fractions of (a) MEA-DMC and (b) MEA-EC as the chain extender.  $^1\text{H}$  NMR spectra of TPUs with (c) MEA-DMC and (d) MEA-EC as chain extender at different  $R$ -values.  $^1\text{H}$  NMR spectra of TPUs (prepared with different molecular weight prepolymers) chain-extended with (e) MEA-DMC and (f) MEA-EC.

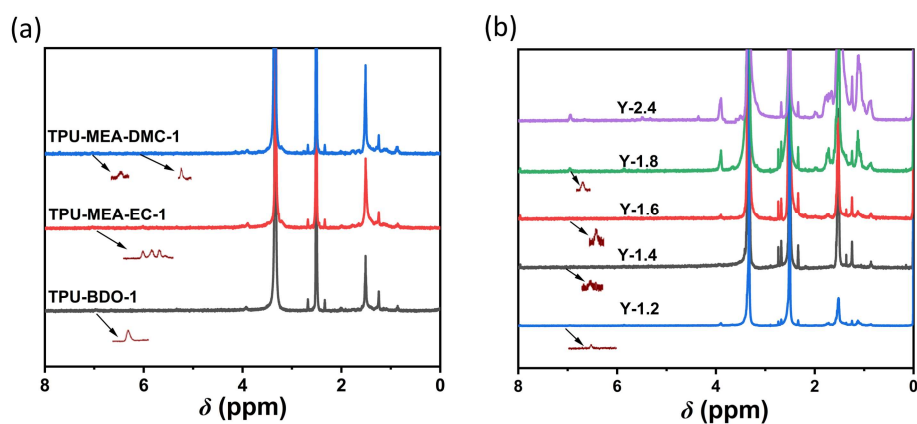


Figure S4.  $^1\text{H}$  NMR spectra of (a) TPUs synthesized with different chain extenders, and (b) prepolymers.

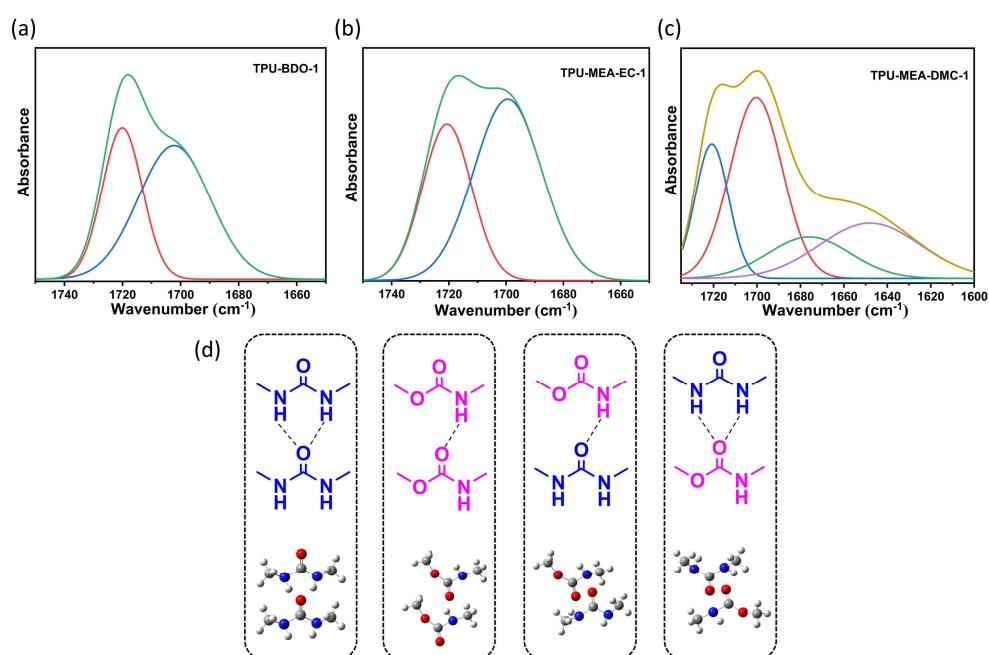


Figure S5. Curve fitting of the carbonyl region of TPUs. (a) TPU-BDO-1, (b) TPU-MEA-EC-1, (c) TPU-MEA-DMC-1. (d) Schematic representation of four types of individual hydrogen bonds, including urea-urea interactions, urea-urethane interactions, urethane-urethane interactions, and urethane-urea interactions.

Table S1. FTIR curve-fitting results of TPUs in carbonyl stretching region.

Assignment		Wavenumber(cm <sup>-1</sup> )				Area (%)	
		TPU-BDO-1	TPU-MEA-EC-1	TPU-MEA-DMC-1	TPU-BDO-1	TPU-MEA-EC-1	TPU-MEA-DMC-1
V (C=O) urethane amide	Free	I <sub>(1720)</sub>	I <sub>(1719)</sub>	I <sub>(1720)</sub>	39.1	38.3	19.7
	H-bonded	II <sub>(1700)</sub>	II <sub>(1700)</sub>	II <sub>(1700)</sub>	60.9	61.7	41.3
V (C=O) urea amide	Free			III <sub>(1675)</sub>			15.0
	H-bonded			IV <sub>(1645)</sub>			23.9
Total number of hydrogen bonding					60.9	61.7	65.2

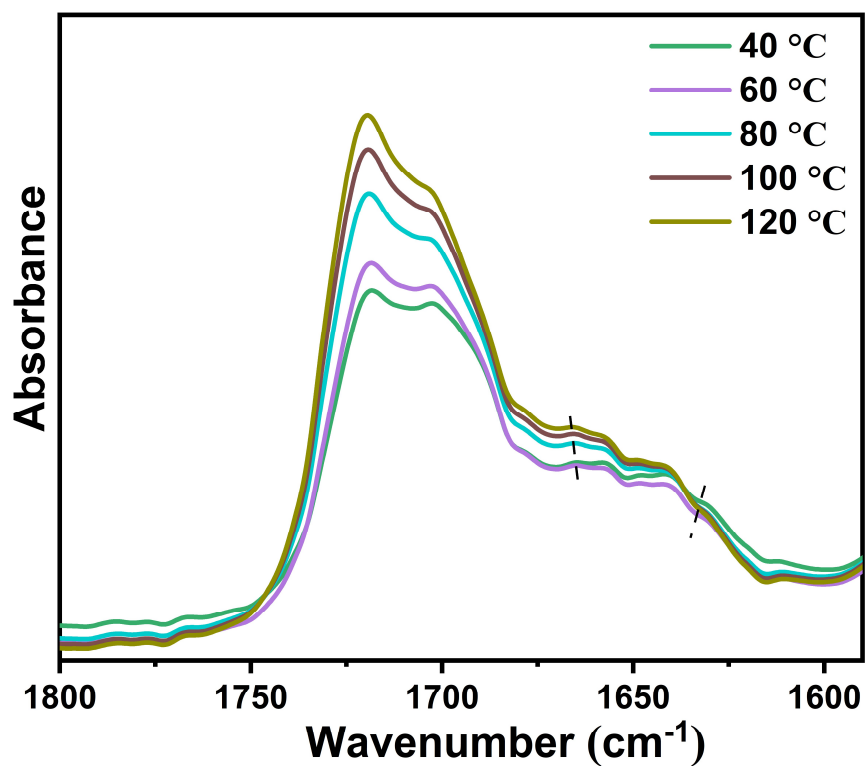


Figure S6. Temperature-dependent FTIR spectra in the C=O region of 1650-1750  $\text{cm}^{-1}$  of TPU-MEA-DMC-1 upon heating from 40 °C to 120 °C.

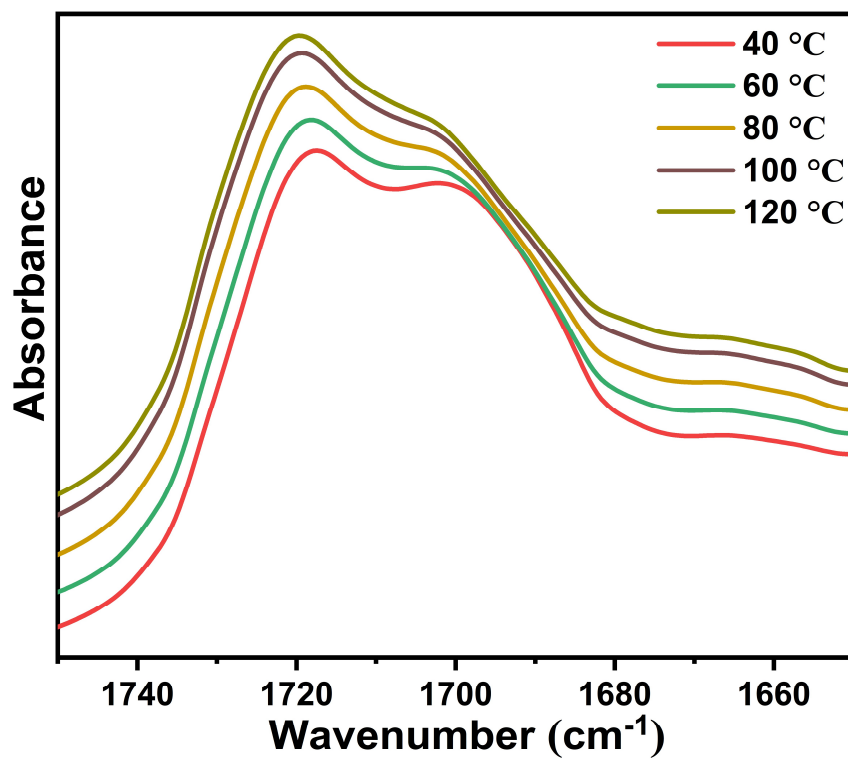


Figure S7. Temperature-dependent FTIR spectra in the C=O region of 1650-1750  $\text{cm}^{-1}$  of TPU-MEA-EC-1 upon heating from 40 °C to 120 °C.

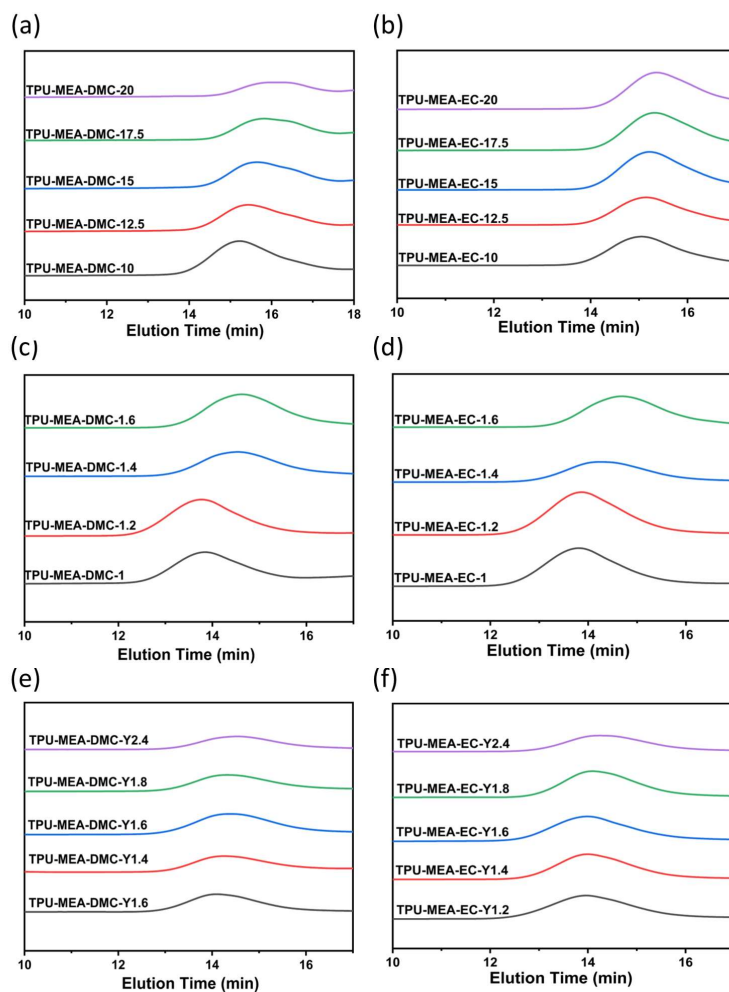


Figure S8. GPC traces of various TPU samples with varying mass fractions of (a) MEA-DMC and (b) MEA-EC as the chain extender. GPC traces of polyurethane synthesized with (c) MEA-DMC and (d) MEA-EC as chain extender at different  $R$ -values. GPC traces of TPUs (prepared with different molecular weight prepolymers) chain-extended with (e) MEA-DMC and (f) MEA-EC.

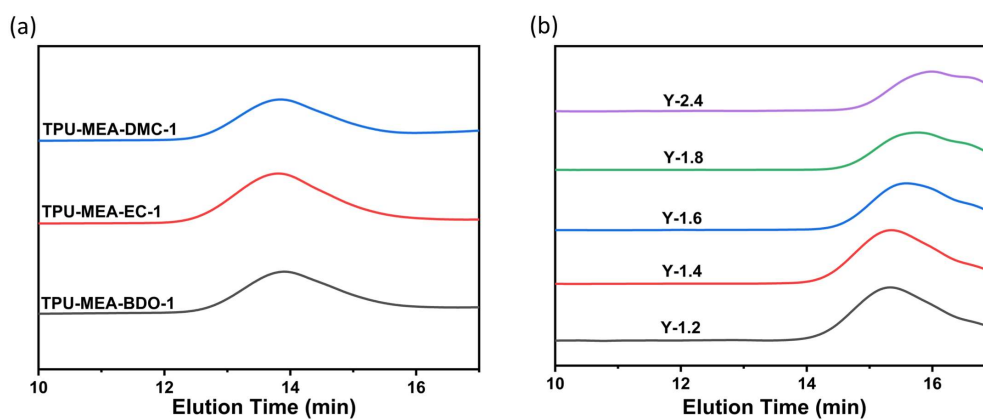


Figure S9. (a) GPC traces of TPUs synthesized with different chain extenders, (b) GPC traces of prepolymers.

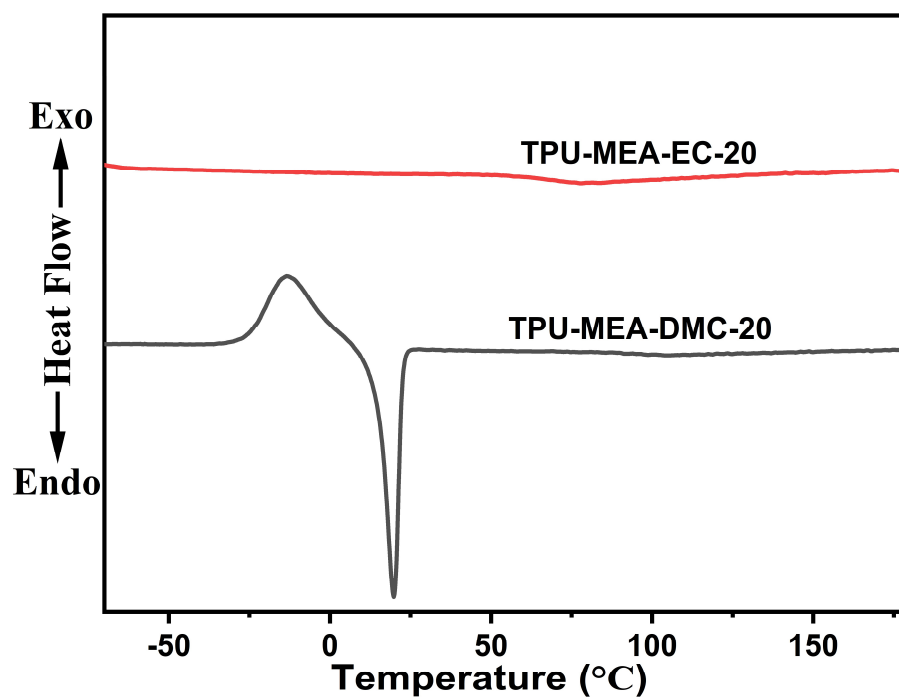


Figure S10. DSC curves of as-prepared TPUs.

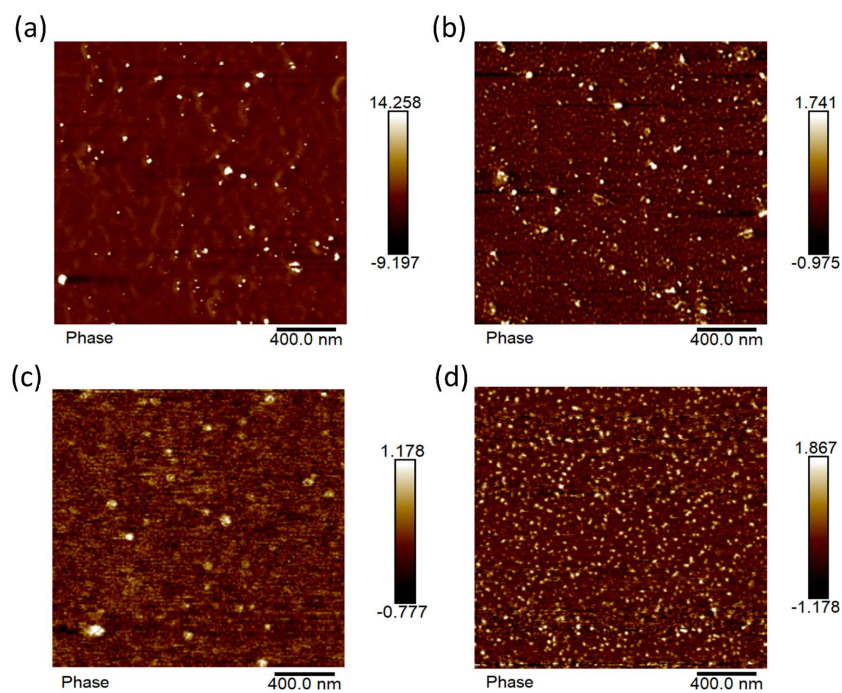


Figure S11. AFM images of (a) for TPU-MEA-DMC-10, (b) for TPU-MEA-DMC-20, (c) for TPU-MEA-EC-10 and (d) for TPU-MEA-EC-20.

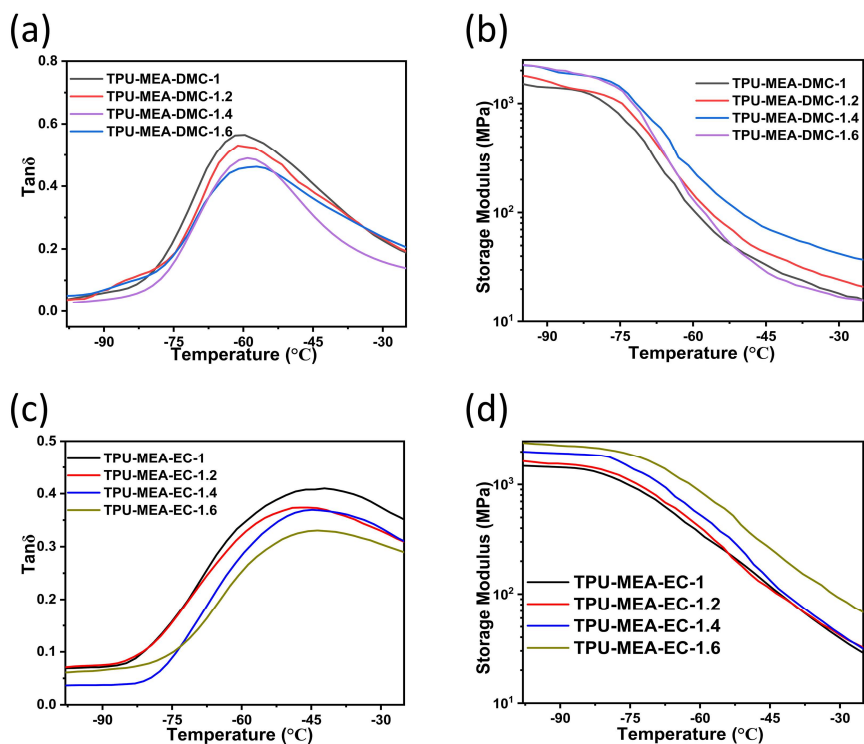


Figure S12. (a)  $\text{Tan}\delta$  diagrams of TPUs synthesized with MEA-DMC as chain extender at different  $R$ -value, (b)  $E'$  diagrams of TPUs synthesized with MEA-DMC as chain extender at different  $R$ -value, (c)  $\text{Tan}\delta$  diagrams of TPUs synthesized with MEA-EC as chain extender at different  $R$ -value, (d)  $E'$  diagrams of TPUs synthesized with MEA-EC as chain extender at different  $R$ -value.

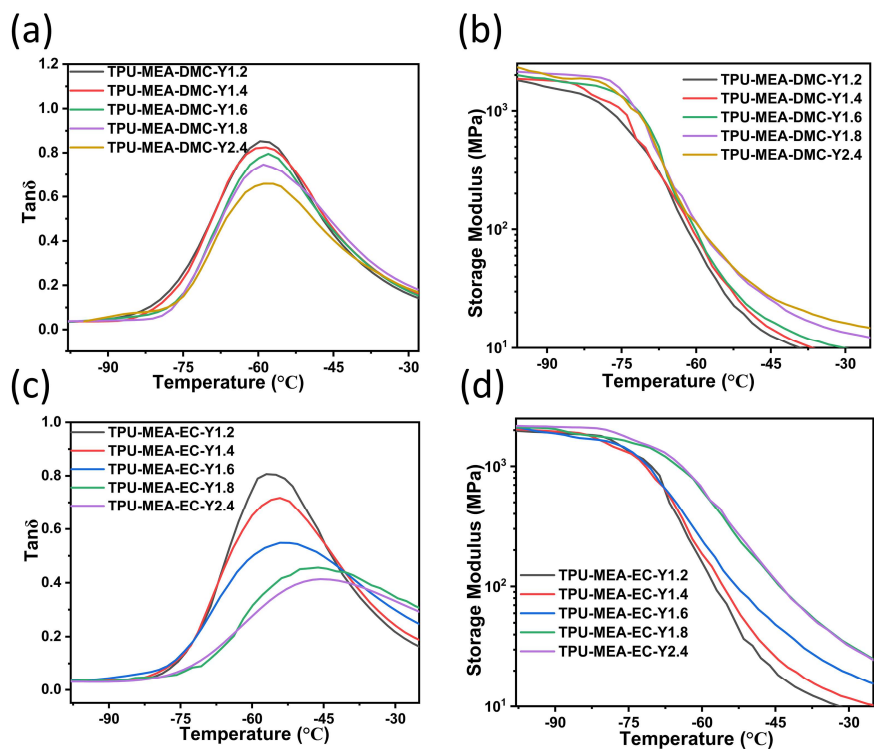


Figure S13. (a)  $\tan\delta$  curves of polyurethane prepolymers (varying molecular weights) chain-extended with MEA-DMC, (b)  $E'$  curves of polyurethane prepolymers (varying molecular weights) chain-extended with MEA-DMC, (c)  $\tan\delta$  curves of polyurethane prepolymers (varying molecular weights) chain-extended with MEA-EC, (d)  $E'$  curves of TPUs (prepared with different molecular weight prepolymers) chain-extended with MEA-EC.

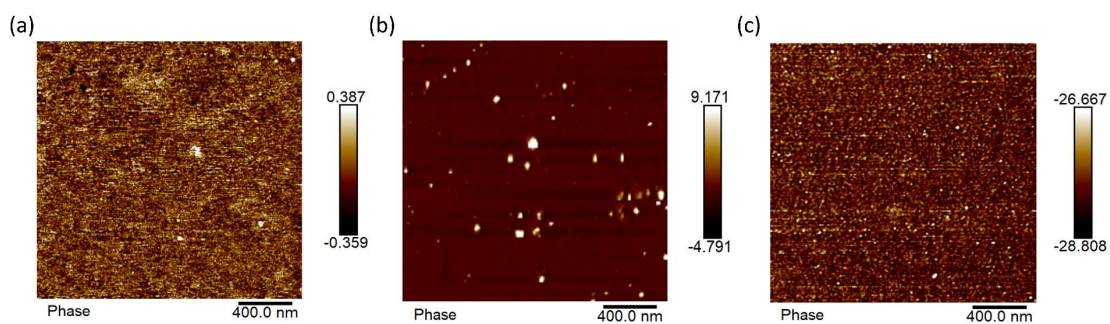


Figure S14. AFM images of (a) for TPU-MEA-BDO-1, (b) for TPU-MEA-DMC-1, and (c) for TPU-MEA-EC-1.

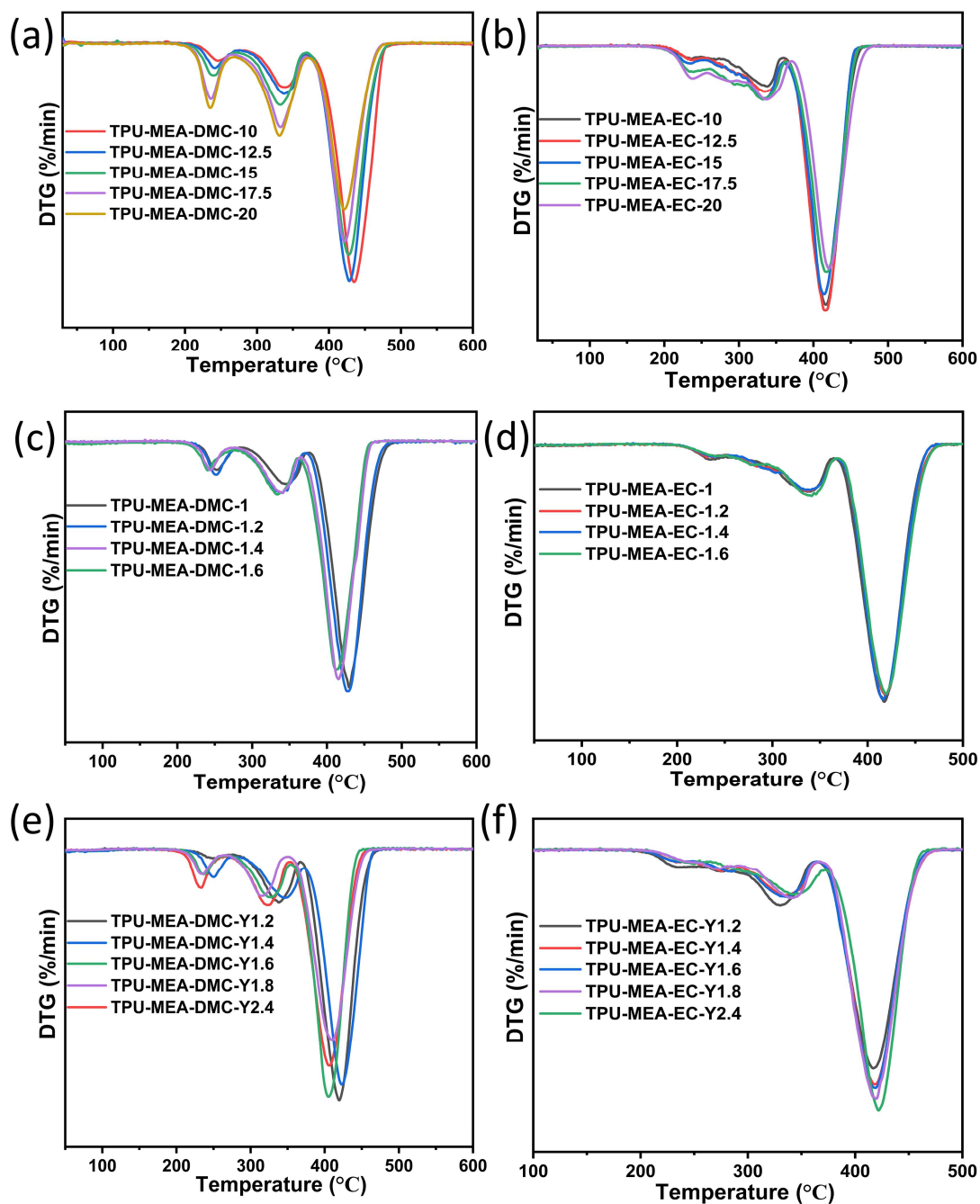


Figure S15. (a) DTG curves of TPUs with varying mass fractions of MEA-DMC as the chain extender, (b) DTG curves of TPUs with varying mass fractions of MEA-EC as the chain extender, (c) DTG diagrams of TPUs synthesized with MEA-DMC as chain extender at different  $R$ -value, (d) DTG diagrams of TPUs synthesized with MEA-EC as chain extender at different  $R$ -value, (e) DTG curves of TPUs (varying molecular weights) chain-extended with MEA-DMC, (f) DTG curves of TPUs (varying molecular weights) chain-extended with MEA-EC.

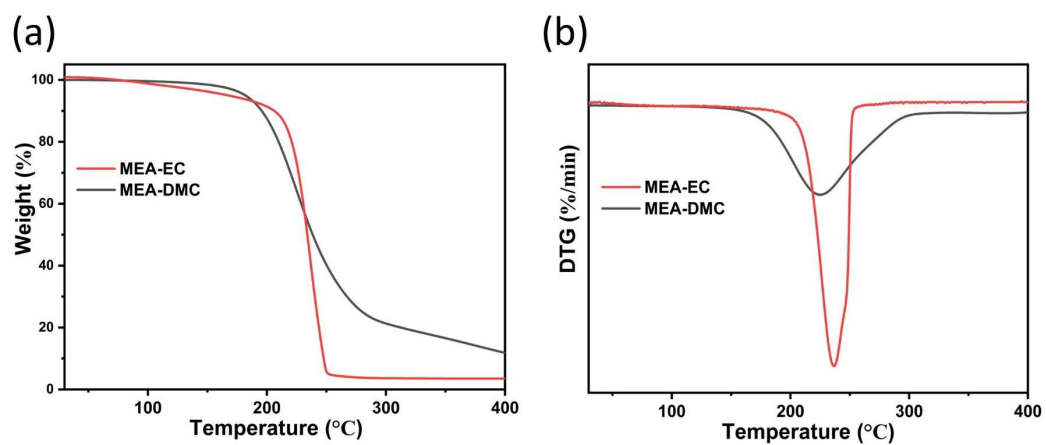


Figure S16. (a) TGA of the two chain extenders, (b) DTG of the two chain extenders.

Table S2. Feed ratios used in the synthesis of TPUs.

Elastomer	HMDI <sup>a</sup> (mmol)	PTMG2000 (mmol)	HMDI <sup>b</sup> (mmol)	MEA-DMC (mmol)	MEA-EC (mmol)	BDO (mmol)
TPU-MEA-DMC-10	2	0.64	/	1.36	/	/
TPU-MEA-DMC-12.5	2	0.52	/	1.48	/	/
TPU-MEA-DMC-15	2	0.41	/	1.59	/	/
TPU-MEA-DMC-17.5	2	0.32	/	1.68	/	/
TPU-MEA-DMC-20	2	0.26	/	1.74	/	/
TPU-MEA-DMC-1	2	1	/	1	/	/
TPU-MEA-DMC-1.2	2.2	1	/	1	/	/
TPU-MEA-DMC-1.4	2.4	1	/	1	/	/
TPU-MEA-DMC-1.6	2.6	1	/	1	/	/
TPU-MEA-DMC-Y1.2	6	5	6	5	/	/
TPU-MEA-DMC-Y1.4	7	5	5	5	/	/
TPU-MEA-DMC-Y1.6	8	5	4	5	/	/
TPU-MEA-DMC-Y1.8	9	5	3	5	/	/
TPU-MEA-DMC-Y2.4	12	5	/	5	/	/
TPU-MEA-EC-10	2	0.64	/	/	1.36	/
TPU-MEA-EC-12.5	2	0.52	/	/	1.48	/
TPU-MEA-EC-15	2	0.41	/	/	1.59	/
TPU-MEA-EC-17.5	2	0.32	/	/	1.68	/
TPU-MEA-EC-20	2	0.26	/	/	1.74	/
TPU-MEA-EC-1	1	0.5	/	/	0.5	/
TPU-MEA-EC-1.2	1.2	0.55	/	/	0.55	/
TPU-MEA-EC-1.4	1.4	0.58	/	/	0.58	/
TPU-MEA-EC-1.6	1.6	0.62	/	/	0.62	/
TPU-MEA-EC-Y1.2	6	5	6	/	5	/
TPU-MEA-EC-Y1.4	7	5	5	/	5	/
TPU-MEA-EC-Y1.6	8	5	4	/	5	/
TPU-MEA-EC-Y1.8	9	5	3	/	5	/
TPU-MEA-EC-Y-2.4	12	5	/	/	5	/
TPU-BDO-1	2	1	/	/	/	1
Y-1.2	1.2	1	/	/	/	/
Y-1.4	1.4	1	/	/	/	/
Y-1.6	1.6	1	/	/	/	/
Y-1.8	1.8	1	/	/	/	/
Y-2.4	2.4	1	/	/	/	/

a: Prepolymer addition, b: Upon completion of the prepolymer reaction, the chain extender was supplemented in Step 2. TPU-MEA-DMC(EC)-X: An X value between 10 and 20 indicates that the mass fraction of the chain extender is 10-20 wt%, with the *R*-value fixed at 1. TPU-MEA-DMC(EC)-X: An X value ranging from 1 to 1.6. The specific ratio ranges from PTMG: HMDI: chain extender = 1:2:1 to 1:2.6:1.

TPU-BDO-1: TPU synthesized with BDO as the chain extender, with an *R*-value of 1. TPU-MEA-DMC(EC)-X: when X is expressed in the form of Y1.2-Y2.4, it indicates that the ratio of PTMG to HMDI in the prepolymer is controlled within the range of 1.2 to 2.4. Subsequently, HMDI and the chain extender are added while maintaining an overall molar ratio of PTMG: HMDI: chain extender at 1:2.4:1. The prepolymers, directly named Y-1.2 to Y-2.4, are formed by the direct reaction of PTMG and HMDI, with the HMDI to PTMG molar ratio varying from 1.2 to 2.4.

Table S3. DMA and DSC data.

Elastomer	DMA- $T_g$ [°C]	DSC- $T_c$ [°C]
TPU-MEA-DMC-10	-62.8	-22.2
TPU-MEA-DMC-12.5	-67.3	-20.7
TPU-MEA-DMC-15	-69.6	-17.3
TPU-MEA-DMC-17.5	-74.5	-16.4
TPU-MEA-DMC-20	-75.8	-13.2
TPU-MEA-DMC-1	-56.8	-25.6
TPU-MEA-DMC-1.2	-58.3	-23.5
TPU-MEA-DMC-1.4	-60.3	/
TPU-MEA-DMC-1.6	-61.6	/
TPU-MEA-DMC-Y1.2	-59.6	-22.8
TPU-MEA-DMC-Y1.4	-59.0	-19.5
TPU-MEA-DMC-Y1.6	-58.8	-17.8
TPU-MEA-DMC-Y1.8	-58.0	-17.0
TPU-MEA-DMC-Y2.4	-58.0	/
TPU-MEA-EC-10	-53.1	/
TPU-MEA-EC-12.5	-59.3	/
TPU-MEA-EC-15	-59.8	/
TPU-MEA-EC-17.5	-62.9	/
TPU-MEA-EC-20	-64.1	/
TPU-MEA-EC-1	-46.0	/
TPU-MEA-EC-1.2	-45.0	/
TPU-MEA-EC-1.4	-43.6	/
TPU-MEA-EC-1.6	-43.6	/
TPU-MEA-EC-Y1.2	-57.0	/
TPU-MEA-EC-Y1.4	-55.9	/
TPU-MEA-EC-Y1.6	-54.2	/
TPU-MEA-EC-Y1.8	-48.0	/
TPU-MEA-EC-Y-2.4	-45.7	-
TPU-BDO-1	-42.5	/

Table S4. TGA and DTG data of TPUs

Elastomer	$T_{5\%}$ [°C]	$T_{10\%}$ [°C]	$T_{\max1}$ [°C]	$T_{\max2}$ [°C]	$T_{\max3}$ [°C]
TPU-MEA-DMC-10	290.5	325.7	245.7	336.9	434.7
TPU-MEA-DMC-12.5	255.5	314.3	240.4	337.1	427.7
TPU-MEA-DMC-15	243.6	295.3	238.7	332.2	426.9
TPU-MEA-DMC-17.5	232.0	247.0	234.6	331.5	422.0
TPU-MEA-DMC-20	229.8	241.8	235.3	330.5	421.2
TPU-MEA-DMC-1	257.1	317.6	252.1	344.7	428.6
TPU-MEA-DMC-1.2	257.7	313.0	251.3	336.0	428.2
TPU-MEA-DMC-1.4	248.7	311.7	242.7	339.8	414.3
TPU-MEA-DMC-1.6	242.3	297.8	239.1	333.7	411.0
TPU-MEA-DMC-Y1.2	307.0	329.0	248.3	337.3	418.2
TPU-MEA-DMC-Y1.4	252.5	309.9	251.43	347.1	423.6
TPU-MEA-DMC-Y1.6	251.3	307.8	235.3	326.8	405.3
TPU-MEA-DMC-Y1.8	247.9	307.8	233.7	314.9	409.2
TPU-MEA-DMC-Y2.4	232.9	279.8	231.8	322.4	405.2
TPU-MEA-EC-10	273.5	314.5	234.3	336.2	416.7
TPU-MEA-EC-12.5	273.8	306.8	235.0	334.5	415.8
TPU-MEA-EC-15	257.7	296.3	230.3	332.8	412.5
TPU-MEA-EC-17.5	242.0	274.8	234.5	332.3	417.3
TPU-MEA-EC-20	240.7	269.0	236.3	336.8	422.0
TPU-MEA-EC-1	266.3	307.7	233.2	337.0	417.3
TPU-MEA-EC-1.2	271.5	307.5	233.8	337.5	419.5
TPU-MEA-EC-1.4	271.5	310.2	234.5	336.7	416.0
TPU-MEA-EC-1.6	279.0	312.2	236.3	338.0	417.7
TPU-MEA-EC-Y1.2	249.7	287.3	231.7	329.7	415.6
TPU-MEA-EC-Y1.4	265.0	303.3	231.3	335.5	418.0
TPU-MEA-EC-Y1.6	267.2	302.8	233.5	334.5	417.2
TPU-MEA-EC-Y1.8	268.0	309.3	241.2	341.5	418.5
TPU-MEA-EC-Y-2.4	273.5	310.4	247.1	344.3	421.6
TPU-BDO-1	294.5	318.3	/	337.5	417.5

$T_{5\%}$  ( $T_{10\%}$ ): The temperature at 5% (10%) mass loss.

$T_{\max1}$  ( $T_{\max2}$  or  $T_{\max3}$ ): The temperature at the maximum mass loss in the first (second or third) stage.