

## Supporting information

*of*

### SO<sub>2</sub>-based thermoplastic polyurethane elastomer: Synthesis, microstructure, and mechanical properties

#### 1. Materials and characterization techniques

##### 1.1. Materials

PO was purchased from Acros, propylene glycol and 1,4-butanediol (BDO) were procured from Energy Chemical, were all distilled over calcium hydride under nitrogen. SO<sub>2</sub> (99.9%), provided by Dalian Guangming special gas products company, dibutyltin dilaurate (DBTDL) and methylene diphenyl diisocyanate (MDI) purchased from TCI, were all used as received. Bis(triphenylphosphoranylidene)ammonium chloride (PPNCl) was procured from Shanghai Aladding Biochemical Technology Co., Ltd., and further purified by recrystallization. Polypropylene glycol (PPG) with  $M_n$  of 1000 and 2000 were supplied by Macklin reagent and heated under vacuum for water removal.

##### 1.2. Synthesis of polysulfite diol

The specific procedure in our previous work could be used as reference for polysulfite diol synthesis.<sup>1</sup> Polysulfite diol was obtained by the copolymerization of SO<sub>2</sub> with PO using PPNCl as initiator in the presence of propylene glycol as the chain transfer reagent. Reaction was performed in an autoclave at 40 °C for 12 h. The crude oligomer diol was dissolved in small amount of CH<sub>2</sub>Cl<sub>2</sub>, and then precipitated with excess n-Hexane. This process was repeated 3 times to remove cyclic byproduct and the unreacted PO, and colorless transparent oligomer diol was obtained by vacuum-drying at 70 °C for solvent and water removal.

##### 1.3. Characterization techniques

###### 1.3.1. Matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF MS)

MALDI-TOF mass spectrometric measurements were carried on a Waters MALDI micro MX mass spectrometer, equipped with a nitrogen laser delivering 3 ns laser pulses at 337 nm. Trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB) was used as a matrix. CH<sub>3</sub>COONa (Aldrich, 98%) was added for ion formation.

###### 1.3.2. <sup>1</sup>H nuclear magnetic resonance (<sup>1</sup>H NMR)

<sup>1</sup>H NMR spectra of samples were measured on a nuclear magnetic resonance instrument (Varian INOVA-400 MHz). DMF-d<sub>7</sub> and CDCl<sub>3</sub> were used as the solvent for SO<sub>2</sub>-based TPU elastomers and polysulfite respectively.

###### 1.3.3. Differential scanning calorimetry (DSC)

DSC analysis of the samples were performed on a NETZSCH DSC 206 equipment, and heated from -30 to 100 °C at a scanning rate of 10 °C min<sup>-1</sup> under a constant nitrogen flow.

###### 1.3.4. Thermo-gravimetric analysis (TGA)

Thermal stability of TGA of samples were carried on a Mettler-Toledo TGA/SDTA851e in the range from 25 to 600 °C at a heating rate of 10 °C min<sup>-1</sup> under a constant nitrogen flow.

###### 1.3.5. Gel permeation chromatography (GPC)

The number-average molecular weight ( $M_n$ ) and dispersity ( $\mathcal{D}$ ) of TPU elastomer/polysulfite were determined by GPC technique at 30 °C and a flow rate of 1.0 mL/min, with DMF as the eluent on an Agilent 1260 instrument. The curve was calibrated using monodisperse polystyrene standards.

### 1.3.6. Fourier transform infrared spectroscopy (FT-IR)

FT-IR spectra were performed on a Bruker EQUINOX55 spectrometer in the range from 4000 to 600  $\text{cm}^{-1}$  at a resolution of 2  $\text{cm}^{-1}$  and 32 times for each test.

### 1.3.7. X-ray diffraction (XRD)

The XRD patterns were recorded on Bruker D8 Advance diffractometer with Cu K radiation (40 kV, 200 mA) in the range from 5° to 90° with a scan rate of 5°·min<sup>-1</sup>.

### 1.3.8. Small angle X-Ray scattering (SAXS)

Measurements were carried out at a SAXS instrument (Rigaku NANOPIX) in the range of scattering angle from 0° to 7° with a wavelength of 1.5418 Å. Silver behenate ( $d_{001} = 58.380$  Å) powder was used as the standard material to calibrate the scattering angle.

### 1.3.9. Scanning electron microscope (SEM)

Ultrahigh Resolution Field Emission Scanning Electron Microscopy (JSM-7900F) equipped with a RBED detector was employed to observe the morphology of samples under 20000 times magnification.

### 1.3.10. Dynamic mechanical analysis (DMA)

Dynamic mechanical properties of samples were investigated on a DMA technique (METTLER TOLEDO, DMA/SDTA1+) in tensile mode. The approximate dimension of samples for testing was 8 mm in length, 2 mm in width and 1 mm in thickness. The test temperature was varied from -40 °C to 80 °C at a rate of 3 °C·min<sup>-1</sup> with the testing frequency of 10 Hz and an amplitude of  $\epsilon = 0.3\%$ .

### 1.3.11. Tensile test

Mechanical properties of samples were evaluated by a tensile test device (Instron 6800 universal testing system, 10 kN load cell) at 25 °C at a rate of 500 mm·min<sup>-1</sup>.

## 1.4. Sample preparation

Thin film was prepared via compression molding using a Plate Vulcanizing Machine (GT-7014-H30C) equipped with a hydraulic unit (maximum force 30000 psi). Dried copolymer materials were loaded between non-stick Teflon paper sheets into a stainless-steel mold with inset dimensions 50 mm × 50 mm × 1 mm fabricated inhouse, and compressed between two 80 mm × 80 mm steel electrically heated platens clamp force 5000 psi. All the elastomers were placed in a glass desiccator at room temperature (25 °C) for 7 days.

Tensile stress/strain test was performed by an Instron 6800 universal testing system (10 kN load cell) on dumbbell-shaped test specimens. Specimens for analysis were generated by cutting the prepared films using a cutting die to standard dimensions. Three standard dumbbell-shaped specimens could be cut from the prepared films, and 3–4 dumbbell-shaped specimens for each sample were prepared for the analysis. Mechanical behavior was averaged for all the specimens measured for each individual species investigated (Tables S5 and S6). Thickness ( $1.00 \pm 0.01$  mm), width (3.18 mm), and grip length ( $25.5 \pm 0.1$  mm) of the measured dumbbell-shaped specimens were measured for normalization of data by the Bluehill measurement software. Test specimens were affixed into the screw-tight grip frame. Tensile stress and strain were measured to the point of material break at a grip extension speed of 10.0 mm/min at ambient conditions.

Dynamic Mechanical Analysis (DMA). A rectangular spline for the Dynamic Mechanical Properties Test with a scale of 16 mm × 3.5 mm × 1.0 mm was obtained by cutting the melt-processed film. The test was performed at small tension film mode, 0.3% strain, 1 Hz, 2 °C min<sup>-1</sup> (from -60 °C to 100 °C) on a Mettler-Toledo DMA/SDTA 1+.

Scanning electron microscope (SEM). The sample with a scale of 5 mm × 1.5 mm × 1.0 mm, was adhered to the sample table through conductive adhesive. Nitrogen gas gun was used to remove powder and dust from the sample. And then spray gold on the surface of the sample to enhance the conductivity before SEM testing.

## 2. Figures and Tables

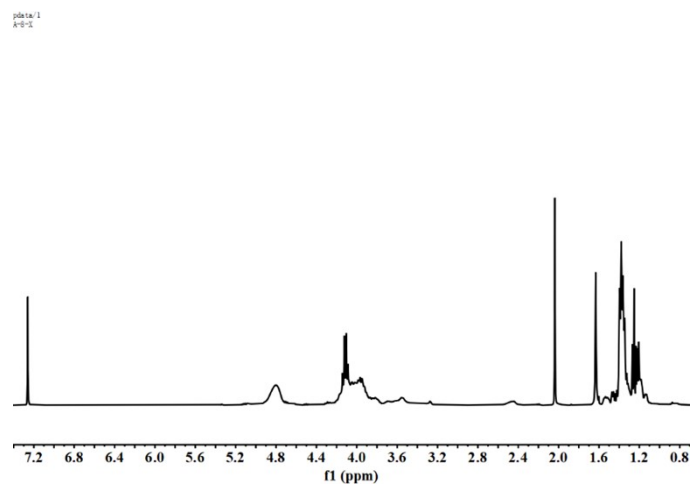


Figure S1.  $^1\text{H}$  NMR of polysulfite oligomer diol with  $M_n$  of 2000 g/mol dissolved in  $\text{CDCl}_3$ .

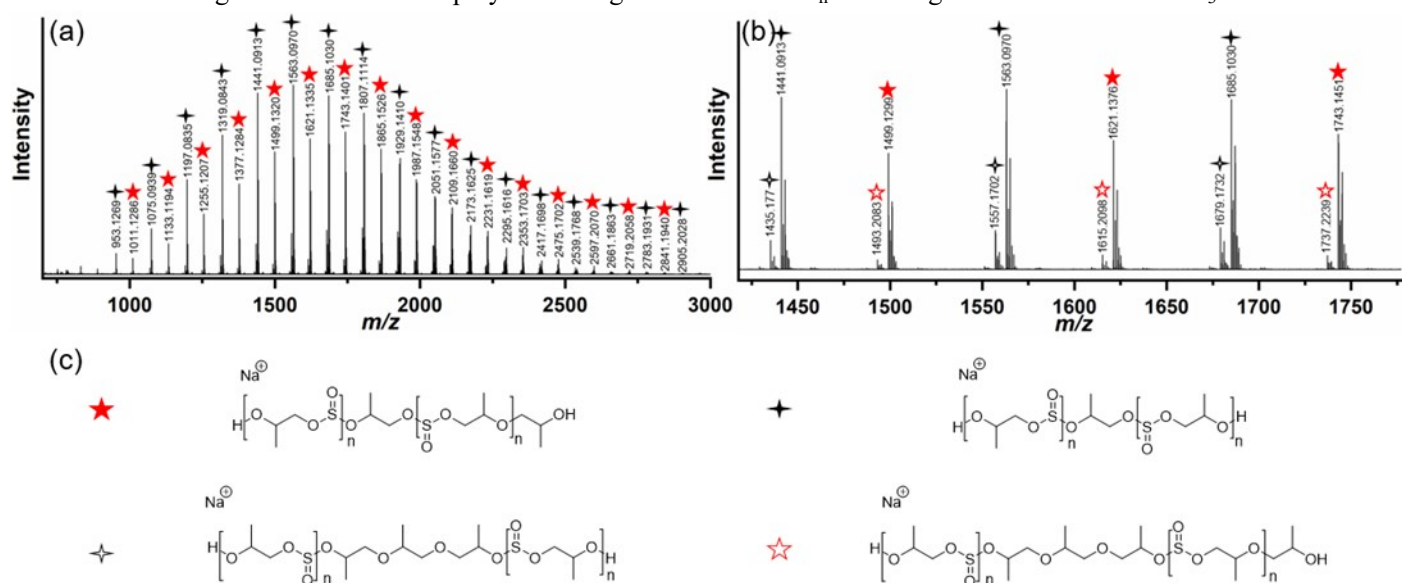


Figure S2 MALDI-TOF MS spectrum of the polysulfite oligomer diol with  $M_n$  of 2000 g/mol (a) along with its partial magnified one (b) and the corresponding structures of four mass series (c).

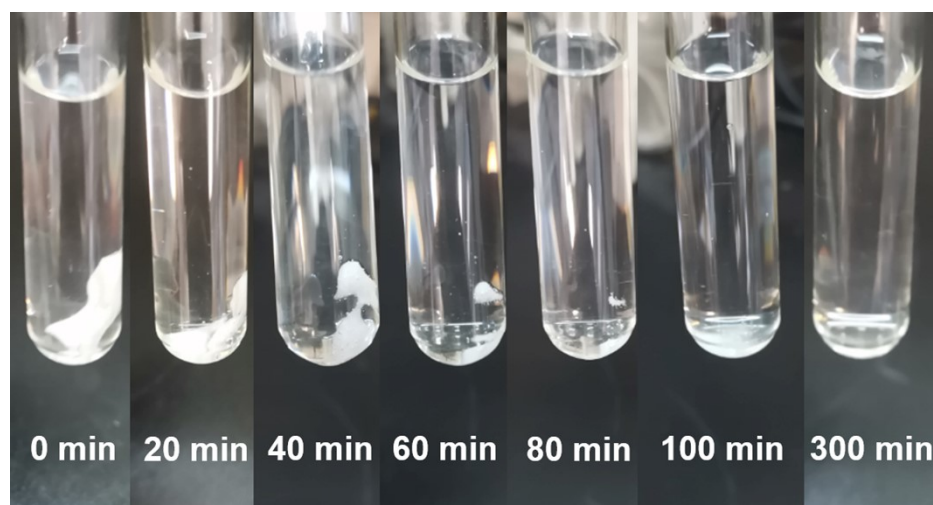


Figure S3. Dissolution test of  $\text{SO}_2$ -based TPU elastomer.

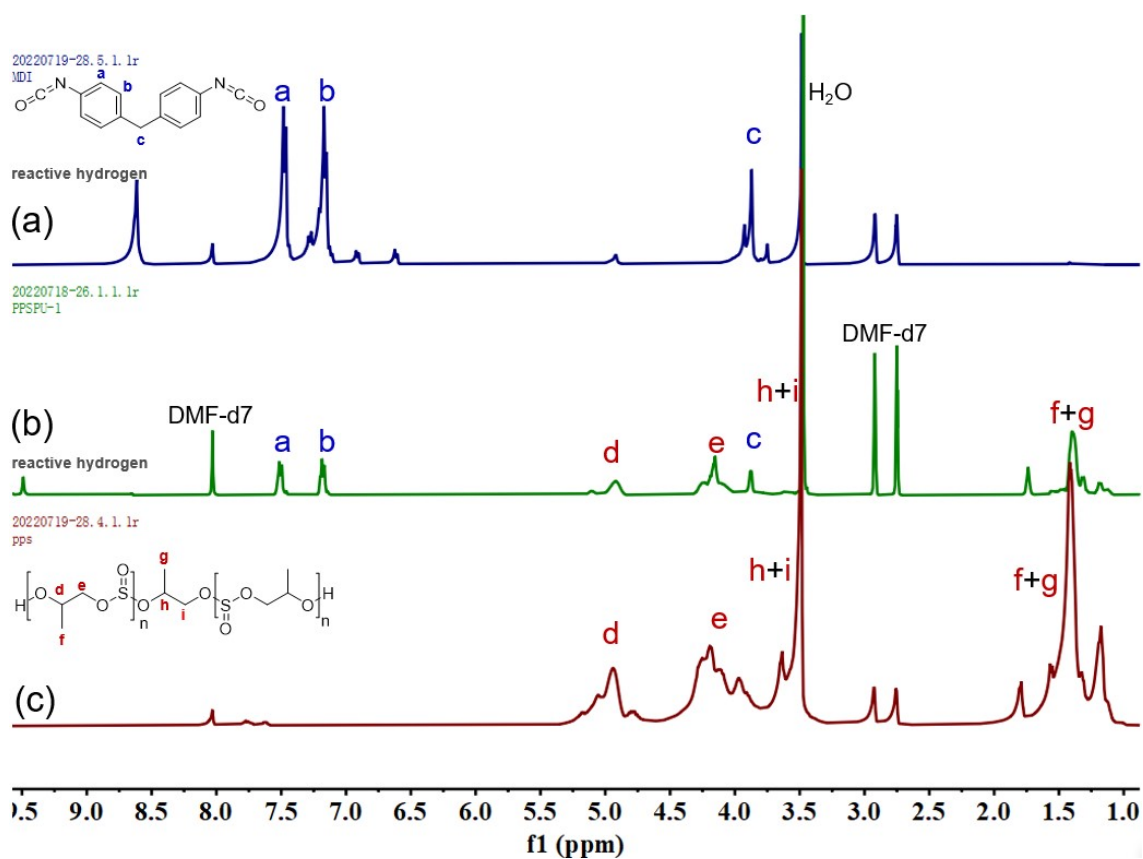


Figure S4.  $^1\text{H}$  NMR of MDI (a), SO<sub>2</sub>-based TPU elastomer (b) and polysulfite oligomer diol (c).

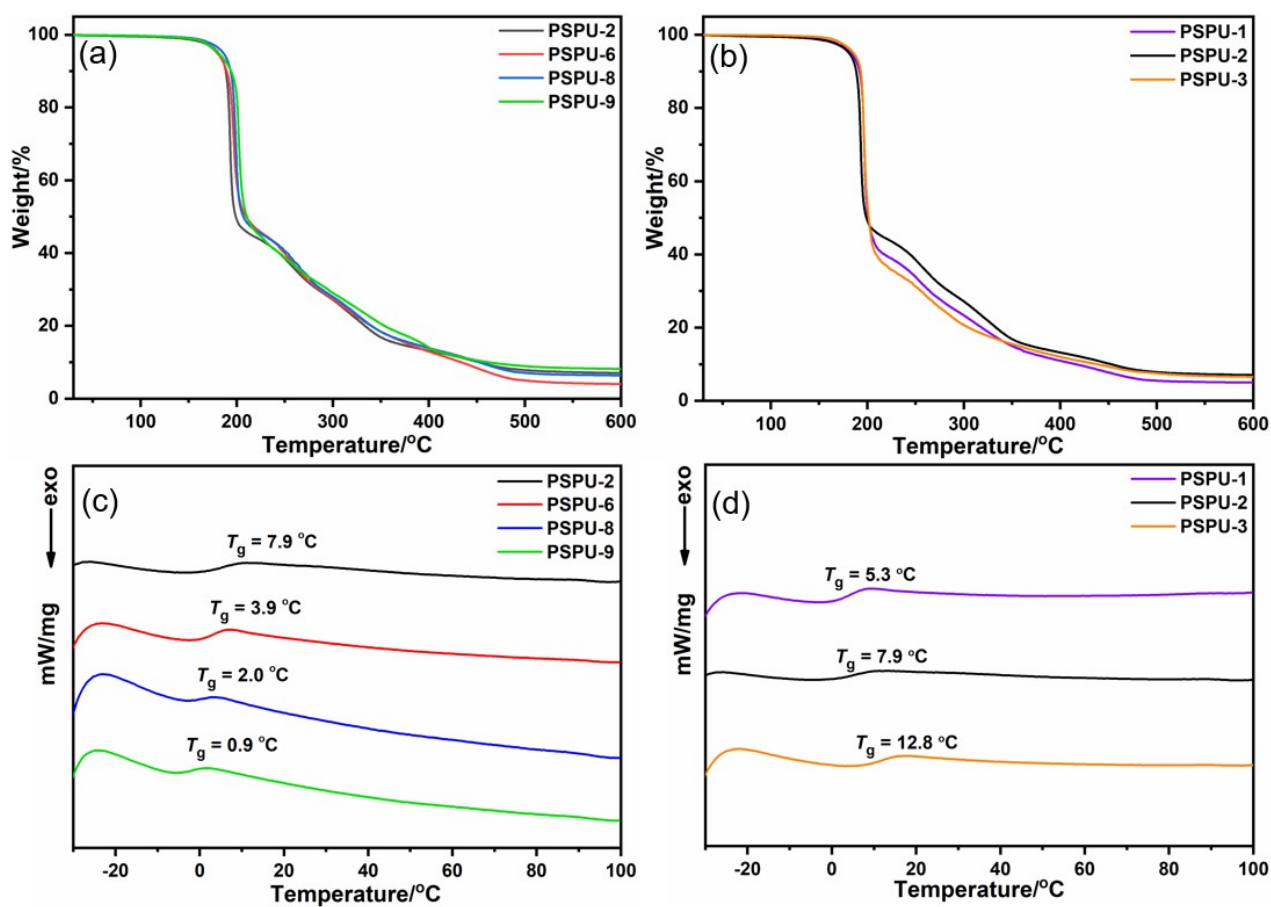


Figure S5. TGA and DSC results of SO<sub>2</sub>-based TPU elastomer.

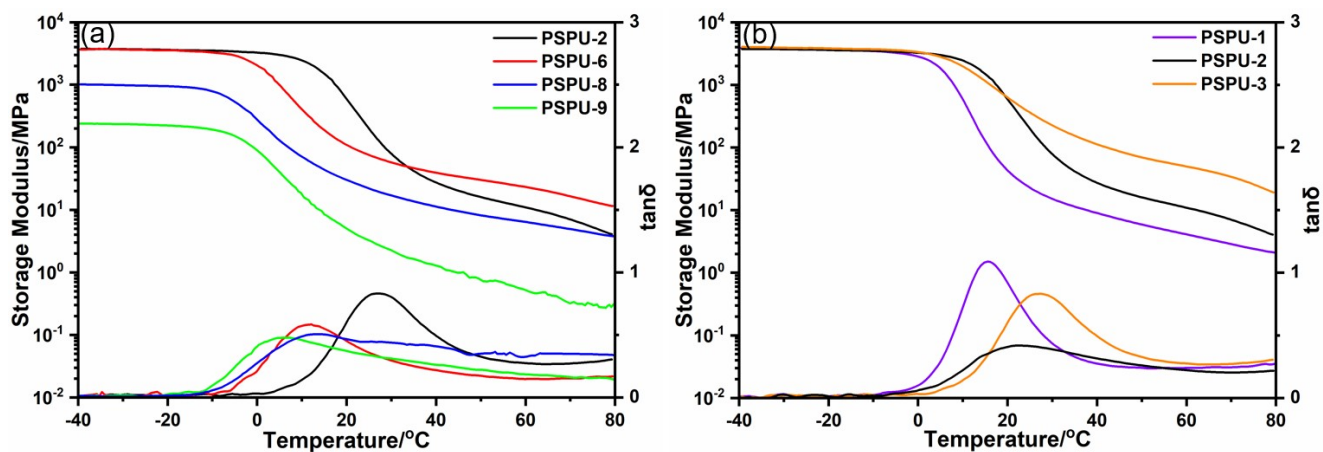


Figure S6. DMA results of SO<sub>2</sub>-based TPU elastomers.

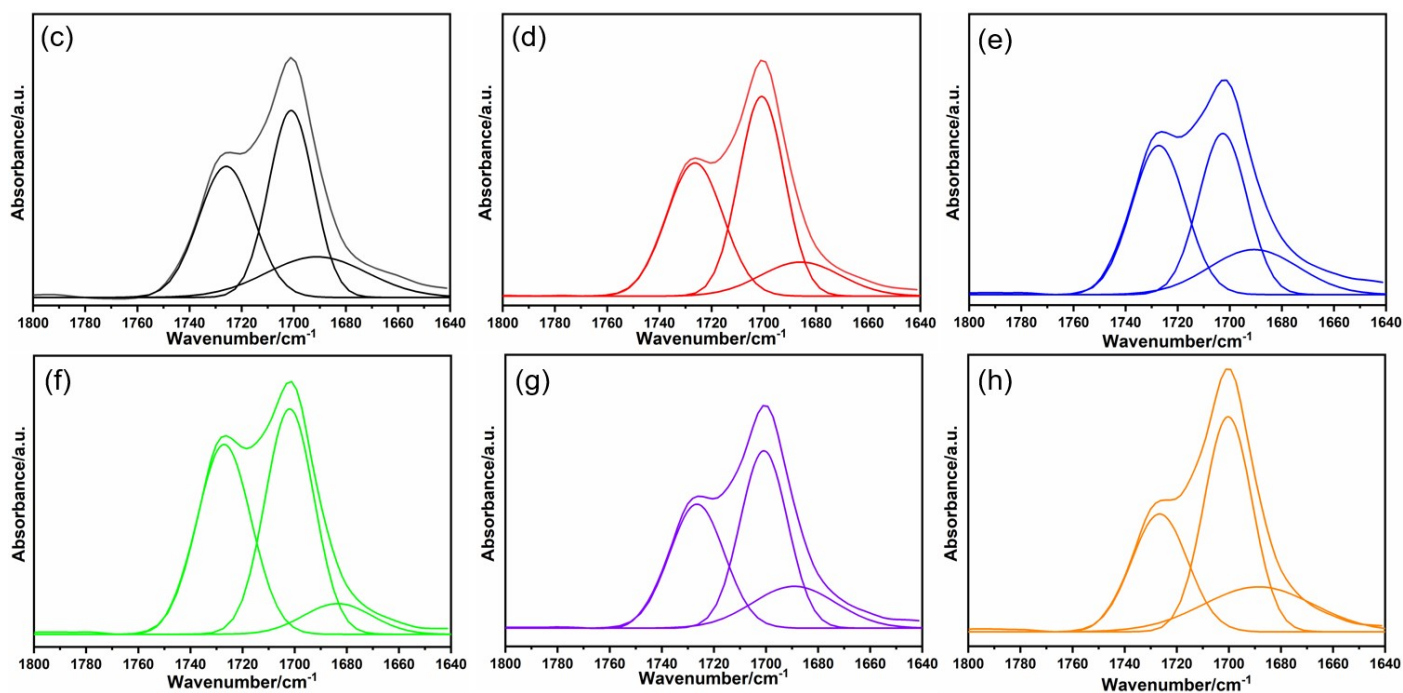
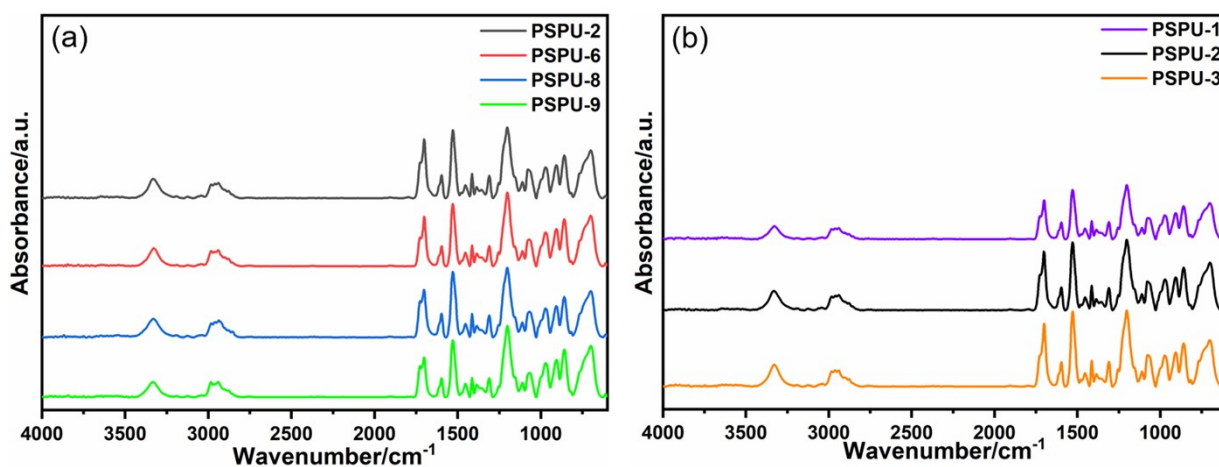


Figure S7. FT-IR results of SO<sub>2</sub>-based TPU elastomers with different SS  $M_n$  (a) and different HS contents (b). Curve fitting results of carbonyl group peaks in FT-IR. (c) PSPU-2, (d) PSPU-6, (e) PSPU-8, (f) PSPU-9, (g) PSPU-1 and (h) PSPU-3.

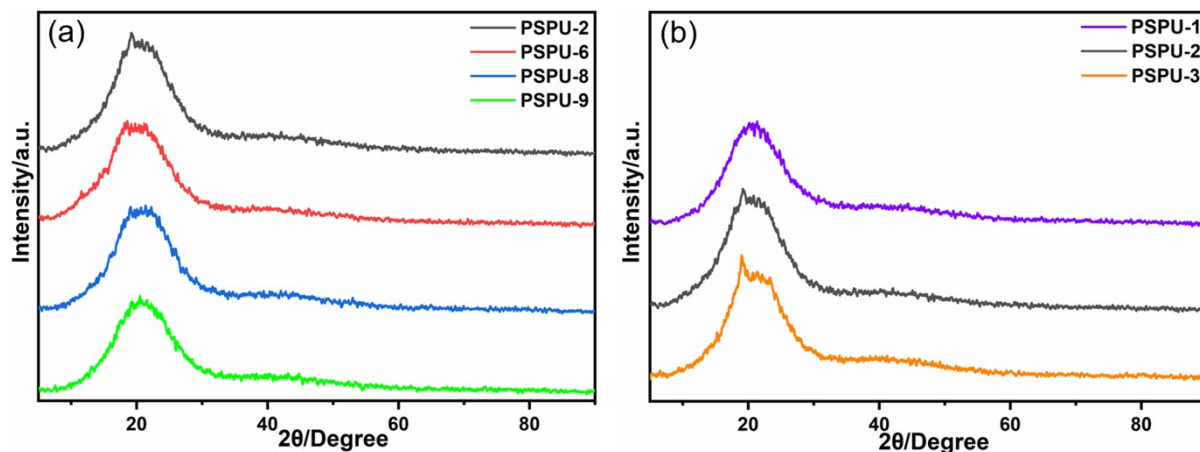


Figure S8. XRD results of SO<sub>2</sub>-based TPU elastomers with different SS  $M_n$  (a) and different HS contents (b).

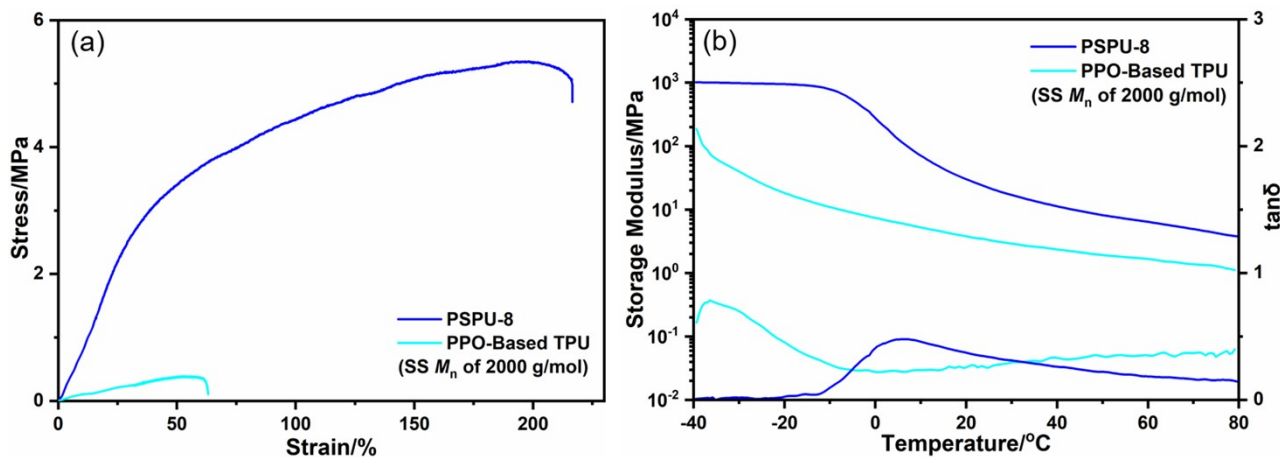


Figure S9. Comparison of tensile test (a) and DMA (b) result between SO<sub>2</sub>-based (entry 8, Table 1) and PPO-based TPU elastomers with 2000 g/mol SS  $M_n$  obtained from the same method.

Table S1. Synthesis of polysulfite diols with various  $M_n$ s<sup>a</sup>.

entry	PO/SO <sub>2</sub> /initiator/chain transfer agent <sup>b</sup>	time (h)	temp. (°C)	conv. <sup>c</sup> (%)	selectivity <sup>d</sup> (% Polymer)	$M_n^e$ (kg/mol)	$D^e$
1	1000/1500/1/100	12	50	>99	90	1.0	1.16
2	1000/1500/1/70	12	50	>99	89	1.5	1.13
3	1000/1500/1/54	12	50	>99	90	2.0	1.12
4	1000/1500/1/36	12	50	>99	91	3.0	1.12

<sup>a</sup>Polysulfite diols with various  $M_n$ s was prepared following a previous literature procedure developed in this lab<sup>1</sup>. <sup>b</sup>Reactions were performed in the presence of PPnCl as the initiator and propylene glycol as the chain transfer reagent with different feed ratio (molar ratio). <sup>c</sup>The conversion of PO, determined by <sup>1</sup>H NMR. <sup>d</sup>Selectivity for polymer over cyclic sulfite, determined by <sup>1</sup>H NMR. <sup>e</sup>Determined by gel permeation chromatography (GPC) in tetrahydrofuran and calibrated with polystyrene.



Table S2. Tensile test results of SO<sub>2</sub>-based TPU elastomers<sup>a</sup>.

sample <sup>b</sup>	$\sigma^1$ (MPa)	$\sigma^2$ (MPa)	$\sigma^3$ (MPa)	$\sigma$ -AVG	$\varepsilon^1$ (%)	$\varepsilon^2$ (%)	$\varepsilon^3$ (%)	$\varepsilon$ -AVG
PSPU-1	8.8	8.0	8.7	8.8±0.4	505	478	480	487±12
PSPU-2	16.7	15.0	16.5	16.0±0.8	376	351	363	363±10
PSPU-3	16.2	15.8	14.3	15.4±0.8	207	189	181	192±11
PSPU-4	6.6	6.0	5.1	5.9±0.7	33	30	28	30±4
PSPU-5	7.8	7.2	6.2	7.3±0.6	302	279	270	283±13
PSPU-6	7.9	7.9	6.8	7.5±0.5	245	228	234	236±12
PSPU-7	5.9	5.6	5.1	5.5±0.3	61	64	52	59±9
PSPU-8	5.4	5.0	4.3	4.9±0.4	217	205	197	206±8
PSPU-9	5.1	5.0	4.4	4.8±0.3	191	203	182	192±14

a.  $\sigma$ , ultimate tensile strength;  $\varepsilon$ , elongation at break. Average values and standard deviations were obtained from the tensile test of three samples with an extension rate of 10 mm·min<sup>-1</sup>.

b. The numbers represent the  $M_n$ s (1000–3000 g/mol) of SS and weight content (0.3–0.45) of HS of SO<sub>2</sub>-based TPU elastomers.

Table S3.  $q$  and  $L$  of SO<sub>2</sub>-based TPU elastomers.

sample <sup>a</sup>	$q_{\max}/\text{nm}^{-1b}$	$L/\text{nm}^c$
PSPU-1	4.63	1.357
PSPU-2	4.61	1.363
PSPU-3	4.64	1.354

a. The numbers represent the  $M_n$ s (1000–3000 g/mol) of SS and weight content (0.3–0.45) of HS of SO<sub>2</sub>-based TPU elastomers.

b.  $q_{\max}$  is the  $q$  value at maximum intensity of the scattering peak, determined by SAXS.

c.  $L$ , the approximate length between two micro-phase domain, calculated by  $L = 2\pi/q_{\max}$ .

Table S4. Curve-fitted results of the carbonyl groups of FT-IR spectra at 25 °C of SO<sub>2</sub>-based TPU elastomers.

sample <sup>a</sup>	free carbonyl groups <sup>b</sup> (%)	disordered hydrogen bonded groups <sup>c</sup> (%)	ordered hydrogen bonded groups <sup>d</sup> (%)
PSPU-2	36.6	42.7	20.7
PSPU-6	38.7	47.2	14.1
PSPU-8	40.4	39.3	20.3
PSPU-9	43.9	47.1	9.0
PSPU-1	36.4	45.0	18.6
PSPU-3	36.0	43.3	20.7
PSPU-4	30.1	47.2	22.7

a. The numbers represent the  $M_n$ s (1000–3000 g/mol) of SS and weight content (0.3–0.45) of HS of SO<sub>2</sub>-based TPU elastomers.

b. The proportion of free carbonyl groups (C=O), assigned to the curve-fitted peak at approximately 1720 cm<sup>-1</sup>.

c. The proportion of disordered hydrogen-bonded carbonyl groups (C=O), assigned to the curve-fitted peak at approximately 1700 cm<sup>-1</sup>.

d. The proportion of ordered hydrogen-bonded carbonyl groups (C=O), assigned to the curve-fitted peak at approximately 1680 cm<sup>-1</sup>.

Table S5. Hydroxyl value of polysulfite diols<sup>a</sup>

$M_n$ of polysulfite diol (g/mol)	1000	1500	2000	3000
Hydroxyl value (mg KOH/g)	102~110	69~74	52~56	32~37

a. Hydroxyl value was determined by national standard code for Chinese characters HGT 2709-1995.

## References

[1] Jin, X.-C.; Ren, B.-H.; Gu, G.-G.; Yue, T.-J.; Ren, W.-M. The copolymerization of SO<sub>2</sub> with propylene oxide mediated

by organic ammonium salts: a comprehensive study of the main-chain structure, living polymerization character and regioselectivity. *Polym. Chem.* **2022**, *13*, 3136–3143.