# **Supporting Information**

## Preparation of Muti-Functional Polyamides Vitrimers via Ugi Four-Component

# **Polymerization and Oxime-Promoted Transcarbamoylation Reaction**

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#### 1. Materials

Hexamethylenediamine (> 99%), Ethyl formate (> 99%), Polyetheramine (Mn = 230 g/mol, 400 g/mol, 2000 g/mol) were purchased from MACKLIN Chemicals Ltd. Phosphoryl chloride (> 98%) was purchased from Xiya Regent Chemicals Ltd. Isobutyraldehyde (> 99%), Triethylamine (> 99%), Hydroxylamine hydrochloride (> 99%), Sodium acetate (> 99%), Potassium carbonate (> 99%) Hexamethylene diisocyanate (HDI) (> 99%) and Levulinic acid (> 99%) were purchased from Adamas Chemistry Co Ltd.

# 2. Experimental Procedures

#### Synthesis of 1, 6-diisocyanohexane:



This compound was prepared according to a literature procedure.<sup>1</sup> A solution of hexamethylenediamine (2.91 g, 25.0 mmol, 1.0 equiv.) in ethyl formate (35.5 mL, 465 mmol, 18.6 equiv.) was refluxed at 80 °C overnight. Then the crude product was concentrated in vacuo and dissolved in CH<sub>2</sub>Cl<sub>2</sub> (100 mL) with triethylamine (35 mL, 251 mmol, 10 equiv.) at 0 °C. When the temperature was stable, phosphorus oxychloride (5.5 mL, 50.0 mmol, 2.4 equiv.) was added dropwise into the solution over 20 min. The mixture was stirred at room temperature for 6 h. Ice water (200 mL) containing K<sub>2</sub>CO<sub>3</sub> (20.0 g) was added and was stirred for another 30 min. The mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 50 mL). The organic layers were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated in vacuum. The crude product was purified by column chromatography (silica gel) using PE/EA (4:1) as eluent. 1, 6-diisocyanohexane was obtained as a yellow oil (2.30 g, 70% yield). The spectral data are in accordance with the literature.<sup>1</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 3.43-3.41 (m, 4H), 1.71 (m, 4H), 1.52-1.49 (m, 4H) ppm (Figure S1a).



**Fig. S1. (a).** <sup>1</sup>H NMR spectrum of 1,6-diisocyanohexane. **(b) (c) (d).** Comparison of <sup>1</sup>H NMR spectrum before and after functional group transformation.

Synthesis of D230-U: This polymer chain was prepared according to a literature procedure.<sup>2</sup> In a100 mL flask, polyetheramine ( $M_n$  = 230 g/mol, 4.6 g, 20.0 mmol) and isobutyraldehyde (5.21 g, 60.0 mmol) were dissolved in methanol (20 mL) and stirred at room temperature for 1 h. Then the mixture of 1,6-diisocyanohexane (2.72 g, 20.0 mmol), levulinic acid (6.96 g, 60.0 mmol) and THF (7.5 mL) were added. The mixture was stirred for 48 h at room temperature. Then the solvent was removed in vacuo, and the mixture was dissolved in dichloromethane (12 mL). Precipitation in cold hexane (twice) and dry in vacuum at 50°C for 12 h got polymer chain D230-U (7.12 g, 46% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) spectra of D400-U as an example was shown in Fig. S2, GPC curve were shown in Fig. S3 and Mn, Mw, PDI were recorded in Table

S1.

Synthesis of D2000-U: This polymer chain was prepared according to a literature procedure.<sup>2</sup> In a 100 mL flask, polyetheramine ( $M_n$  = 2000 g/mol, 4.0 g, 2.0 mmol) and isobutyraldehyde (0.521 g, 6.0 mmol) were dissolved in methanol (10 mL) and stirred at room temperature for 1 h. Then the mixture of 1, 6-diisocyanohexane (0.27 g, 2.0 mmol), levulinic acid (0.67 g, 6.0 mmol) and THF (5.0 mL) were added. The mixture was stirred for 48 h at room temperature. Then the solvent was removed in vacuo, and the mixture was dissolved in dichloromethane (12 mL). Precipitation in cold hexane (twice) and dry in vacuum at 50 °C for 12 h got polymer chain D2000-U (2.03g, 40% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) spectra of D400-U as an example was shown in Fig. S2, GPC curves were shown in Fig. S3 and Mn, Mw, PDI were recorded in Table S1.

Synthesis of D230-OH: In a 250 mL flask, D230-U, (2.0 g), NaOAc (3.39 g) and hydroxylamine hydrochloride (1.80 g) were dissolved in a mixture of ethanol (80 mL) and water (40 mL) and refluxed at 100 °C overnight. Then the mixture was extracted with  $CH_2Cl_2$  (3 × 50 mL). The organic layers were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, precipitated in cold diethyl ether (twice) and placed in vacuum at 50 °C for 12h to yield polymer chain D230-OH (1.62 g, 80% yield). Characteristic peak changes of D230-U and D230-OH in <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) spectra were shown in Fig. S1b.

**Synthesis of D2000-OH:** In a 250 mL flask, D2000-U, (2.0 g), NaOAc (1.06g) and hydroxylamine hydrochloride (0.56 g) were dissolved in a mixture of ethanol (80

mL) and water (40 mL) and refluxed at 100 °C overnight. Then the mixture was extracted with  $CH_2Cl_2$  (3 × 50 mL). The organic layers were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, precipitated in cold diethyl ether (twice) and placed in vacuum at 50 °C for 12 h to yield polymer chain D2000-OH (1.60 g, 79% yield). Characteristic peak changes of D2000-U and D2000-OH in <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) spectra were shown in Fig. S1d.

**Synthesis of D230-Poly:** D230-OH (2.0 g) was dissolved in an appropriate amount of THF (10 wt%), then HDI (0.48 g) was added dropwise into the solution and stirred at room temperature for 10 min. Immediately, the mixture was poured into a square PTFE mould and evaporated solvent in fume hood to get the D230-Poly film. Then the film was further cured in vacuum at 60 °C for 24 h and the D230-Poly film was obtained.

**Synthesis of 2000-Poly:** D2000-OH (2.0 g) was dissolved in an appropriate amount of THF (10 wt%), then HDI (0.14 g) was added dropwise into the solution and stirred at room temperature for 10 min. Immediately, the mixture was poured into a square PTFE mould and evaporated solvent in fume hood to get the D2000-Poly film. Then the film was further cured in vacuum at 60 °C for 24 h and the D2000-Poly film was obtained.

**Swelling experiments:** Swelling experiments of Dx-Poly were performed in DMF. Approximately 50 mg fragments of each material were immersed in DMF for 72 h at 25 °C, respectively.

swelling ratio = 
$$(m_s - m_i)/m_i$$

 $m_i$ ,  $m_s$ , were the mass of sample in initial, swollen state, respectively. The  $m_s$ ,  $m_i$  and swelling ratio were record in Table S2.

### 3. Characterization Methods

**Nuclear Magnetic Resonance Spectroscopy.** Nuclear magnetic resonance (NMR) spectra were obtained by using a Bruker AV400 spectrometer (400 MHz). The solution is CDCl<sub>3</sub>, and the internal reference is tetramethyl silane.

**Gel Permeation Chromatography.** Number-average molecular weights (M<sub>n</sub>) and polydispersity indexes (PDI) were determined by gel permeation chromatography (GPC) equipped with a 2414 refractive index detector, a Waters 1525 binary HPLC pump, and three Waters Styragel HT columns (HT2, HT3, HT4). The columns were thermostated at 35 °C, and DMF was used as an eluent at a flow rate of 1.0 mL/min. Calibration was made against standard monodisperse linear polystyrene (PSt); the obtained datum was processed on professional software.

**Thermogravimetric Analyses**. Thermogravimetric analyses (TGA) were performed with a Mettler Toledo TGA/DSC3<sup>+</sup> instrument under nitrogen atmosphere at heating rate of 10 °C /min from 40 °C to 800 °C.

**Dynamic Mechanical Analysis.** Dynamic mechanical analysis (DMA) performed on Mettler DMA1 were used to performing stress–relaxation experiments and measuring the glass transition temperature ( $T_g$ ). Stress–relaxation experiments were conducted with samples of dimension (30 × 4 × 2 mm<sup>3</sup>). Samples were initially preloaded at a force of -0.01 N to maintain straightness, 4 % strain was applied and maintained at the corresponding temperature during the test. The decrease of stress was recorded and the stress relaxation modulus was calculated.  $T_g$  analyses have been carried out with samples of dimension ( $30 \times 4 \times 2 \text{ mm}^3$ ) at the frequency of 1 Hz, from -20 to 100 °C at 3 °C/min (D230-Poly and D400-Poly) and from -60 to 70 °C at 3 °C/min (D2000-Poly).

**Static Tensile Testing.** The mechanical performances were analyzed by a Shimadzu AGS-X Tester (equipped with 50 N sensor) at a strain rate of 5 mm/min with dumbbell-shaped samples (gauge length = 15 mm). Each sample was tested in at least five dumbbell-shaped specimens, and the reported results were obtained by calculating the average values of each group.



Fig. S2. <sup>1</sup>H NMR spectrum of D400-U as an example.



Fig. S3. GPC curves of Dx-U.

Table S1. GPC data of Dx-U

Sample	Mn (g/mol)	Mw (g/mol)	PDI
D230-U	12400	17300	1.39
D400-U	14500	22100	1.52
D2000-U	30200	51200	1.69



**Fig. S4.** (a), (b), (c), (d), (e), (f), (g) and (h). The <sup>1</sup>H NMR spectra of different reaction times (2 h, 4 h, 6 h, 8 h, 12 h, 24 h, 36 h and 48 h respectively), (i). The relationship between functional group conversion rate and reaction time.



**Fig. S5.** (a). GPC curves of D230-U 12 h, D230-U 24h and D230-U 48 h. (b). Infrared spectrum of D230-U (48 h) and Step-1.

Sample	$m_{i}\left(g ight)$	$m_{s}\left(g ight)$	Swelling ratio (%)
D230-U	0.0349	0.0740	112
D400-U	0.0572	0.123	115
D2000-U	0.0312	0.0702	125

 Table S2. Swelling data in DMF of Dx-Poly

Table S3. Tensile mechanical property and healing efficiency of Dx-Poly.

Sample	Stress (original)	Strain (original)	Stress (reprocessed)	Strain (reprocessed)	Healing efficiency of	Healing efficiency of
	[MPa]	[%]	[MPa]	[%]	stress (%)	strain (%)
D230-U	$7.79 \pm 0.23$	$179 \pm 3$	$6.47\pm0.14$	$168 \pm 4$	83 ± 3	$93 \pm 4$
D400-U	$8.75 \pm 0.18$	$255 \pm 6$	$8.25 \pm 0.31$	$244\pm7$	$94 \pm 4$	$95 \pm 3$
D2000-U	$2.60\pm0.07$	$147\pm2$	$2.43 \pm 0.09$	$144 \pm 3$	$93 \pm 3$	$97 \pm 3$

(a)

(b)





**Fig. S6.** Swelling experiment of Dx-Poly and Dx-Poly could not be soluble in DMF for 7 days at 25 °C.



Fig. S7. TGA curves of Dx-Poly



Fig. S8. Stress-relaxation curves of Dx-Poly at 150 °C.



Fig. S9. Optical microscope images (a) before, (b) after the healing process at 80°C for 5 h and (c) after the healing process at 80°C for 20 h.



Fig. S10. Stress-strain curves of (a) D230-Poly and (b) D2000-Poly before and after hot pressing.

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