Electronic Supplementary Information

Long-chain polyamide covalent adaptable networks based on renewable ethylene

brassylate and disulfide exchange

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The ESI contains 25 figures and 3 tables in 17 pages.



FTIR spectra of the EB/Cys/TAEA mixtures after 18 h at 100 °C

Fig. S1 FTIR spectra of the EB/Cys/TAEA networks after curing at 100 °C for 18 h. The signal at 1736 cm⁻¹ is due to the unreacted EB monomer, resulting in low gel content and indicating that the reaction required higher temperature and longer time to proceed towards completeness.

¹H NMR spectra



Fig. S2 ¹H NMR (400 MHz, CDCl₃) spectra of pure cystamine (bottom) and the cystamine/TBD mixture (top) after heating to dissolve TBD. Signals a' and b' are attributed to partially deprotonated Cys.



Fig. S3 ¹H NMR spectrum (400 MHz, CDCl₃) of the combined dissolved phases after swelling the four PA CANs. TBD is prevalent while some residual monomers and/or linear oligomers are observed (4.2-3.8, 2.7-2.1, 1.6-1.2 ppm). *corresponds to residual HFIP.

EDS analysis of the PA CANs



Fig. S4 Elemental map of Cys30; carbon is presented in green, nitrogen in blue, oxygen in red and sulfur in yellow (the brightness has been increased after obtaining the maps).



Fig. S5 Elemental map of Cys40; carbon is presented in green, nitrogen in blue, oxygen in red and sulfur in yellow (the brightness has been increased after obtaining the maps).



Fig. S6 Elemental map of Cys50; carbon is presented in green, nitrogen in blue, oxygen in red and sulfur in yellow (the brightness has been increased after obtaining the maps).



Fig. S7 Elemental map of Cys60; carbon is presented in green, nitrogen in blue, oxygen in red and sulfur in yellow (the brightness has been increased after obtaining the maps).





Fig. S9 Representative E'' curves of the pristine PA CANs with varying cystamine content. If the T_g is taken as the maximum of the curve the values for each network are: Cys30 18 \pm 1; Cys40 14 \pm 0.2; Cys50 11 \pm 1; Cys60 15 \pm 1.



Fig. S10 DMA triplicate analysis of Cys50 (top row) and Cys60 (bottom row) showing that not all of the samples had multiple peaks in the tan δ curves.



Fig. S11 Stress relaxation curves of Cys60 at 70 and 120 °C.

Characterization of the EDOBA:Cys reference networks

Three networks with different fractions of dynamic bonds were prepared as references. To do so, the total diamine:triamine ratio was kept constant at 50:50 and the non-dynamic:dynamic diamine ratio was varied, Fig. S13.



Fig. S12 Ratios of EDOBA:Cys to prepare reference networks with different fractions of dynamic bonds.

Table S1. Properties of the EDOBA: Cys reference r	networks
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EDOBA:Cys	Gel content	$T_{g, DSC}$	T _{g, DMA}	T_{m}	ΔH_m	v_{e}	τ
	(%)	$(^{\circ}C)^{a}$	$(^{\circ}\mathrm{C})^{b}$	$(^{\circ}C)^{a}$	$(J g^{-1})^a$	$(\text{mol } \text{m}^{-3})^c$	$(\mathbf{s})^d$
40:10	92 ± 1.2	16 ± 0.9	39 ± 2	82 ± 0.1	$33\pm\ 0.1$	324 ± 39	-
25:25	91 ± 0.9	19 ± 0.8	37 ± 1	81 ± 2	$33\pm\ 0.3$	332 ± 39	-
10:40	87 ± 1.4	21 ± 0.5	45 ± 2	$84\pm\ 0.5$	$35\pm\ 0.7$	255 ± 8	28.5



Fig. S13 Stacked FTIR spectra of the EDOBA:Cys reference networks.



Fig. S14 Representative E' (left) and $tan\delta$ (right) curves of the EDOBA:Cys networks.



Fig. S15 Stress relaxation curves of the EDOBA:Cys networks.







Fig. S18 Strain sweep (100 °C) of Cys50.



Fig. S19 Strain sweep (100 °C) of Cys60.



Fig. S20 Strain sweep (100 °C) of EDOBA50.

Calculation of crystal plane distance (d).

According to Bragg's law:

$$d = \frac{n\lambda}{2sin\theta}$$

where $\lambda_{CuKa} = 1.54$ nm and θ is the incident angle for which constructive interference occurs. For the EDOBA50 control network and the EB/TAEA network:

 $2\theta = 21.7^{\circ}$ therefore $\theta = 10.85^{\circ}$

$$d = \frac{1.54}{2\sin(10.85)} = \frac{1.54}{0.376} \approx 4.1 \text{ nm} = 41 \text{ Å}$$

For the PA CANs containing S atoms:

 $2\theta = 21.4^{\circ}$ therefore $\theta = 10.7^{\circ}$

$$d = \frac{1.54}{2 \sin(10.7)} = \frac{1.54}{0.371} \approx 4.15 \text{ nm} = 41.5 \text{ Å}$$

Characterization of the reference EDOBA50 and Hex50 control networks

Note: The EDOBA50 and Hex50 networks were synthesized by curing the respective EB/EDOBA or Hex/TAEA mixture at 100 °C for 24 h. The FTIR spectra showed at that time complete disappearance of the C=O stretching band of EB (1736 cm⁻¹), Fig. S22, and the gel content was sufficiently high to stop the curing.

Table S2. Properties of the EDOBA50 and Hex50 networks.

Network	Gel content	T _{g,DSC}	$T_{g,DMA}$	T_m	De	T _{d,5%}
	(%)	$(^{\circ}\mathrm{C})^{a}$	$(^{\circ}C)^{b}$	(°C)	$(\text{mol } \text{m}^{-3})^c$	(°C)
EDOBA50	87 ± 0.7	18 ± 0.8	16 ± 2	84 ± 0.6	364 ± 46	222
Hex50	84 ± 0.8	20 ± 0.9	6 ± 0.8	68 ± 1	284 ± 50	n.d. ^d
				123 ± 0.8		

^{*a*}Obtained from the second heating scan. Scans run between -30-200 °C with 10 K min⁻¹. ^{*b*}Maximum of tan δ . ^{*c*}Calculated through eq. 1. E' in rubbery plateau for EDOBA50 and Hex50 was taken at 100 °C and 175 °C, respectively. ^{*d*}Not determined.



Fig. S21 FTIR spectrum of (a) EDOBA50 and (b) Hex50 networks.



Fig. S22 Representative E' and $\tan \delta$ curves of EDOBA50 and Hex50 networks.



Fig. S23 Comparison of representative DSC traces (2^{nd} heating scan, -30-200 °C) of Hex50, EDOBA50 and Cys50 networks. Only Hex50 presented a second melting transition at high temperature ($T_{m,2} = 124$ °C) while EDOBA50 and Cys50 displayed only one $T_m > T_{m,1}$ of Hex50, indicating that the heteroatoms (O and S) are likely participating in secondary interactions.



DMA results of the reprocessed PA CANs

Fig. S24 Representative E', E" and $\tan \delta$ curves of the reprocessed PA CANs; Cys30 first row, Cys40 second row, Cys50 third row, Cys60 fourth row, respectively.





Fig. S25 FTIR spectra of the PA CANs after each reprocessing cycle. The dashed lines indicate the amide I and II band.

Chemical resistance of Cys40

Note: Specimens of Cys40 that were hot-pressed once were immersed in each solvent for 24 h. After 24 h, the solvent from each vial was decanted off and the remaining solids were collected and washed with copious amounts of acetone, followed by drying at 100 °C under vacuum. It is possible that the high-boiling point solvents (DMF, DMSO) were not completely removed, but to avoid decomposition of the network the temperature was not increased any further. The reported final mass in Table S3 refers to the value measured after the above-described procedure.

Solvent	Initial mass (g)	Final mass (g)	Mass loss (%)
Hex	0.046	0.046	0
PhMe	0.052	0.050	4
Et ₂ O	0.051	0.050	2
DCM	0.086	0.076	12
THF	0.048	0.047	2
EtOAc	0.050	0.050	0
Me ₂ CO	0.065	0.063	3
MeOH	0.041	0.039	5
MeCN	0.051	0.050	2
DMF	0.061	0.057	7
DMSO	0.100	0.093	7
H_2O	0.051	0.049	4
HCl (aq 1M)	0.059	0.057	3
NaOH (aq 1M)	0.065	0.060	8

Table S3. Chemical resistance of Cys40 against different solvents.