Supporting Information Quantity or Quality: Are Self-Healing Polymers and Elastomers Always Tougher with more Hydrogen Bonds?

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Experimental

Materials

All materials were obtained from commercial suppliers and used as received unless otherwise stated.

Synthesis of 2-(propionic acid)yldodecyl trithiocarbonate (PADTC)

PADTC was synthesized as outlined in the literature.¹

Synthesis of 2-(((6-(3-(6-methyl-4-oxo-1,4-dihydropyrimidin-2yl)ureido)hexyl)carbamoyl)oxy)ethyl acrylate (UPyA)

UPyA was synthesized as outlined in the literature.²

Synthesis of furfuryl methacrylate (FMA)

FMA was synthesized as outlined in the literature.³

Synthesis of a typical RAFT UPy HEA polymer (Poly(HEA100-UPyA7.5))

To a 50 mL round bottom flask containing a magnetic stirrer bar, UPyA powder (1.3268 g, 0.0032 mol) and 9.9855 g dimethylformamide (DMF) were added. The reaction mixture was capped with a rubber septum, and then allowed to homogenize for 5 minutes at 65 °C, followed by deoxygenating with nitrogen for 20 min at ambient temperature. Meanwhile, PADTC (0.3019 g, 0.0009 mol), azobisisobutyronitrile (AIBN, 0.0282 g, 0.0002 mol), hydroxyethyl acrylate (HEA, 5.0000 g, 0.0431 mol) were added in a small vial and the prepared reaction mixture was transferred to the round bottom flask via syringe, while the whole system was still being purged with nitrogen. After deoxygenation, the reaction was stirred at 65 °C overnight. The resulting Poly(HEA₁₀₀-UPyA_{7.5}) polymer solution was confirmed by 500 MHz 1H-NMR with above 95% conversion. The materials were analyzed by size exclusion chromatography (SEC) to evaluate molecular weight distribution.

Synthesis of a typical RAFT UPy EA polymer (Poly(EA100-UPyA7.5))

To a 50 mL round bottom flask containing a magnetic stirrer bar, UPyA powder (1.5389 g, 0.0037 mol) and 10.0956 g dimethylformamide (DMF) were added. The reaction mixture was

capped with a rubber septum, and then allowed to homogenize for 5 minutes at 65 °C, followed by deoxygenating with nitrogen for 20 min at ambient temperature. Meanwhile, PADTC (0.1751 g, 0.0005 mol), azobisisobutyronitrile (AIBN, 0.0164 g, 0.0001 mol), ethyl acrylate (EA, 5.0000 g, 0.0499 mol) were added in a small vial and the prepared reaction mixture was transferred to the round bottom flask via syringe, while the whole system was still being purged with nitrogen. After deoxygenation, the reaction was stirred at 65 °C overnight. The resulting Poly(EA₁₀₀-UPyA7.5) polymer solution was confirmed by 500 MHz 1H-NMR with above 95% conversion. The materials were analyzed by size exclusion chromatography (SEC) to evaluate molecular weight distribution.

Synthesis of a typical RAFT FMA HEA polymer (Poly(HEA100-FMA7.5))

To a 50 mL round bottom flask equipped with a magnetic stirrer bar, PADTC (0.1510 g, 0.0004 mol), AIBN (0.0141 g, 0.0001 mol), HEA (5.0000 g, 0.0431 mol), FMA (0.5367 g, 0.0032 mol) and 8.5526 g dimethylformamide (DMF) were added. The reaction mixture was capped with a rubber septum and purged with nitrogen for 20 min. The reaction was stirred at 65 °C for 2 h. The resulting Poly(HEA₁₀₀-FMA_{7.5}) polymer solution was confirmed by 500 MHz 1H-NMR with above 80% conversion. The crude product was precipitated by dropwise addition to stirred diethyl ether. The product was dried overnight in a vacuum oven giving Poly(HEA₁₀₀-FMA_{7.5}). The materials were analyzed by SEC to evaluate molecular weight distribution.

Synthesis of a typical RAFT FMA EA polymer (Poly(EA100-FMA7.5))

To a 50 mL round bottom flask equipped with a magnetic stirrer bar, PADTC (0.1751 g, 0.0005 mol), AIBN (0.0164 g, 0.0001 mol), EA (5.0000 g, 0.0499 mol), FMA (0.6224 g, 0.0037 mol)

and 8.7208 g dimethylformamide (DMF) were added. The reaction mixture was capped with a rubber septum and purged with nitrogen for 20 min. The reaction was stirred at 65 °C for 5 h. The resulting Poly(EA100-FMA7.5) polymer solution was confirmed by 500 MHz 1H-NMR with above 80% conversion. The crude product was precipitated by dropwise addition to stirred hexanes. The product was dried overnight in a vacuum oven giving Poly(EA100-FMA7.5). The materials were analyzed by SEC to evaluate molecular weight distribution.

Synthesis of a typical RAFT EA polymer (Poly(EA100))

To a 50 mL round bottom flask equipped with a magnetic stirrer bar, PADTC (0.1751 g, 0.0005 mol), AIBN (0.0164 g, 0.0001 mol), EA (5.0000 g, 0.0499 mol), and 7.7872 g dimethylformamide (DMF) were added. The reaction mixture was capped with a rubber septum and purged with nitrogen for 20 min. The reaction was stirred at 65 °C for 8 h. The resulting Poly(EA₁₀₀) polymer solution was confirmed by 500 MHz 1H-NMR with above 95% conversion. The crude product was precipitated by dropwise addition to stirred 50:50 mixture of ethanol and water. The product was dried overnight in a vacuum oven giving Poly(EA₁₀₀). The materials were analyzed by SEC to evaluate molecular weight distribution.

Synthesis of a typical RAFT HEA polymer (Poly(HEA100))

To a 50 mL round bottom flask equipped with a magnetic stirrer bar, PADTC (0.1509 g, 0.0004 mol), AIBN (0.0141 g, 0.0001 mol), HEA (5.0000 g, 0.0431 mol), and 7.7903 g dimethylformamide (DMF) were added. The reaction mixture was capped with a rubber septum and purged with nitrogen for 20 min. The reaction was stirred at 65 °C for 8 h. The resulting Poly(HEA₁₀₀) polymer solution was confirmed by 500 MHz 1H-NMR with above 95%

conversion. The crude product was precipitated by dropwise addition to stirred Toluene. The product was dried overnight in a vacuum oven giving Poly(HEA₁₀₀). The materials were analyzed by SEC to evaluate molecular weight distribution.

Typical Interpenetrated Network Polymer Synthesis

Poly(EA₁₀₀-FMA_{7.5}-UPyA_{7.5}) is used here as an example to demonstrate the general procedure of making interpenetrated networks. The prepared dry Poly(EA₁₀₀-FMA_{7.5}) polymer was weighed and the realized mass (4.8734 g, 0.0004 mol) was taken to calculate the theoretical weight of Poly(EA₁₀₀-UPyA_{7.5}) polymer-DMF solution, in order to combine two polymers as 1 : 1 ratio with respect to polymer weight (mass basis). In this case, 12.1835 g Poly(EA₁₀₀-UPyA_{7.5}) polymer-DMF solution was added to the Erlenmeyer flask containing precipitated Poly(EA₁₀₀-FMA_{7.5}) polymer and homogenized via sonicator. In a separate vial, 1,1′ (methylenedi-4,1 phenylene)bismaleimide (BMI) (0.6072 g, 0.0014 mol) was dissolved in 2.4367 g of DMF and, then transferred into the flask containing the prepared polymer mixture solution. Once fully dissolved and homogenized, the contents of the flask were transferred to a Teflon mold to process polymerization at 45–50 °C for 48 h. After crosslinking, the materials were removed from the Teflon mold and allowed to dry in the fume hood for 24 h and overnight in a thermal oven.

Nuclear Magnetic Resonance (NMR)

All NMR experiments were performed on a Bruker Advance 300 or 500 MHz spectrometer.

Determination of number average molecular weight (Mn) and composition by NMR

Typical PHEA-FMA materials, 0.88 ppm (PADTC-CH₃) was calibrated to 3H, 4.1 ppm (HEA-CH₂ at ester) was integrated and divided by 2 (2H from HEA) delivering the HEA units. Then, 6.49 ppm (FMA-aromatic) was integrated and divided by 2 (2H from FMA) delivering FMA units. Typical PHEA-UPyA materials, 0.88 ppm (PADTC-CH₃) was calibrated to 3H, 3.58 ppm (HEA-CH₂ adjacent to OH group) was integrated and divided by 2 (2H from HEA) delivering the HEA units. The 3.58 ppm (HEA) integral value was subtracted from 4.1 ppm (HEA+UPyA) integral value, the result was divided by 4 (4H from UPyA from CH₂ at UPyA ester and CH₂ at UPyA NHCOOCH₂ urethane) delivering the UPyA units.

Typical PEA-FMA materials, 3.36 ppm (PADTC-CH₂ at trithiocarbonate) was calibrated to 2H, 4.1 ppm (EA-CH₂ at ester) was integrated and divided by 2 (2H from EA) delivering EA units. Peak at 6.41 ppm (FMA-aromatic) was integrated and divided by 2 (2H from FMA) delivering the FMA units.

Typical PEA-UPyA materials, 0.88 ppm (PADTC-CH₃) was calibrated to 3H, the peaks near 3.20 ppm (UPyA) were integrated and divided by 4 (2H from UPyA urethane protons <u>CH₂NHCOOCH₂</u> and 2H from UPyA urea protons <u>CH₂NHCONH</u>) delivering the UPyA units. The peak at 4.10 ppm was integrated, and the resulting integral at 4.1 ppm had the integral values of the peaks near 3.2 ppm subtracted (4H from UPyA from CH₂ at UPyA ester and CH₂ at UPyA NHCOO<u>CH₂</u> urethane), and the remaining signal, divided by 2 (2H from EA CH₂ ester protons) delivering the EA units.

 M_n by NMR is typically calculated via multiplying monomer units by their respective molecular weights, a sum of the resulting values and the molecular weight of the chain transfer agent (PADTC) gives the experimental M_n value (See Table S1 and S2).

Infrared (IR) spectroscopy

All IR spectra were collected using a Bruker IFS 66/S Fourier transform spectrometer equipped with a tungsten halogen lamp, a CaF2 beam splitter, and a liquid nitrogen cooled InSb detector.

Differential Scanning Calorimetry (DSC)

All DSC experiments were performed on a TA instruments Q20 or Q2000 DSC system using a heating, cooling, heating cycle. For polymer networks, heat flow was monitored between -40 and 150 °C with a heating rate of 10 °C/min and a cooling rate of 5 °C/min. For homopolymers, heat flow was monitored between -60 and 150 °C with a heating rate of 10 °C/min and a cooling rate of 5 °C/min and a cooling rate of 5 °C/min. Only data from the second heating cycle was analyzed.

Size Exclusion Chromatography (SEC)

SEC was used to determine polymer molecular weight and dispersity data using an Agilent 1260 SEC system equipped with an autosampler, an Agilent 1260 isocratic pump, Agilent 1 guard and 2 analytical Polar Gel-M columns, degasser, and Agilent 1260 refractive index (RI detector). *N*,*N*-Dimethylformamide (DMF) + 0.1 wt% LiBr at 50 °C was the eluent at a flow rate of 1 mL/min. Each sample was filtered before injection. The SEC system was calibrated with poly(methyl methacrylate) standards, with conventional calibration for the determination of molecular weights and dispersities.

Tensile methods

An Instron 3344 universal testing system equipped with a 100 N load cell was used at room temperature for all tensile tests. The elongation of the materials was increased at rate of 0.05 mm s⁻¹. The fracture toughness and self-healing experiments were performed until failure for notched samples all self-healed samples respectively.

Young's Modulus Calculations

The Ogden hyperelastic model was used to determine the Young's modulus (E). The engineering stress (σ) was fitted with the following equation⁴:

$$S = \frac{2G}{a} \notin I^{a-1} - I^{-1-(a/2)} \notin Eq. S1$$

where, *G* is the shear modulus, α is the strain hardening exponent, and λ is the stretch ratio given by $\lambda = \varepsilon + 1$, where ε is the applied strain. *G* and α were found for each sample by fitting Eq. S1 to the experimental stress-strain data, and the elastic modulus (*E*) was found from Eq. S2:

$$E = 2G(1+\upsilon)$$
 Eq. S2

where v is Poisson's ratio (taken as 0.5 for an incompressible material). The mean and standard error were determined by fitting 3 replicates.

Fracture energy determination

An Instron 3344 universal testing system equipped with a 100 N load cell was used at room temperature for all fracture test. Samples were divided into two groups designate "notched" and

"unnotched". Materials of the cut group were notched half way through their respective width before being loaded onto the Instron in a manner that maintains the notch on a horizontal plane. The samples were then subjected to tensile tests. Unnotched materials were left without a notch and subject to the same tensile tests. Fracture energy was determined by integrating the stressstrain curve of the uncut samples up to the mean strain at break for the cut samples.

Self-Healing Procedures

Materials subjected to self-healing was first sliced in half with a razor blade and the two separate ends of such material was then pressed backed together at the sliced area using mild pressure from fingers. Afterwards all of the materials, both cut and uncut were placed into an oven at 90 °C for 24 hours to expose the materials to equivalent thermal conditions. Samples were then subjected to tensile tests. For cold self-healing performed under ambient conditions, the similar steps were followed except, the materials were not heated.

Additional experimental data

Table S1. Molecular weight data for RAFT PEA polymers synthesized. M_{n-NMR} is calculated as $M_{CTA}+Units_{EA}\times M_{EA}+Units_{UPyA}\times M_{UPyA}+Units_{FMA}\times M_{FMA}$. M_{n-th} is calculated as $M_{CTA}+TarUnits_{EA}\times Conv.eA}\times M_{EA}+TarUnits_{UPyA}\times Conv.UPyA}\times M_{UPyA}+TarUnits_{FMA}\times Conv.FMA}\times M_{FMA}$.HereTarUnits is the targeted number of units and Units is the number of units measured by NMR, and Conv.refers to monomer conversion.Total H-bond donor is the calculated total number of hydrogen bond donors given by CTA + 4 × Units_UPyA, since each CTA has 1 hydrogen bond donor on the initiating group and each UPyA unit has 4 hydrogen bond donors.

Polymer	Conv.	Units	Conv.	Units	Units	Total	M_{n-Th}	M _{n-NMR}	M _{n-SEC}	$M_w\!/M_{n\text{-}SEC}$
	EA	EA	UPyA	UPyA	FMA	H-				
			or			bond				
			FMA			donor				
PEA100-FMA5	88	98	>95	0	5	1	10000	11000	12000	1.44
PEA100-UPyA5	>95	92	>95	5	0	21	12000	12000	16000	1.20
PEA100-FMA7.5	86	99	>95	0	8	1	10000	12000	12000	1.48
PEA100-UPyA7.5	>95	90	>95	7	0	29	13000	12000	17000	1.23
PEA50-FMA3.75	90	63	>95	0	4	1	5500	7300	6300	1.34
PEA50-UPyA3.75	>95	41	>95	3	0	13	6600	5700	9000	1.21
PEA ₅₀	>95	57	-	0	0	1	5300	6100	5500	1.20
PEA100	>95	119	-	0	0	1	10000	12000	11000	1.18

Table S2. Molecular weight data for RAFT PHEA polymers synthesized. M_{n-NMR} is calculated as $M_{CTA}+Units_{HEA}\times M_{HEA}+Units_{UPyA}\times M_{UPyA}+Units_{FMA}\times M_{FMA}$. M_{n-th} is calculated as $M_{CTA}+TarUnits_{HEA}\times Conv._{HEA}\times M_{HEA}+TarUnits_{UPyA}\times Conv._{UPyA}\times M_{UPyA}+TarUnits_{FMA}\times Conv._{FMA}\times M_{FMA}$.Here TarUnits is the targeted number of units and Units is the number of units measured by NMR, andConv. refers to monomer conversion. Total H-bond donor is the calculated total number ofhydrogen bond donors given by CTA + 4 × Units_{UPyA} + Units_{HEA}, since each CTA has 1 hydrogen bonddonor on the initiating group, each HEA unit has 1 hydrogen bond donor, and each UPyA unit has 4hydrogen bond donors.

Polymer	Conv.	Units	Conv	Units	Units	Total	M_{n-Th}	Mn-NMR	Mn-SEC	$M_w\!/M_{n\text{-}SEC}$
	HEA	HEA	UPYA	ОРУА	FMA	н-				
			or			bond				
			FMA			donor				
PHEA100-FMA5	79	92	>95	0	5	93	10000	12000	18000	1.29
PHEA100-UPyA5	>95	112	>95	5	0	123	14000	15000	22000	1.23
PHEA100-FMA7.5	74	79	>95	0	7	80	10000	11000	16000	1.33
PHEA100-UPyA7.5	>95	102	>95	7	0	131	15000	15000	25000	1.17
PHEA50-FMA3.75	73	41	>95	0	4	42	5300	5800	7700	1.22
PHEA50-UPyA3.75	>95	56	>95	4	0	77	7700	8500	12000	1.19
PHEA ₅₀	>95	55	-	0	0	56	6000	6700	9600	1.25
PHEA ₁₀₀	>95	110	-	0	0	111	12000	13000	17000	1.25



Figure S1. SEC traces of PEA50-FMA3.75, PEA50-UPyA3.75, PHEA50-FMA3.75, and PHEA50-UPyA3.75.



Figure S2. NMR data for PEA50-FMA3.75, PEA50-UPyA3.75.



Figure S3. NMR data for PHEA50-FMA3.75, PHEA50-UPyA3.75.



Figure S4. Infrared spectra of PEA₁₀₀-7.5%. & PHEA₁₀₀-7.5% materials.



Figure S5. A) Self-healing at ambient temperature of PEA₁₀₀-7.5%. B) Self-healing at ambient temperature of PHEA₁₀₀-7.5%.



Figure S6. A) Self-healing at ambient temperature of PEA₅₀-7.5%. B) Self-healing at ambient temperature of PHEA₅₀-7.5%.

References

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