Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting information

Dynamic Covalent Exchange in Poly(thioether anhydrides)

Kelly R. Tillman, Rebecca Meacham, Julian F. Highmoore, Mikenzie Barankovich, Ana M. Witkowski, Patrick T. Mather,[2] Tyler Graf,[2"] Devon A. Shipp*

Department of Chemistry & Biomolecular Science, Clarkson University, Potsdam NY 13699-5810

[2]Department of Chemical Engineering, Bucknell University, Lewisburg PA.

"Current Address:

Murray State University

Department of Chemistry

1201 Jesse D. Jones Hall

Murray, KY 42071

270-809-6540

tgraf@murraystate.edu

* To whom correspondence should be addressed

dshipp@clarkson.edu

Orchid ID: 0000-0002-8709-1667

Patrick T. Mather: Orcid ID: 0000-0002-2267-0457

Table S1: Monomer amounts used in preparation of cross-linked polyanhydrides

Composition	PNA (g)	HDT (g)	PETMP (g)
100:80:20	0.6090	0.4152	0.1562
100:70:30	0.7074	0.4145	0.2937
100:60:40	0.6614	0.3526	0.3769
100:50:50	0.7019	0.3075	0.4771
100:20:80	0.7082	0.1214	0.7552
100:0:100	0.7202	0	0.9626

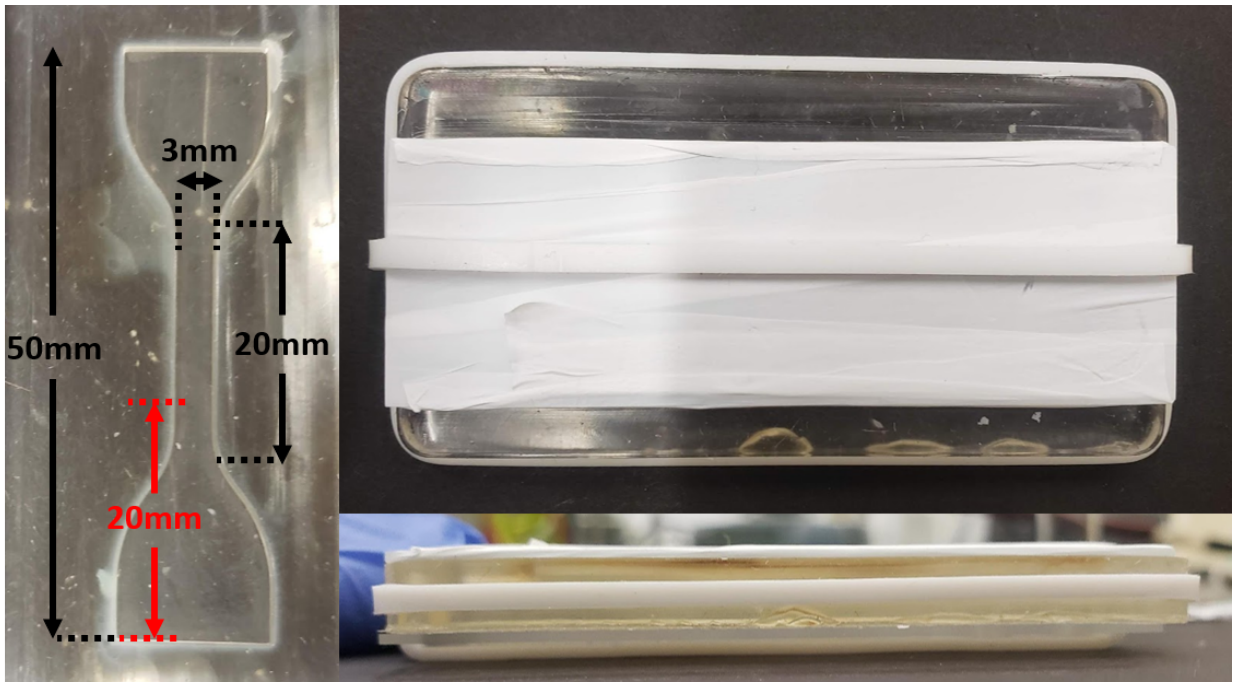

Figure S1: The 1mm deep PDMS dog-bone mold (left) used for the self-healing study shows the dimensions of the polymer mold and the position of the razor incision used to keep microscope imaging consistent. An image of the self-healing apparatus (right) uses heat resistant rubber bands around the PDMS dog-bone mold and Teflon wrapped glass slides providing a closed environment.

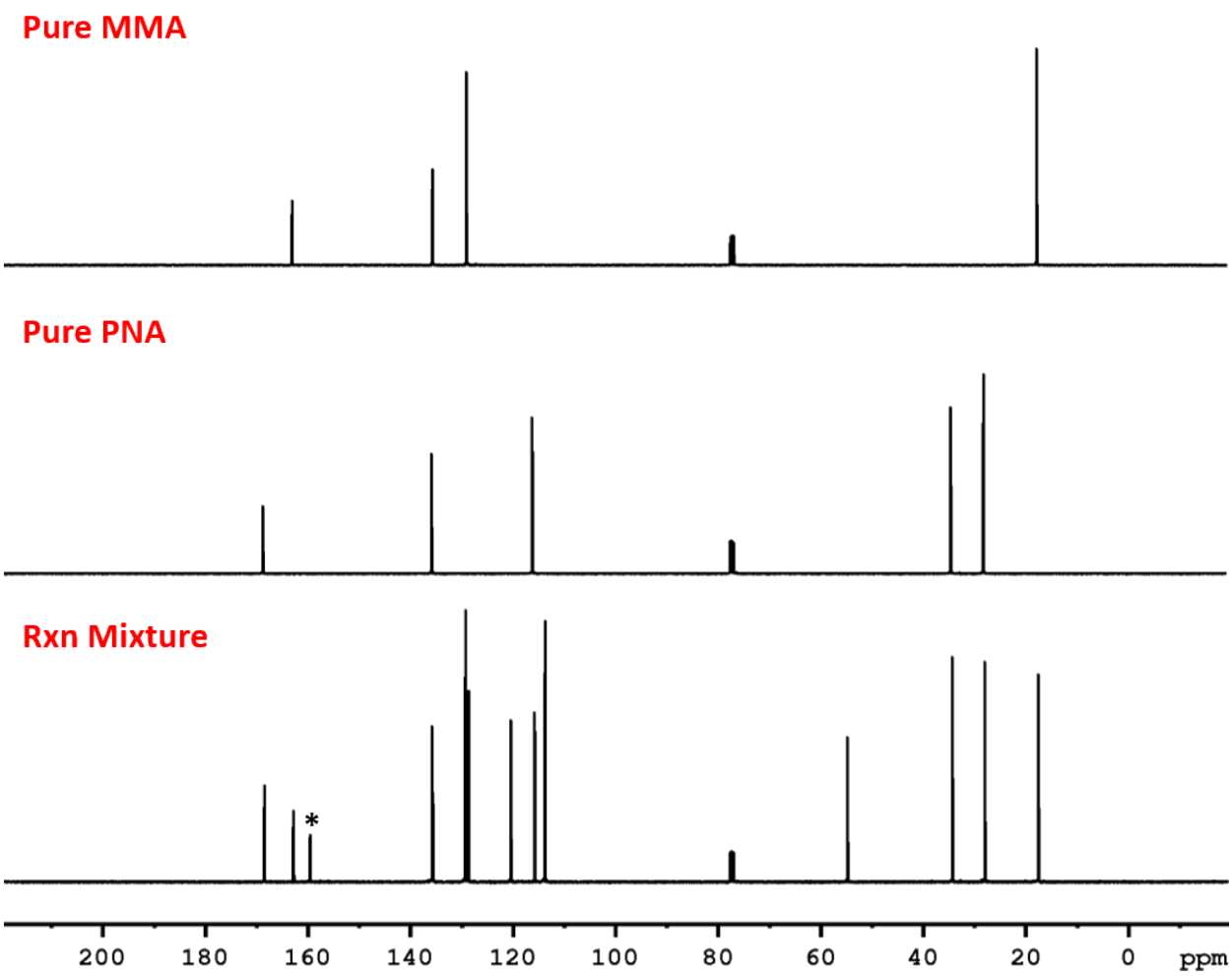

Figure S2: ^{13}C NMR Spectra comparing pure compounds to reaction mixture for peak tracking comparison. *represents internal standard, anisole.

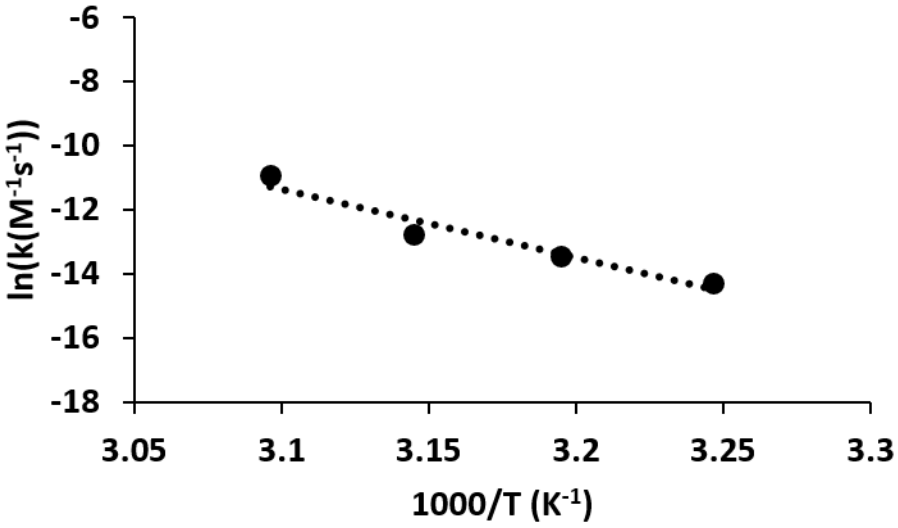

Figure S3: Arrhenius plot of k_f for the PNA + MAAn exchange reaction.

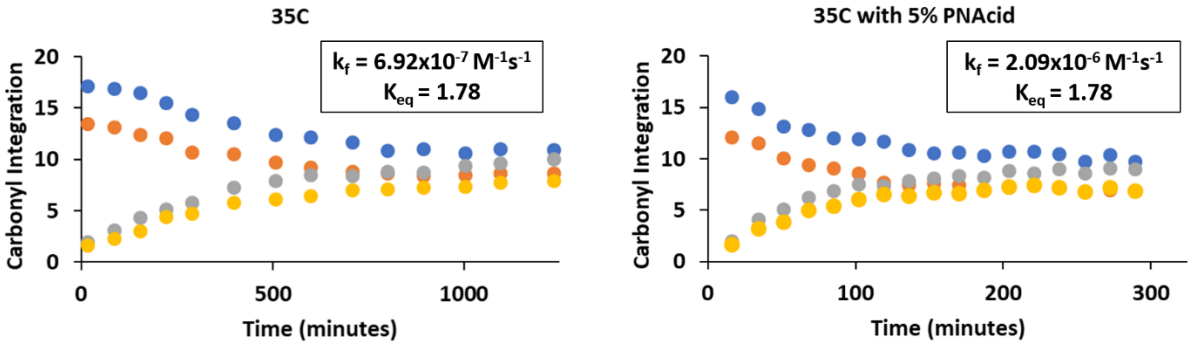

Figure S4: Comparison of rates of small molecule DCE reaction at 35°C (left) and 35°C with addition of carboxylic acid 4-pentenoic acid (right).

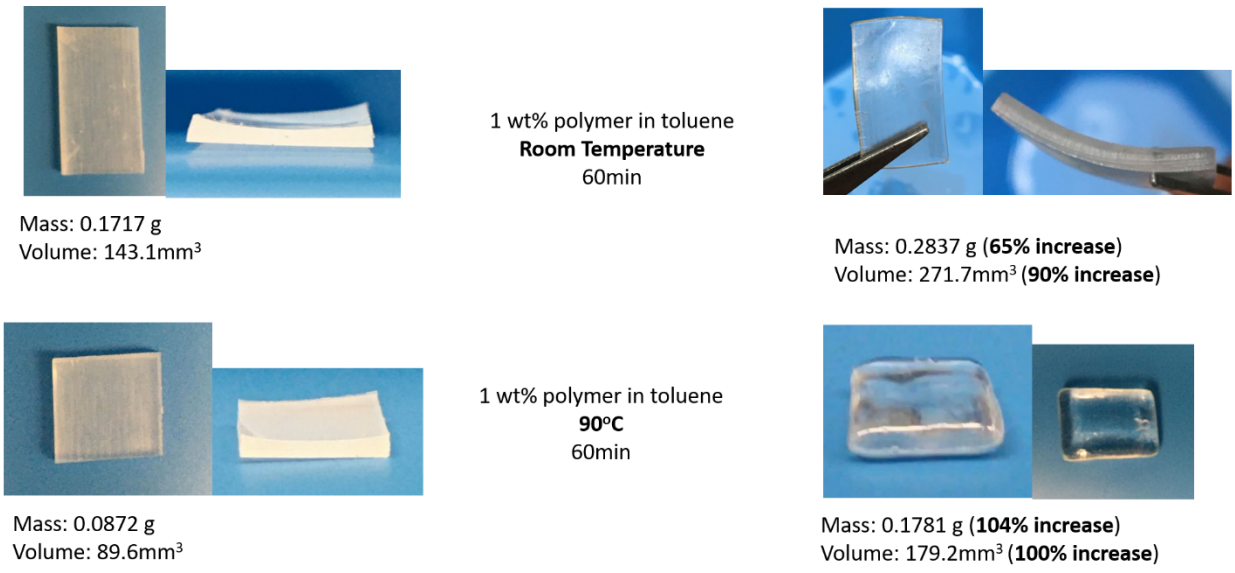

Figure S5: Solvent resistance test of PNA:HDT:PETMP 100:80:20 (least cross-linked) in toluene at room temperature (top) and 90°C (bottom).

Swelling Test: Polymer was cut with a razor blade, dimensions and mass were determined, and the sample was placed in a vial with toluene at a concentration of 1wt% polymer. For the sample that was heated, a PTFE sleeve was cut and placed at the bottom of the vial to prevent adhesion to the glass. One sample sat at room temperature, while the other was placed in an oil bath at 90°C. The duration of the test was 60 min, allowing for sufficient exchange to occur. The temperature was selected to prove that at elevated temperatures where exchange is occurring, the material maintains cross-link connectivity. The results show an increase in swelling at elevated temperatures, which occurs from the DCE relaxing the stressed cross-links, in return allowing for further swelling.

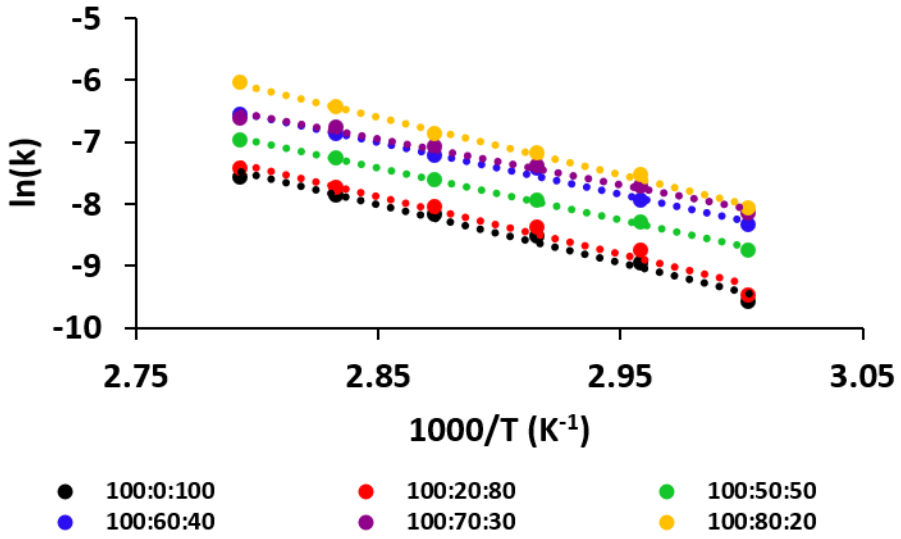

Figure S6. Arrhenius plot of stress relaxation rates in poly(thioether anhydrides) measured by DMA.

Table S2. Statistical Data for tensile data collected on the original, notched, and healed samples.

	ORIGINAL			NOTCHED			HEALED		
	Strain at break	Peak Stress (MPa)	Tensile Toughness (MJ/m^3)	Strain at break	Peak Stress (MPa)	Tensile Toughness (MJ/m^3)	Strain at break	Peak Stress (MPa)	Tensile Toughness (MJ/m^3)
SAMPLE 1	0.34	5.2	136	0.06	1.3	4.9	0.4	6.3	180
SAMPLE 2	0.28	5.1	103	0.06	1.5	5.3	0.28	5.6	116
SAMPLE 3	0.29	6.2	135	0.06	1.5	5.3	0.4	7.8	233
AVG.	0.31	5.5	125	0.06	1.4	5.2	0.36	6.6	176
ST. DEV.	0.03	0.6	19	0	0.1	0.3	0.07	1.1	58

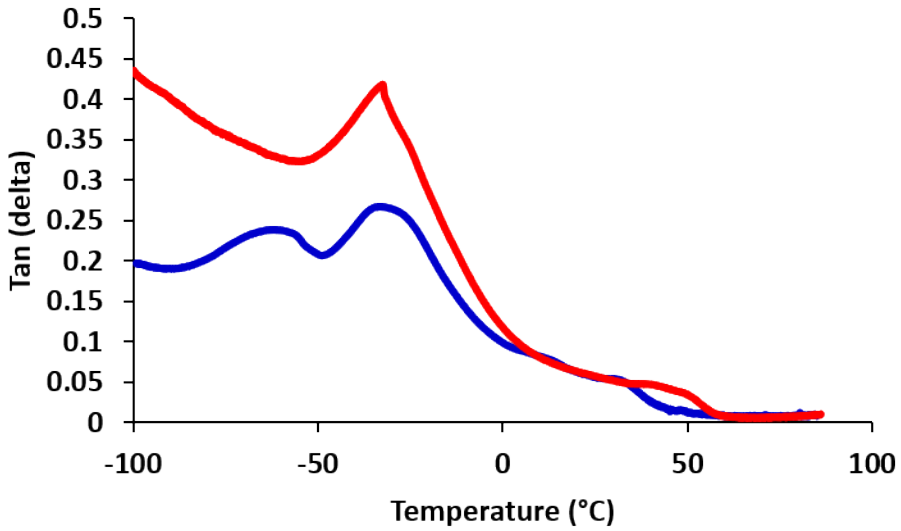

Figure S7. Tan δ plot in correlation to DMA Oscillation Temperature Sweep data of the original (blue) and recycled (red) poly(thioether anhydride) samples displayed in Figure 8.