Electronic Supplementary Material (ESI) for Polymer Chemistry.


# Supplementary Information

## Photo-Oxidative Cross-Linking of Thiol Polydimethylsiloxane Co-Polymers Via Disulfide Formation

*Taylor Wright,[a] Ziyue Zhang, [b] Carl A. Michal,[c,a] Savvas G. Hatzikiriakos,[b] Michael O. Wolf*[a]*

a. Department of Chemistry, 2036 Main Mall, University of British Columbia, Vancouver, BC V6T 1Z1, Canada.

b. Department of Chemical and Biological Engineering, 2360 East Mall, University of British Columbia, Vancouver, BC V6T 1Z3, Canada

c. Department of Physics and Astronomy, University of British Columbia, Vancouver, BC, Canada, V6T 1Z1

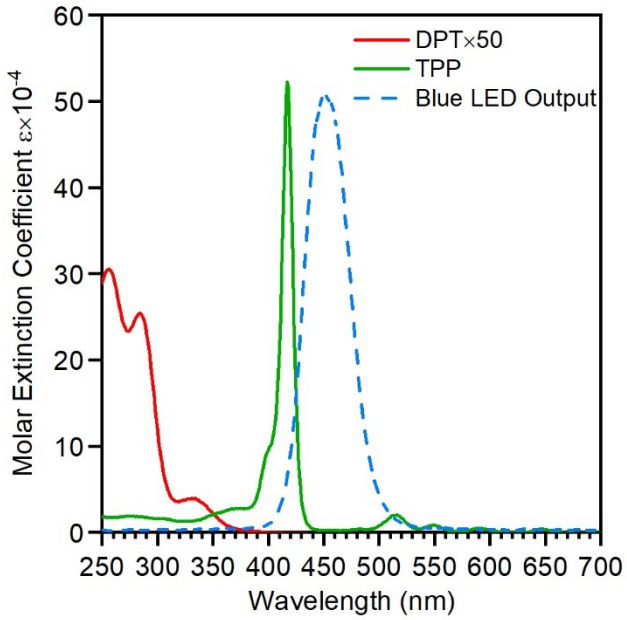


**Figure S1**. UV-Vis absorbance of DTP and TPP in DCM. $\varepsilon_{DPT}$ has been multiplied by 50 for display purposes. The spectral output of the blue LED used for these experiments is included (arbitrary intensity).

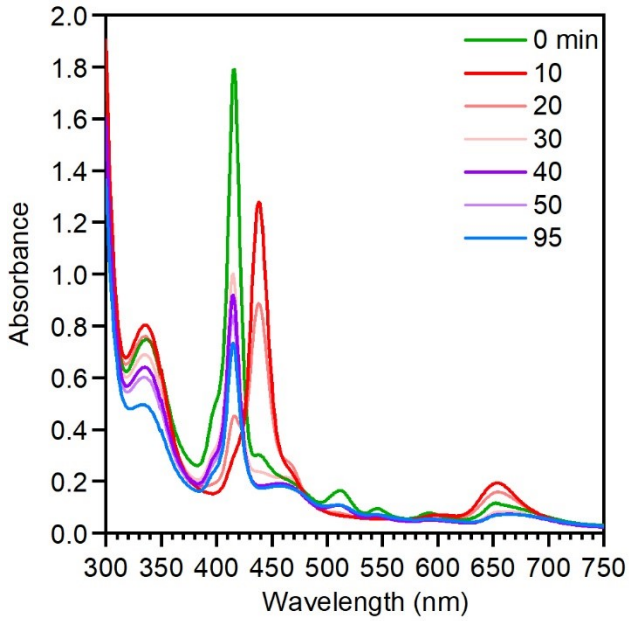


**Figure S2**. Change in UV-Vis absorbance of a thin film of **PA** irradiated using 430 nm light for 95 minutes.

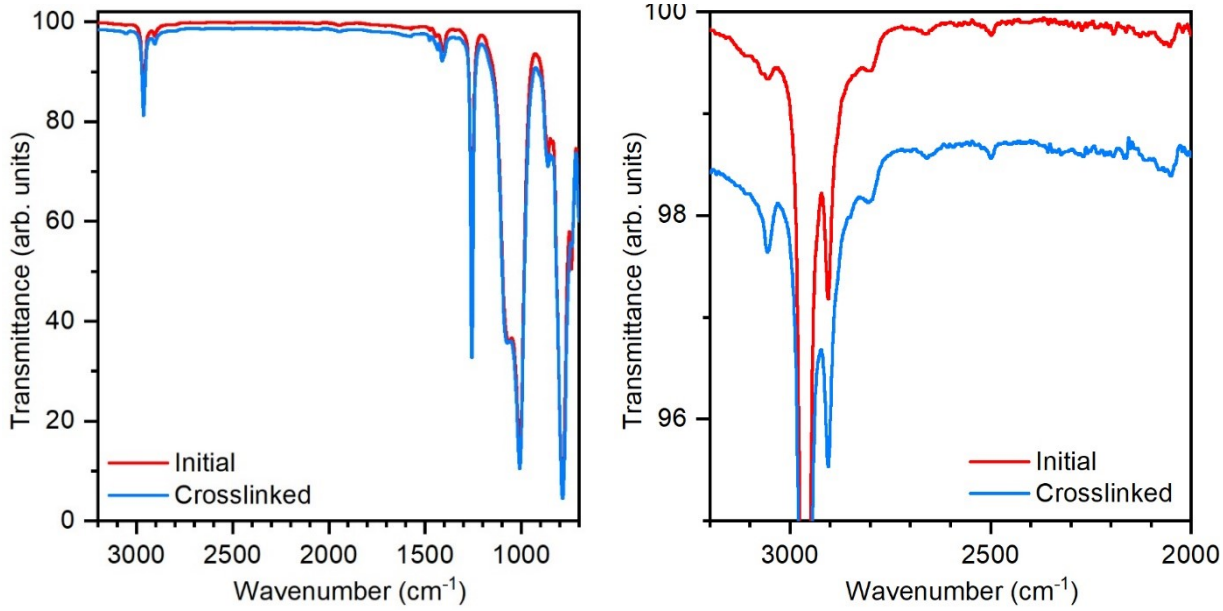


**Figure S3**. Left: The full FT-IR spectra of polymer sample **PA** before and after cross-linking. Right: the same spectra showing a smaller wavenumber range. No change in the vibrational spectrum is observed as the thiol S-H stretch expected at approximately 2560 $cm^{-1}$ is too weak to be observed in these low thiol-content materials.

**Figure S4**. Cross-linked sample of **PA** used for Raman measurements, showing surface wrinkling not observed for samples with a high content of **PB**.

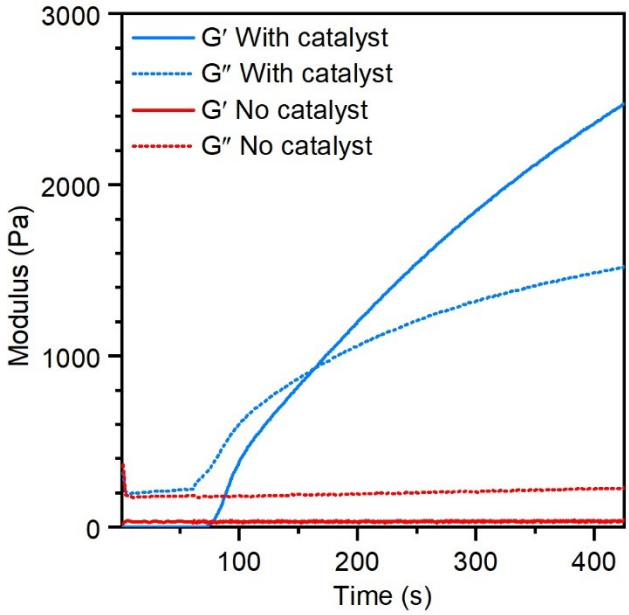


**Figure S5**. Photo-rheology experiments of samples of **P100** measured with and without DPT catalyst, measured at 23 mW/cm$^2$ light intensity. The absence of change in G' for the sample without DPT demonstrates that $^1O_2$ by itself does not result in cross-linking in this system.

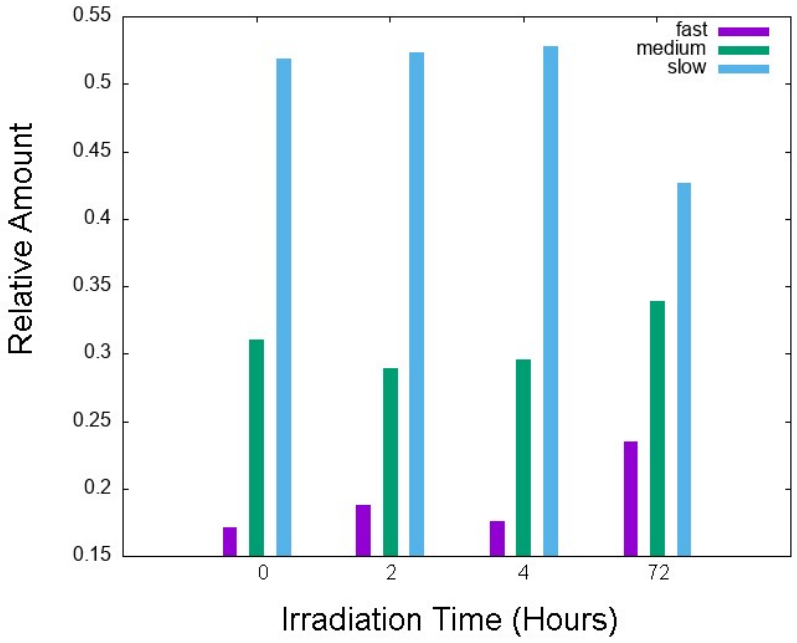


**Figure S6**. Relative amount of the three translation diffusion coefficients measured for the polymer backbone in sample **P100** as a function of irradiation time, determined using $^{1}$H PFG-NMR.

| Irradiation Time (hours) | Toluene $D_t$ (cm$^2$/s) | $CF_3Py$ $D_t$ (cm$^2$/s) | PDMS-1 $D_t$ (cm$^2$/s) | PDMS-2 $D_t$ (cm$^2$/s) | PDMS-3 $D_t$ (cm$^2$/s) |
|---|---|---|---|---|---|
| 0 | $5.4 \pm 0.2 \times 10^{-6}$ | $4.1 \pm 0.2 \times 10^{-6}$ | $2.0 \pm 0.3 \times 10^{-7}$ | $1.3 \pm 0.1 \times 10^{-8}$ | $1.0 \pm 0.045 \times 10^{-9}$ |
| 2 | $4.4 \pm 0.2 \times 10^{-6}$ | $3.8 \pm 0.4 \times 10^{-6}$ | $1.9 \pm 0.4 \times 10^{-7}$ | $1.4 \pm 0.2 \times 10^{-8}$ | $9.8 \pm 0.6 \times 10^{-10}$ |
| 4 | $4.7 \pm 0.2 \times 10^{-6}$ | $3.8 \pm 0.1 \times 10^{-6}$ | $1.2 \pm 0.2 \times 10^{-7}$ | $1.3 \pm 0.2 \times 10^{-8}$ | $9.3 \pm 0.4 \times 10^{-10}$ |
| 72 | $3.7 \pm 0.2 \times 10^{-6}$ | $3.0 \pm 0.4 \times 10^{-6}$ | $5.5 \pm 0.9 \times 10^{-8}$ | $5.5 \pm 1 \times 10^{-9}$ | $6.1 \pm 2 \times 10^{-10}$ |

**Table S1**. Translational diffusion coefficient measured for sample **P100** as a function of irradiation time, determined using PFG-NMR.

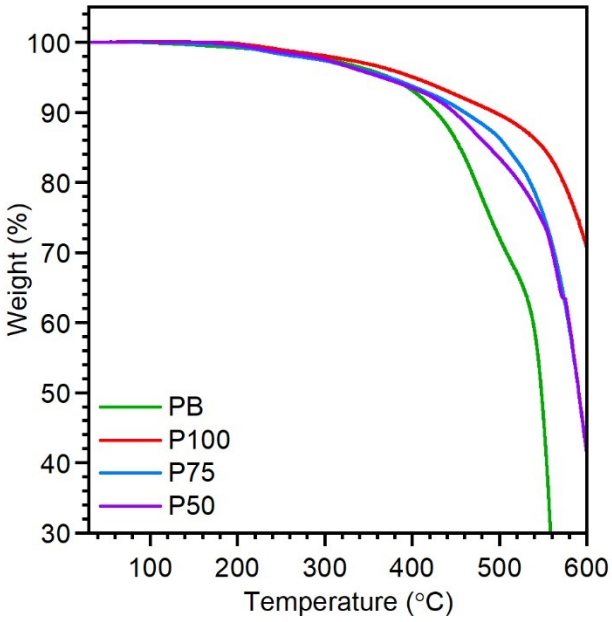


**Figure S7**. TGA curves of **PB** and cross-linked polymer samples, measured at 10 °C / min under $N_2$.

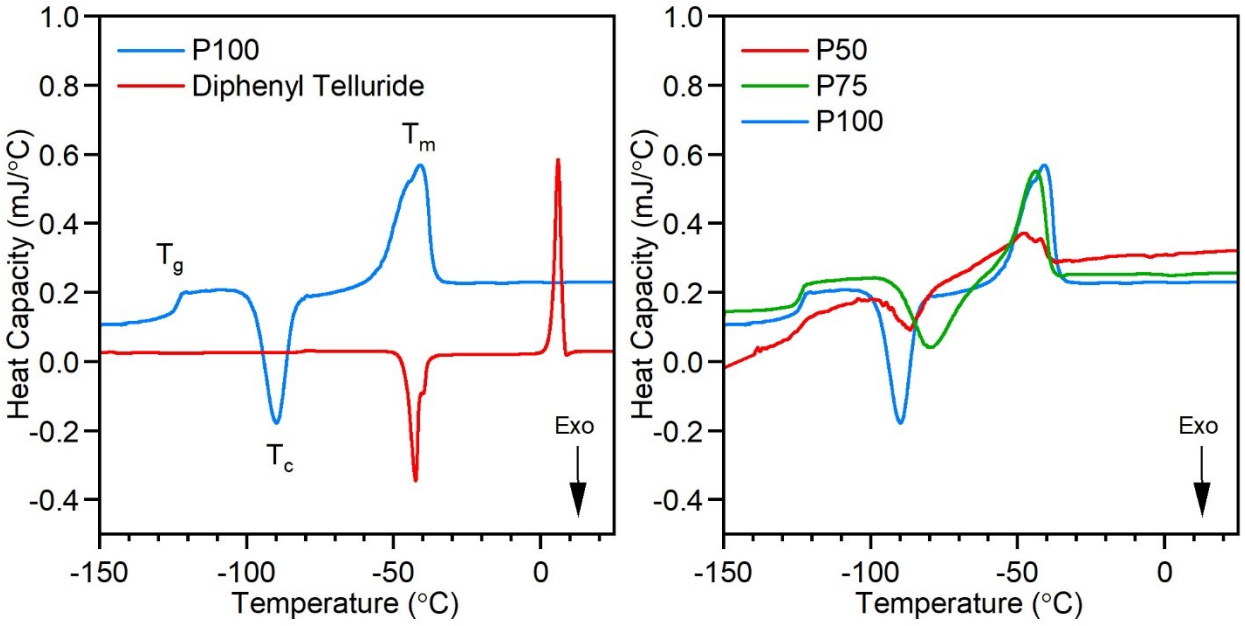


**Figure S8**. Left: DSC curves of **P100** and **DPT.** Right: DSC curves of **P50**, **P100**, and **P75**. Measured at 10 °C / min under $N_2$, traces scaled for display purposes. A strong crystallization and melting point can be observed for **DPT**, while polymer samples have a $T_g$ transition and shifted $T_c$ and $T_m$.

| Sample ID | Mass % PA | Mass % PB | $T_g$ (°C) |
|---|---|---|---|
| P100 | 0 | 100 | -123.5 |
| P75 | 25 | 75 | -124.0 |
| P50 | 50 | 50 | -122.6 |

**Table S2**. Composition and Tg of cross-linked polymer samples, measured at 10 °C / min under. All cross-linked samples had the same melting/crystallization peaks associated with **DPT**.

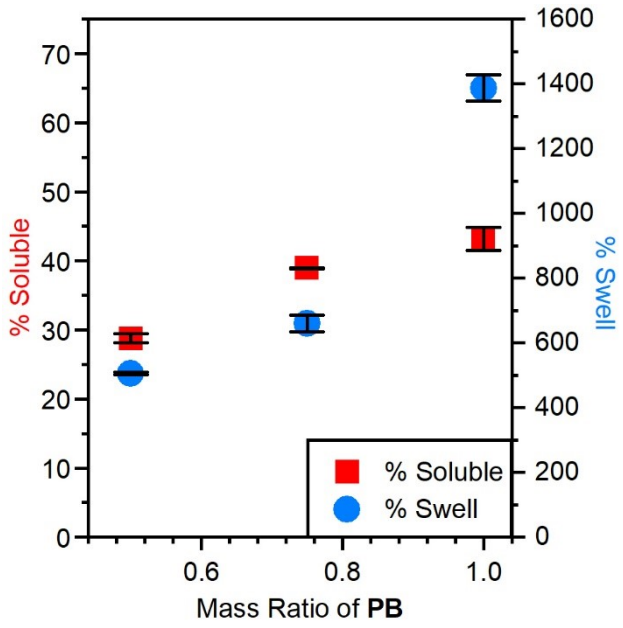


**Figure S9**. % Soluble and Swell for samples **P100**, **P75**, and **P50**. Samples were pre-weighed and then soaked with excess THF overnight. The samples were weighed to determine the % Swell, and then rinsed thoroughly with clean THF and dried overnight under vacuum. The resulting mass was used to determine the % Soluble, using the equations below.

$$\%\, Swell = \frac{Swollen\ Mass}{Initial\ Mass} \times 100 \qquad \%\, Soluble = 100 - \left(\frac{Dried\ Mass\ After\ Soak}{Initial\ Mass} \times 100\right)$$

| Constant | Symbol | Units | Value |
|---|---|---|---|
| Solubility parameter for solvent | $\delta_s$ | $(J/cm^3)^{0.5}$ | 18.6 |
| Solubility parameter for polymer | $\delta_p$ | $(J/cm^3)^{0.5}$ | 20.5 |
| Density of polymer | $\rho_s$ | g/mL | 0.98 |
| Density of solvent | $\rho_p$ | g/mL | 0.889 |
| Molar mass of solvent | $M$ | g/mol | 72.11 |
| Molar volume of solvent | $V_s$ | mL/mol | 81.1 |
| Flory-Huggins Interaction Parameter | $\chi$ | | 0.12 |
| Swollen mass | $m_1$ | g | |
| Initial polymer mass | $m_0$ | g | |

**Table S3**. Values used for the calculation of number average molar mass between cross-links for **P100**. Calculations for **P50** and **P75** were not performed due to the complex molar mass and thiol content resulting from the mixture of two different polymers.

The Flory-Huggins interaction parameter was calculated using the equation:

$$\chi = \frac{\left(V_s(\delta_p - \delta_s)^2\right)}{RT}$$

The degree of swelling ($Q$) and volume fraction of polymer ($V_p$) was calculated using the equation:

$$Q = \frac{1}{V_p} = \frac{\left(\frac{m_0}{\rho_p}\right) + \left(\frac{m_1 - m_0}{\rho_s}\right)}{\frac{m_0}{\rho_p}}$$

The number average molar mass between cross-links ($M_c$) was calculated using the Flory-Rehner equation:

$$M_c = \frac{V_s(V_p^{\frac{1}{3}} - \frac{1}{2}V_p)}{\ln(1 - V_p) + V_p + \chi V_p^2}$$

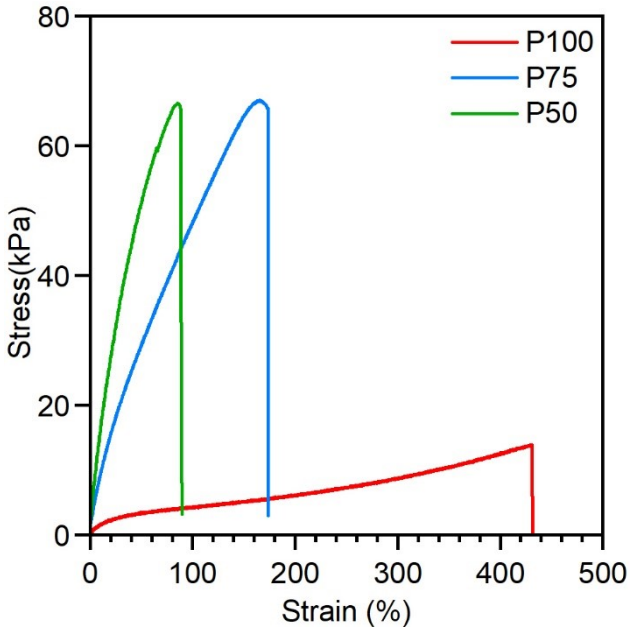


**Figure S10.** Example stress-strain curves for samples **P100**, **P75**, and **P50**, measured from tensile test experiments.

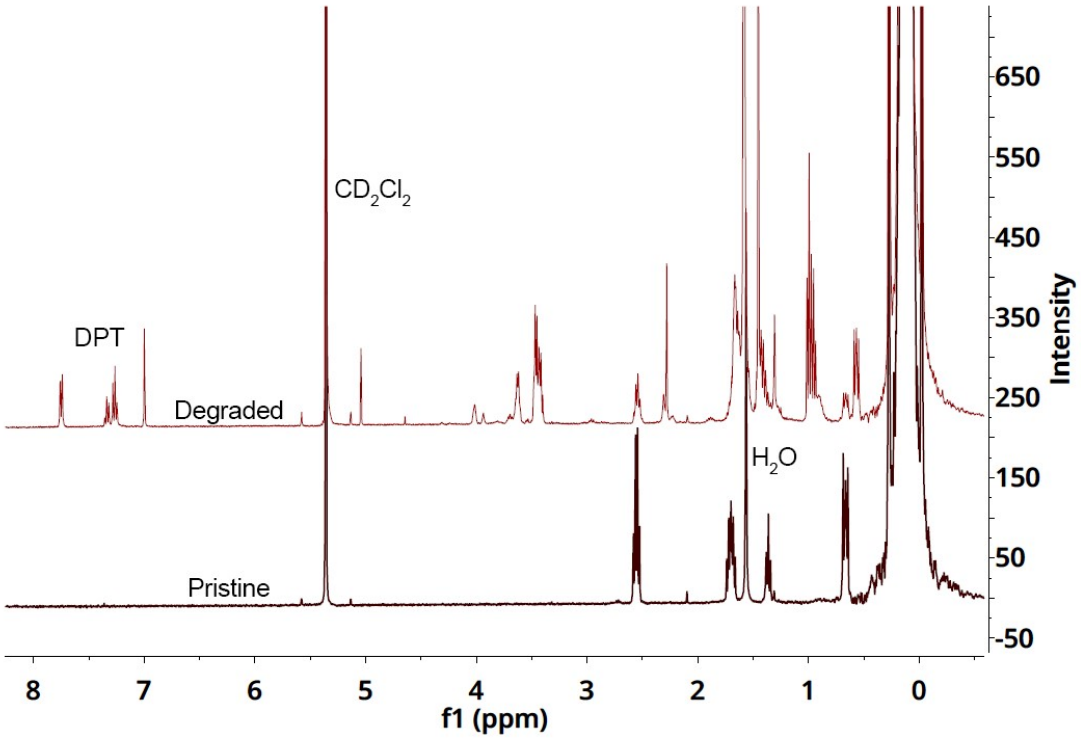

**Figure S11.** $^{1}$H NMR spectra of pristine **PB** and degraded **PB** recovered after reductive cleavage of the disulfide linkages using $ZrCl_4/NaBH_4$. 400 MHz, $CD_2Cl_2$, RT.

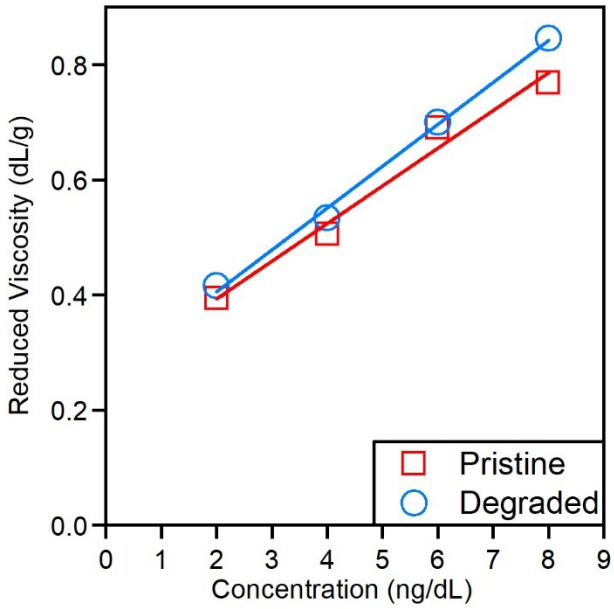


**Figure S12.** Intrinsic viscosity plot for samples of pristine and degraded **PB** at different concentrations in toluene.

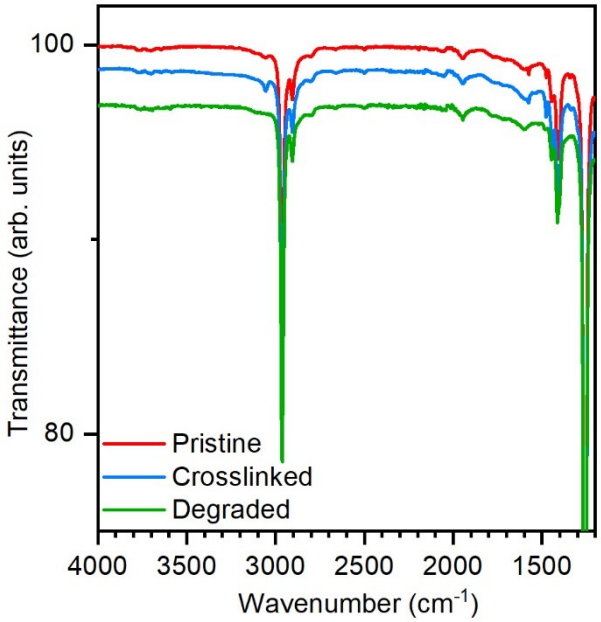

**Figure S13.** FT-IR spectra of pristine **PB**, cross-linked **P100**, and degraded **PB**.