Supporting Information

Synthesis of Polyurethane/Vinyl Polymer Hybrids with Unexpected Mechanical Properties Using a Macro Chain Transfer Agent

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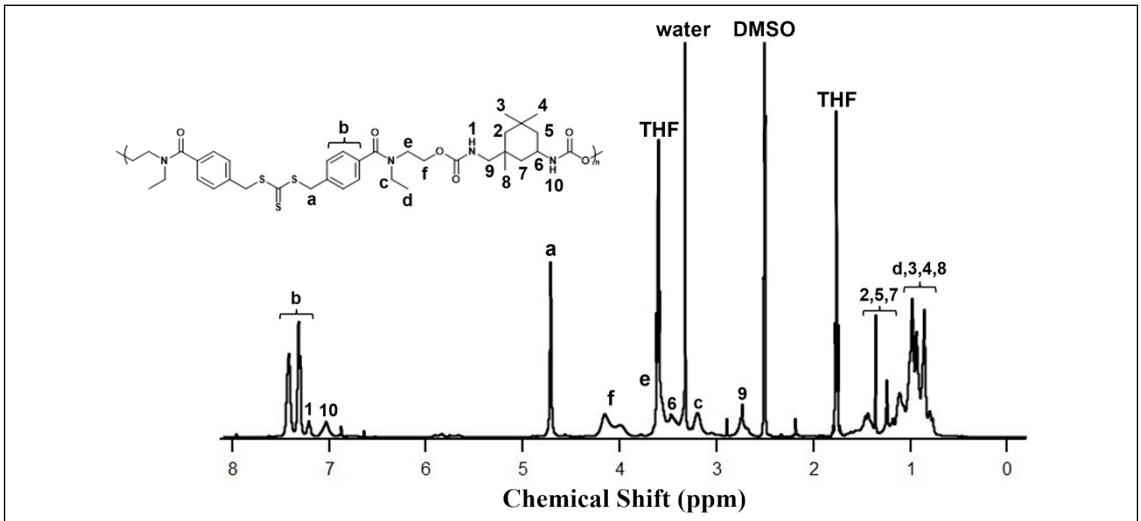

Figure S1. ^{1}H NMR spectrum of PU-TTC from Run 3 in Table 1 prepared in DMSO-d_6.

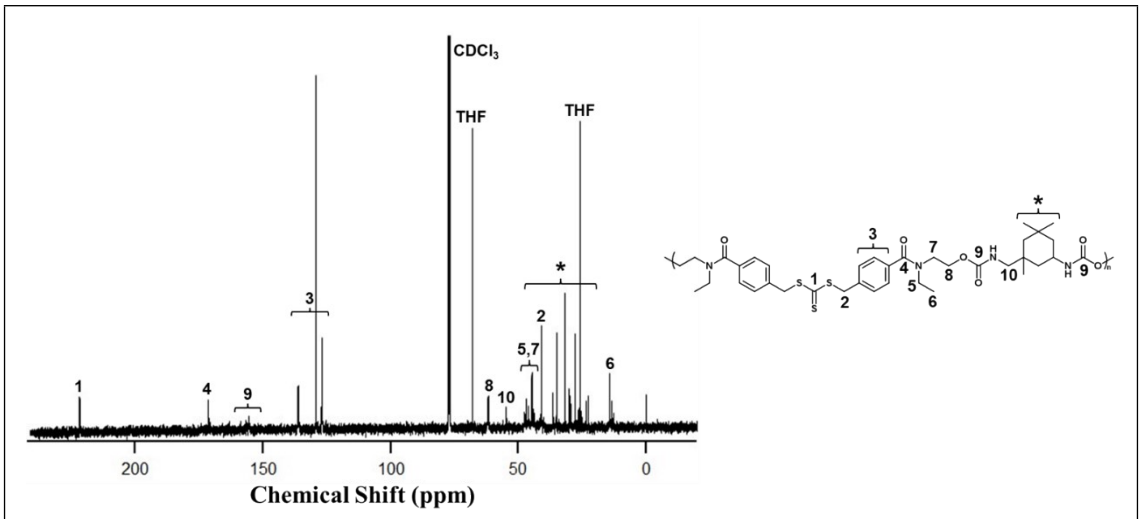

Figure S2. ^{13}C NMR spectrum of PU-TTC from Run 3 in Table 1 prepared in $CDCl_3$.

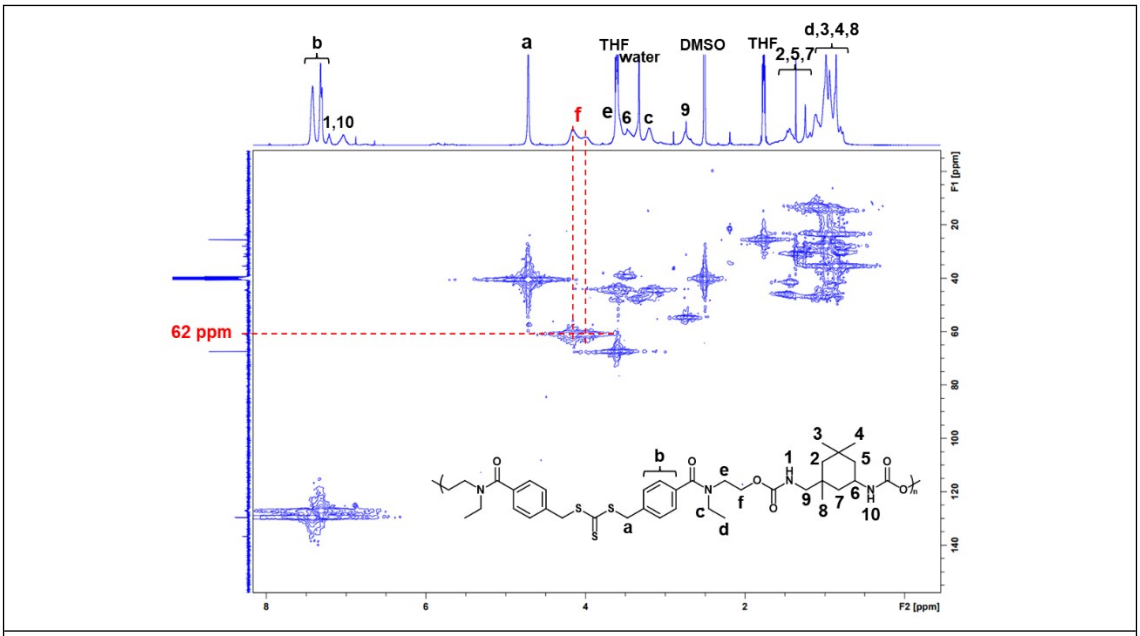

Figure S3. HMQC spectrum of PU-TTC from Run 3 in Table 1 prepared in DMSO-d_6.

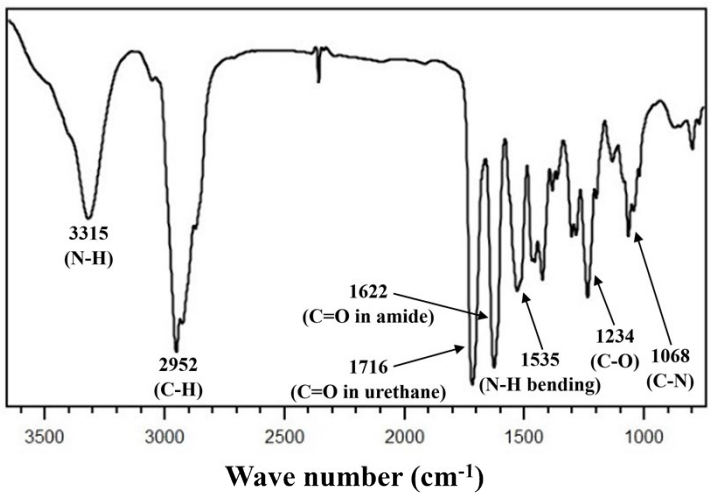

Figure S4. IR spectrum of PU-TTC from Run 3 in Table 1.

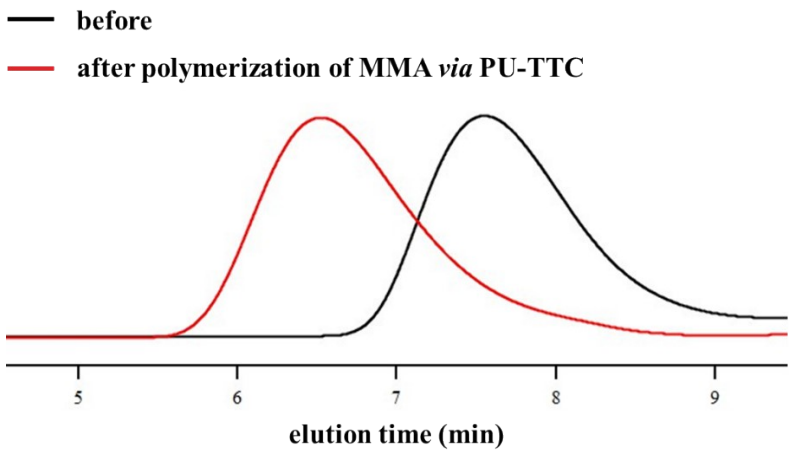

Figure S5. SEC trace of polyurethane-poly(MMA) hybrid synthesized *via* PU-TTC (black line = PU-TTC, red line = synthesized polyurethane-poly(MMA) hybrid *via* PU-TTC) (Run 4 in Table 2)

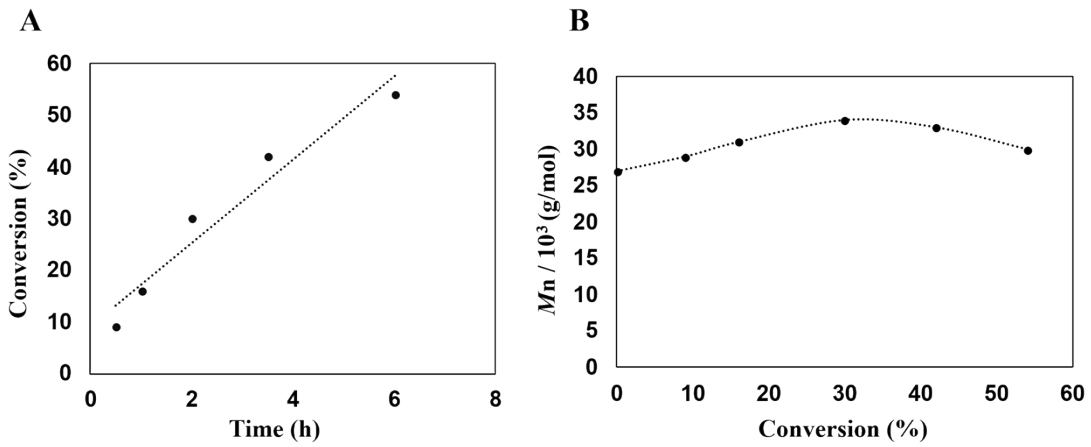

Figure S6. (A) Plot of monomer conversion (%) vs time (h) (Run 1 in Table S1); (B) Plot of *M*n vs monomer conversion (%) (Run 1 in Table S1).

Table S1. RAFT polymerization of MMA using PU-TTC.[a,b]

Run	$[M]_0/[TTC]_0$	$[M]_0$ (mol/L)	Radical trigger	Time (h)	Conv.[c] (%)	M_n[d] (kg/mol)
1	100	2.0	Redox-LED	8	54	30.4

[a] Polymerization using PU-TTC (run 3 in Table 1) as chain transfer agent. [b] Polymerization with $Ir(ppy)_3$ as a redox catalyst by blue-LED irradiation. [c] Calculated from ^1H NMR in $CDCl_3$. [d] Determined by SEC with poly(methyl methacrylate) standards.

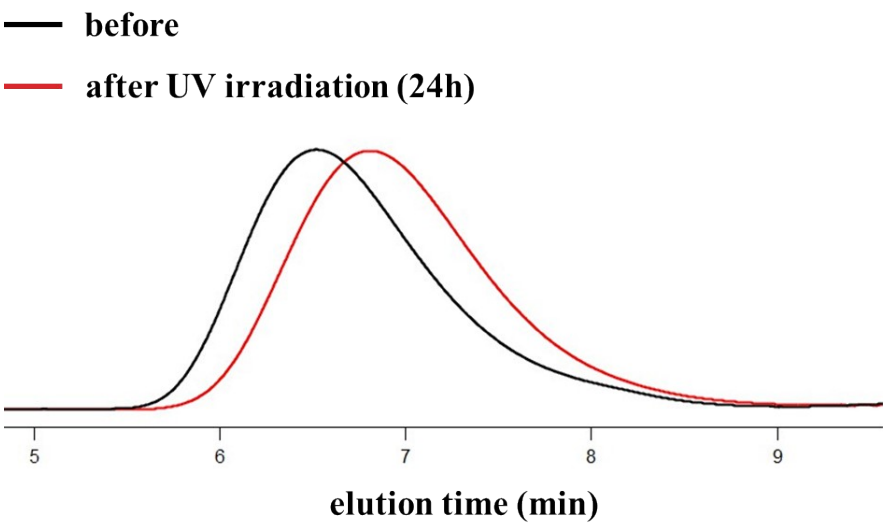

Figure S7. Evolution of molecular weight of polyurethane-poly(MMA) hybrid resulting from UV irradiation.

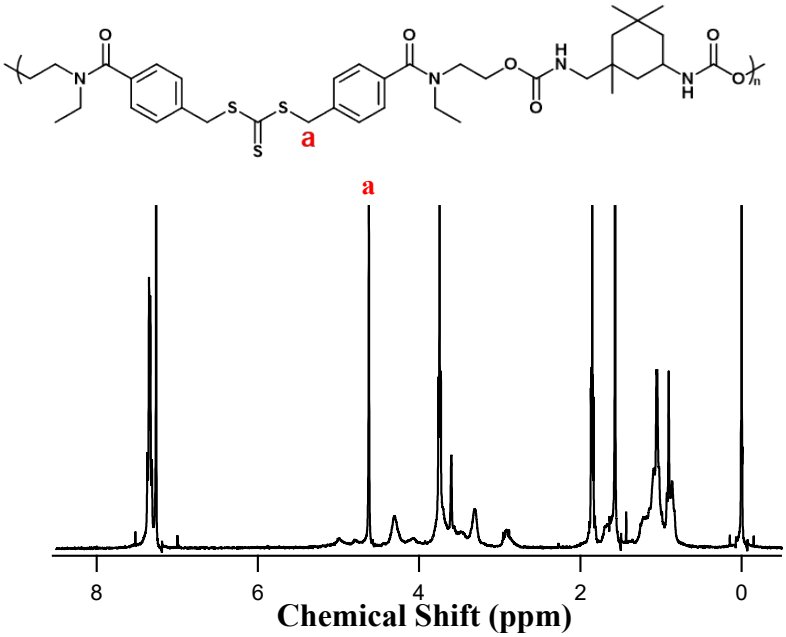

Figure S8. ^{1}H NMR spectrum of PU-TTC in $CDCl_3$.

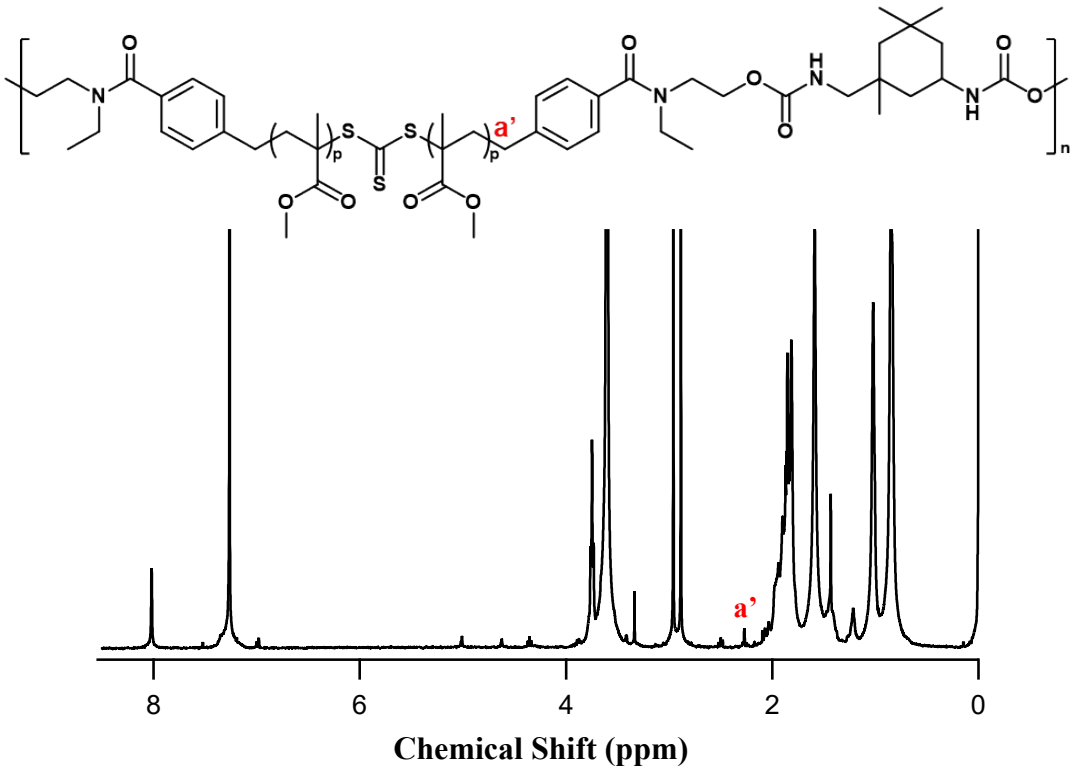

Figure S9. ^{1}H NMR spectrum of polyurethane-PMMA hybrid in $CDCl_3$.

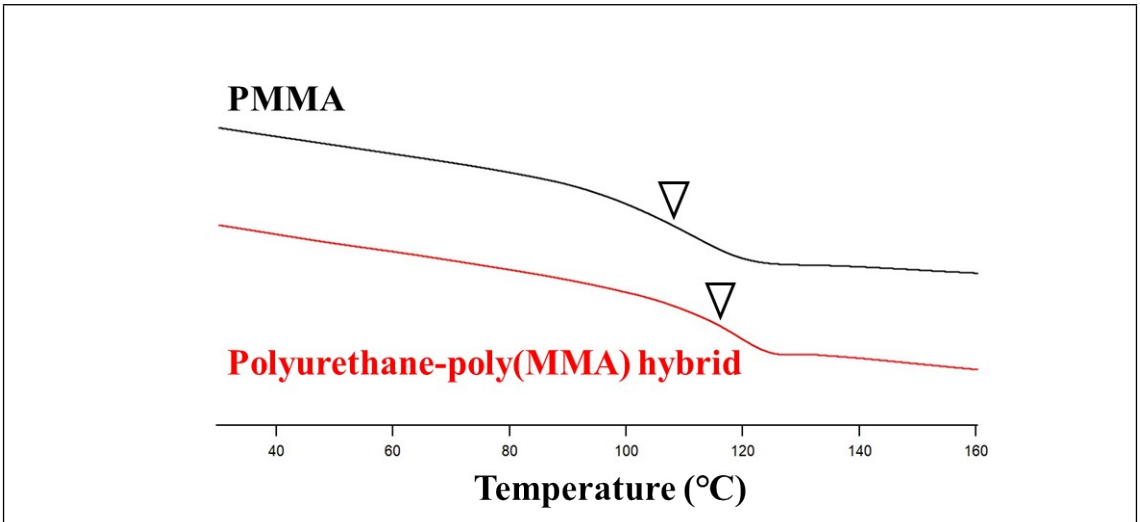

Figure S10. DSC chart in 2nd heating of polyurethane-poly(MMA) hybrid (Run 3 in Table 2) and PMMA homopolymer

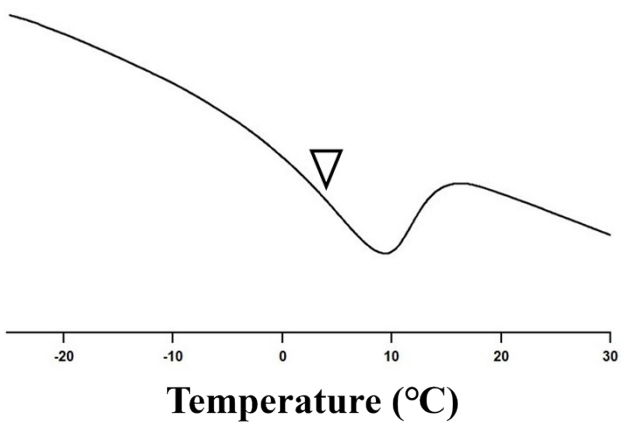

Figure S11. DSC chart in 2nd heating of PU-TTC from Run 3 in Table 1.

Table S2. Transmittance of polyurethane-poly(MMA) and PMMA homopolymer.

Sample	M_n[a] (kg/mol)	M_w/M_n[a]	Transmittance(590nm) (%)
PMMA homopolymer[b]	173	1.98	86.0
Poly(urethane-MMA)[b]	79.8	2.20	7.3

[a]Determined by SEC with a standard series of poly(methyl methacrylate)s.

[b]Thickness of the specimen were 0.90 mm (PMMA homopolymer) and 0.96 mm (poly(urethane-MMA)) respectively.

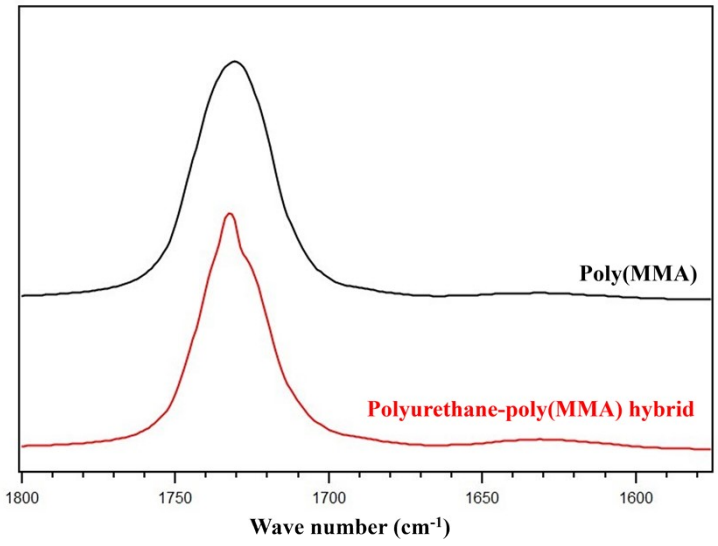

Figure S12. IR spectra of poly(MMA) and polyurethane-poly(MMA) hybrid from Run 3 in Table

2.

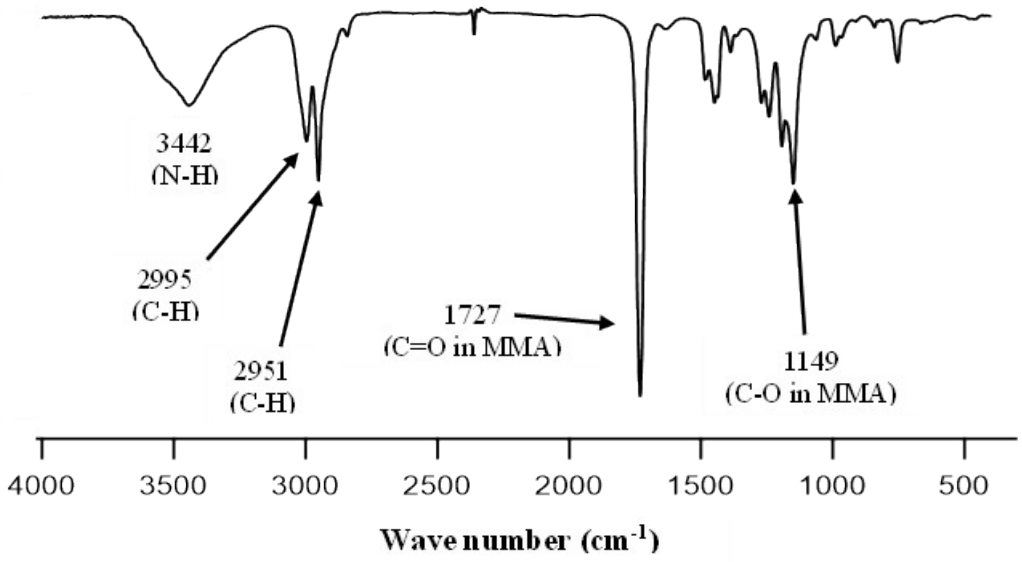

Figure S13. IR spectrum of poly(urethane-MMA).

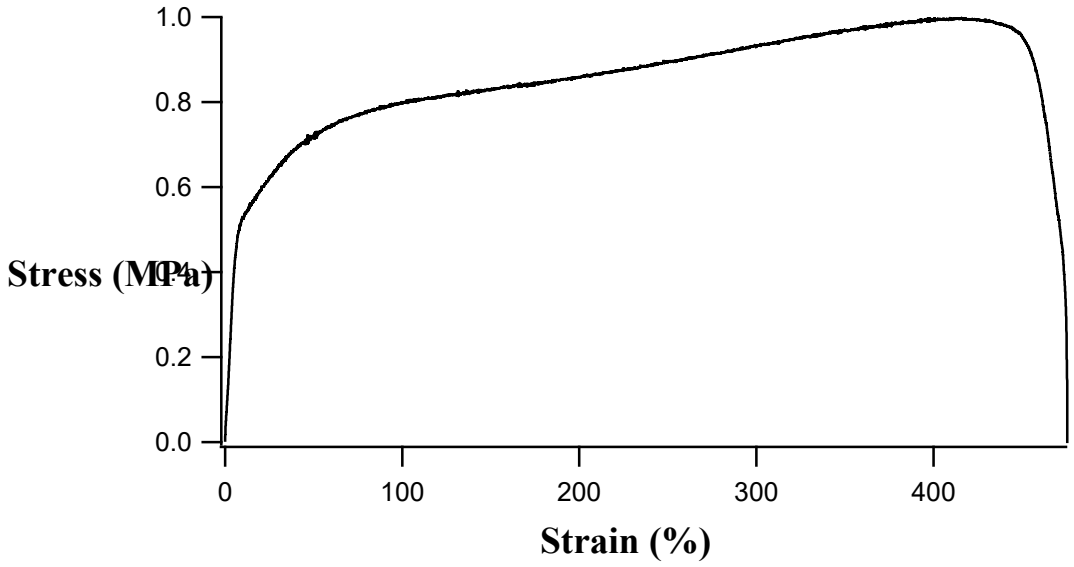

Figure S14. Stress-strain curves of PU-TTC.