Supporting Information

Toughening Polylactide with Nonlinear, degradable Analogues of PEG and its copolymers

Huanting Li,[a] Yuhua Yan,[a] Xing Jiang,[a] Jingjing Lin[a] and Minfeng Li[a]*

[a] College of Chemistry, Beijing Normal University, Beijing 100875, China.

E-mail: minfeng_li@ bnu.edu.cn

Content

Examples of ^{1}H NMR Analysis

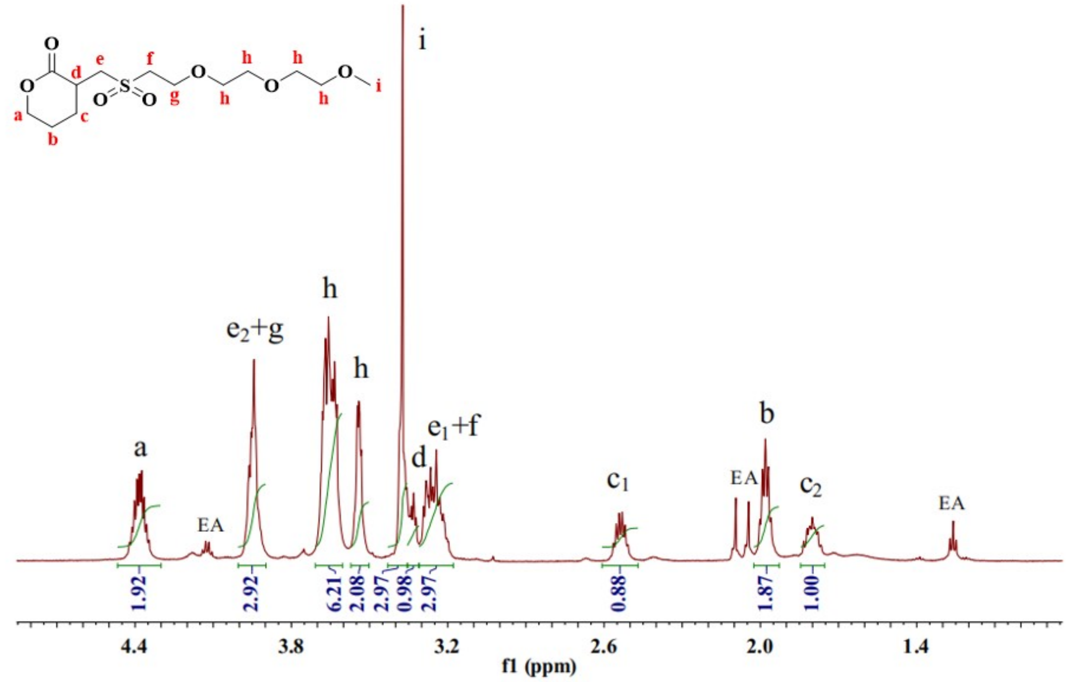

Figure S1. ^{1}H NMR spectra of monomer VL-Teg in $CDCl_3$.

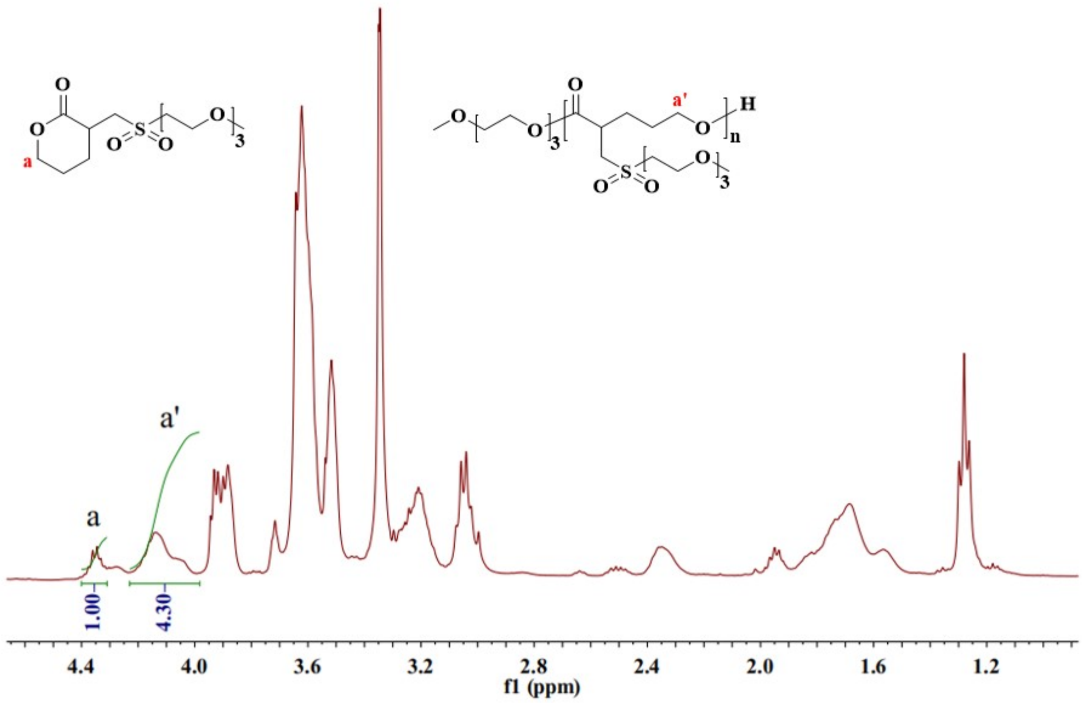

Figure S2. ^{1}H NMR spectrum of homopolymer reaction mixture in $CDCl_3$.

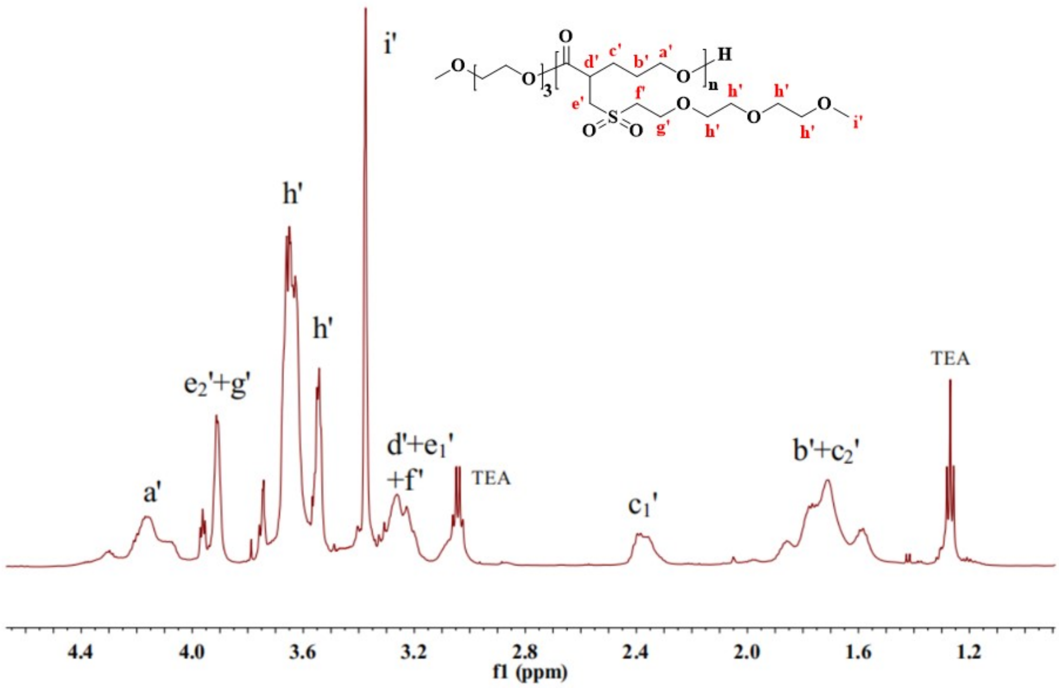

Figure S3. ^{1}H NMR spectrum of purified homopolymer $P(VL\text{-}Teg)_{40}$ in $CDCl_3$.

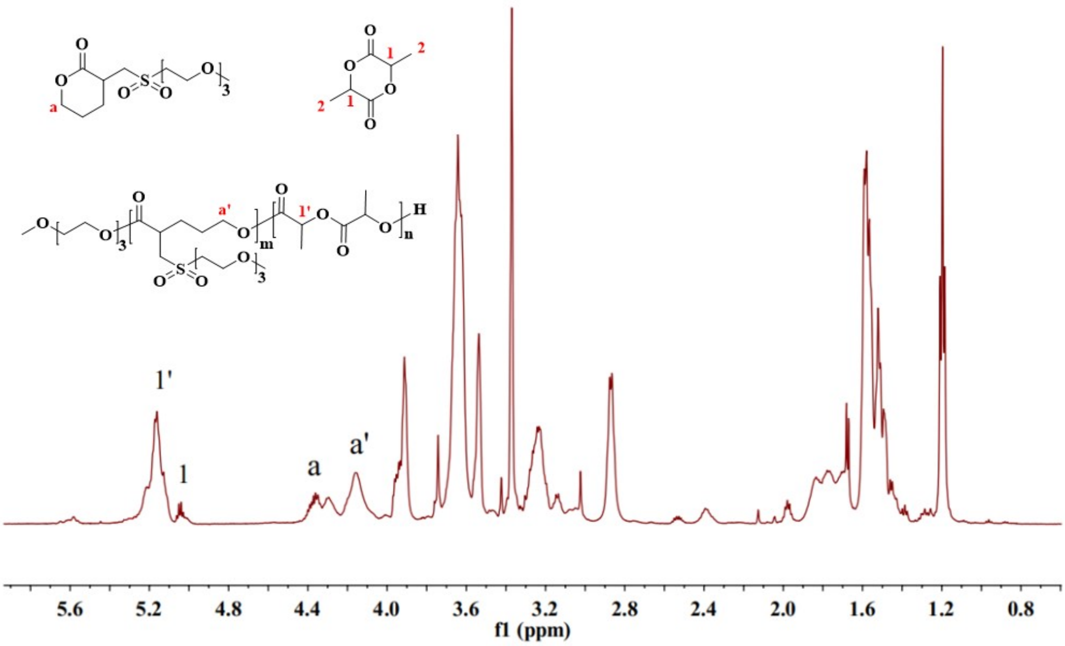

Figure S4. ^{1}H NMR spectrum of block copolymer reaction mixture in $CDCl_3$.

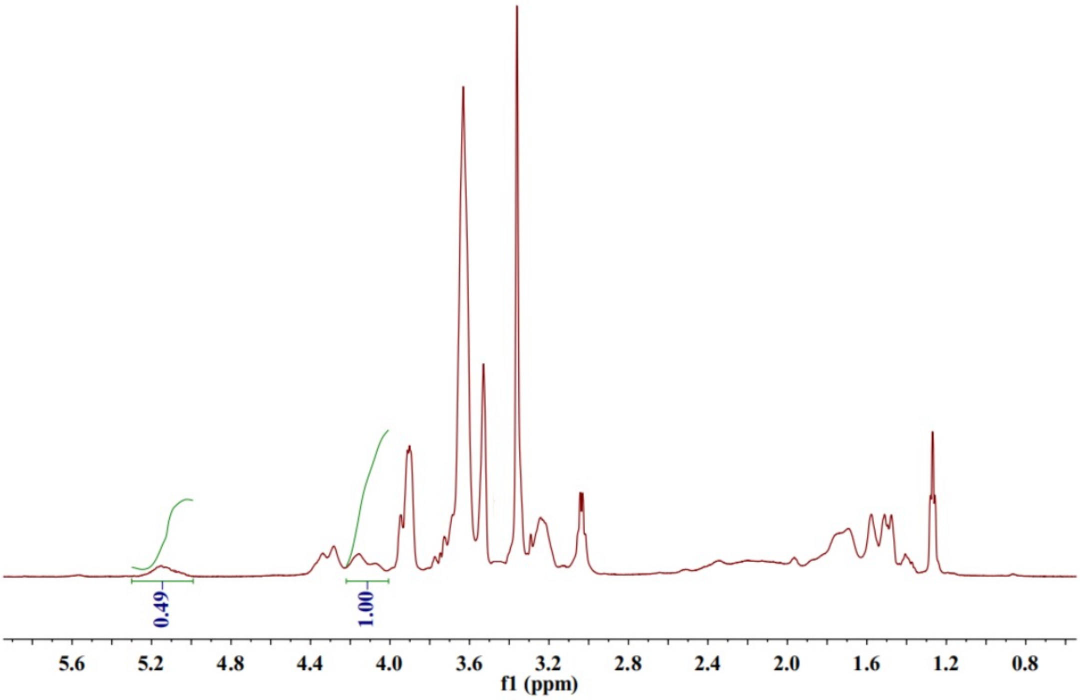

Figure S5. ^{1}H NMR spectrum of the purified block copolymer P(VL-Teg)$_{40}$-*b*-PLA$_{20}$ in $CDCl_3$.

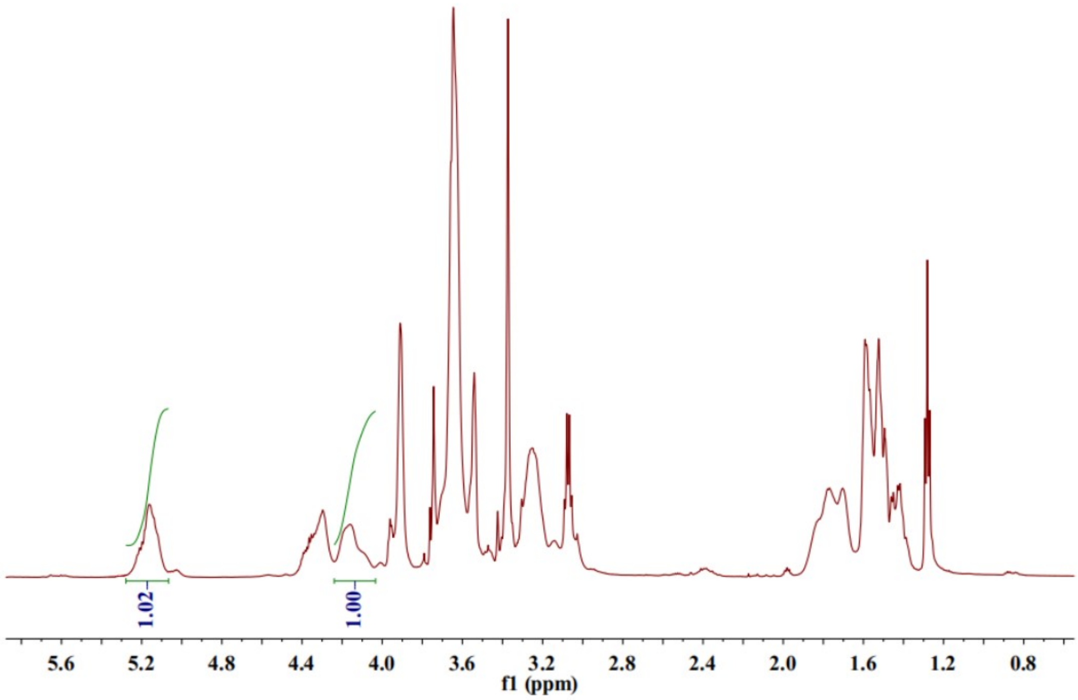

Figure S6. ^{1}H NMR spectrum of the purified block copolymer P(VL-Teg)$_{40}$-*b*-PLA$_{40}$ in $CDCl_3$.

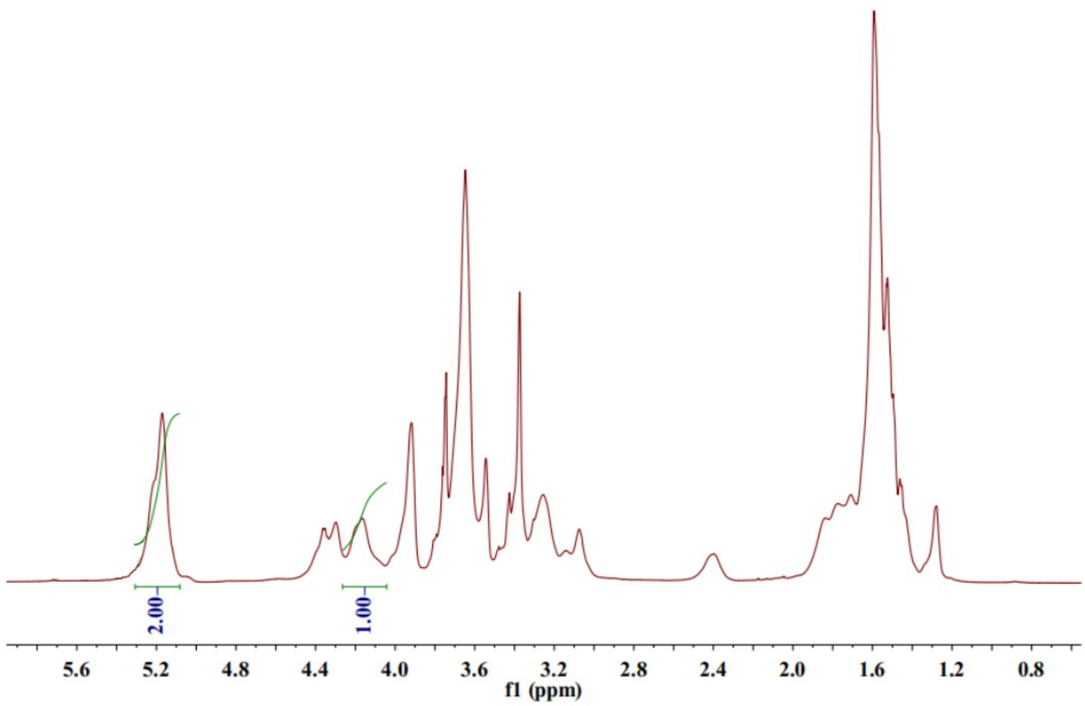

Figure S7. ^{1}H NMR spectrum of the purified block copolymer P(VL-Teg)$_{40}$-*b*-PLA$_{80}$ in $CDCl_3$.

Ring-open Polymerization of Lactide

Table S1 PLA with different degrees of polymerization

Entry	Polymer	$[M]_0/[I]_0$ ^{a}	Conv. ^{b} (%)	$M_{n,theory}$ (g/mol)	M_n ^{c} (g/mol)	M_w/M_n ^{c}	Yield ^{d} (%)
1	LA	25/1	92	3423	3637	1.21	36
2	LA	50/1	93	6810	6935	1.24	44
3	LA	100/1	95	13801	16694	1.23	76
4	LA	150/1	90	19566	20939	1.31	91
5	LA	200/1	86	24899	22008	1.33	81

^{a} 120°C; benzyl alcohol as the initiator; catalyst loading 0.2 mol% with respect to the monomer; [HOTf]/[DPP] =1/2. ^{b} Conversion determined *via* ^{1}H NMR. ^{c} Determined by GPC in dimethylformamide (DMF) *versus* polystyrene standards. ^{d} Conversion taken into account.

We investigated the ROP kinetics of a mixture of LA and HOTf/DPP (1/2). The results showed that the molecular weight (M_n) was in good agreement with the theoretical value, the monomer conversion increased linearly and the dispersion remained low (**Fig. S8**). The linear dependence of

$\ln([M]_0/[M])$ on polymerization time is shown in **Fig. S8b**, exhibited as first-order kinetics, indicating that the rate of monomer consumption remains constant during polymerization. These observed linear relationships suggest the controlled nature of the HOTf/DPP (1/2) mixture catalyzing the bulk ROP of LA.

Entry	Time (min)	Conv. (%) ^{a}	$M_{n,\,GPC}$ ^{b}	$\ln([M]_0/[M])$	PDI ^{b}
1	10	30	1106	0.357	1.09
2	20	49	4497	0.673	1.12
3	30	57	8151	0.844	1.14
4	40	70	10866	1.204	1.16
5	50	79	12491	1.561	1.19
6	75	90	17361	2.303	1.24

Table S2. Data of ^{a} Determined by ^{1}H NMR. ^{b} Determined by GPC in DMF with polystyrene as standards (1 mL/min, 35°C).

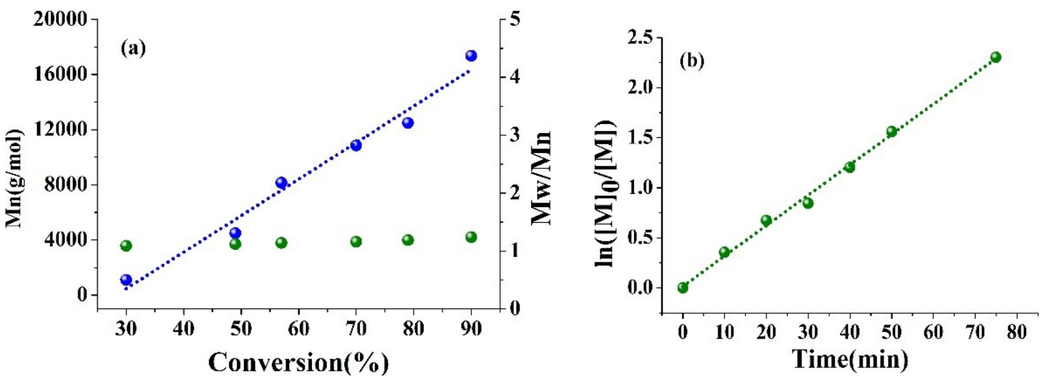

Figure. S8. (a) Plot of molecular weight (M_n) versus monomer conversion. (b) Semi-logarithmic plot of monomer consumption against time.

Examples of GPC Analysis

With the addition of the second block and the successive increase in the blocking ratio, it was observed that the GPC traces shifted significantly to higher molar masses, while the shape of the chromatogram remained unimodal. Although the peak broadens slowly as the length of the second segment increases, it remains at a relatively low level. (P(VL-Teg)$_{40}$-*b*-PLA$_{80}$, M_n=14694, Đ=1.33)

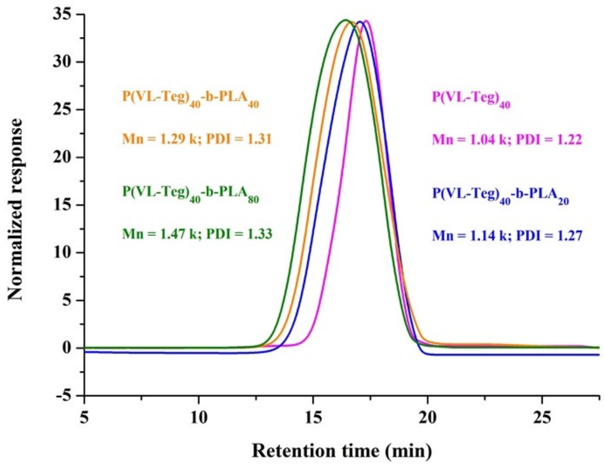

Figure. S9. GPC traces: the magenta line corresponds to P(VL-Teg) homopolymer and the rest correspond to the P(VL-Teg)-*b*-PLA copolymers with different block ratios.

Examples of Mechanical Property Analysis

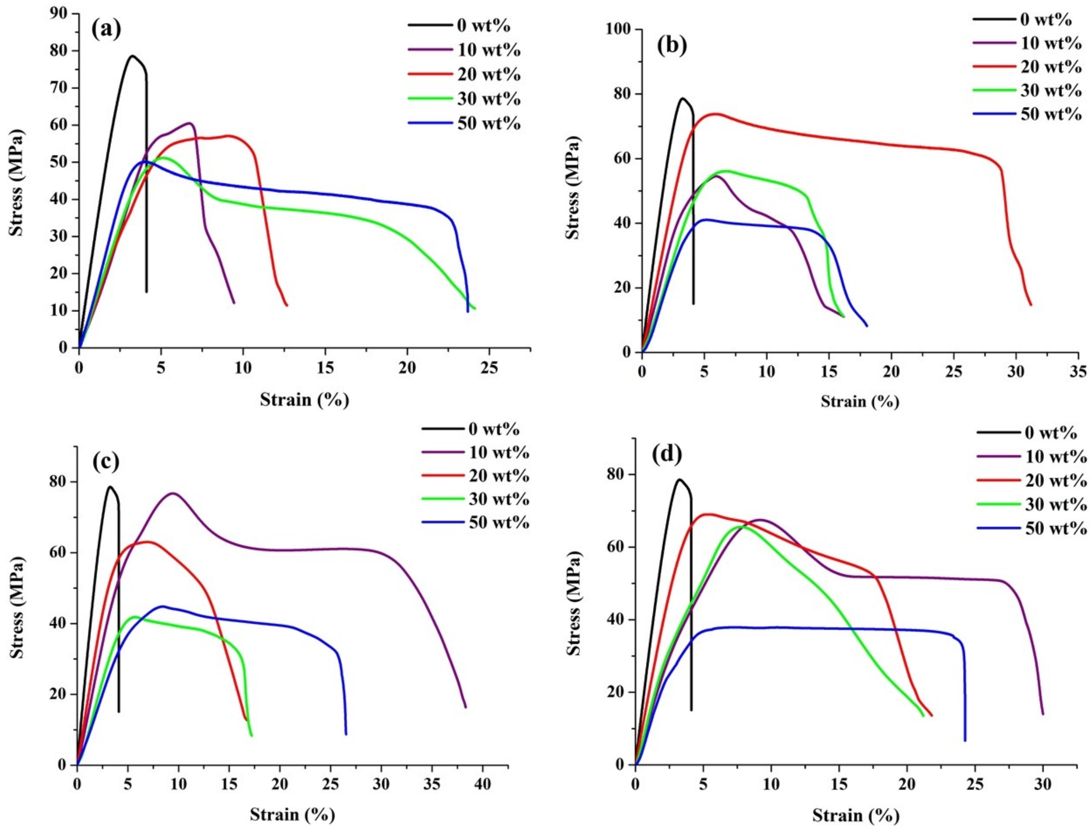

Figure. S10. The tensile curves of (a) P(VL-Teg)$_{40}$/PLA blend; (b) P(VL-Teg)$_{40}$-*b*-PLA$_{20}$/PLA blend; (c) P(VL-Teg)$_{40}$-*b*-PLA$_{40}$/PLA blend; (d) P(VL-Teg)$_{40}$-*b*-PLA$_{80}$/PLA blend.

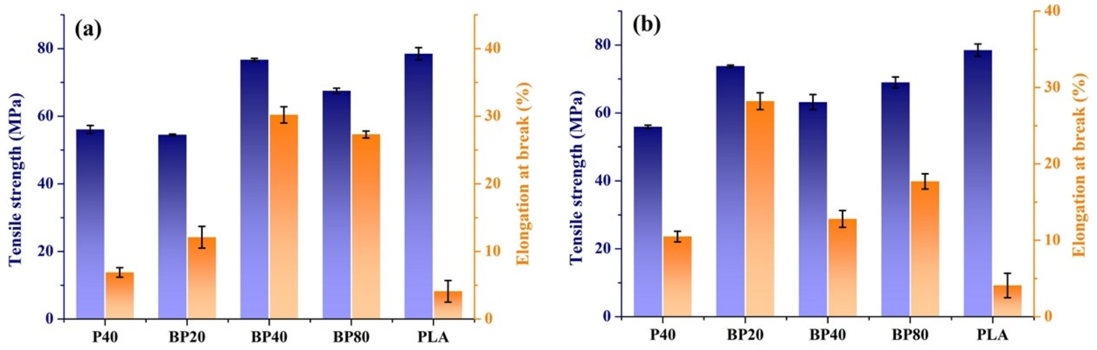

Figure. S11. Tensile strength and elongation at break of various polymers at different loading: (a) 10 wt%; (b) 20 wt%.

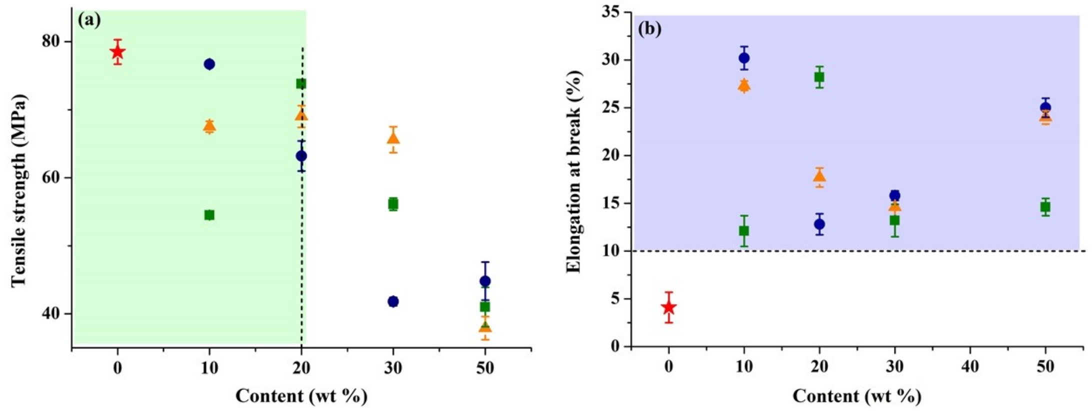

Figure. S12. (a) Plot of tensile strength as a function of content; (b) Plot of elongation at break as a function of content. ★ Neat PLA; ■ P(FVLSF)$_{40}$-*b*-PLA$_{20}$; ● P(FVLSF)$_{40}$-*b*-PLA$_{40}$; ▲ P(FVLSF)$_{40}$-*b*-PLA$_{80}$.