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Electronic Supplementary Information for

Interphase synergistic effects of dynamic bonds in multiphase thermoplastic elastomers

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Experimental

Materials.

5-phenyl-2-norbornene (PhN)[1], dodecanyl 5-norbornene-2-caboxylate (DN)[2], and protected UPy monomer (pUN), [(2*S*)-bicyclo[2.2.1]hept-5-en-2-ylmethyl-6-(3-(4-methyl-6-(2-nitrobenzyloxy)pyrimidin-2-yl)ureido)hexylcarbamate][3], were synthesized according to the literatures. The ^{1}H NMR spectra of these monomers are shown in Fig. S1. Dichloromethane (DCM) (Wako, Japan), ethyl vinyl ether (Tokyo Chemical Industry, Japan), Grubbs' 3rd generation catalyst (Sigma Aldrich, USA), and methanol (Wako, Japan) were used as received.

General procedure for the synthesis of triblock copolymers.

Here we describe the synthetic procedure for TPE(5-10-5) as an example. The other triblock copolymers were synthesized similarly with different ratios of the monomers in each step which have been listed in Table 1 in the main text. First, Grubbs' 3rd generation catalyst 4.79 mg (5.41 μmol, 1 eq.) was weighed in a 50 mL glass vial equipped with a rubber septum. The vial was cooled in an ice bath and purged with nitrogen. DCM 8 mL was added through the septum to dissolve the catalyst. To this vial a solution of PhN 50.7 mg (0.298 mmol, 55 eq.) and pUN 15.0 mg (0.027 mmol, 5.0 eq.) in DCM 4 mL was swiftly injected with vigorous stirring. After stirring for 5 min, a solution of D 780 mg (2.54 mmol, 470 eq.) and pUN 29.9 mg (0.0541 mmol, 10 eq.) in DCM 8 mL was injected and stirred for 30 min. In the final polymerization step, a solution of PhN 50.7 mg (0.298 mmol, 55 eq.) and pUN 15.0 mg (0.027 mmol, 5.0 eq.) in DCM 4 mL was injected into the vial and the solution was stirred for another 5 min. Then the reaction was quenched by adding ~ 20 drops of ethyl vinyl ether followed by stirring for 2 h at room temperature. Precipitation in excess methanol yielded brown rubbery solid. Deprotection of UPy moiety was carried out by irradiating UV light with the wavelength of 365 nm from a UV-LED curing device (8332A controller with AC8361 LED head, CCS, Japan) to a dilute chloroform solution of the protected polymer (ca. 0.3wt%) for 3 h. The deprotected polymer was isolated by concentrating the solution by a rotavapor, precipitating in excess methanol, and drying in vacuum. The UV deprotection process was not done to TPE(0-0-0) without UPy moiety.

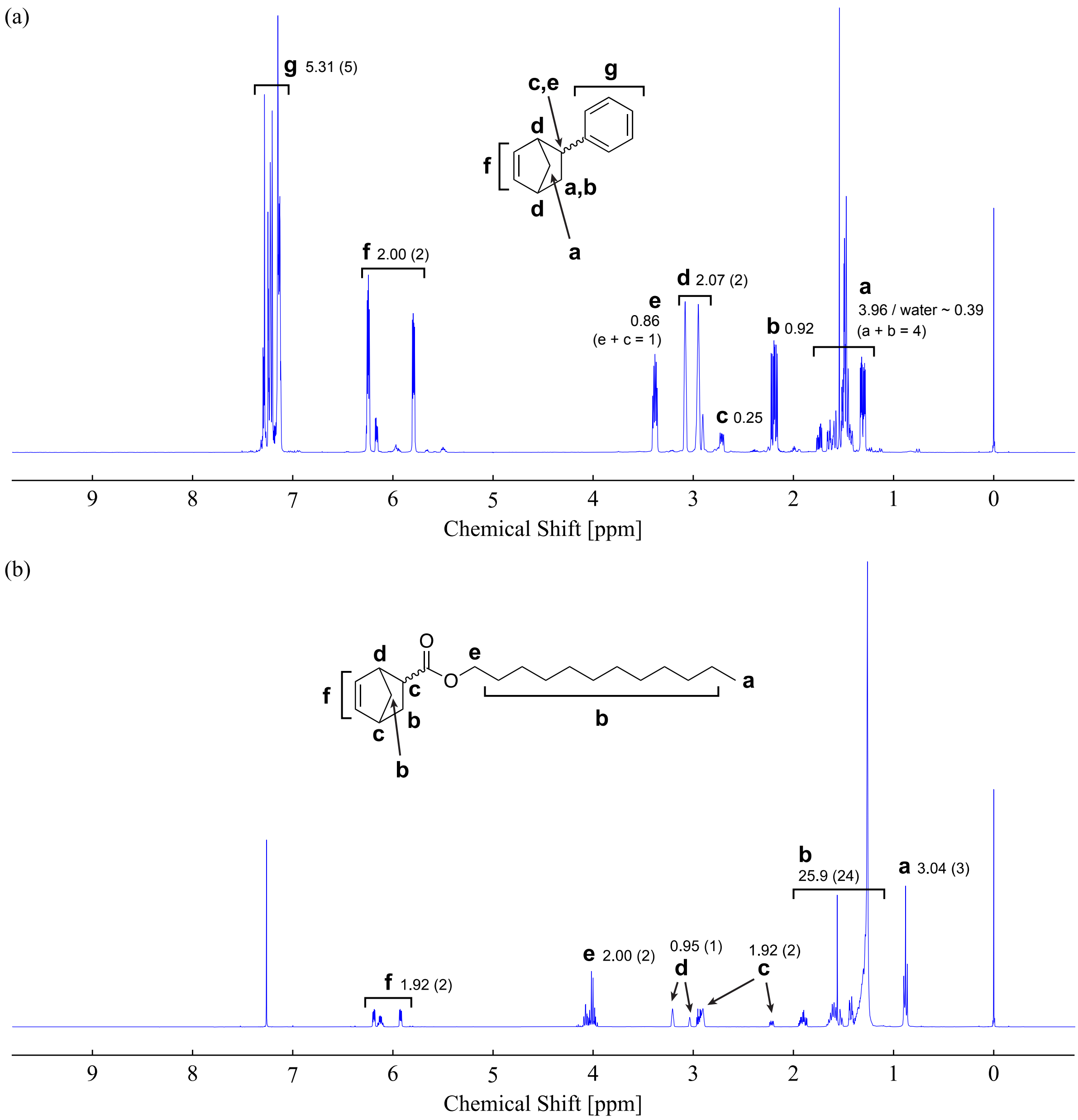

Fig. S1. ^{1}H NMR spectrum of PhN (a), DN (b), and pUN (c) ($CDCl_3$, 400 MHz). Numbers indicate observed integral intensity, together with the corresponding theoretical values in the parentheses. The peak assignment on DN (b) was done according to the literature[4].

(c)

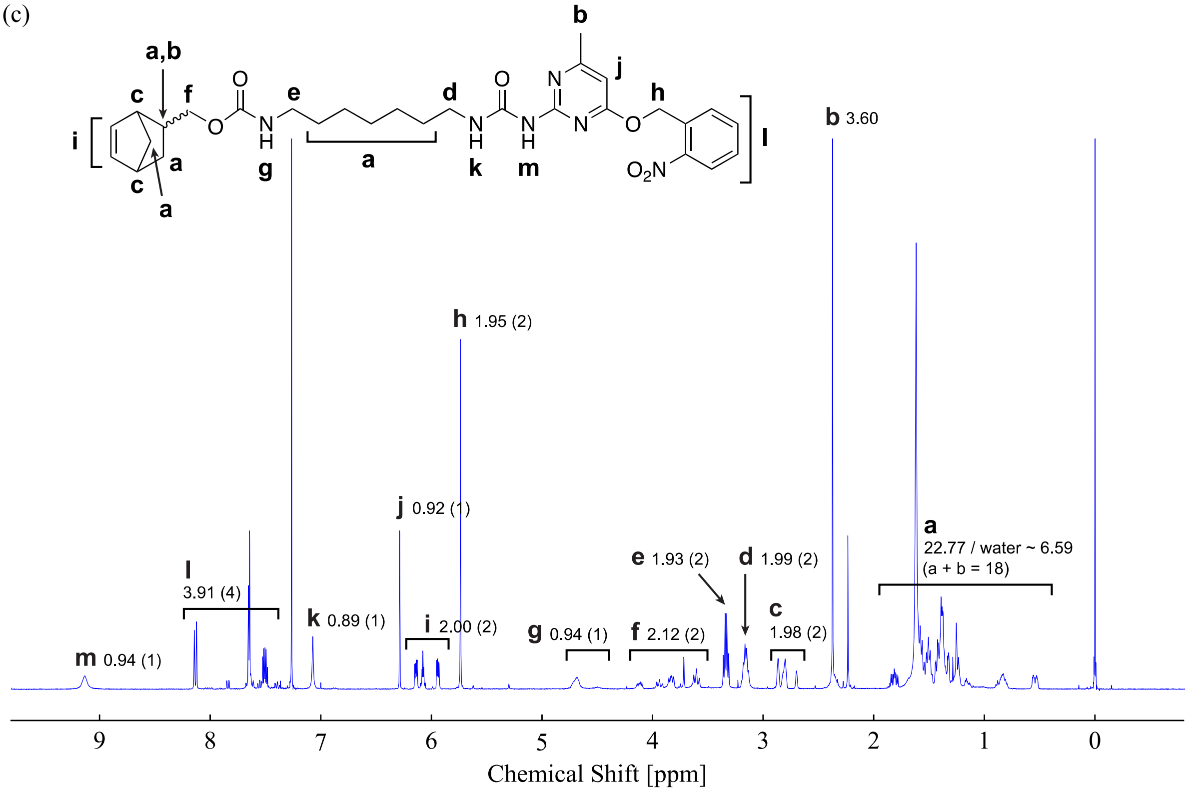

Fig. S1. (continued)

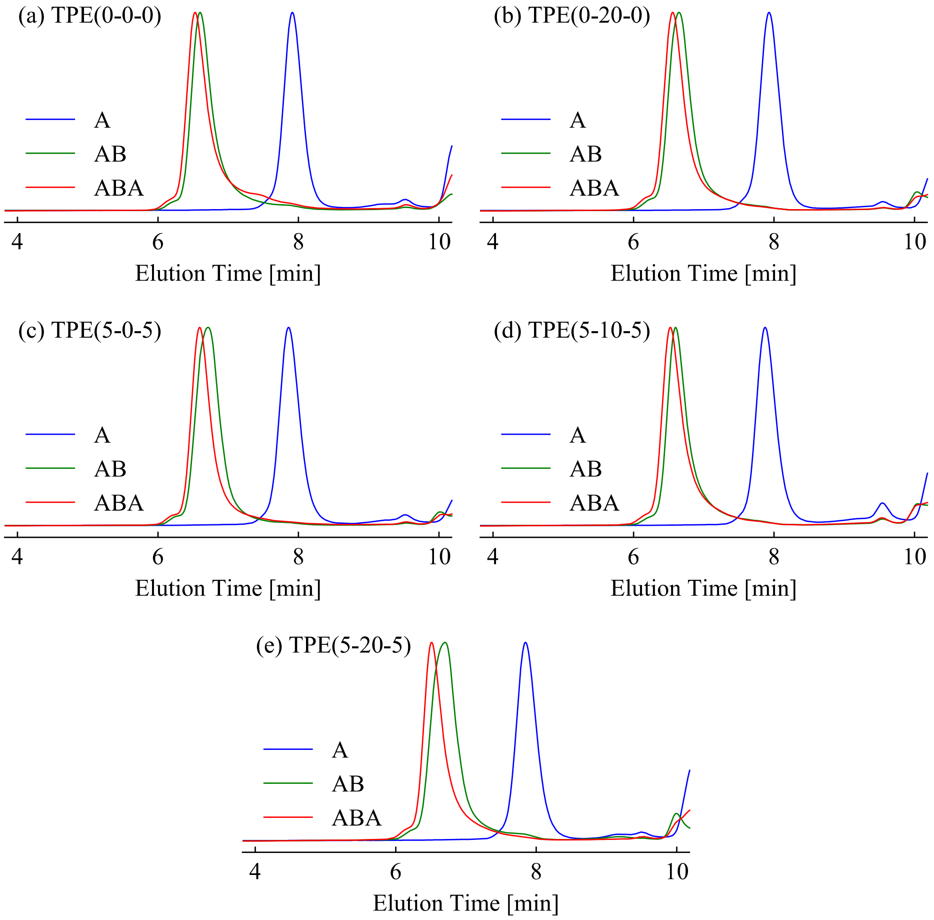

Fig. S2. SEC chromatograms of the reaction mixture at the end of each step of block copolymerization for TPE(0-0-0) (a), TPE(0-20-0) (b), TPE(5-0-5) (c), TPE(5-10-5) (d), and TPE(5-20-5) (e). The measurements were performed on the samples before UV deprotection of UPy moiety using an SEC column (GMHHR-M, Tosoh, Japan) and 0.5% triethylamine/tetrahydrofuran as an eluent.

Table S1. Results of the SEC analysis of the reaction mixture at the end of each polymerization step [a].

Code	M_p (SEC) [b] [kg mol^{-1}]			M_n (SEC) [c] [kg mol^{-1}]			M_w/M_n		
	A	AB	ABA	A	AB	ABA	A	AB	ABA
TPE(0-0-0)	14	198	232	13	112	103	1.09	1.61	1.92
TPE(0-20-0)	13	178	219	13	119	132	1.09	1.50	1.57
TPE(5-0-5)	15	154	201	14	118	116	1.11	1.37	1.63
TPE(5-10-5)	15	199	236	14	121	136	1.09	1.50	1.56
TPE(5-20-5)	16	157	243	14	113	140	1.10	2.12	1.56

a: Characterization was performed on the samples before deprotection of UPy. b: Apparent peak molecular weight calibrated by polystyrene standards. c: Apparent number-averaged molecular weight calibrated by polystyrene standards.

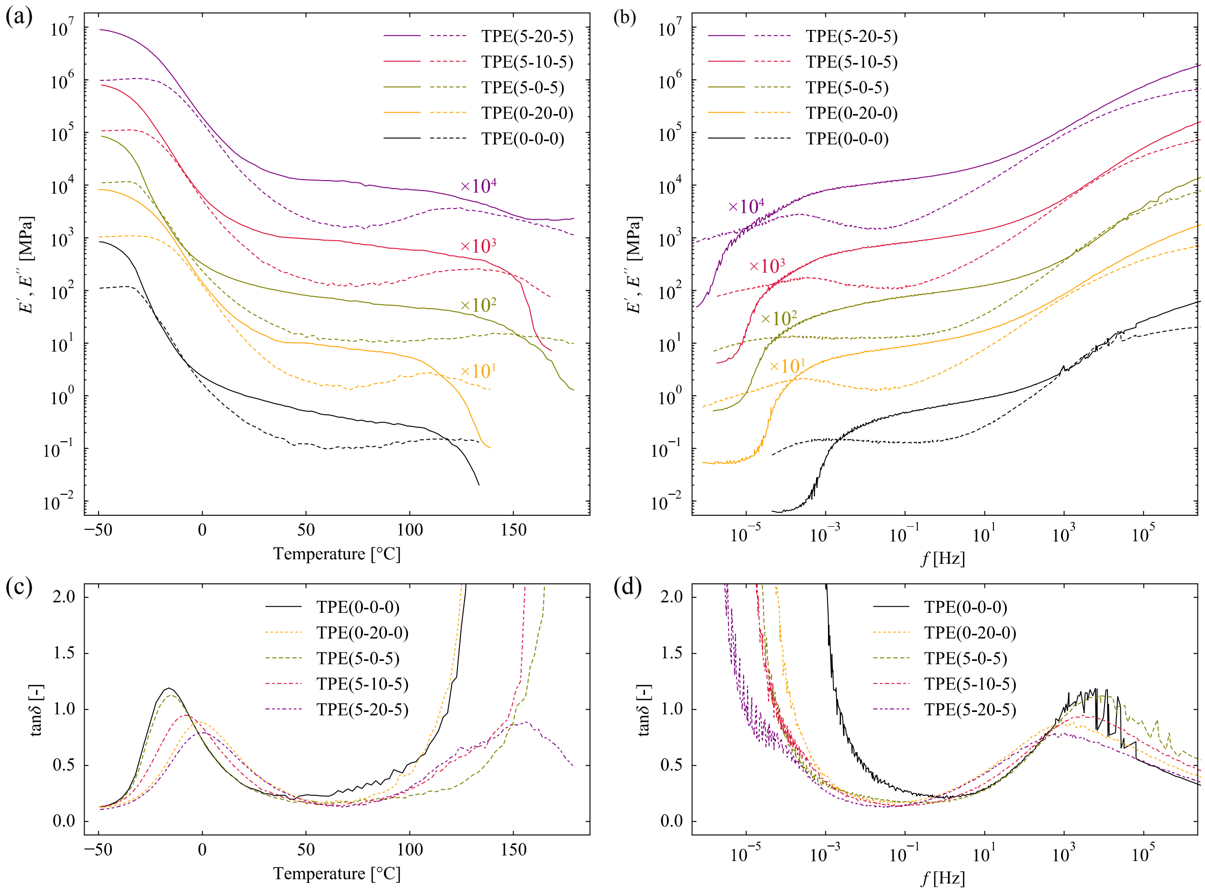

Fig. S3. Linear viscoelastic spectra of the TPEs. Storage modulus E' and loss modulus E'' at $f = 10$ Hz as a function of temperature (a) and master curves of E' and E'' as a function of frequency f constructed at $T_{\mathrm{ref}} = 25$ °C (b). The curves have been vertically shifted by an indicated factor for the sake of legibility. Loss tangent as a function of temperature (c) and f (d).

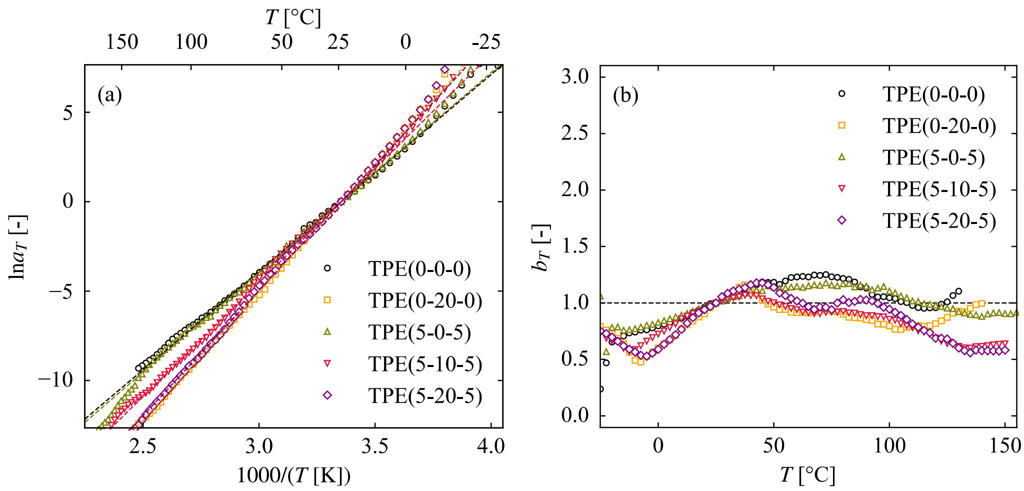

Fig. S4. Horizontal shift factor a_T (a) and vertical shift factor b_T (b) used to construct the master curves in Fig. S3. a_T is displayed as an Arrhenius plot and the dashed lines are the results of linear fitting in the range of 50 °C $\leq T \leq$ 100 °C, the slope of which yields the apparent activation energy E_a. The horizontal dashed line in panel b indicates $b_T = 1$ (= no vertical shifting).

Table S2. Linear viscoelastic properties of the TPEs.

Code	T_1 [a] [°C]	T_2 [b] [°C]	E_a [c] [kJ mol^{-1}]
TPE(0-0-0)	−16	118	92
TPE(0-20-0)	−1	115	119
TPE(5-0-5)	−15	152	93
TPE(5-10-5)	−8	148	106
TPE(5-20-5)	0	- [d]	116

a: Temperature at the peak of tan δ measured at f = 10 Hz. b: Temperature at the crossover of E' and E''. c: Apparent activation energy estimated from the horizontal shift factor in the temperature range of 50 °C $\leq T \leq$ 100 °C. d: T_2 could not be determined because E' did not become lower than E'' even at the highest temperature employed.

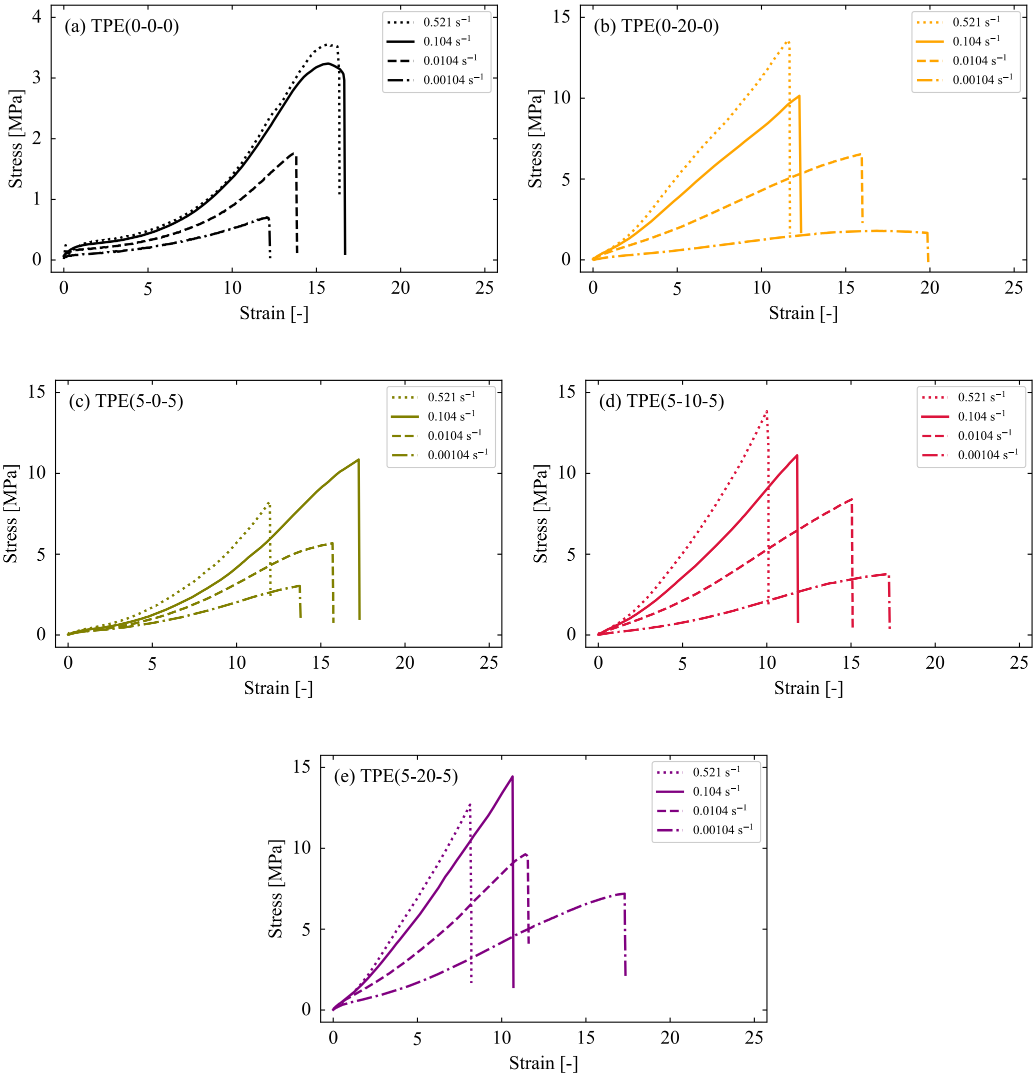

Fig. S5. Stress-strain curves of the TPEs measured at different strain rates for TPE(0-0-0) (a), TPE(0-20-0) (b), TPE(5-0-5) (c), TPE(5-10-5) (d), and TPE(5-20-5) (e).

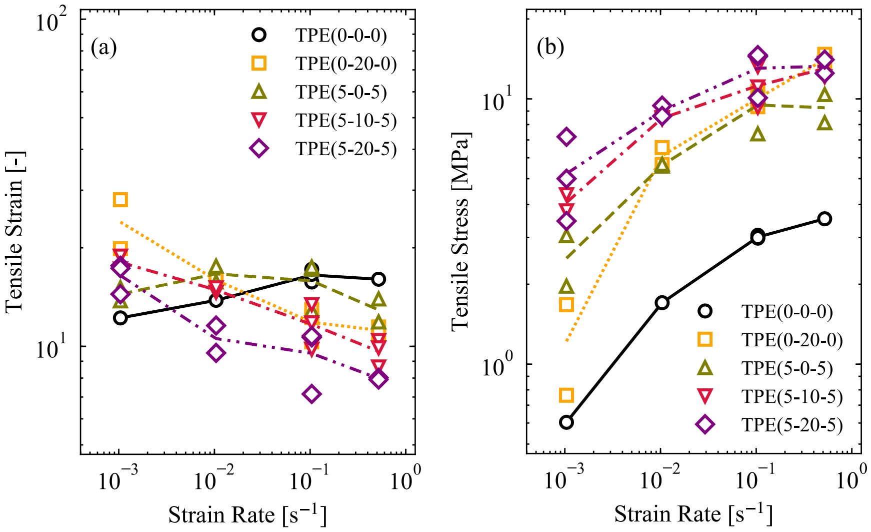

Fig. S6. Strain rate dependence of the tensile strain (a) and tensile stress (b). Multiple data points at the same strain rate are those from different test pieces. The lines connect the averages over the test pieces at each strain rate.

Table S3. Prescribed strain and resulting work in the 1st loading for the TPE samples.

Code	ε_c	W_1 [MJ m^{-3}]
TPE(0-0-0)	12.60	9.1
TPE(0-20-0)	5.30	9.5
TPE(5-0-5)	8.45	11.0
TPE(5-10-5)	5.00	10.5
TPE(5-20-5)	4.40	9.9

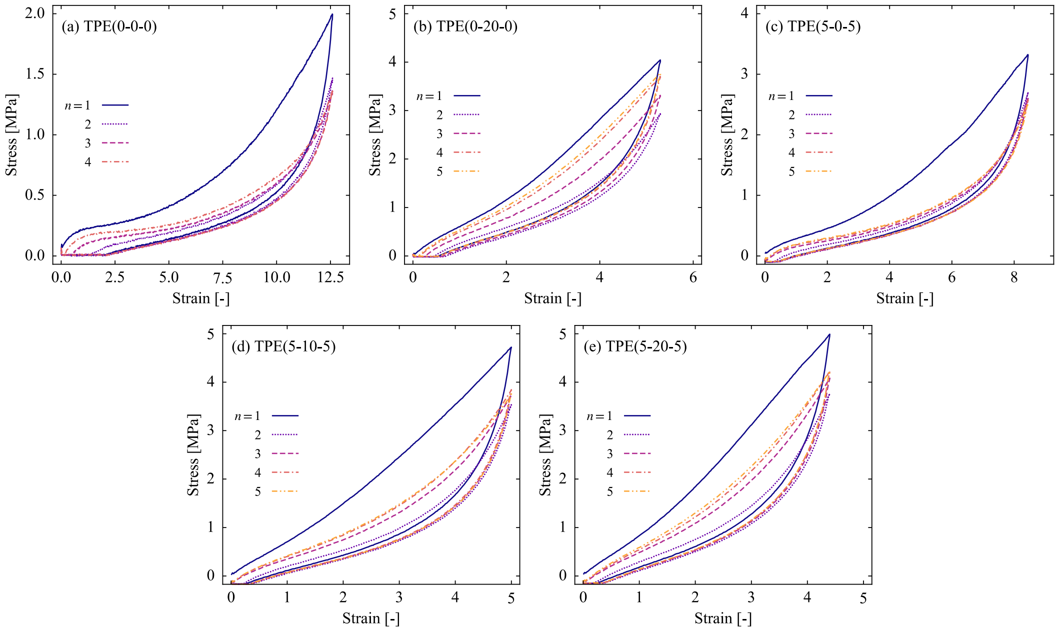

Fig. S7. Stress-strain curves in cyclic tensile tests for TPE(0-0-0) (a), TPE(0-20-0) (b), TPE(5-0-5) (c), TPE(0-10-0) (d), and TPE(5-20-5) (e). Data at *n* = 5 for TPE(0-0-0) is not shown because the sample ruptured during the loading process.

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