Supporting Information for

Mechanical properties of supramolecular polymeric materials cross-linked by donor−acceptor interactions.

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Materials

All the reagents and solvents were commercially available and used as received without further purification. *N*-picrylethylenediamine derivative (TNB derivative)[1] was prepared according to previously described methods.

Measurements

The ^{1}H NMR spectra were obtained using a JEOL JNM-ECS 400 NMR spectrometer. The concentration of each sample was adjusted to 1.4 wt%. Chemical shifts were referenced to the tetramethylsilane (TMS) value. Gel permeation chromatography (GPC) measurements were performed in DMSO (0.40 mL/min, 40 °C) using an TOSOH HLC-8320GPC EcoSEC® equipped with a TOSOH TSK gel α-M column. Molecular weight was calibrated using polyethylene glycol standard. The rheology measurement was performed using Physica MCR302 rheometer. Mechanical properties of materials were measured by the mechanical tension testing system (Rheoner, RE–33005 (Yamaden Ltd.) and Autograph AG-X plus (Shimadzu Co.).

Calculation of binding constant for DA complex between Py derivative and TNB derivative

We performed the ^{1}H NMR measurement to estimate apparent association constant (K_a) of the DA complex between TNB derivative and 1-pyrenemethylamine hydrochloride (Py derivative) using a Scatchard plot. As concentration of Py derivative was increased, clear up-field shifts of the black circle protons of TNB were observed, indicating the interaction of TNB derivative with Py derivative (Fig. S1). We constructed a Scatchard plot based on the ^{1}H NMR data using as follows equation (Fig. S2).

$$\frac{\Delta}{[D]_0} =- K\Delta + K\Delta_0$$

The slope gave the value of K_a = 1.6 M^{-1}.

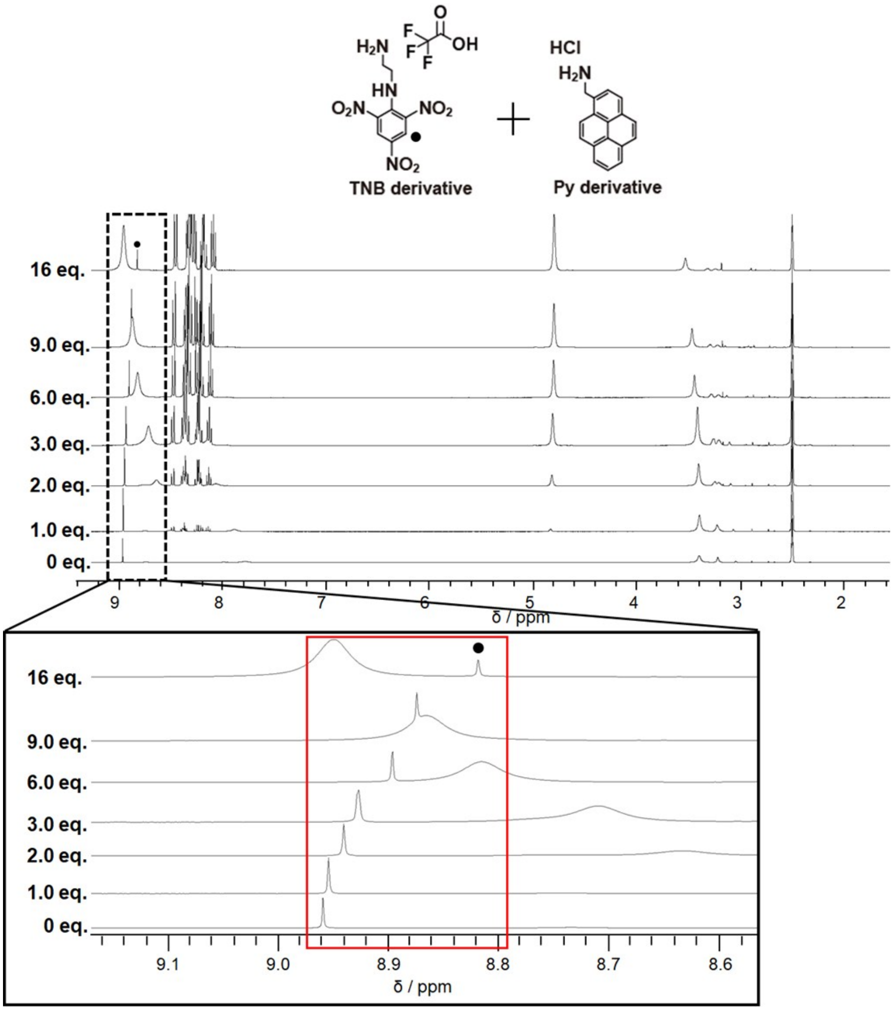


Figure S1. ^{1}H NMR spectra of TNB derivative (5 mM) in the presence of various concentrations of Py in DMSO-d_6 at 25 °C.

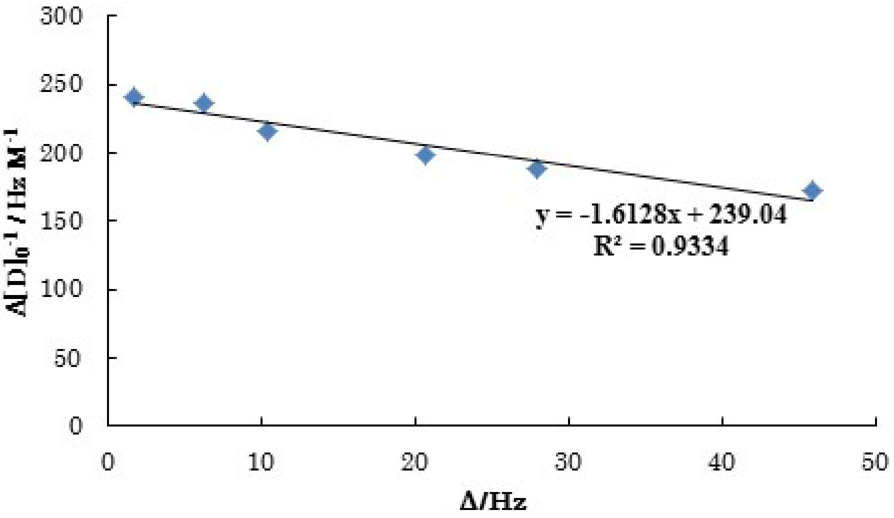
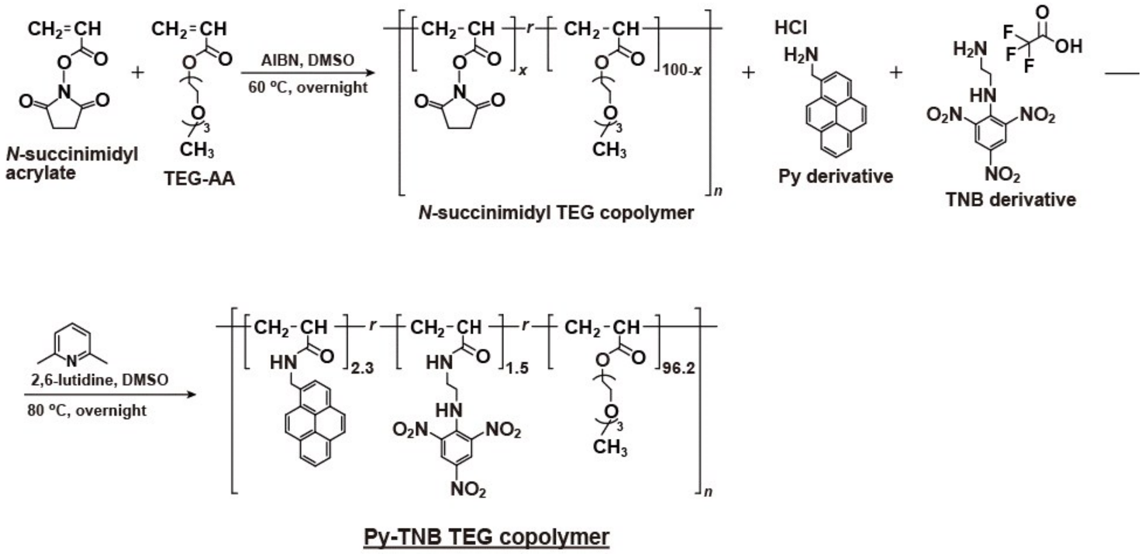


Figure S2. Scatchard plots relating to the shift of aromatic proton in TNB with various concentrations [D]$_0$ of Py in DMSO-d_6.

Preparation of the Py-TNB TEG copolymer



Scheme S1. Preparaiton of Py-TNB TEG copolymer

Methyl triethylene glycol acrylate (TEG-AA) (3.7 g, 17 mmol), *N*-succinimidyl acrylate (0.16 g, 0.96 mmol), and 2,2'-azobis(isobutyronitrile) (AIBN) (30 mg, 0.14 mmol) were mixed in DMSO (18 mL). The copolymerization was carried out at 60 °C under Ar for overnight. The polymeric product, Py derivative (0.15 g, 0.57 mmol), TNB derivative (0.22 g, 0.57 mmol), and 2,6-lutidine (0.44 mL, 3.8 mmol) were mixed in DMSO at 80°C for overnight. The solution was dialyzed with methanol and then dried under reduced pressure at room temperature. Yield 3.6 g, M_n; 7.1×10^5.

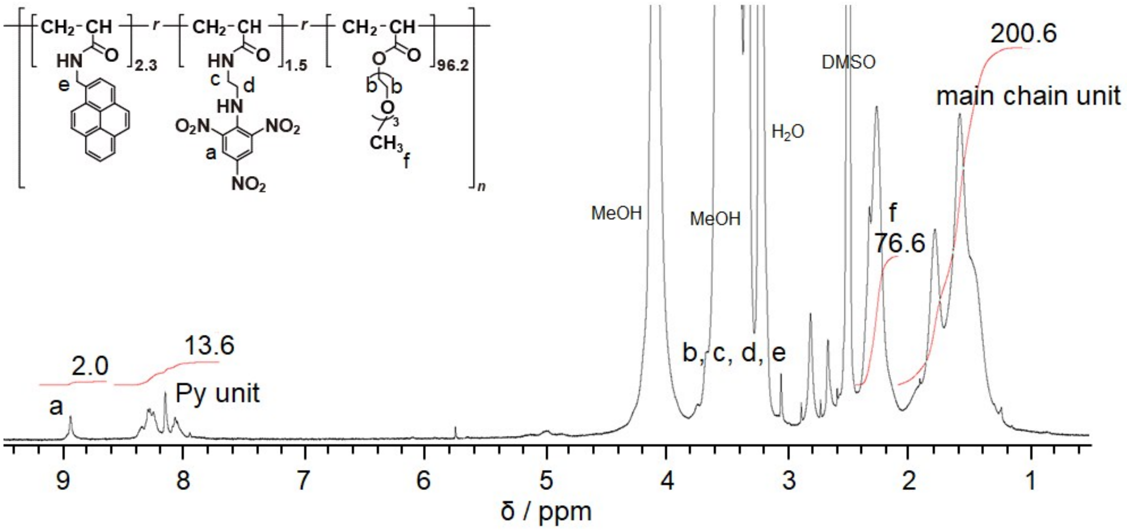
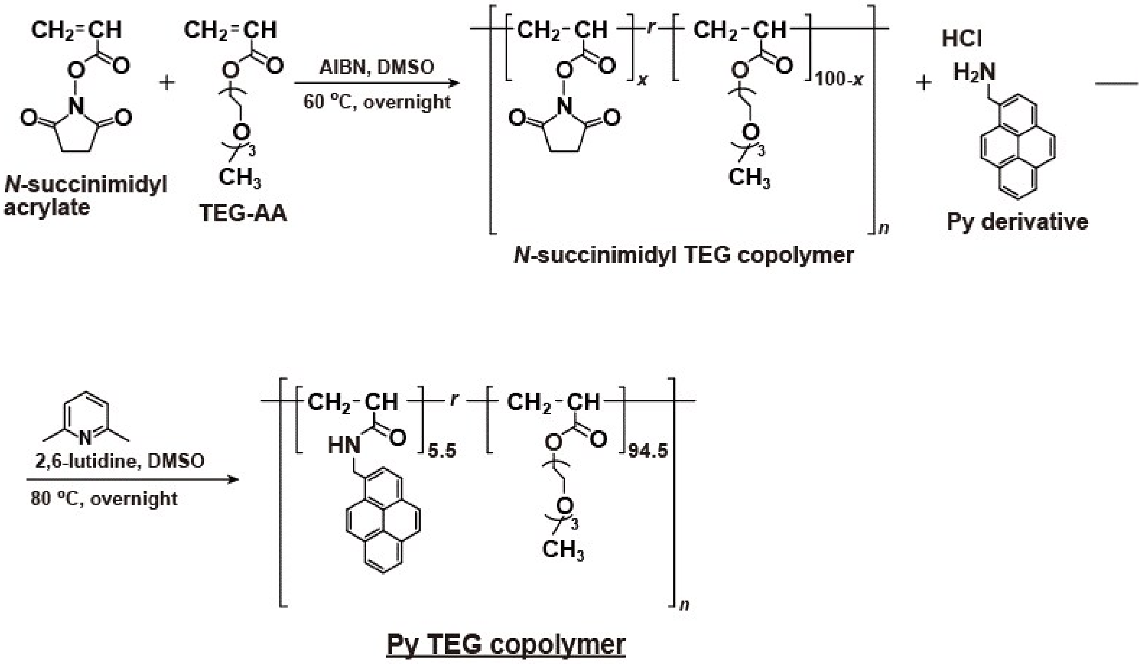


Figure S3. ^{1}H NMR spectrum of Py-TNB TEG copolymer (DMSO-d_6, 25 ^{o}C).

^{1}H NMR (400 MHz, DMSO-d_6, TMS): δ = 8.94 (*H* of TNB unit), 8.40-7.99 (*H* of Py unit), 3.70-3.10 (-CH_2CH_2O- of TEG unit, -NCH_2CH_2N- of TNB unit, and -NCH_2C- of Py unit over laps with -CH_3 of MeOH), 2.41-2.07 (-CH_3 of TEG terminal unit), 2.00-1.19 (-CH_2CH- of main chain).

Prepration of the Py TEG copolymer



Scheme S2. Preparation of the Py TEG copolymer.

TEG-AA (3.7 g, 17 mmol), *N*-succinimidyl acrylate (0.16 g, 0.96 mmol), and AIBN (30 mg, 0.14 mmol) were mixed in DMSO (18 mL). The copolymerization was carried out at 60 °C under Ar for overnight. The polymeric product, Py derivative (0.25 g, 0.96 mmol), and 2,6-lutidine (0.44 mL, 3.8 mmol) were mixed in DMSO at 80°C for overnight. The solution was dialyzed with methanol and then dried under reduced pressure at room temperature. Yield 3.4 g, M_n; 4.6×10^5.

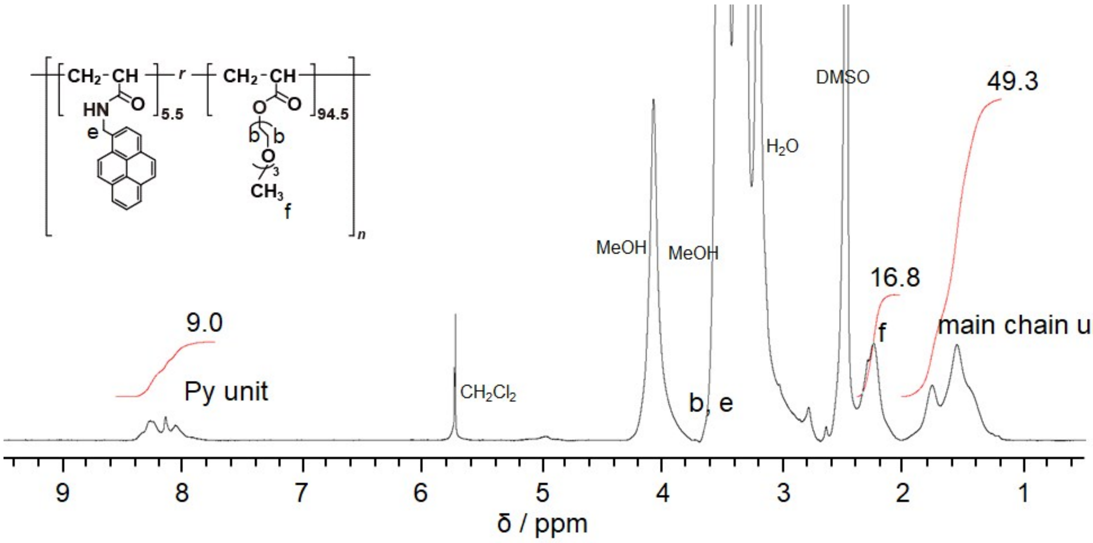
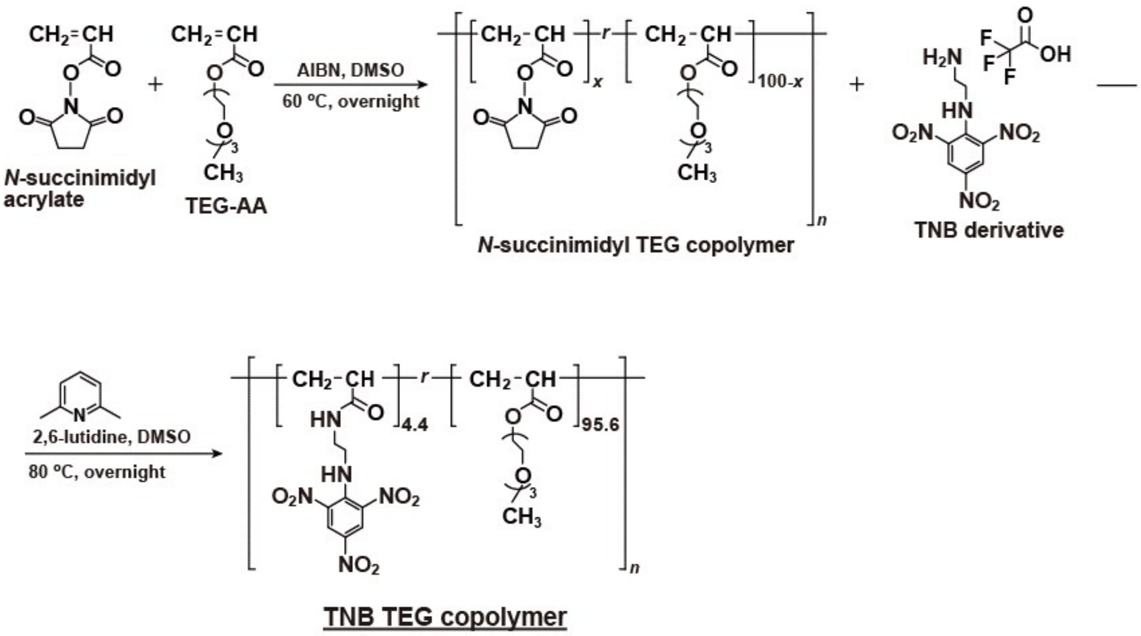


Figure S4. ^{1}H NMR spectrum of Py TEG copolymer in DMSO-d_6 at 25 ^{o}C.

^{1}H NMR (400 MHz, DMSO-d_6, TMS): δ = 8.37-7.95 (*H* of Py unit), 3.75-3.20 (-CH_2CH_2O- of TEG unit and -NCH_2C- of Py unit over laps with -CH_3 of MeOH), 2.39-2.15 (-CH_3 of TEG terminal unit), 1.95-1.10 (-CH_2CH- of main chain).

Preparation of the TNB TEG copolymer



Scheme S3. Preparation of the TNB TEG copolymer.

TEG-AA (3.7 g, 17 mmol), *N*-Succinimidyl Acrylate (0.16 g, 0.96 mmol), and AIBN (30 mg, 0.14 mmol) were mixed in DMSO (18 mL). The copolymerization was carried out at 60 °C under Ar for overnight. The polymeric product, TNB derivative (0.37 g, 0.96 mmol), and 2,6-lutidine (0.44 mL, 3.8 mmol) were mixed in DMSO at 80°C for overnight. The solution was dialyzed with methanol and then dried under reduced pressure at room temperature. Yield 3.1 g, M_n; 4.4×10^5.

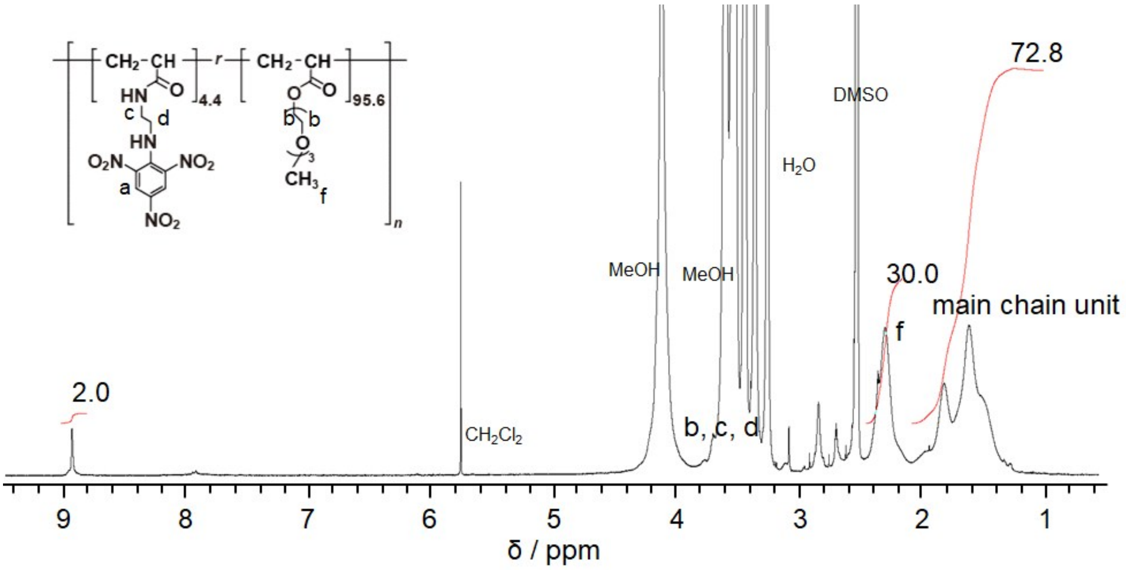


Figure S5. ^{1}H NMR spectrum of TNB TEG polymer in DMSO-d_6 at 25 ^{o}C.

^{1}H NMR (400 MHz, DMSO-d_6, TMS): δ = 8.90 (*H* of TNB unit), 3.70-3.10 (-CH_2CH_2O- of TEG unit and -NCH_2CH_2N- of TNB unit over laps with -CH_3 of MeOH), 2.35-2.11 (-CH_3 of TEG terminal unit), 1.95-1.20 (-CH_2CH- of main chain).

Preparation of elastomers

Figure S6 shows preparation of elastomers. The polymers (1.0 g) (Table S1) were dissolved in DMSO (10 mL) and then these polymer solutions were poured into a mold and dried at 60 °C under reduced pressure for overnight to obtain elastomers.

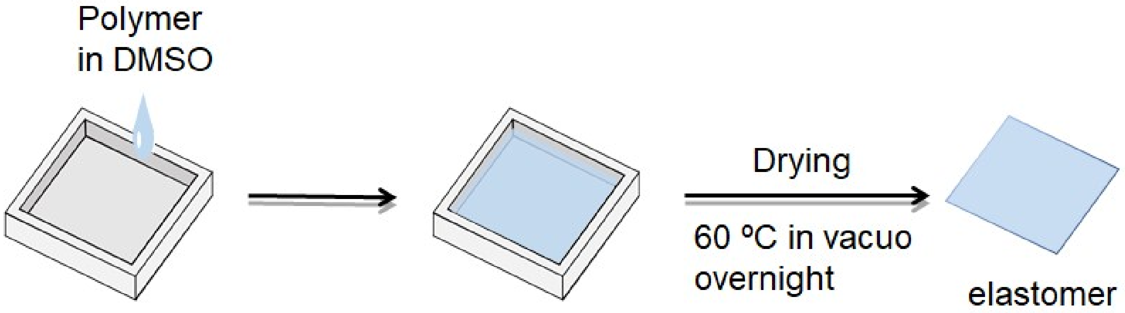


Figure S6. Preparation of elastomers.

Table S1. Preparation of elastomers

Elastomer	Polymer	Weight (g)	DMSO (mL)
Py-TNB TEG elastomer	Py-TNB TEG copolymer	1.0	10
Py TEG elastomer	Py TEG polymer	1.0	
TNB TEG elastomer	TNB TEG polymer	1.0	
Py TEG + TNB TEG elasotmer	Py TEG poymer	0.45	
	+	+	
	TNB TEG polymer	0.55	

Preparation of TEG elastomer

Figure S7 shows preparation of TEGelastomer. TEG gel was obtained by radical copolymerization of TEG-AA (0.43 g, 2.0 mmol) and *N*,*N*'-methylenebis(acrylamide) (MBAAm) (4.6 mg, 30 μmol) using ammonium peroxodisulfate (APS) as initiator and *N*,*N*,*N*',*N*'-tetramethyl ethylenediamine (TEMED) as the cocatalyst. The TEG gel was immersed in excess water to remove impurities. The TEG gel was dried at 60 °C under reduced pressure to obtain TEG elastomer.

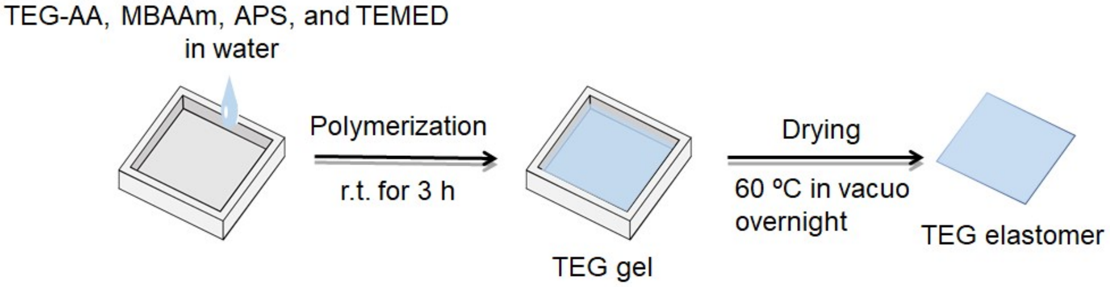


Figure S7. Preparation of TEG elastomer.

Viscoelastic properties of elastomers

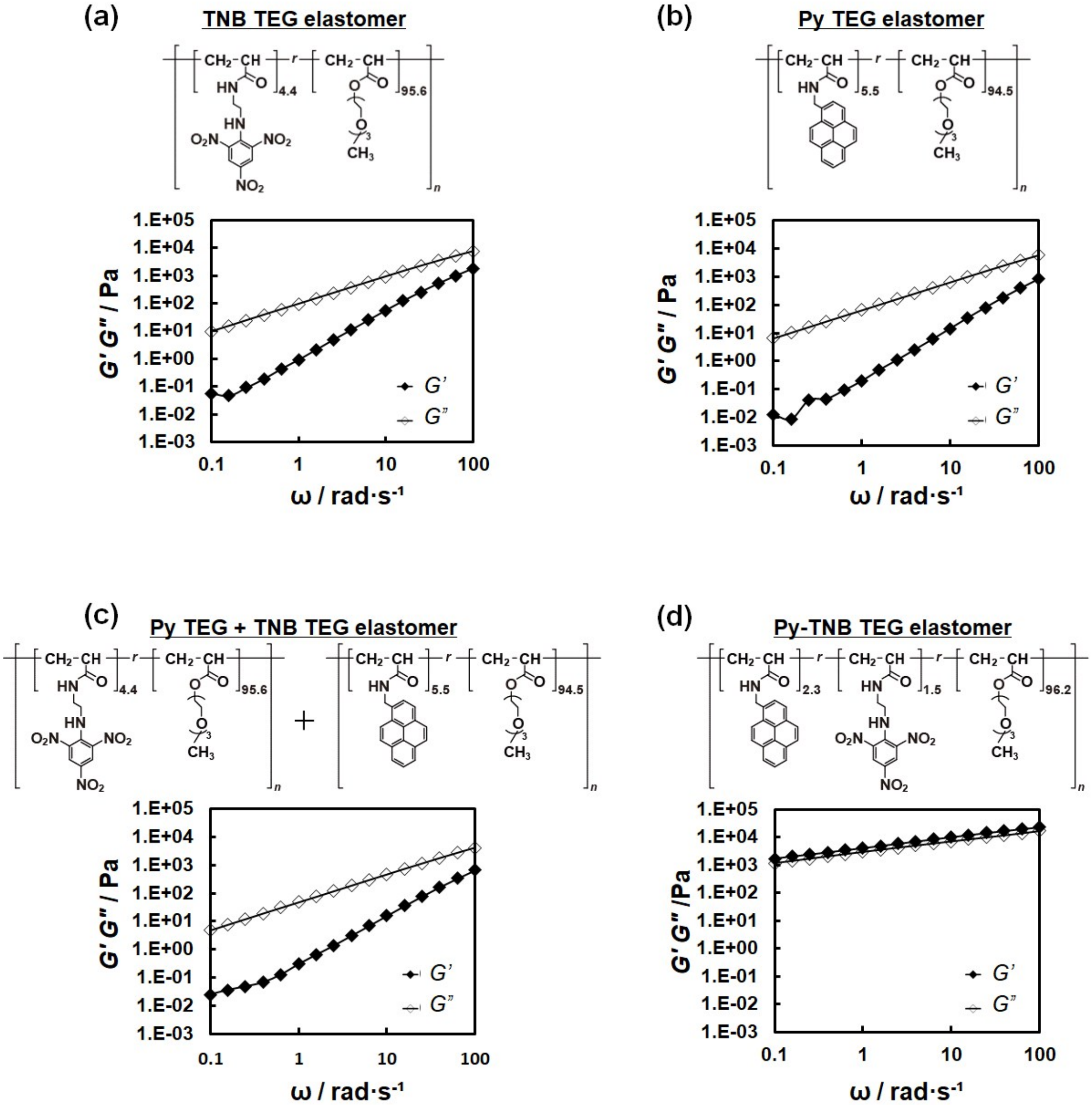


Figure S8. Viscoelastic properties of (a) TNB TEG elastomer, (b) Py TEG elastomer, (c) Py TEG + TNB TEG elastomer, and (d) Py-TNB TEG elastomer.

Competitive experiment

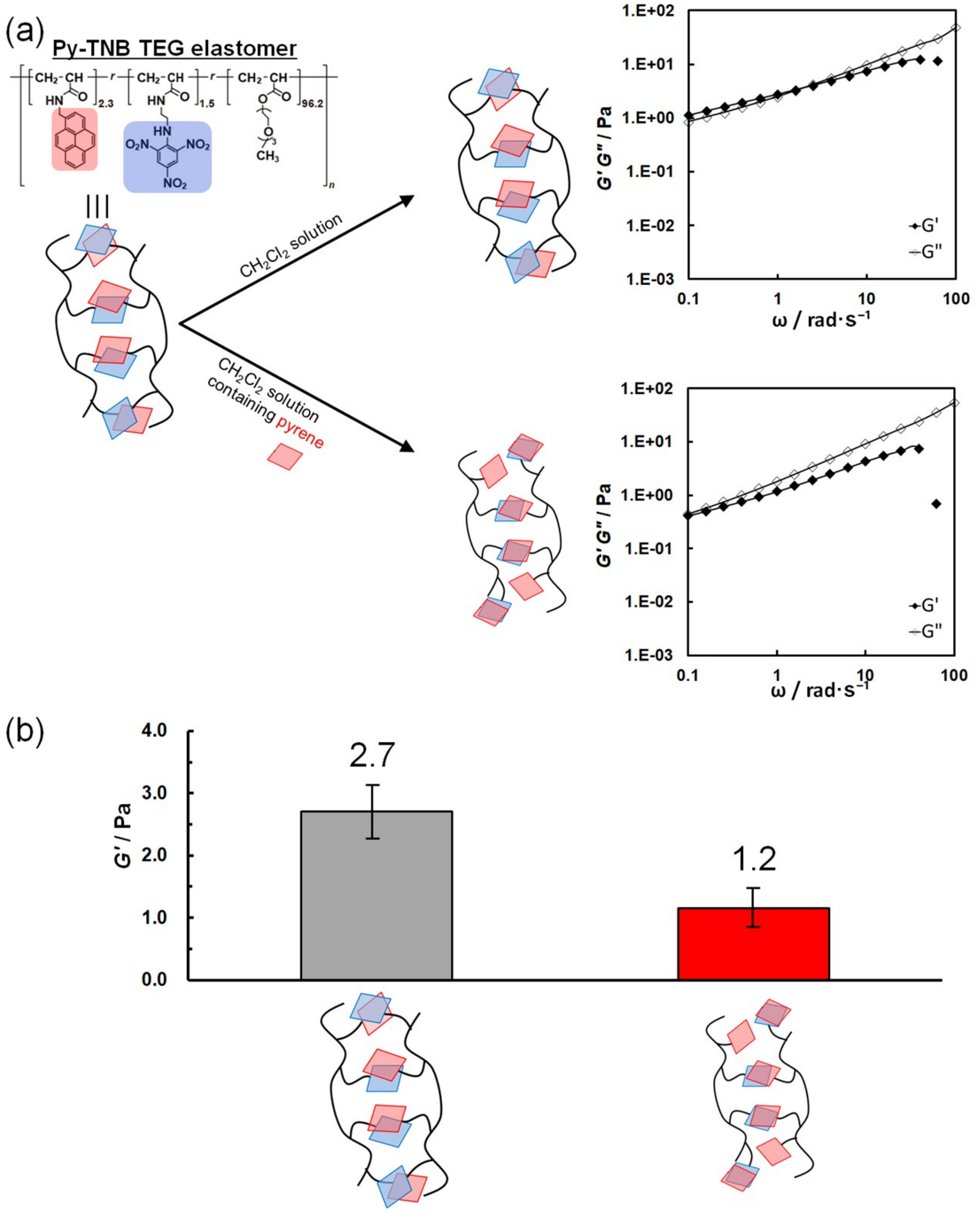


Figure S9. (a) Viscoelastic properties of Py-TNB TEG organogel (up) and Py-TNB TEG organogel containing Py (down). (b) Storage elastic modulus (G') of Py-TNB TEG organogel (gray) and Py-TNB TEG organogel containing Py (red) at the angular frequency (ω) = 1 rad/sec.

Cycle test of Py-TNB TEG elastomer and TEG elastomer.

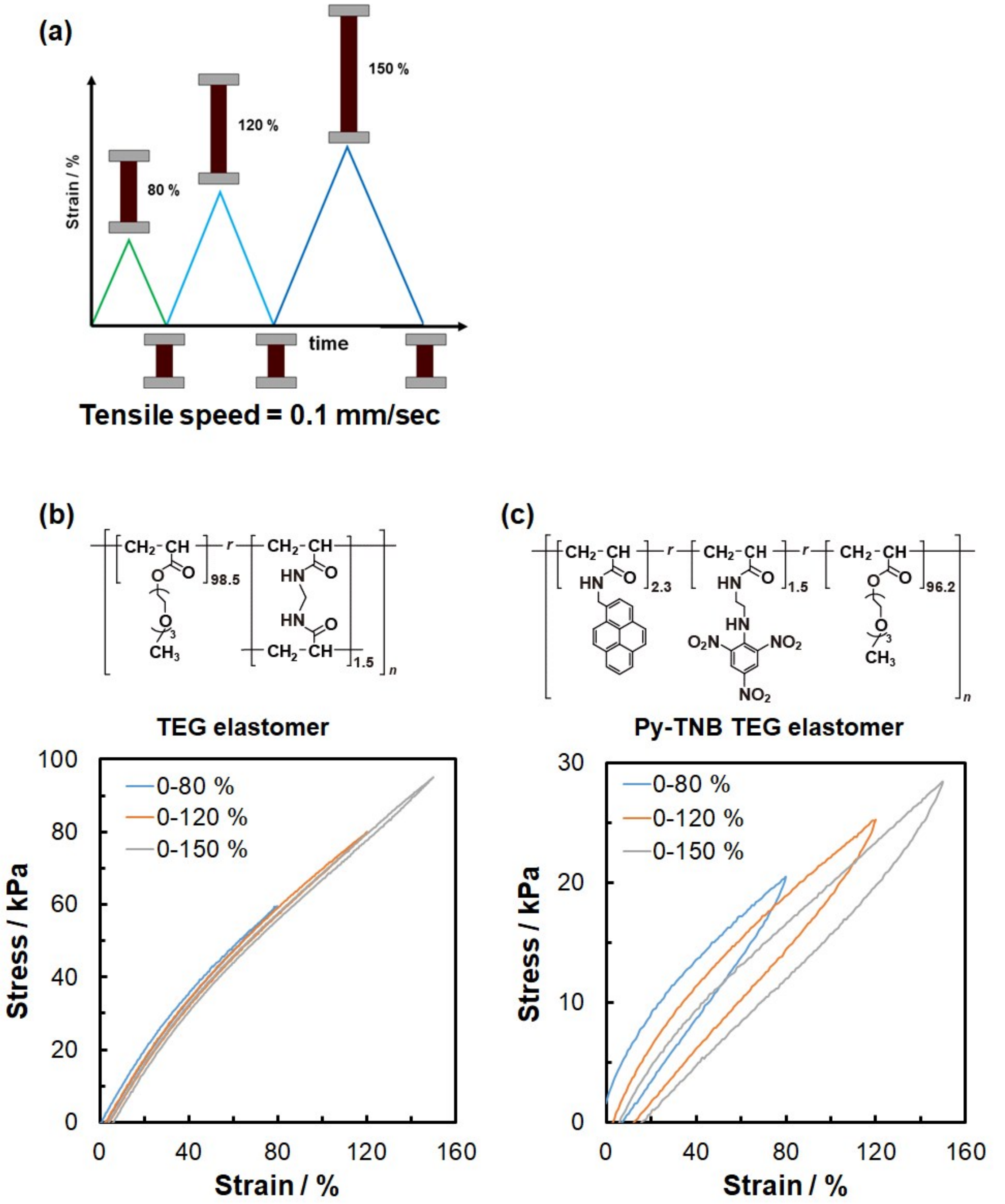


Figure S10. (a) Experimental procedure of cycle test. The maximum strains were set to 80-150% for the elastomers at a deformation rate of 0.1 mm/s. The test pieces were continuously stretched and recovered without interval. Stress–strain curves of the cycle test of (b) TEG elastomer and (c) Py-TNB TEG elastomer.

Tensile tests at different tensile speed

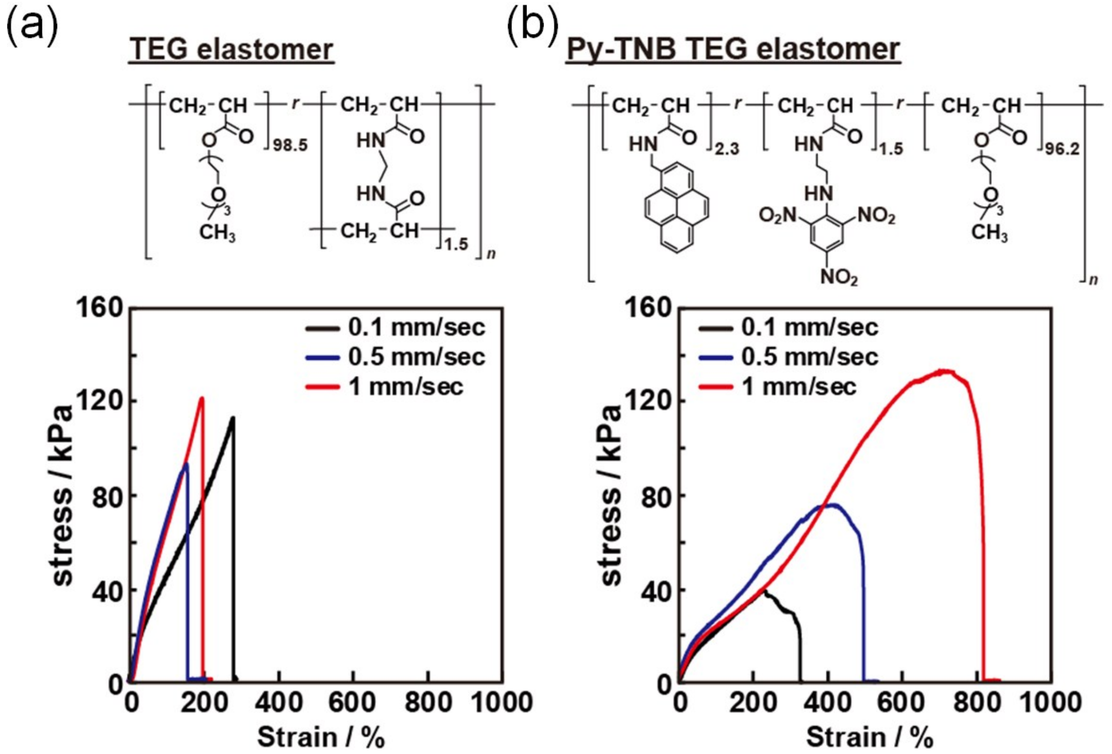


Figure S11. Stress–strain curve of (a) TEG elastomer and (b) Py-TNB TEG elastomer at 0.1 (black), 0.5 (blue), and 1 (red) mm/sec.

Stability of DA complex between Py and TNB for temperature

We performed the ^{1}H NMR measurement to investigate the thermal stability of the DA complex between TNB derivative and Py. Down-field shifts of the black circle protons of TNB were observed by increasing temperature (Fig. S12). This result indicates the dissociation of DA complex between TNB derivative and Py.

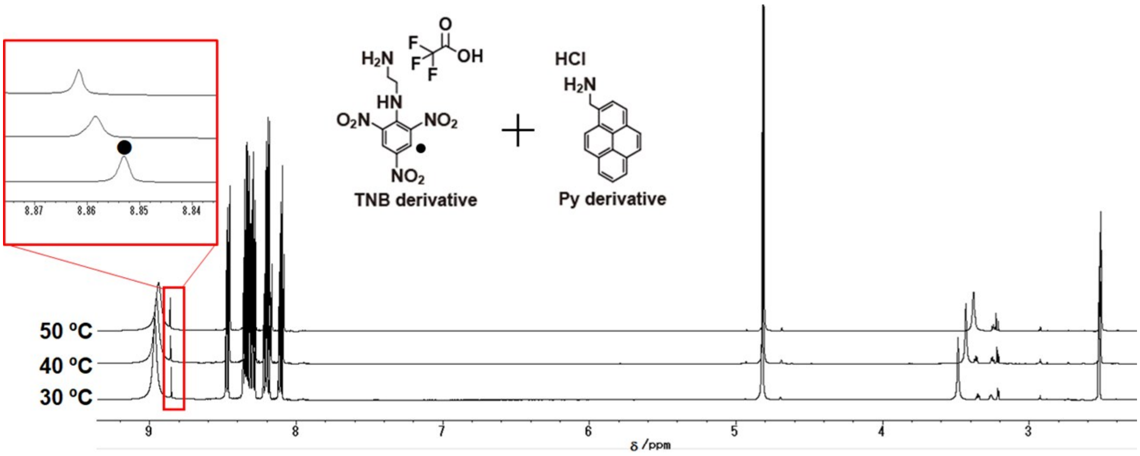


Figure S12. ^{1}H NMR spectra of DA complex between TNB derivative and Py derivative at various temperatures (30, 40, and 50 °C) in DMSO-d_6.

References

1. E. Buncel, M. Hamaguchi and A. R. Norris, *Can. J. Chem.-Rev. Can. Chim.*, 1981, **59**, 795.