Electronic Supplementary Information (ESI) for Soft Matter

Controlling the dynamics of elastomer networks with multivalent brush architectures

Michika Onoda,[a,b] Fei Jia,[a] Yukikazu Takeoka,[b] and Robert J. Macfarlane[*a]

[a.] **Department of Materials Science and Engineering, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, Massachusetts 02139, USA.**

[b.] **Department of Molecular Design and Engineering, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, 464-8603, Japan**

Table of contents

1. Experimental section p. S2

1.1. Materials p. S2

1.2. Synthesis p. S2

1.2.1. Synthesis of modified 3rd generation Grubbs catalyst p. S2

1.2.2. Synthesis of ethylene bis(2-bromoisobutyrate) (bis-bibb) p. S2

1.2.3. Synthesis of exo-5-norbornene-2-methanol (NB-OH) p. S2

1.2.4. Synthesis of exo-5-norbornene-2-methyl 2-bromoisobutyrate (NB-BiBB) p. S3

1.2.5. Synthesis of Br-PnBA-Br p. S3

1.2.6. Synthesis of NB-PnBA-Br p. S3

1.2.7. Synthesis of P(PnBA-Br) p. S4

1.2.8. Synthesis of imidazole-functionalized PnBA and PPnBA p. S4

1.3. Measurements p. S4

1.3.1. Characterization p. S4

1.3.2. Elastomer preparation p. S5

1.2.3. Rheological measurements p. S5

2. Results and discussion p. S6

Figure S1 p. S6

Figure S2 p. S7

Figure S3 p. S8

Figure S4 p. S9

Figure S5 p. S10

Figure S6 p. S11

Figure S7 p. S12

Figure S8 p. S13

Supplementary discussion p. S14

Figure S9 p. S15

Figure S10 p. S16

References p. S17

1. Experimental Section

1.1. Materials

n-Butyl acrylate (nBA) purchased from Sigma-Aldrich Co. was purified by passing through a basic activated alumina oxide column to remove the inhibitor. All other materials were purchased from Sigma-Aldrich Co., VWR International LLC, or Fisher Scientific Inc., and used without further purification, unless otherwise indicated.

1.2. Synthesis

1.2.1. Synthesis of modified 3rd generation Grubbs catalyst

Third-generation Grubbs catalyst (G3) was synthesized based on a published protocol.[1] In brief, 2nd-generation Grubbs catalyst (500 mg, 5.89×10^{-4} mol) and excess 3-bromopyridine (1.64 g, 1.0 mL, 1.04×10^{-2} mol) were mixed in a 15 mL centrifuge tube. The reaction mixture was then precipitated thrice in anhydrous pentane (10 mL). The resulting green powder was dried *in vacuo* and stored at −20 °C.

1.2.2. Synthesis of ethylene bis(2-bromoisobutyrate) (bis-bibb)

In a glove box, ethylene glycol (5.00 mL, 8.94×10^{-2} mol), anhydrous dichloromethane (200 mL), and triethylamine (37.4 mL 2.68×10^{-1} mol, 3.0 eq.) were added to a round-bottom flask equipped with a magnetic stir bar and dropping funnel. Subsequently, the dropping funnel was charged with 2-bromoisobutyryl bromide (27.6 mL, 2.24×10^{-1} mol, 2.5 eq.) and anhydrous dichloromethane (20 mL). The flask was then removed from the glovebox and allowed to cool to 0 °C in an ice bath. After cooling, the 2-bromoisobutyryl bromide solution in the dropping funnel was added dropwise to the reaction mixture. After the complete addition, the reaction mixture was slowly warmed to 25 °C. The resulting reaction mixture was filtered, concentrated by rotary evaporation, and dissolved in chloroform (200 mL). The obtained brown solution was washed sequentially with a hydrochloric acid solution (100 mL, 1.0 M), saturated sodium bicarbonate solution (100 mL), and deionized water for three times (100 mL×3). The organic layer was dried over sodium sulfate, filtered, and passed twice through a basic activated aluminum oxide column. The resulting solution was concentrated by rotary evaporation to obtain a light brown solid. The crude product was further purified by recrystallizing twice from ethyl acetate to recover a clear transparent solid (25.1 g, 6.97×10^{-2} mol, 78% yield).

1.2.3. Synthesis of *exo*-5-norbornene-2-methanol (NB-OH)

In a glove box, *exo*-5-norbornenecarboxylic acid (5.0 g, 3.62×10^{-2} mol) and anhydrous tetrahydrofuran (150 mL) were added to a round-bottom flask equipped with a glass-coated magnetic stir bar, dropping funnel, and reflux tube. The dropping funnel was charged with a lithium aluminum hydride (LAH) solution (1.0 M in tetrahydrofuran, 4.52×10^{-2} mol, 45.2 mL, 1.25 eq.). The flask was removed from the glovebox and allowed to cool to 0 °C in an ice bath. Then, the LAH solution in the dropping funnel was added dropwise to the reaction mixture after a N_2-filled bubbler was connected to the flask to evacuate excess gas during the reaction. After the complete addition, the reaction mixture was refluxed at 70 °C overnight. Then, the resulting mixture was cooled to 0 °C in an ice bath. To quench the reaction, 1.7 mL of deionized water was added dropwise,

followed by 1.7 mL of 10% sodium hydroxide solution, and finally 5.0 mL of deionized water. The flask was allowed to warm to room temperature and the reaction mixture was diluted with diethyl ether (300 mL). The white precipitate was removed via Celite filtration. The obtained transparent filtrate was washed thrice with brine (100 mL), dried over sodium sulfate, filtered, and concentrated by rotary evaporation to obtain *exo*-5-norbornene-2-methanol as a viscous colorless liquid (4.18 g, 3.36×10^{-2} mol, 92% yield).

1.2.4. Synthesis of *exo*-5-norbornene-2-methyl 2-bromoisobutyrate (NB-bibb)

In a glovebox, *exo*-5-norbornene-2-methanol (1.00 g, 8.05×10^{-3} mol), anhydrous tetrahydrofuran (50 mL), and triethylamine (1.68 mL, 1.21×10^{-2} mol, 1.5 eq.) were added to a round-bottom flask equipped with a magnetic stir bar and dropping funnel. The dropping funnel was charged with 2-bromoisobutyryl bromide (1.29 mL, 1.05×10^{-2} mol, 1.3 eq.) and anhydrous tetrahydrofuran (10 mL). The flask was removed from the glovebox and allowed to cool to 0 °C in an ice bath. Then, a 2-bromoisobutyryl bromide solution was added dropwise to the reaction mixture. After the complete addition, the reaction mixture was slowly warmed to room temperature and stirred overnight. Subsequently, the reaction mixture was filtered, concentrated by rotary evaporation, and dissolved in diethyl ether (200 mL). The obtained brown solution was washed sequentially with deionized water (100 mL), saturated sodium bicarbonate solution (100 mL), and deionized water (100 mL). The organic layer was dried over sodium sulfate, filtered, and concentrated by rotary evaporation. The crude product was purified by column chromatography with a mobile phase of 10:1 hexanes/ethyl acetate to recover a viscous colorless liquid (1.29 g, 6.68×10^{-3} mol, 83% yield).

1.2.5. Synthesis of Br-PnBA-Br

To a round-bottom flask with a magnetic stir bar, nBA (24.9 g, 27.9 mL, 1.94×10^{-1} mol), bis-bibb (1.00 g, 2.78×10^{-3} mol), *N,N,N′,N″,N‴*-pentamethyldiethylenetriamine (PMDETA) (0.72 g, 870 µL, 4.17×10^{-3} mol), and anisole (49.0 mL) were added, and the flask was purged with N_2 for 30 min. Then, copper(I) bromide (CuBr) (598 mg, 4.17×10^{-3} mol) was added to the reaction mixture under N_2 flow, and the resulting mixture was stirred for an additional 10 min at room temperature with N_2 purge. Atom transfer radical polymerization (ATRP) was carried out at 80 °C for 100 min, and the reaction was quenched in a dry ice bath. The resulting solution with the unreacted monomer was concentrated by rotary evaporation and diluted with chloroform (300 mL). The obtained solution was washed thrice with a saturated ethylenediaminetetraacetic acid (EDTA) disodium salt solution (150 mL) to remove the copper catalyst. The organic layer was dried over sodium sulfate, filtered, and concentrated by rotary evaporation. The crude product was diluted with dichloromethane and further purified by reprecipitating thrice from a cold 9:1 methanol/water solution. The precipitated viscous liquid was dried *in vacuo* for 1 d at room temperature to recover Br-PnBA-Br as a viscous colorless liquid (12.1 g, 64% conversion). The results of characterization are summarized in **Table S1**.

1.2.6. Synthesis of NB-PnBA-Br

To a round-bottom flask with a magnetic stir bar, nBA (113 g, 126 mL, 8.79×10^{-1} mol), NB-bibb (2.00 g, 7.32×10^{-3} mol), PMDETA (952 mg, 1.15 mL, 5.49×10^{-3} mol), and anisole (92.5 mL) were added, and the mixture was purged with N_2 for 60 min. Then, CuBr (788 mg, 5.49×10^{-3} mol) was added under N_2 flow and

the resulting reaction mixture was stirred for an additional 10 min at room temperature with N_2 purge. ATRP was carried out at 70 °C for 2 h, and the reaction was quenched in a dry ice bath. The final mixture with the unreacted monomer was concentrated by rotary evaporation, and the residue was diluted with chloroform (300 mL). The obtained solution was washed thrice with a saturated EDTA disodium salt solution (150 mL). The organic layer was dried over sodium sulfate, filtered, and concentrated by rotary evaporation. The crude product was diluted with dichloromethane and further purified by reprecipitating thrice from a cold 9:1 methanol/water solution. The precipitated viscous liquid was dried *in vacuo* for 1 d at room temperature to obtain NB-PnBA-Br as a viscous colorless liquid (31.2 g, 34% conversion). The results of characterization are summarized in **Table S1**.

1.2.7. Synthesis of P(PnBA-Br)

In a glovebox, NB-PnBA-Br (5.0 g, 9.56×10^{-4} mol) and anhydrous dichloromethane (29 mL) were added to a round-bottom flask with a magnetic stir bar. Then, the G3 dissolved in 1.0 mL dichloromethane (16.9 mg, 1.91×10^{-5} mol) was quickly added to the reaction mixture. The resulting mixture was stirred at room temperature for 2 h. To quench the reaction, excess ethyl vinyl ether (EVE) (5.0 mL, 5.22×10^{-2} mol) was added, and the reaction mixture was stirred for 1 h. The crude product was diluted with dichloromethane and purified by reprecipitating thrice from a cold 9:1 methanol/H_2O solution. The precipitated viscous liquid was dried *in vacuo* for 2 d at 60 °C to obtain P(PnBA-Br) as a viscous colorless liquid (4.8 g, 96% yield).

1.2.8. Synthesis of imidazole-functionalized PnBA and PPnBA

To a round-bottom flask with a magnetic stir bar, P(PnBA-Br) (4.28 g, 8.18×10^{-4} mol of Br group), *m*-phenylenediamine (MPD) (86.5 mg, 103 µL, 9.82×10^{-4} mol, 1.2 eq.), and *N,N*-dimethylformamide (DMF) (5.0 mL) were added. Then, methimazole (467 mg, 4.09×10^{-3} mol, 5.0 eq.) was added, and the resulting mixture was stirred overnight. The solution was concentrated by rotary evaporation and the residue was dissolved in dichloromethane. The product was precipitated thrice from a cold 9:1 methanol/water solution. The precipitated viscous liquid was dried *in vacuo* for 2 d at room temperature to obtain imidazole-functionalized PPnBA as a viscous yellow liquid (3.96 g, 93% yield). The imidazole-functionalized linear polymer, imi-PnBA-imi, was synthesized using the same protocol.

1.3. Measurements

1.3.1. Characterization

The polymers synthesized in this study were characterized by ^{1}H-NMR (JEOL502, 500 MHz) and size exclusion column chromatography (SEC, Agilent Technologies, 1260 Infinity II) using tetrahydrofuran as the carrier solvent and calibrated using polystyrene standards. The results are presented in **Figure S1-S3** and

Table S1.

Table S1 Characterization of the polymers synthesized in this study.

Polymer Formula[a)]	M_n/ kDa[b)]	$Đ$[c)]
Br-PnBA$_{45}$-Br	5.7	1.10
imi-PnBA$_{45}$-imi	5.8	1.10
NB-PnBA$_{41}$-Br	5.2	1.28
P(PnBA$_{41}$-Br)$_{50}$	262	1.08
P(PnBA$_{41}$-imi)$_{50}$	263	1.09

[a)] Abbreviations: Br, bromide; imi, 1-methylimidazole; NB, norbornene; nBA, *n*-butyl acrylate. Numbers following the abbreviations of monomers indicate the average number of repeating units.

[b)] Number-averaged molecular weight of the polymer. The conversion of the monomer to polymer was calculated based on the decrease in the integrated intensity of the ^{1}H-NMR signal of the double bonds of the unreacted monomer before and after polymerization.

[c)] Dispersity of polymers, calculated from SEC using tetrahydrofuran as the carrier solvent and calibrated using polystyrene standards.

1.3.2. Elastomer preparation

Imidazole-functionalized polymer (1.0 g) was dissolved in dichloromethane (3.0 mL). A known amount of zinc di[bis(trifluoromethylsulfonyl)imide] ($Zn(NTf_2)_2$; imidazole:Zn(II) = 4:1) dissolved in 1.0 mL of acetonitrile was then added to the polymer solution. The obtained pale yellow solution was then transferred to a Petri dish, and the solvent was evaporated overnight at 80 °C. The resulting polymer sample was further dried *in vacuo* for 24 h at 80 °C.

1.3.3. Rheological measurements

Rheological measurements were performed using an MCR302 rheometer (Anton Paar) in the parallel plate geometry with a 20 mm diameter plate. The temperature was controlled using a Peltier temperature controller. Approximately 0.5 g of the elastomer was loaded on the stage at room temperature, and then heated to 80 °C ($>T_m$). Subsequently, the parallel plate was contacted to the sample, ensuring a gap of 0.3 mm between the plates. The sample was then slowly cooled to 10 °C over 30 min to release the internal stress. The temperature dependences of G' and G'' were evaluated at an angular frequency of 10 rad/s with a strain amplitude of 1% and heating rate of 0.1 °C/s. After the temperature sweep measurement, the sample was cooled to 10 °C and allowed to stand for 15 min for stabilization. Dynamic frequency sweeps (frequency range: 0.1 to 100 rad/s) were performed with a strain amplitude of 1% by varying the temperature from 10 to 90 °C in 10 °C steps. Samples were equilibrated at each temperature for 5 min before data collection. The measurements were repeated three times to ensure data reliability.

2. Results and Discussion

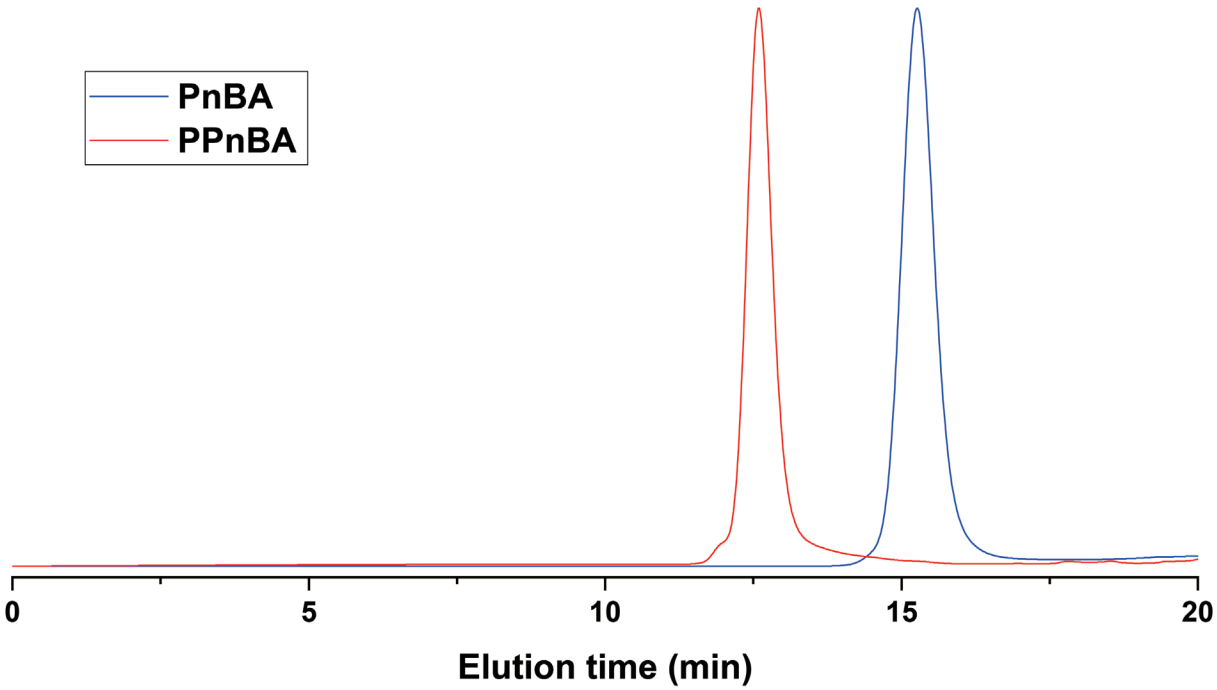

Figure S1. GPC traces of imidazole-functionalized PnBA (imi-PnBA$_{45}$-imi) and PPnBA (P(PnBA$_{41}$-imi)$_{50}$) synthesized in this study.

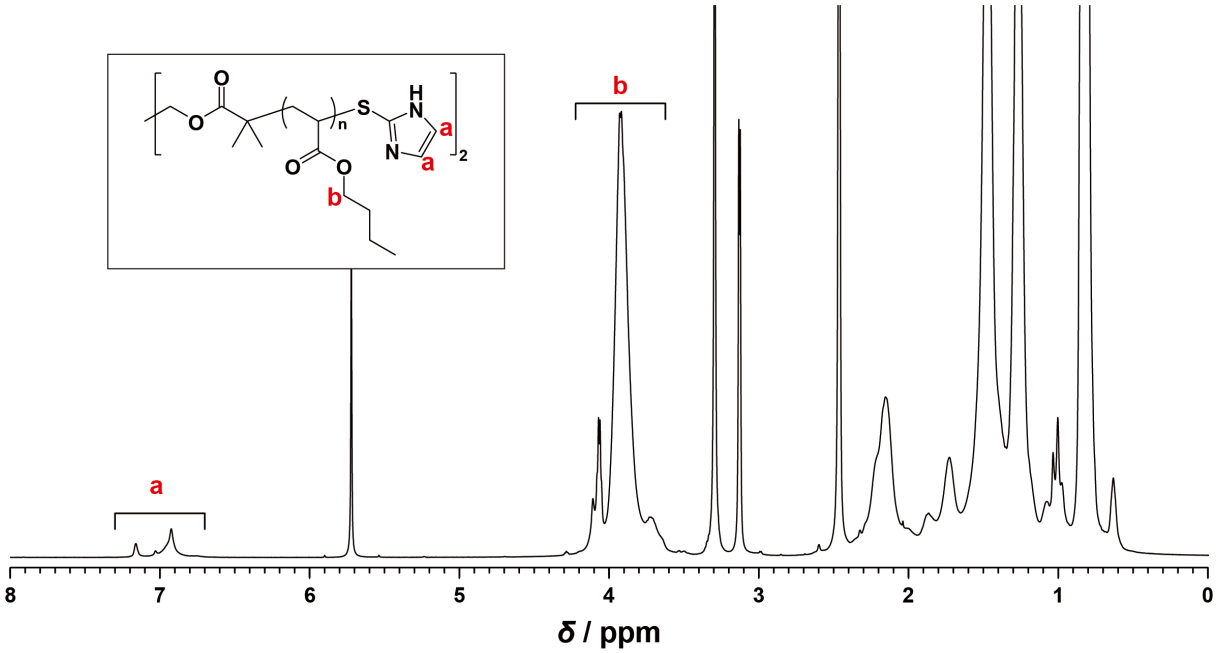

Figure S2. ^{1}H-NMR spectrum of imidazole-functionalized PnBA (imi-PnBA$_{45}$-imi).

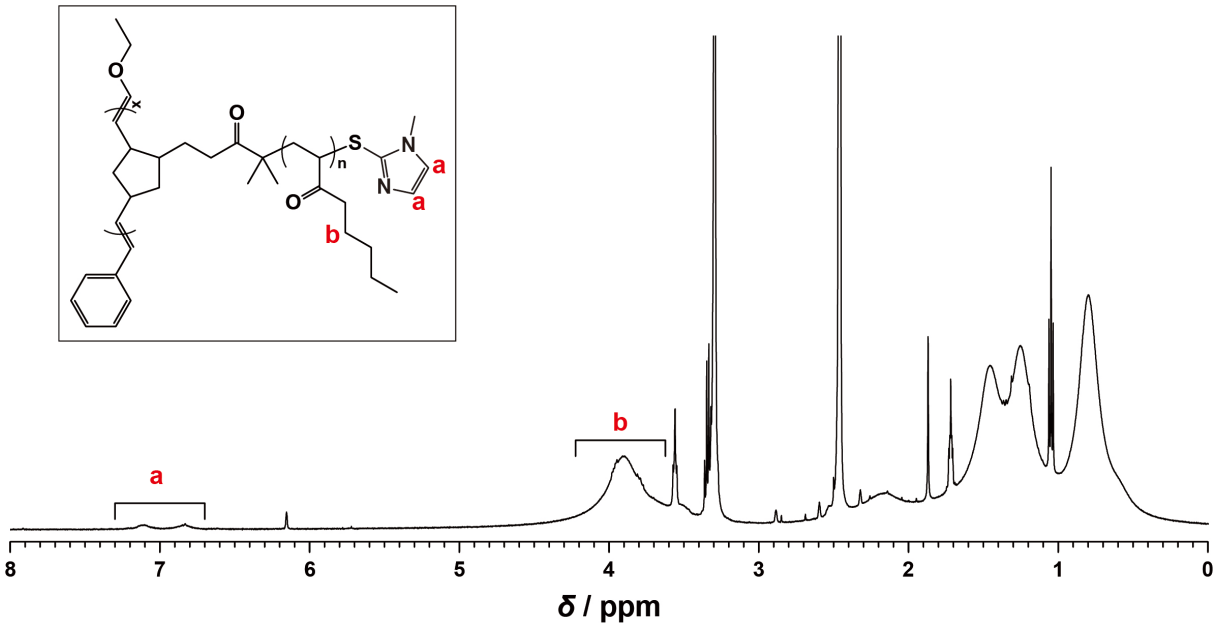

Figure S3. ^{1}H-NMR spectrum of imidazole-functionalized PPnBA (P($PnBA_{41}$-imi)$_{50}$).

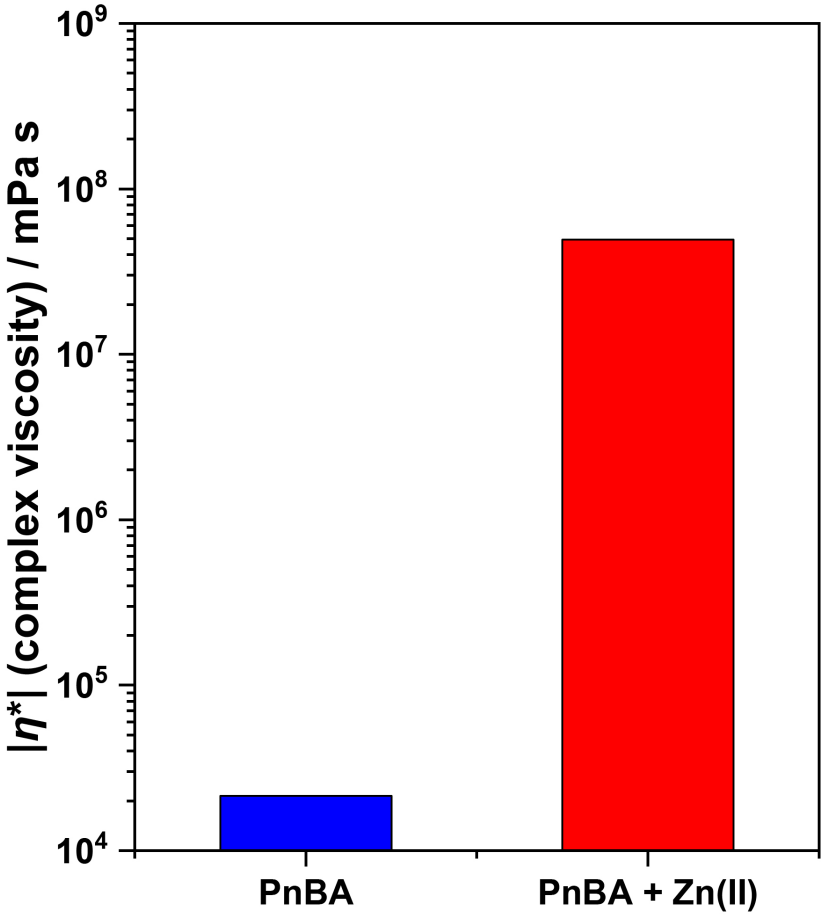

Figure S4. Complex viscosities of the PnBA melt and PnBA elastomer crosslinked by Zn(II) at 20 °C.

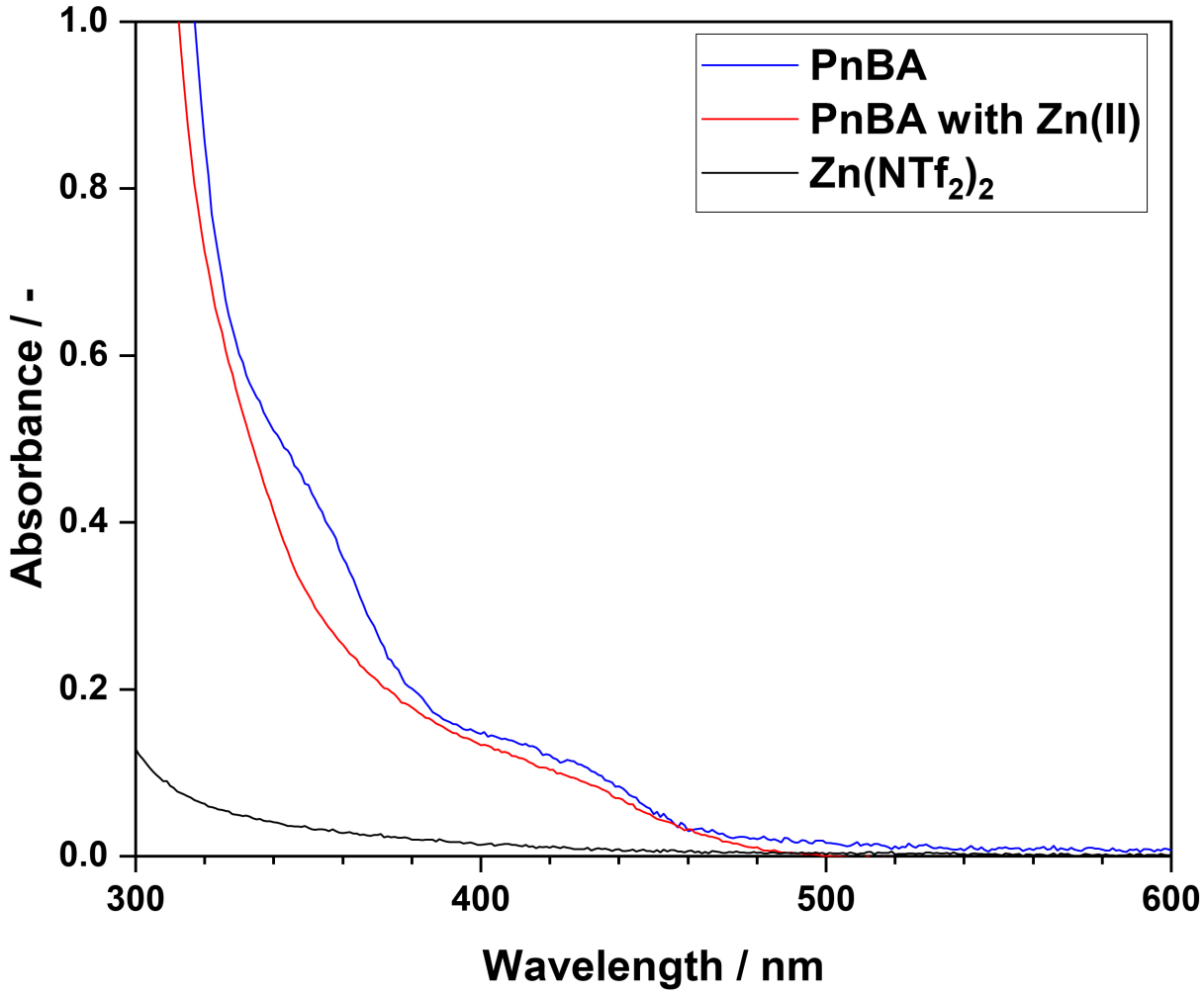

Figure S5. UV-Vis spectra of PnBA and PnBA added with Zn(II) and $Zn(NTf_2)_2$ in acetonitrile. The polymer concentrations were fixed at 0.2 wt%.

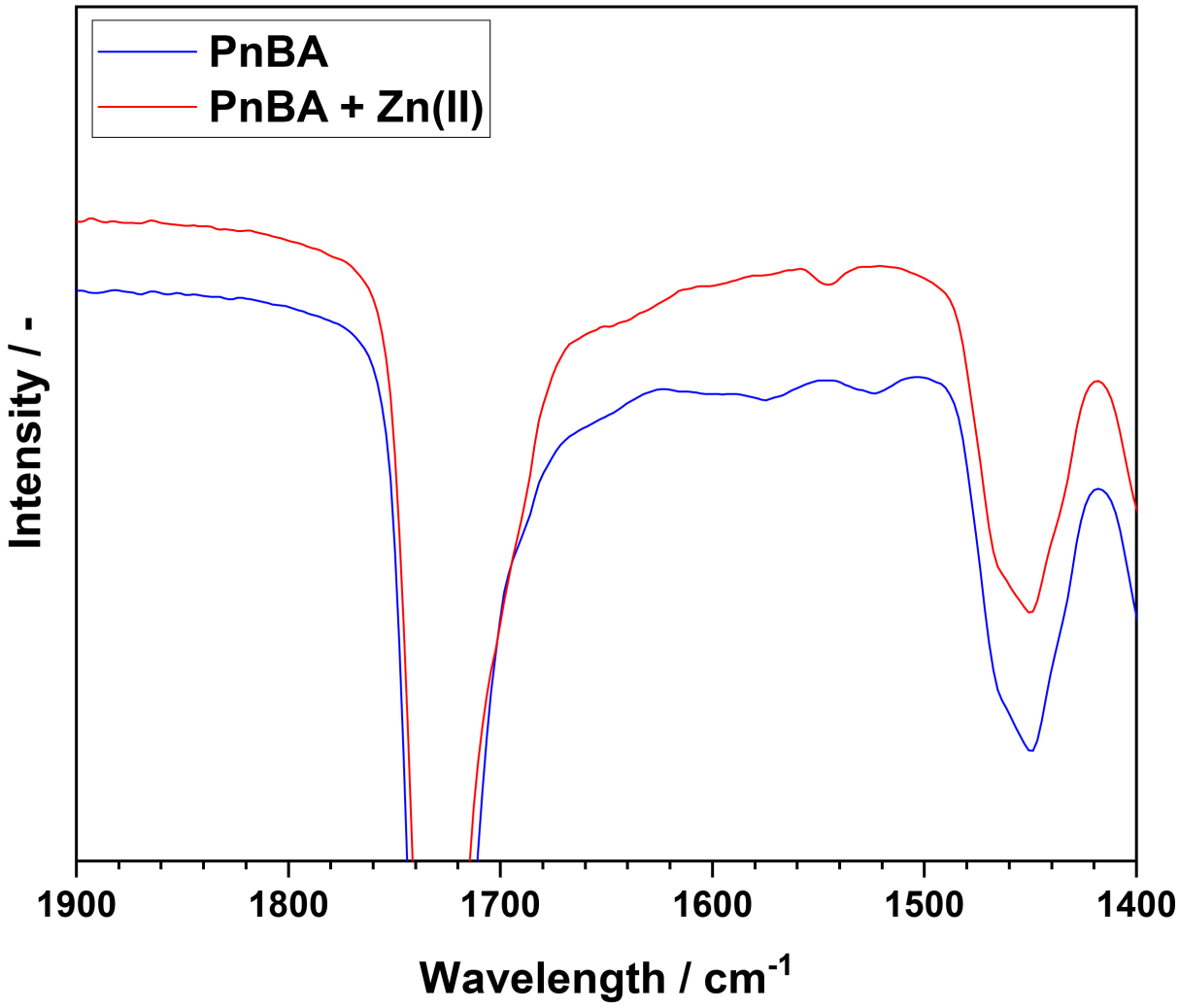

Figure S6. Fourier-transform infrared (FT-IR) spectra of PnBA and PnBA added with Zn(II).

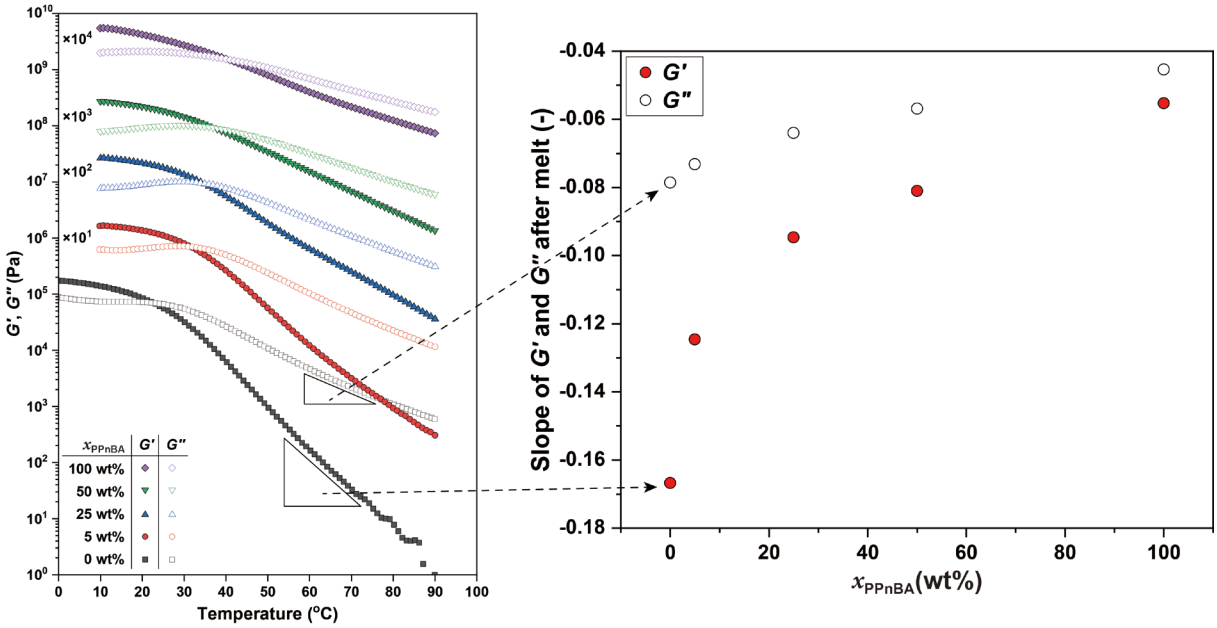

Figure S7. Slope of G' and G'' as a function of x_{PPnBA} after melting. The slopes were obtained by fitting the experimental data with the equation, $G(T) = a\exp(bT)$.

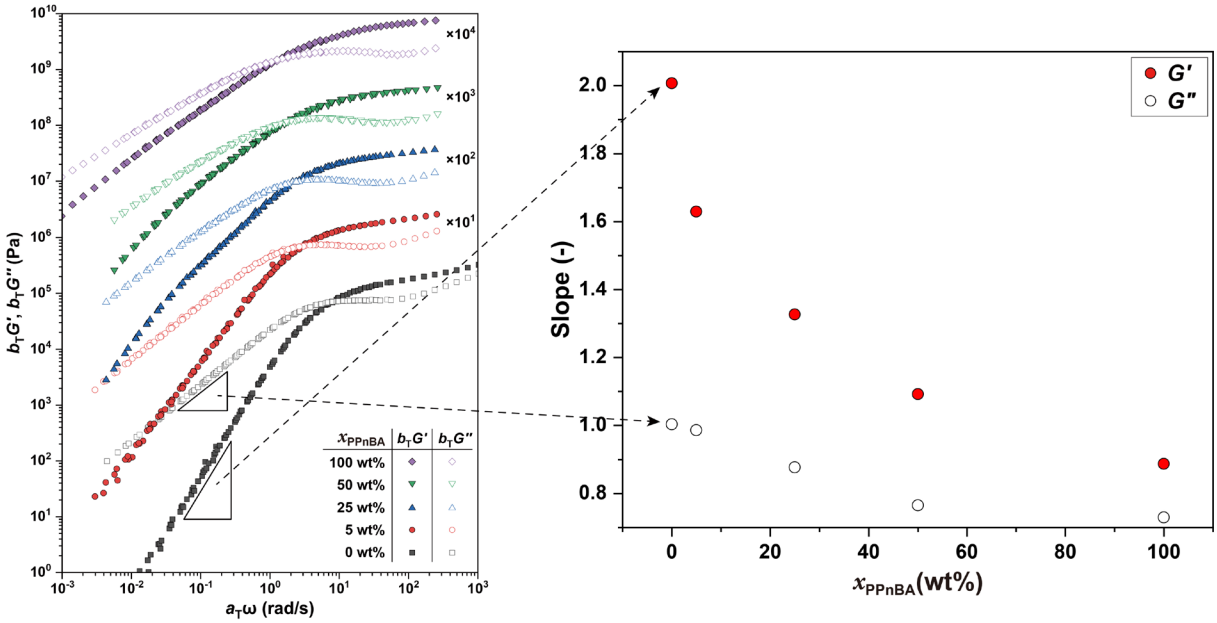

Figure S8. Slope of G' and G'' in the lower frequency range as a function of x_{PPnBA}. The slopes were obtained by fitting the experimental data with the equation, $G(T) = a\exp(b\omega)$.

Supplementary Discussion

Considering the complicated polymer network with PnBA and PPnBA chains, we used the affine network model[2] and ignored the effect of junction and high-dimensional loops to simplify the estimation of the theoretical value of G_N (G_{theo}) using the following relationship:

$$G_{theo} = \nu k_B T \tag{S1}$$

where ν is the number density of elastically effective strands (EES), k_B is the Boltzmann constant, and T is the absolute temperature.

Here, four imidazole groups and one Zn(II) ion produce four-branched (f_4) crosslinking points. Therefore, the number density of f_4 crosslinking points ($n(4)$) of the defect-free PnBA/PPnBA-blended elastomer is given by,

$$n(4) = \frac{n_{\mathrm{imi}}}{4} \tag{S2}$$

where n_{imi} is the number density of imidazole groups. In addition to the f_4 crosslinking points, PPnBA has covalent crosslinking points in the backbone. These branch points can be considered as f_3 crosslinking points. Considering that one end of the poly(*n*-butylacrylate) side chain of PPnBA is functionalized with an imidazole group and the other chain end is connected to the backbone, the number density of f_3 crosslinking points, $n(3)$ produced by the PPnBA network can be calculated as,

$$n(3) = n_{\mathrm{imi}} \tag{S3}$$

In addition, one f_x crosslinking point produces $x/2$ EES. Thus, we obtain,

$$\nu(x) = \frac{x}{2} n(x) \tag{S4}$$

where $\nu(x)$ is the number density of the EES from f_x crosslinking points. Furthermore, n_{imi} of PnBA and n_{imi} of PPnBA can be calculated as follows:

$$\text{PnBA: } n_{\mathrm{imi}} = 2n_{\mathrm{PnBA}} \tag{S5}$$

$$\text{PPnBA: } n_{\mathrm{imi}} = 50n_{\mathrm{PPnBA}} \tag{S6}$$

where n_{PnBA} and n_{PPnBA} are the number densities of PnBA and PPnBA, respectively. In Eq. S5, 2 represents the imidazole groups at both chain ends of PnBA. In Eq. S6, 50 represents the polymerization degree of the PPnBA backbone with imidazole-functionalized side chains. Using Equations S1 to S6, G_{theo} can be calculated as follows:

$$G_{theo} = (n_{PnBA} + 100\ n_{PPnBA})k_B T \tag{S7}$$

n_{PnBA} and n_{PPnBA} are calculated as,

$$n = \frac{\rho}{M_{\mathrm{n}}} N_{\mathrm{A}} \tag{S8}$$

where N_A is the Avogadro constant, M_{n} is the number-averaged molecular weight, and ρ is the physical density of the polymer. For the calculation of G_{theo} using **Equation S7** substituted with **Equation S8**, the following values were used: $N_{\mathrm{A}} = 6.22 \times 10^{23}$ mol^{-1}, $M_{\mathrm{n,PnBA}} =$ 5.6 kg mol^{-1}, $M_{\mathrm{n,PPnBA}} =$ 260 kg mol^{-1}, $\rho_{\mathrm{PnBA}} = 1080$ kg m^{-3}, $k_{\mathrm{B}} = 1.38 \times 10^{-23}$ m^2 kg s^{-2} K^{-1}, $T = 293.15$ K. The results are shown in **Figure S9**.

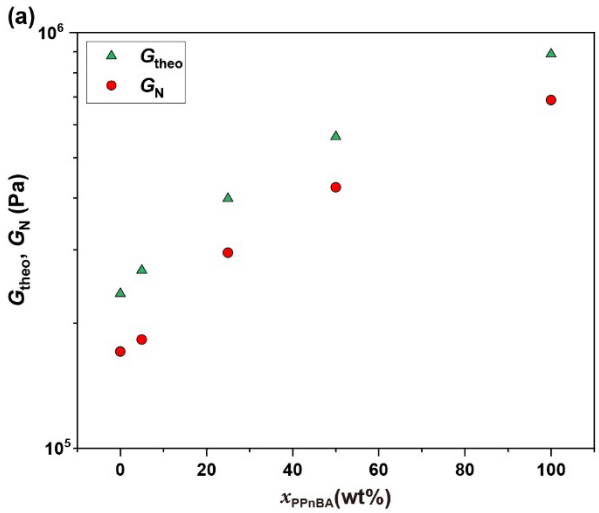

Figure S9. Plateau modulus (G) as a function of xPPnBA for defect-free elastomers. Comparison of the experimentally obtained plateau modulus (G_{N}) with the theoretically calculated plateau modulus (G_{theo}).

The overall trend of G_{theo} follows that of the experimental G_{N}, which implies that our simplified model is valid. However, G_{theo} is 20–30% smaller than G_{N}. This result indicates the presence of defects. Considering that the annealing time of the elastomer can be considered as ∞, the defects derived from spatial heterogeneity and concentration fluctuation can be ignored. Thus, we hypothesized that the defects originate from the unreacted imidazole chain ends, which produce dangling ends.

To estimate the coordination efficiency (p), we further imposed a constraint on the system. If imidazole ends can only produce f_4 crosslinking points or dangling ends, $n(4)$ and $n(3)$ can be modified as,

$$n(x) = n(x)_{p=1} \times p \tag{S9}$$

Note that not only $n(4)$, but also $n(3)$ should be modified because the branched point at the backbone is no longer elastically effective when the branch is not connected to other branches via Zn(II). Using **Equation S9**, we determined the variation in p with x_{PPnBA} (**Figure S10**).

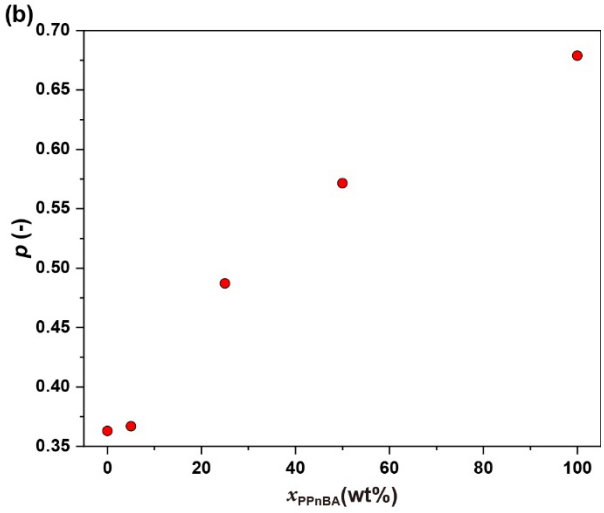

Figure S10. Calculated end-group reactivity of the PnBA/PPnBA blended elastomer as a function of x_{PPnBA}.

References

[1] Love, J. A.; Morgan, J. P.; Trnka, T. M.; Grubbs, R. H. *Angew. Chem. Int. Ed.* 2002, **41**, 4035.

[2] P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca and London, 1953.