Supplementary information

Functionalization of triblock copolymer elastomers by cross-linking the end blocks via trans-N-alkylation-based exchangeable bonds

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1. Materials

4,4'-meththylene bis(phenyl isocyanate) (MDI), 4-vinyl pyridine (4VP), α bromoisobutyryl bromide (BIBB) were purchased from Aldrich. 4VP was purified by passing them through alumina prior to use. Polyethylene glycol with $M_n \sim 400$ g/mol (PEG-400), trimethylamine (TEA), 1,6-dibromohexane (DBH) were purchased from TCI. Copper(I) bromide (CuBr) and *N*,*N*,*N*'',*N*''-pentamethyl diethylene triamine (PMDETA) were purchased from Wako Pure Chemical. These chemicals, except for 4VP, and other organic solvents were used as recieved.

2. Analytical methods

Molecular chracterization: Dispersity indices (M_w/M_n) for the polymers were determined by size exclusion chromatography (SEC). The measurements were conducted at 40 °C by using Shodex KD803+804 columns, combined with a Tosoh DP8020 pump system and an RI (Tosoh RI-8020) detector. DMF with LiBr (0.05 wt%) was used as the eluent with a flow rate of 0.5 ml/min. The elution volume was calibrated with standard series of poly(methyl methacrylate). The syntheses of PU macro-initiator and triblock copolymers were confirmed by ¹H-NMR in DMSO-*d*₆ with using a Bruker Analytik DPX400 spectrometer (400 MHz). The number averaged molecular weight (M_n) for PU macro-initiator was first determined by using multi-angle laser light scattering (WYATT, µDAWN) combined with SEC (Waters, Acquity), where the eluent was THF and the refractive index increment (dn/dc) was 0.1307 determined by using *M*_n of the PU macro-initiator and by comparing the integral ratios of characteristic signals for the PU macro-initiator and poly(4VP) segments in ¹H-NMR (see later section for estimation procedure). The densities of polymers were measured using gas pycnometer (Micro-UltraPyc 1200e, Anton Paar).

Fourier transform infrared spectroscopy (FT-IR): The quaternization of pyridine groups was confirmed by FT-IR. The instrument was a FT/IR-6300 spectrometer (JASCO) combined with a microscopic positioning tool. The measurement samples were prepared by drop casting method. The temperature dependence of FT-IR spectra were made using the same set-up combined with a Linkam hot stage. The equipart time for each target temperature was set to be 3 min. The measurements were conducted under N₂ gas atomosphere.

X-ray photoelectron spectroscopy (XPS): XPS data were obtained by the M-Probe electron spectrometer (Surface Science Instruments). X-rays were generated from a monochromatic Alk α source with 20 mA and 10 kV irradiation. The analysis was performed with a spot size of 800 μ m at a takeoff angle of 35° from the surface plane.

Scattering analysis: Small-angle X-ray scattering (SAXS) measurements were performed at BL-6A beamline in Photon Factory, Tsukuba, Japan, equipped with a Pilatus detector. The sample-to-detector distance was 2.0 m and the X-ray wavelength was 1.5 Å. The sample was seiled by kapton films and a stainless steel washer to avoid sample flowing at high

temperatures. The scattering from the kapton films were substracted for the analysis. The logarithmic intensity was expressed as a function of the scattering vector $q (= 4\pi(\sin\theta)/\lambda)$, where λ and 2θ is the wavelength of X-rays (Cu K α) and the scattering angle, respectively. For temperature-ramp tests, the heating rate was fixed to be 10 °C/min and the samples were equiribarated for 2 min at each target temperature. For constant temperature tests, the sample was kept at 170 °C (i.e., the maximum temperature for the stress-relaxation tests) for 60 min. The measurements were conducted under N₂ gas atmosphere.

Rheology: Viscoelastic property was measured by temperature-ramp rheology. MCR302 (Anton Paar) was used with 8 mm parallel plates. The measurements were performed within a linear regime at a frequency of 6.28 rad/s under N_2 gas atmosphere. The cooling spectra was shown in the main text, where the temperature ramp rate was 5 °C/min.

Dilatometry: Dilatometry test was conducted by TMA7100 (HITACHI). The samples were cut to a strip-shape with a size of $10 \times 3 \times 0.5$ mm. The sample length was monitored with increasing temperatures at 3 °C min⁻¹ under a very small constant tension (30 mN) to avoid sample bending.

Stress-relaxation: The stress-relaxation dynamics was measured with an application of 2% strain, using shear-type rheometer (MCR302, TA Anton paar) and 8 mm parallel plates. The measurements were carried out at various temperatures, and the samples were kept for 10 min at each target temperature for thermal equilibration before starting the measurements.

3. Synthesis

The synthesis of triblock copolymer V-PU-V consisted of three steps, as shown in Figure 1 in the main text. In the first step, MDI (10.0 g, 40.0 mmol) was dissolved in 50 mL super dehydrated DMF, and PEG-400 (14.56 g, 36.4 mmol) was added into the above solution. After the reaction was conducted at room temperature under N₂ gas atmosphere for 3 h, an additional PEG-400 (4.36 g, 10.9 mmol) was injected into the mixture by a syringe to react with the residual NCO groups remained from the former 3 h reaction. After continuously reacting for another 21 h, re-precipitations were carried out to remove the unreacted monomers and small molecular weight polymers, where DMF was used as good solvent and methanol was used as poor solvent. A viscous liquid was obtained after three re-precipitations and these were continuously dried in a vacuum oven at 40 °C. The obtained polyurethane was terminated with OH groups (thus coded as PU-OH) according to ¹H-NMR (see Figure S1).

Secondly, PU-OH was further reacted with BIBB to obtain the PU ATRP macro initiator. PU-OH was dissolved in 40 mL anhydrous THF, where TEA was also mixed. After the mixture was immersed in an ice bath and bubbled with using a steady nitrogen flow for 20 min, BIBB (5 eq. to OH group in PU-OH) was injected by a syringe. The ice bath was kept for another 20 min and then removed when the reaction started. After 24 h reaction, filtration was conducted to remove the salts generated from TEA and HBr, which was followed by reprecipitation. After re-precipitation for three times and evaporation of the solvents, a viscous liquid was obtained in this step. The obtained PU ATRP macro initiator was coded as PU-Br.

Finally, triblock copolymer was synthesized by growing 4VP monomers from the ends of PU-Br via ATRP. PU-Br was firstly dissolved in super dehydrated DMF and mixed with ligand PMDETA and monomer 4VP in an ice bath. The mixture was bubbled with a steady N₂ gas flow and stirred for 15 min, following by subsequent addition of catalyst CuBr. The feed mole ratio of macro initiator [I]₀, monomer [M]₀, macro initiator [I]₀, CuBr [CuBr]₀, and ligand [L]₀, was set to be [M]₀ : [I]₀ : [CuBr]₀ : [L]₀ = 100: 1: 5: 10. Then the mixture was further bubbled for another 15 min in ice bath. The ATRP was initiated at 80 °C and continued for 24 h. Then, an air flow was bubbled into the reaction solution to quench the polymerization. The re-precipitation was conducted for three times to remove CuBr and unreacted monomers, where DMF was used as good solvent and methanol was used as poor solvent. The polymer obtained from re-precipitations was dried in vacuum oven.

4.¹H-NMR data

For the ¹H-NMR spectra (Figure S1a and S1b) of OH-terminated PU (PU-OH) and PU macro initiator (PU-Br), signal **a** (3.78 ppm), **b** (7.06 ~ 7.12 ppm), and **c** (7.32 ~ 7.40 ppm) were from the MDI moiety, and signal **d** (9.65 ppm) belonged to the proton of urethane linkage. The signal **g** (4.17 ppm) and **f** (3.62 ppm) belonged to the protons of the terminated ethylene in PEG-400 moiety located adjacent to the urethane linkage. Similarly, the signals from the protons of ethylene inside the PEG-400 appeared as signal **e** at 3.44 ~ 3.56 ppm. The signal **i** (4.56 ~ 4.61 ppm) in the spectrum of PU-OH belonged to the end OH groups. After the reaction of PU-OH and BIBB, the signal from end OH group disspeated. In the spectrum of PU-Br, the signal **j** at 1.89 ppm belonged to the protons of methyl at the BIBB end moiety. These data demonstrated the complete reaction conversion of OH end groups of PU-OH to be converted to PU-Br.

In the spectrum of V-PU-V triblock copolymer (Figure S1c), three new peaks appeared, as signal \mathbf{k} (1.25~1.80 ppm), \mathbf{m} (6.40~6.90 ppm), and \mathbf{n} (8.00~8.45 ppm).



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Figure S1. 1H-NMR spectra in DMSO- d_6 for (a) PU-OH, (b) PU-Br, and (c) triblock copolymer V-PU-V (see the sample abbreviation in the text).

5. SEC data

Figure S2 represents the SEC curves for PU-OH, PU-Br, and triblock copolymer V-PU-V. After polymerization of 4-vinylpyridine, the peak top was shifted to shorter elution time, indicating the increase of molecular weight.



Figure S2. SEC curves for PU-OH, PU-Br, and V-PU-V triblock copolymer. The broken line indicates the peak top position for the curve of PU-OH.

6. Summery of molecular characteristics for V-PU-V

Table S1. Molecular characteristics for V-PO-V										
Code	M _{n,total} (kDa) ^a	$n_{\rm PU}{}^{\rm b}$	$n_{\rm P4VP}{}^{\rm b}$	PDIc	$\phi_{\rm PU}{}^{\rm d}$	$\phi_{4\mathrm{VP}}{}^{\mathrm{d}}$				
V-PU-V	12.3	16	13	1.77	0.90	0.10				

^aTotal molecular weight for triblock copolymers ($M_{n,total}$). ^bAverage degree of polymerization for PU and P4VP blocks (n_{PU} and n_{P4VP}). ^cDispersity index. ^dVolume fraction of PU middle block (ϕ_{PU}) and poly(4VP) end blocks (ϕ_{4VP}) that were determined by the polymer density (1.26 g/cm³ for poly(4VP) and 1.16 g/cm³ for PU) and the molecular weight.

7. Preparation of the blend

DBH was blended with V-PU-V in order to cross-link poly(4VP) blocks. The blend film sample was prepared by solution casting method using DMF. The mole ratio of the functional groups was set to be [Br] / [Py] = 1 : 1, where 480 mg of V-PU-V was blended with 45.6 mg of DBH, corresponding to the mole ratio of functional groups (i.e., bromo [Br] and pyridine [Py]), [Br] / [Py] = 1 : 1. The copolymer and DBH were first separately dissolved in DMF. The solutions were then mixed in a Teflon-made mold, and the solvents were evaporated on a heater at 50 °C for a week, and further dried at 50 °C in a vacuum oven for 1 day. The quaternization reaction was promoted for the dried film at 120 °C for 12 h, where the sufficient curing time was preliminarily determined by monitoring reaction progress for a blend of homo poly(4VP) and DBH (see Figure S3). The homogeneous film with a thickness of 0.5 mm was obtained. The film of neat sample was prepared in the similar way (without DBH).

8. Effect of curing time on the progress of quaternization

The sufficient curing time for the progress of pyridine-quaternization was investigated by using the blend of homo poly(4VP) ($M_n \sim 20$ kDa, $D \sim 1.2$) and DBH. The blend was prepared by solution casting method using DMF. The mole ratio of the functional groups was set to be [Br] / [Py] = 1 : 1. The copolymer and DBH were first separately dissolved in DMF. The solutions were then mixed in a Teflon-made mold, and the solvents were evaporated on a heater at 50 °C for a week, and further dried at 50 °C in a vacuum oven for 1 day. The quaternization reaction was promoted for the dried film at 120 °C. Figure S3 represents the change of FT-IR signals from free pyridine (1600 cm⁻¹) and quaternized pyridine (1640 cm⁻¹) with an increase in the curing time. There are negligible change at curing time ≥ 8 h, showing the sufficient progress of the quaternization at curing time ≥ 8 h. There is some amount of free pyridine left in the FT-IR spectra at curing time ≥ 8 h. This incomplete association formation at the stoichiometric blend ratio should be due to steric hindrance according to the literature (see for example, refs #25 and #45 in the main text).



Figure S3. Change of FT-IR signals originated from free pyridine and quaternized pyridine with an increase in the curing time at 120 °C. The peak intensity was normalized by the signal from the quaternized pyridine. The values represent the curing time. The colors of the curves correspond with the sample codes in the same color.

9. FT-IR spectra at room temperature for neat and blend samples

Figure S4 represents the FT-IR spectra at room temperature for neat and blend samples The absorbance at 1722 cm⁻¹ and 1702 cm⁻¹ corresponded to the C=O vibration of the free and hydrogen-bonded urethane group, respectively. The peaks at 1598 cm⁻¹ and 1640 cm⁻¹ originated from the C–N vibration of the free and quaternized pyridine group, respectively. Please see the references for the assignment of these signals, refs #41-44 in the main text. A small shoulder could be detected at 1615 cm⁻¹ originated from the hydrogen-bonded C=N of the pyridine group (ref #46 in the main text).



Figure S4. FT-IR spectra for neat and blend samples at a wavenumber region for the C=O and pyridine signals.

10. XPS data for blend sample

XPS was perfromed for the blend sample to estimate the fraction of quaternized pyridine. However, the intensity from N atom was too low to estimate the fraction accurately due to the small valume fractoin of the pyridine segments in the triblock copolymer. In addition, the data included the signals from three different N atoms, that is, N-H of urethane, free pyridine, and quaternized pyridine, which also made the analysis complicated.

Therefore, we made another XPS for the blend of homo poly(4VP) and DBH, and compared the XPS data with the FT-IR data for the same specimens for the purpose of estimation of the molar extinction coefficient for quaternized pyridine. The thin film specimens were prepared by solution drop casting (DMF) onto the stainless substrate, where the blend weight ratio between homo poly(4VP) and DBH was varied. Figure S5 shows the example of XPS data when the blend weight ratio of poly(4VP) : DBH = 1 : 0.6. After fitting procedure based on the Gaussian function, the signal area from free pyridine N (399.5 eV) and quaternized pyridine N (402 eV) was compared. The ratio of XPS signal area was then compared with the FT-IR intensity ratio of free pyridine (1598 cm⁻¹) and guaternized pyridine (1620 cm⁻¹), providing the molar extinction coefficient for free pyridine and quaternized pyridine in FT-IR. Regardless of the blend ratio, the molar extinction coefficient for quaternized pyridine was 1.1 times as larger as that for free pyridine. According to this data and FT-IR for the blend of V-PU-V and DBH (Figure S4), the fraction of quaternized pyridine the fraction of quaternized pyridine in the total pyridine units is estimated to be 25%, where the fraction was simply estimated by the ratio of FT-IR peak intensity for the free and quaternized pyridine with considering the estimated value of molar extinction coefficient.



Figure S5. An exmple of XPS data for the blend of homo poly(4VP) and DBH.

11. ¹H-NMR spectrum for the sol component

Figure S6 represents the ¹H-NMR specturm for the sol component, where the spectrum for pure DBH is also shown for comparison (Figure S6a). The signals at 1.8 ppm and 1.4 ppm are characteristic signals from DBH, which are also noticiable in the spectrum for the sol component. The results indicate the uncross-linked V-PU-V triblock copolymer and unassociated DBH existed in the blend.



Figure S6. ¹H-NMR spectra for the sol component of blend (bottom) and DBH (top). The solvent used was *d*-DMSO.

12. FT-IR for the re-casted film obtained from DMF solution

Complete dissolution of the sample was induced by heating the blend at 120 °C in DMF (see Figure 1b). For the solution containing the dissolved blend, an elastomeric film was recovered after evaporation of all DMF (Figure S7a). Figure S7b shows the FT-IR data for the re-casted film, where the data for the original blend is also provided for comparison. The two FT-IR spectra are overlapped with each other, meaning the chemical structure of the re-casted film was identical with the original blend before dissolving in DMF.



Figure S7. (a) Macroscopic appearance of the re-cased film. (b) FT-IR spectra for the original blend film (top) and the re-cased film obtained from DMF solution (bottom).

13. SAXS profiles for neat and blend samples at room temperature

Figure S8 represents SAXS profiles for neat and blend samples measured at room temperature.



Figure S8. SAXS profiles for neat V-PU-V and the blend taken at room temperature.

14. SAXS data for the blend of poly(4VP) and DBH

First, poly(4-vinylpyridine) homopolymer (homo poly(4VP)) was synthesized via reversible addition-fragmentation chain transfer (RAFT) polymerization ($M_n \sim 20$ kDa, $D \sim 1.2$). DBH was blended with homo poly(4VP) by solution casting using DMF, where the mole ratio of the functional groups was set to be [Br] / [Py] = 1 : 1. The solvents were removed by a heater at 50 °C for a week and subsequently by vacuum. Figure S9 represents SAXS data at room temperature for the neat homo poly(4VP) and the blend of homo poly(4VP) + DBH.



Figure S9. SAXS profiles for the neat homo poly(4VP) and the blend of homo poly(4VP) + DBH.

15. Difference of elastic modulus between as-casted blend film and cured blend film

Figure S10 shows the difference of rheological spectra between as-casted blend film and cured blend film, showing effects of sufficient thermal curing on the network fromation. For the cured blend film, quaternization reaction was conducted at 120 °C for 12 h.



Figure S10. Temperature ramp rheological data for as-casted blend film and cured blend film; (a) storage modulus (G'), (b) loss modulus (G'), and (c) loss tangent (tan δ).

16. Effects of temperatures on the urethan hydrogen bonds

For the blend film, FT-IR measurements were conducted with an increase in temperatures. The dissociation behavior of hydrogen bond in increasing temperatures was observed in Figure S11a and S11b; increase of free-NH peak at 3400 cm⁻¹, decrease and higher wavenumber shift of hydrogen bonded NH at 3300 cm⁻¹, higher wavenumber shift of C=O at 1730 cm⁻¹, and lower wavenumber shift of N-H bending at 1530 cm⁻¹.

We also assess changing behavior of the fraction of free and quaternized pyridines during the temperature increase by tentatively comparing the peak top intensity for the corresponding FT-IR signals (at 1600 cm⁻¹ for free pyridine and at 1640 cm⁻¹ for quaternized pyridine). The ratio of these intensities ($R_{Q/F}$) remained nearly constant (Figure S11c) within the measurement temperature range.



Figure S11. Changes of FT-IR spectra for the blend at the wavenumber region for (a) 3200 to 3500 cm⁻¹ and (b) 1460 to 1840 cm⁻¹. The blue arrows indicated the changing manner of each peak with increasing temperatures. (c) Temperature dependence of the ratio of intensity $(R_{Q/F})$ for the quaternized (Q) and free (F) pyridines.

15. SEC data for homo PU after heating

We made a simple experiment to assess the possibility of transcarbomoylation in the present system. First, we heated the PU homopolymers at 180 °C for 3 hours under reduced pressure (note that 3 h is sufficiently longer than the measurement time for stress-relaxation). We then performed SEC measurements for the heated PU homopolymers, and compared the SEC data with the original PU homopolymers (Figure S12). The data were almost overlapped with each other. If bond-exchanges via transcarbamoylation were activated, the widening of distribution of chain length should be observed, but actually not. Therefore, we concluded that the relaxation mainly originated from *trans-N*-alkylation.



Figure S12. Comparison of SEC profiles for the original PU and PU after heating at 180 °C.

16. Temperature-ramp SAXS for the blend sample

Figure S13 summarizes SAXS data with increasing temperatures (see the details of experimental condition in the experimental section). In Figure S13a, the temperature was increased from 30 to 170 °C with an interval of 20 °C. In Figure S13b, the temperature was kept constant at 170 °C (i.e., maximum temperature for the stress-relaxation tests) for 60 min. In both profiles, the scattering did not show significant change, meaning the morphohological features remained unchanged withing the measurement temperature condition.



Figure S13. SAXS profiles for (a) temperature-ramp from 30 to 170 °C with an interval of 20 °C and (b) constant temperature tests at 170 °C for 60 min with an interval of 10 min for the blend.

17. TGA data



Figure S14. TGA data for V-PU-V triblock copolymer. The broken line indicates the 5% weight loss.

18. Normalized stress-relaxation curves

Figure S15 shows the stress-relaxation curves in which the Y axis represents the modulus (*G*) normalized by the initial modulus (G_0). At the highest measurement temperature, the modulus was decaying to 20% of the initial modulus within 20 min.



Figure S15. Normalized stress-relaxation curves at different temperatures.

19. Separated fitting data for the stress-relaxation curves



Figure S16. Experimental stress-relaxation curves and fitting curved for the data at different temperatures.

20. Summary of fitting parameters for the stress-relaxation curves

Temperature	$ au_{ m mid}$ ^a	τ_{ex}^{a}	$eta_{ m mid}$ b	eta_{ex} b	$A_{\rm mid}{}^{\rm d}$	$A_{\mathrm{ex}}{}^{\mathrm{d}}$
140 °C	0.92	8700	0.37	0.61	0.33	0.67
150 °C	0.93	3467	0.37	0.68	0.26	0.74
160 °C	0.89	1481	0.39	0.69	0.21	0.79
170 °C	0.70	622	0.45	0.69	0.21	0.79

Table S2. Summary of fitting parameters for the stress-relaxation curves

^aThe relaxation time corresponded to the middle block relaxation (τ_{mid}) and bond-exchange relaxation (τ_{ex}). ^bRelaxation time distribution for the middle block relaxation (β_{mid}) and bond-exchange relaxation (β_{ex}). ^cContribution fraction of the the middle block relaxation (A_{mid}) and bond-exchange relaxation (A_{ex} (=1- A_{mid})). See the detailed explanation for the above parameters in the main text.

21. Stress-relaxation curve fitting with a single function

Figure S17 compared the experimental stress-relaxation curves and the fitting curves with a single stretched exponential function, where the fitting paramters for the bond-exchange (i.e., τ_{ex} , β_{ex} , and A_{ex}) were used.



Figure S17. Deviation of experimental curves from fitting curves with a single stretched exponential function.