

A Vinylic Rotaxane Cross-Linker for Toughened Network Polymers from the Radical Polymerization of Vinyl Monomers

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Supporting Information

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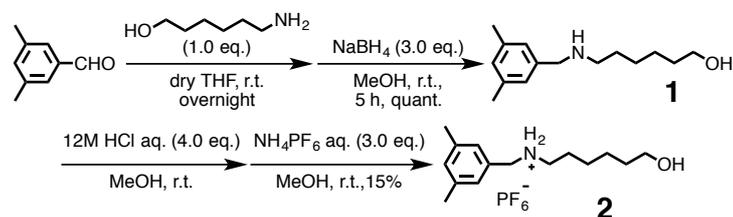
Materials

Dichloromethane was purchased from ASAHI GLASS CO., LTD., and distilled over CaH_2 after being washed with water. 1,6-Hexanediol dimethacrylate (98%, TCI: Tokyo Chemical Industry Co., LTD.), *n*-butyl acrylate (BA) (99%, TCI), and 2-ethylhexyl acrylate (EHA) (99%, TCI) were used without further purification. Other commercially available reagents and solvents were used as received.

Instruments

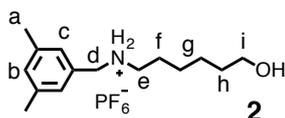
^1H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on a JEOL AL-400 spectrometer using CDCl_3 and $\text{DMSO-}d_6$ as the solvent, calibrated using residual undeuterated tetramethylsilane and solvent as the internal standard. ^1H (500 MHz) and NMR spectra were recorded on a Bruker AVANCEIIIHD500 spectrometer using CDCl_3 as the solvent, calibrated using residual undeuterated tetramethylsilane as the internal standard. IR spectra were recorded on a JASCO FT/IR-230 spectrometer. Melting points were measured on a RFS-10 (Round Science Inc.) instrument. FAB-MS spectra were obtained at the Center for Advanced Material Analysis, Tokyo Institute of Technology on request. Preparative GPC was carried out using a HPLC LC-9210NEXT instrument by Japan Analytical Industry with a Megapak-Gel 201C. The Liquid chromatography (LC) was performed at 40 °C in MeCN/water = 4/1 (v/v) (0.5 mL / min) with mesitylene as an internal standard using a JASCO PU-2080 system equipped with a XBridge® C18 3.5 μm (4.6 x 150 mm). Tensile tests were carried out 24 °C using a SHIMADZU EZ graph equipped with a 50 N load cell at elongation rate of 10 mm/min. Samples were prepared by using a punching blade (No. 7, KOBUNSHI KEIKI CO., LTD.) conformed to ISO 37-4 specimens (dumbbell shape, 12 mm x 2 mm). The UV irradiation was carried out with a high pressure mercury lamp OPM2-250H (USHIO INC.).

Synthesis of axle components



Typical procedure: To a solution of 3,5-dimethylbenzaldehyde (3.3 g, 25 mmol) in dry THF (250 mL) was added the 6-Amino-1-hexanol (2.9 g, 25 mmol), and the reaction mixture was stirred for one night at r.t. After evaporation the residue was diluted with MeOH (250 mL). To a solution of iminoalcohol was added slowly NaBH₄ (2.9 g, 76 mmol) and stirred for about 5 hours at r.t. After evaporation, the residue was dissolved with chloroform. The organic layer was washed with water, then dried over magnesium sulfate, filtered, and concentrated in vacuo to afford *N*-(3,5-dimethylbenzyl)-*N*-(6-hydroxyhexyl) **1** (5.8 g, quant.) as a colorless oil and used for next step without further purification. To a solution of the **1** (2.9 g, 12 mmol) in the least dissolvable amount of methanol was added 12 M hydrochloric acid (4.0 mL, 48 mmol), then the reaction mixture was poured into a large amount of diethyl ether. The precipitates formed were collected by filtration and dried in vacuo. The satd. aq. ammonium hexafluorophosphate was poured into the solution of obtained precipitate in the least amount of methanol until the precipitates were formed. The precipitates formed were collected by filtration, washed with water, and dried in vacuo to give the *N*-(3,5-dimethylbenzyl)-*N*-(6-hydroxyhexyl) ammonium hexafluorophosphate **2** (690 mg, 1.8 mmol, 15%) as a white solid.

m.p. 123–124 °C; ¹H-NMR (500 MHz, DMSO-*d*₆, 298 K): δ (ppm) 8.57 (*br*, 2H, NH₂), 7.08 (*s*, 2H, c), 7.06 (*s*, 1H, b), 4.38 (*t*, *J* = 5 Hz, 1H, OH), 4.05 (*s*, 2H, d), 3.40–3.36 (*m*, 2H, i), 2.90–2.87 (*m*, 2H, e), 2.29 (*s*, 6H, a), 1.63–1.54 (*m*, 2H, f), 1.44–1.37 (*m*, 2H, h), 1.33–1.26 (*m*, 4H, g); ¹³C-NMR (125 MHz, DMSO-*d*₆, 298 K): δ (ppm) 139.7, 131.9, 130.3, 127.5, 60.5, 50.1, 46.7, 32.2, 25.8, 25.4, 25.1, 20.9; FAB-MS (*m/z*): calcd for C₁₅H₂₆NO, 236.2014; found, 236.2013.



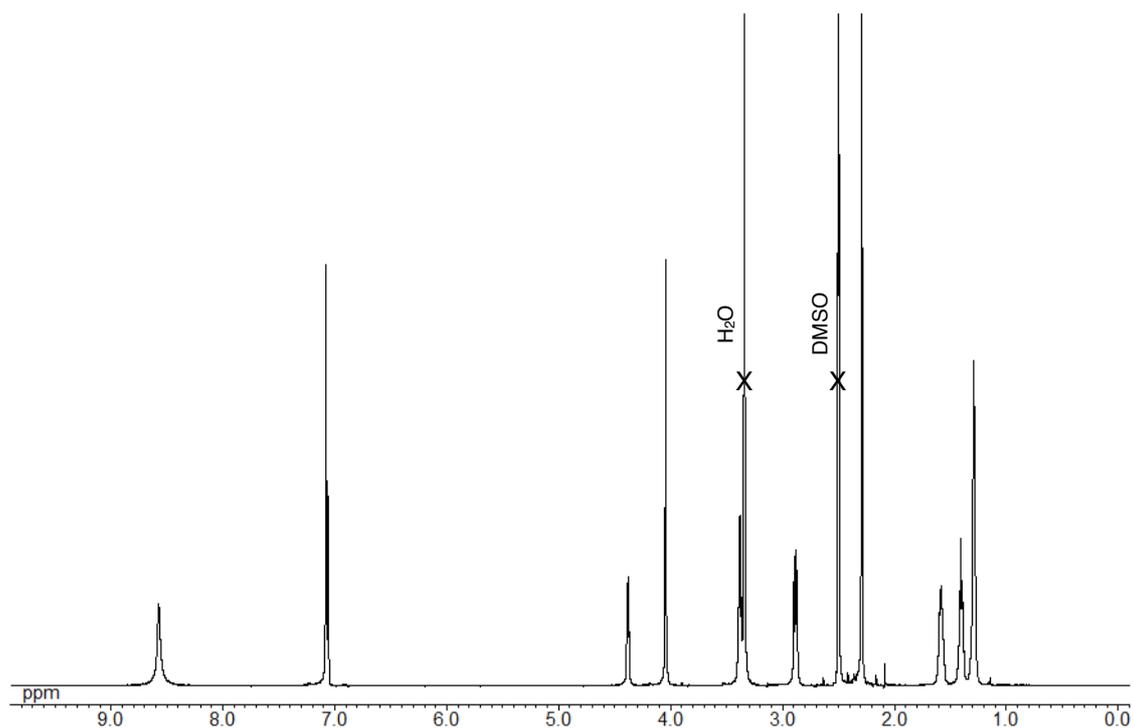


Figure S1. $^1\text{H-NMR}$ spectrum of **2** (500 MHz, $\text{DMSO-}d_6$, 298K)

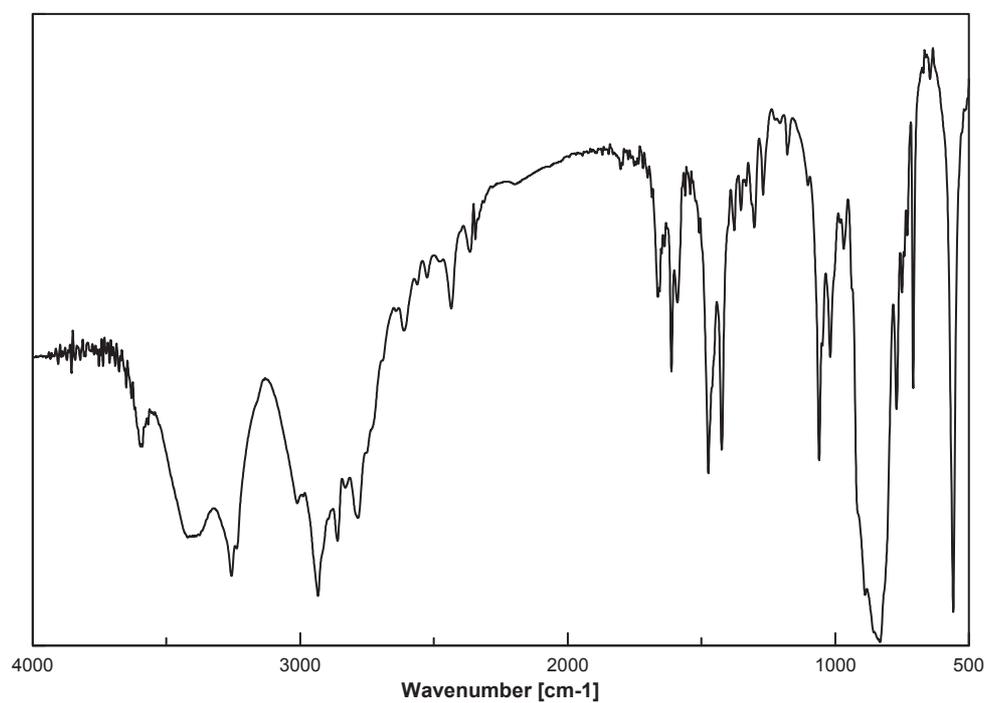
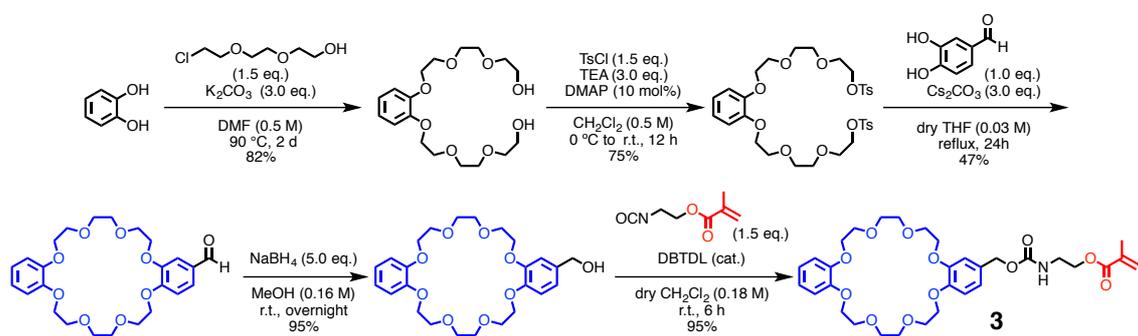


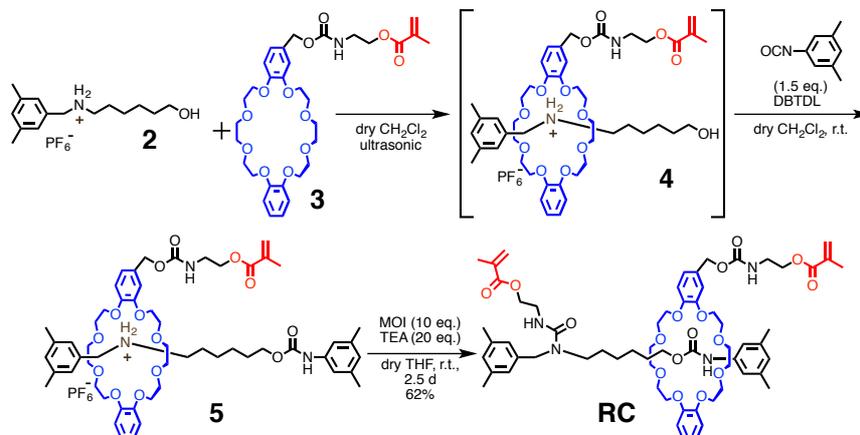
Figure S2. FT-IR spectrum of **2** (KBr)

Synthesis of wheel component



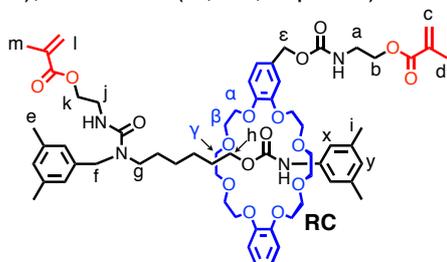
A wheel component with a vinyl group (**3**) was synthesized according to the previously reported procedure^[1].

Synthesis of [2]rotaxane cross-linkers



Typical procedure: A mixture of the axle component **2** (150 mg, 0.41 mmol) and a wheel component **3** (260 mg, 0.41 mmol) in dry CH_2Cl_2 (1.0 mL) was sonicated at r.t. until the solution got transparent to afford a solution of pseudo[2]rotaxane initiator **4**. To a stock solution of **4** was added a little amount of dibutyltin dilaurate (DBTDL) and 3,5-Dimethylphenyl isocyanate (160 mg, 1.1 mmol), and stirred for 5 hours to obtain [2]rotaxane **5** without purification. Then to the mixture was added methanol for quench of excess isocyanate. After evaporation the residue was diluted with dry THF (4.0 mL). To a solution of **5** in THF were added triethylamine (0.81 g, 8.0 mmol) and 2-isocyanate ethylmethacrylate (0.62 g, 4.0 mmol) in order and stirred for 2.5 days at r.t. The crude was purified by column chromatography eluting with EtOAc/hexane = 1/1 (v/v) and preparative GPC eluting with CHCl_3 to give a light pink solid [2]rotaxane cross-linker **RC** (290 mg, 0.25 mmol, 62%).

RC: m.p. 50–51 °C; $^1\text{H-NMR}$ (400 MHz, CDCl_3 , 298 K): δ (ppm) 7.11 (s, 2H, y), 6.96–6.74 (m, 10H, aromatic), 6.52 (s, 1H, x), 6.11 (s, 1H, c), 5.95 (s, 1H, l), 5.76 (s, 1H, c), 5.51 (s, 1H, l), 5.00 (s, 2H, ϵ), 4.35–4.30 (s, 2H, f), 4.30–4.25 (m, 2H, k), 4.24–4.20 (m, 2H, b), 4.20–4.11 (m, 8H, α), 4.12–4.04 (m, 2H, h), 4.12–4.04 (m, 2H, j), 3.85–3.82 (m, 2H, a), 3.98–3.73 (m, 8H, β), 3.60–3.42 (m, 8H, γ), 3.13–2.97 (m, 2H, g), 2.28 (s, 6H, i), 2.11 (s, 6H, e), 1.93 (s, 3H, d), 1.85 (s, 3H, m), 1.49–0.97 (m, 8H, aliphatic)



^{13}C -NMR (100 MHz, CDCl_3 , 298 K): δ (ppm) 167.2, 167.2, 157.9, 156.5, 154.0, 148.7, 148.3, 148.3, 139.5, 138.1, 138.0, 137.8, 135.9, 128.8, 128.6, 126.0, 125.9, 125.7, 124.3, 123.3, 121.6, 121.4, 120.9, 120.6, 115.6, 114.1, 112.3, 111.8, 111.4, 71.0, 69.8, 69.6, 69.5, 69.3, 69.2, 69.2, 68.1, 68.1, 67.9, 66.8, 64.6, 64.0, 63.6, 49.9, 47.4, 46.3, 40.0, 39.9, 28.7, 27.9, 26.5, 25.4, 21.2, 21.2, 18.2, 18.1, 8.5; FAB-MS (m/z): calcd for $\text{C}_{63}\text{H}_{87}\text{N}_4\text{O}_{17}$, 1171.6066; found, 1171.6037.

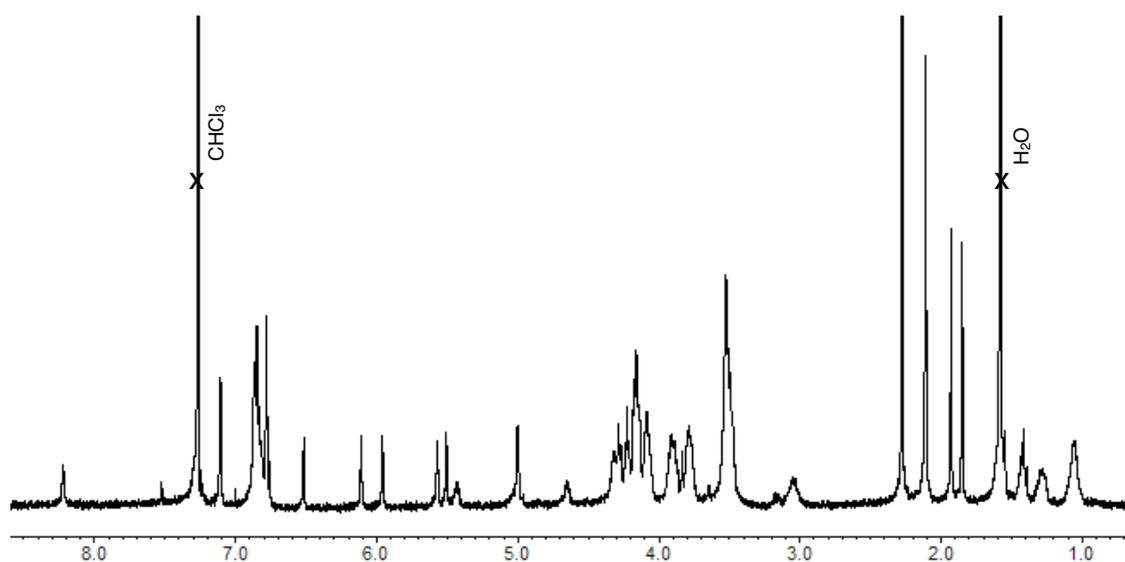


Figure S3. ^1H -NMR spectrum of RC (400 MHz, CDCl_3 , 298K)

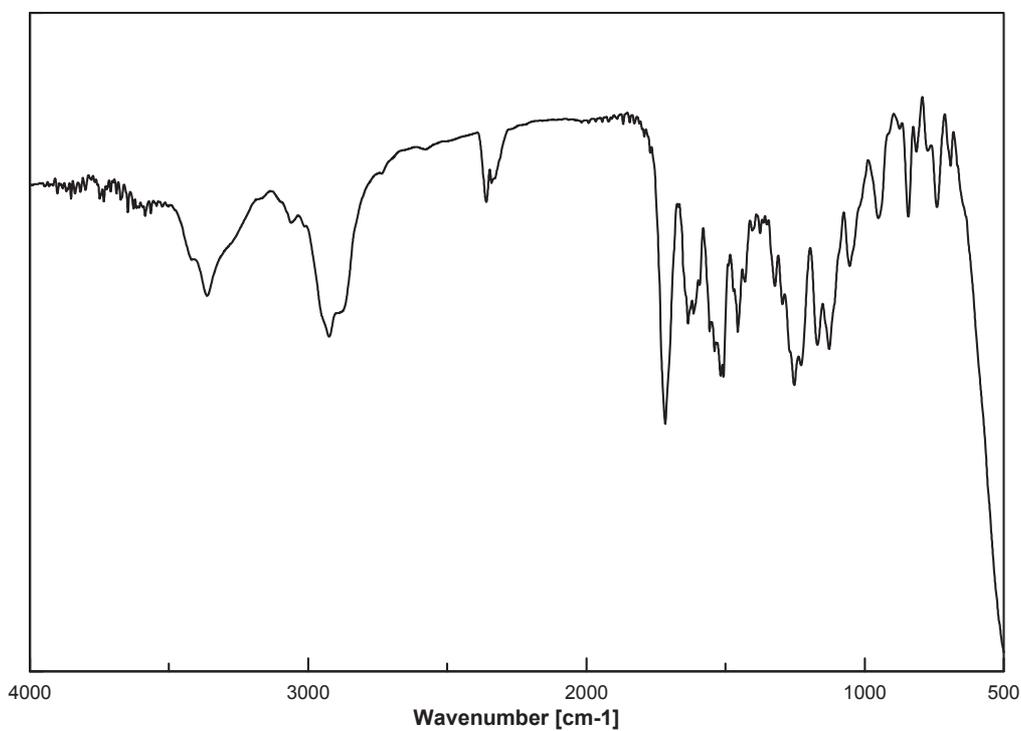


Figure S4. FT-IR spectrum of RC (NaCl)

Synthesis of cross-linked polymers

General procedure: IRGACURE500[®] (200 mg), *n*-butyl acrylate (BA, 2.6 g, 20 mmol) or 2-ethylhexyl acrylate (EHA, 3.7 g, 20 mmol), and a cross-linker (**RC** or **CC**, 0.10 mmol) were degassed three times via the freeze-thaw technique. The mixture was placed on a Teflon plate and covered with glass plate, and UV irradiated for 90 min and then allowed to stand for 12 h at 30 °C. The obtained gelled product was purified by repeated swelling in CH₂Cl₂ and methanol twice, followed by gentle drying at r.t. for 12 h and in vacuo for 12 h to produce the corresponding cross-linked polymer in 57–84% yield. In the case of **RCP_BA**_{0.5}, the conversion of **RC** detected by LC was about 95%.

Characterization of cross-linked polymers

Swelling test

Swelling experiments were performed 5.0–30 mg of cross-linked polymers in CHCl₃, DMF, THF and MeOH (ca. 5.0 mL) at r.t. The swelling ratio was defined as the difference in weight of the swollen gel (W_{swollen}) vs, the dried gel (W_{dry}), according to equation (1).

$$\text{Swelling ratio [\%]} = \frac{W_{\text{swollen}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100 \quad (1)$$

Table S1. Characterizations of all **RCPs** and **CCPs**

Cross-linked polymer	Monomer	Cross-linker	Feed ratio [mol%]	Yield ^a [%]	Swelling test [%]				Tensile test ^b				
					CHCl ₃	DMF	THF	MeOH	Film thickness [μm]	Young's Modulus [MPa] ^c	Fracture Strain [%]	Fracture Stress [MPa]	Fracture Energy [MJ / m ³]
RCP_BA_{0.5}	BA	RC	0.5	67	1000	300	510	90	560	0.27	800	4.4	12.7
RCP_BA_{1.0}			1.0	57	710	240	410	60	570	0.47	470	4.7	7.5
CCP_BA_{0.5}	BA	CC	0.5	77	1100	290	550	80	640	0.35	320	0.63	1.1
CCP_BA_{1.0}			1.0	74	750	230	410	60	660	0.45	190	0.66	0.65
RCP_EHA_{0.5}	EHA	RC	0.5	82	1200	40	640	40	570	0.16	930	2.0	6.4
RCP_EHA_{1.0}			1.0	83	840	70	450	20	680	0.26	550	2.6	5.1
CCP_EHA_{0.5}	EHA	CC	0.5	84	1300	40	690	30	560	0.17	390	0.38	0.76
CCP_EHA_{1.0}			1.0	82	900	40	480	20	730	0.24	140	0.24	0.18

^a Calculated by weight. ^b As an elastomer. ^c Determined by the stress between 0 and 10% strain.

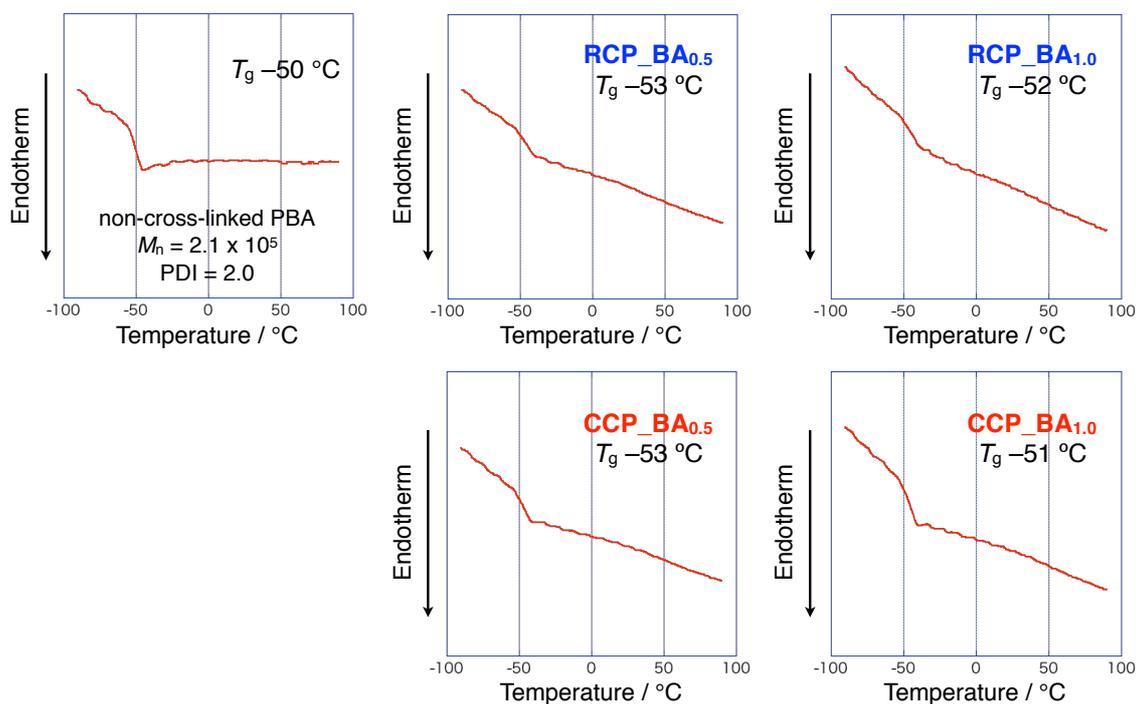


Figure S5. DSC charts of PBA, RCP_BA, and CCP_BA (Heating rate: 10 °C min^{-1} , 2nd heating)

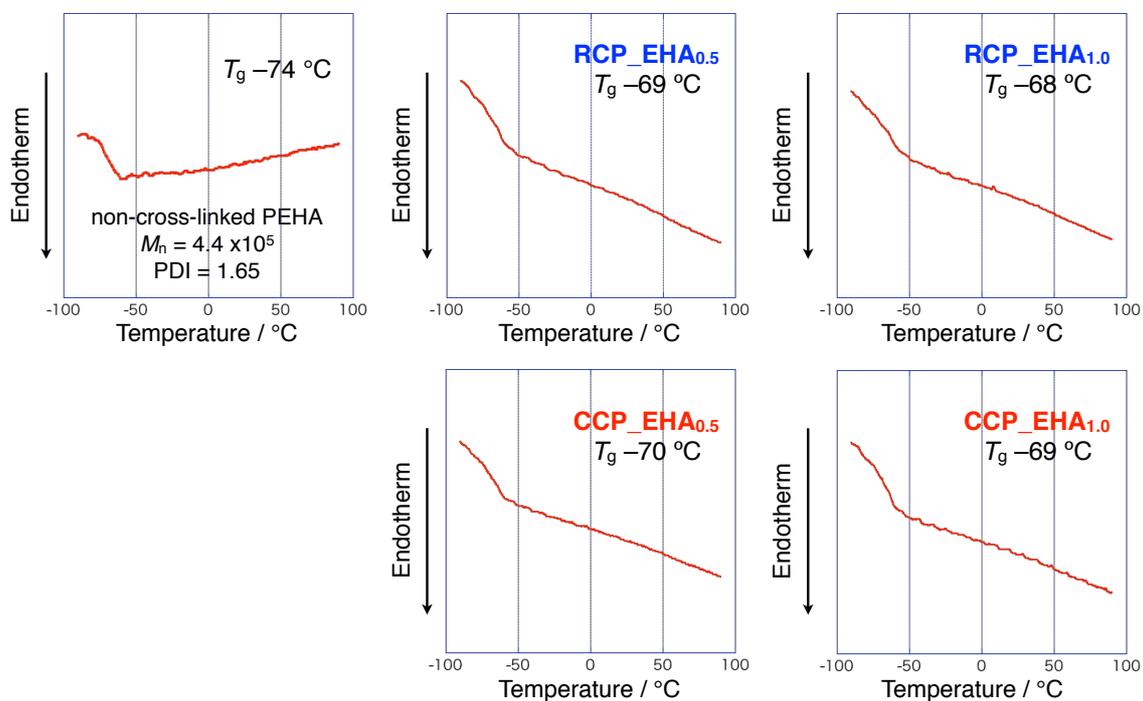


Figure S6. DSC charts of REHA, RCP_EHA and CCP_EHA (Heating rate: 10 °C min^{-1} , 2nd heating)



Figure S7. Pictures of tensile tests of **RCP_BA_{1.0}** and **CCP_BA_{1.0}**, taken just before fracture

Reference

- [1] K. Iijima, Y. Kohsaka, Y. Koyama, K. Nakazono, S. Uchida, S. Asai and T. Takata, *Polym. J.*, **2014**, *46*, 67–72.