Electronic Supplementary Material (ESI) for Materials Advances.

Supporting Information

Effect of Bulky 2,6-Bis(spirocyclohexyl)-Substituted Piperidine Rings in Bis(hindered amino)trisulfide on Thermal Healability of Polymethacrylate Networks

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1 Experimental Section

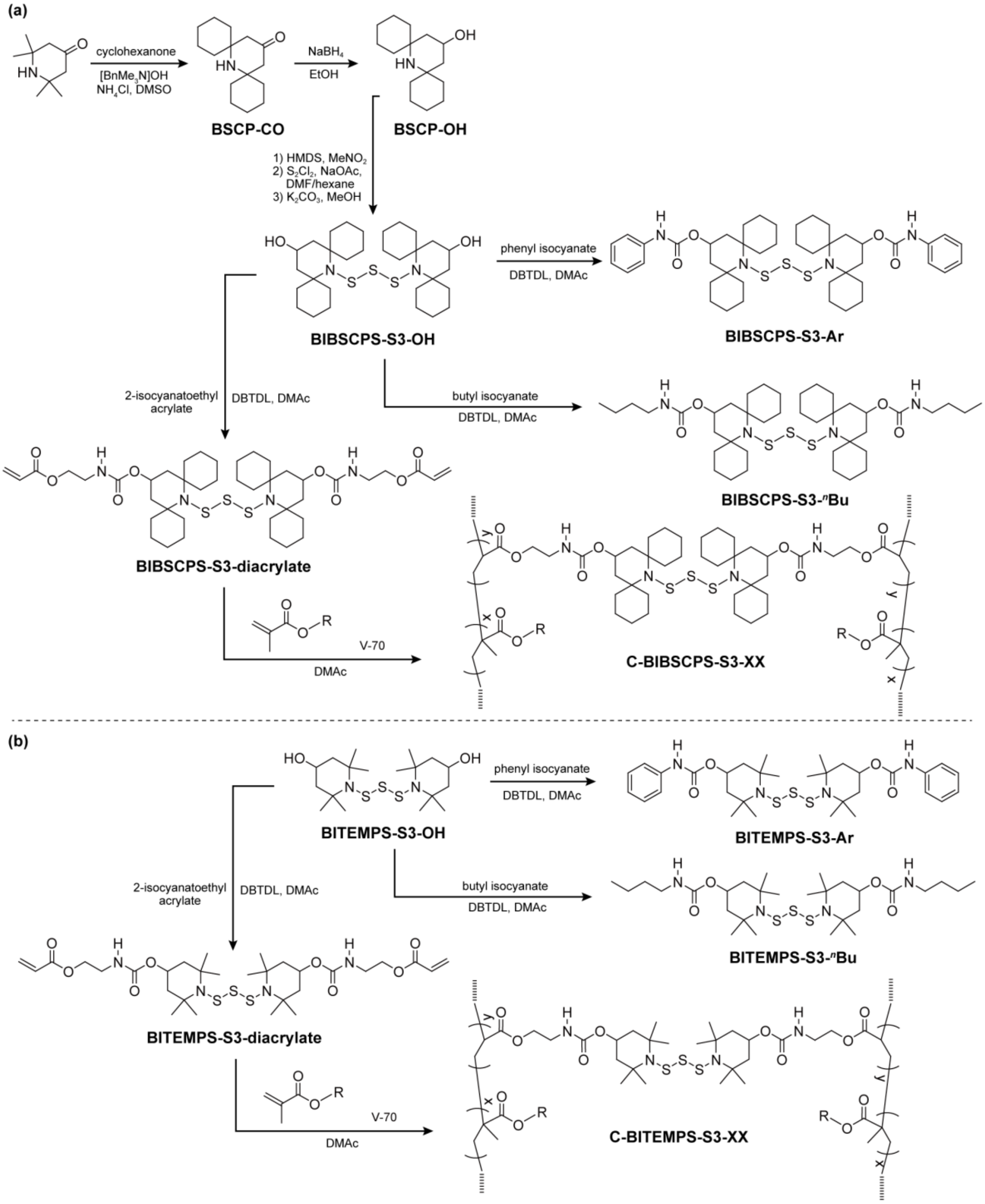
1.1 Materials

Commercially available solvents and reagents were purchased from Sigma Aldrich, TCI, Kanto Chemicals, or FUJIFILM Wako Pure Chemicals and used as received unless otherwise specified. Hexyl methacrylate (HMA), butyl methacrylate (BMA), and ethyl methacrylate (EMA) were purified by distillation under reduced pressure before use. BITEMPS-S3-OH, BITEMPS-S3-Ar, and BITEMPS-S3-diacrylate were prepared according to a previous report.[1]

1.2 Characterization

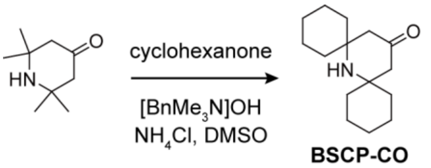
^{1}H and ^{13}C NMR spectra were recorded with a Bruker AVANCEIII400HD and a Varian INOVA400 spectrometer instrument. Fourier transform infrared (FT-IR) spectra were recorded on a Perkin Elmer Frontier spectrometer. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements were performed under a nitrogen atmosphere at a heating rate of 10 °C min^{-1} and 20 °C min^{-1}, respectively, by using an SII EXSTAR DSC 7020 instrument and an SII EXSTAR TG/DTA 7200 instrument. ESI-MS were measured on an Waters Xevo G2-XS QTof instrument. Tensile tests for healability evaluation and cyclic tensile tests were performed on INSTRON5582 using dogbone-shaped samples (0.7–1.2 mm (T) x 4 mm (W) x 13 mm (L)) prepared with a cutting die with a strain rate 10 mm/min at room temperature. Stress-relaxation analysis was performed on an SII EXSTAR TMA/SS 7100 instrument under nitrogen flow. Molecular weights of polymers were measured with a SHIMADZU prominence GPC system equipped with polystyrene gel column using a $CHCl_3$ eluent and polystyrene standards. The number- and weight-average molecular weights (M_n and M_w, respectively) were calculated on the basis of the refractive index data.

1.3 Synthesis



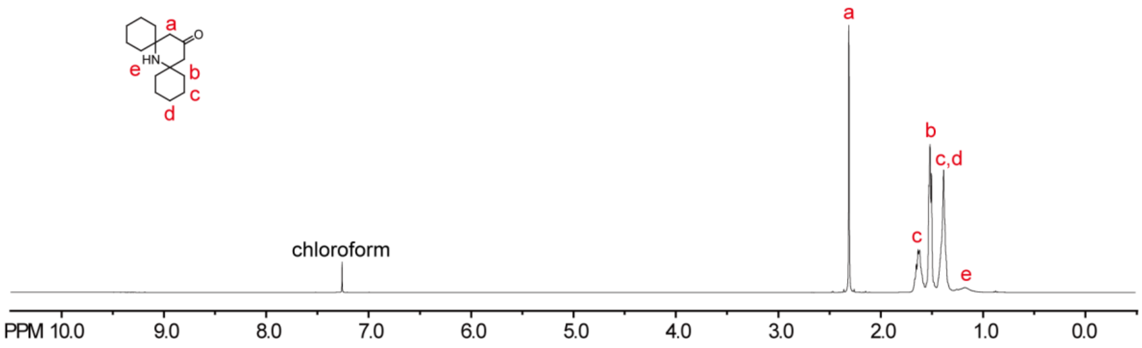
Scheme S1 Synthetic pathway toward diol, diacrylate, model compounds, and cross-linked polymers sterically hindered with (a) two spirocyclohexyl moieties or (b) four methyl groups in a piperidine ring.

1.3.1 BSCP-CO

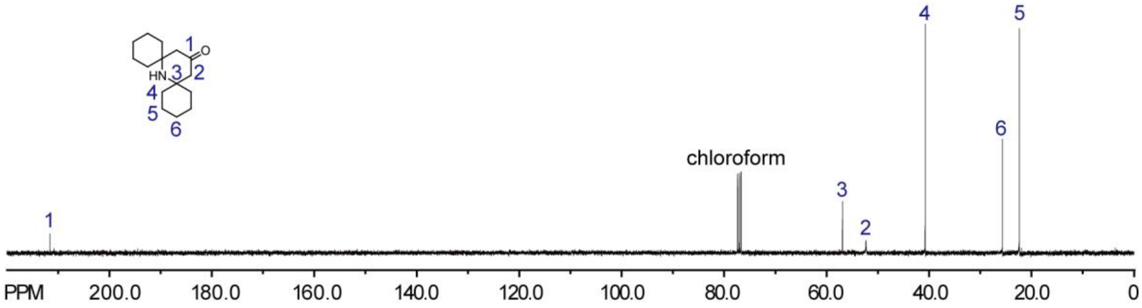


The title compound, 2,6-bis(spirocyclohexyl)-4-piperidone (BSCP), was prepared according to the previous report.[2] DMSO (30 mL), 2,2,6,6-tetramethylpiperidone (6.98 g, 45 mmol), cyclohexanone (14 mL, 135 mmol), and NH_4Cl (12.0 g, 225 mmol) were added to a flask under argon atmosphere. Triton B (40% in methanol, 9 mL) was slowly added and the reaction mixture was stirred at 50 °C for 43 h. After the reaction mixture diluted with water (100 mL) was stirred for a further 30 min, the solution was acidified with conc. HCl (10 mL). Then, the reaction mixture was extracted with diethyl ether to remove a neutral fraction. The aqueous DMSO solution was adjusted to pH > 9 with 6 M NaOH solution, extracted with ethyl acetate, dried over Na_2SO_4, and the obtained mixture was then purified via column chromatography (hexane/ethyl acetate = 4/1, v/v) to give a crude product. Subsequent recrystallization afforded BSCP-CO as a light-yellow solid.

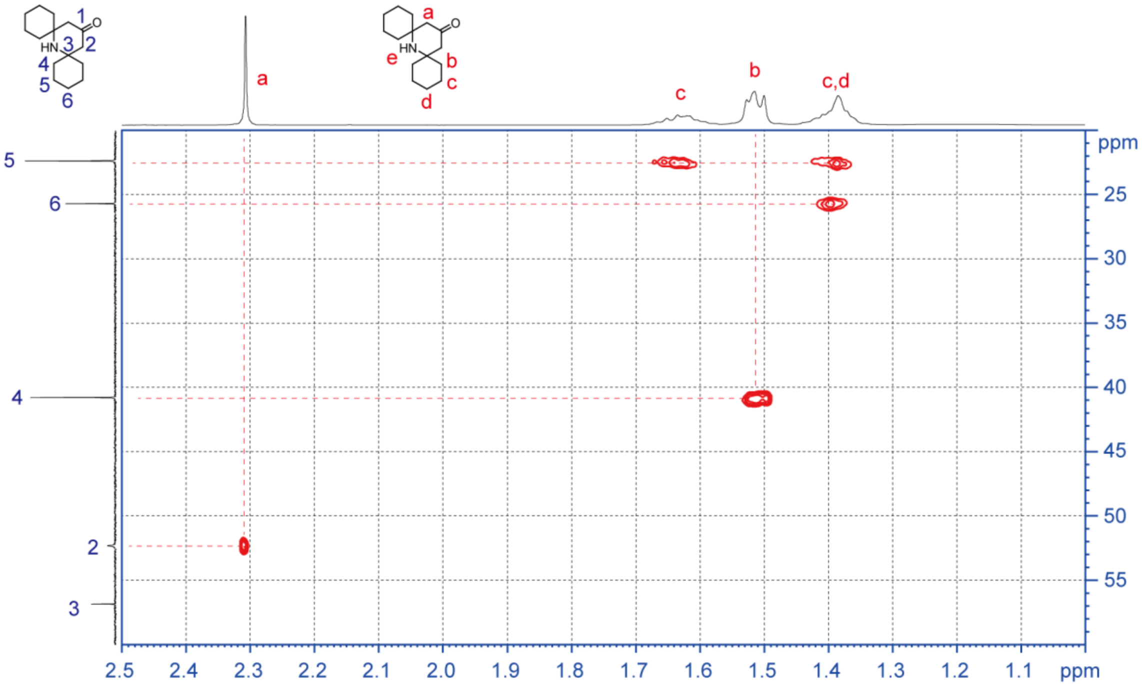
BSCP-CO: Yield: 3.12 g (29 %). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 2.30 (s, 4H), 1.68-1.56 (m, 4H), 1.54-1.48 (m, 8H), 1.44-1.32 (m, 8H), 1.16 (br, 1H). ^{13}C NMR (100 MHz, DMSO-d_6, δ): 211.4 56.9, 40.7, 25.6, 22.3. IR (ATR): 3304, 2932, 2915, 2857, 2670, 1692, 1499, 1461, 1440, 1421, 1356, 1301, 1285, 1271, 1248, 1222, 1200, 1165, 1157, 1147, 1137, 1117, 1090, 1066, 1012, 987, 968, 945, 929, 916, 856, 774, 721.



^{1}H NMR spectrum of BSCP-CO

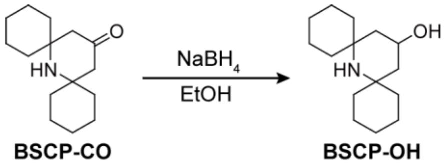


^{13}C NMR spectrum of BSCP-CO



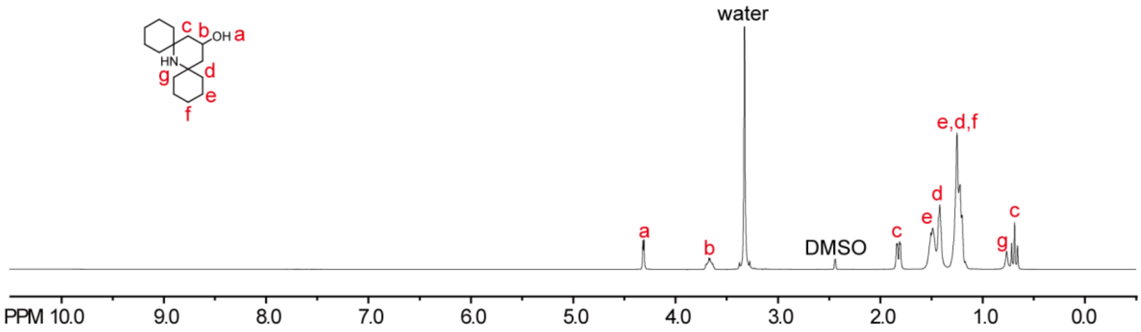
HSQC spectrum of BSCP-CO

1.3.2 BSCP-OH

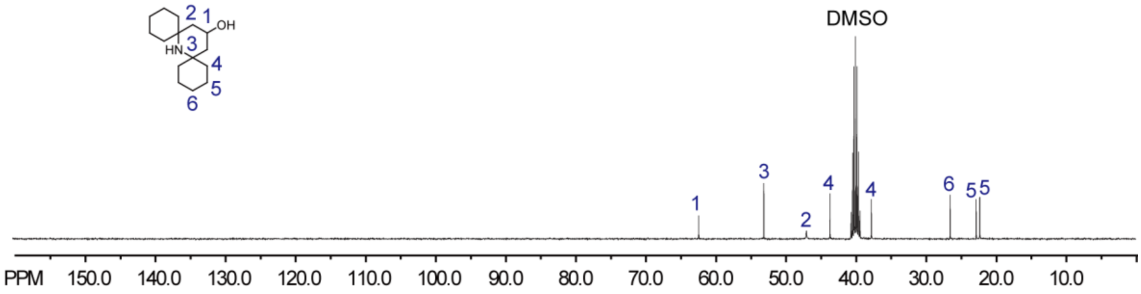


The title compound, 4-hydroxy-2,6-bis(spirocyclohexyl)piperidine (BSCP-OH), was synthesized according to the previous report.[2] Into a flask, BSCP-CO (600 mg, 2.5 mmol) and dry ethanol (5 mL) were added and cooled to 0 °C. After $NaBH_4$ (97 mg, 2.5 mmol) was carefully added, the reaction mixture was stirred overnight at room temperature. The reaction mixture was extracted with diethyl ether, dried over Na_2SO_4, and the solvent was removed under reduced pressure to give a crude product. Subsequent recrystallization with hexane afforded BSCP-OH as a white solid.

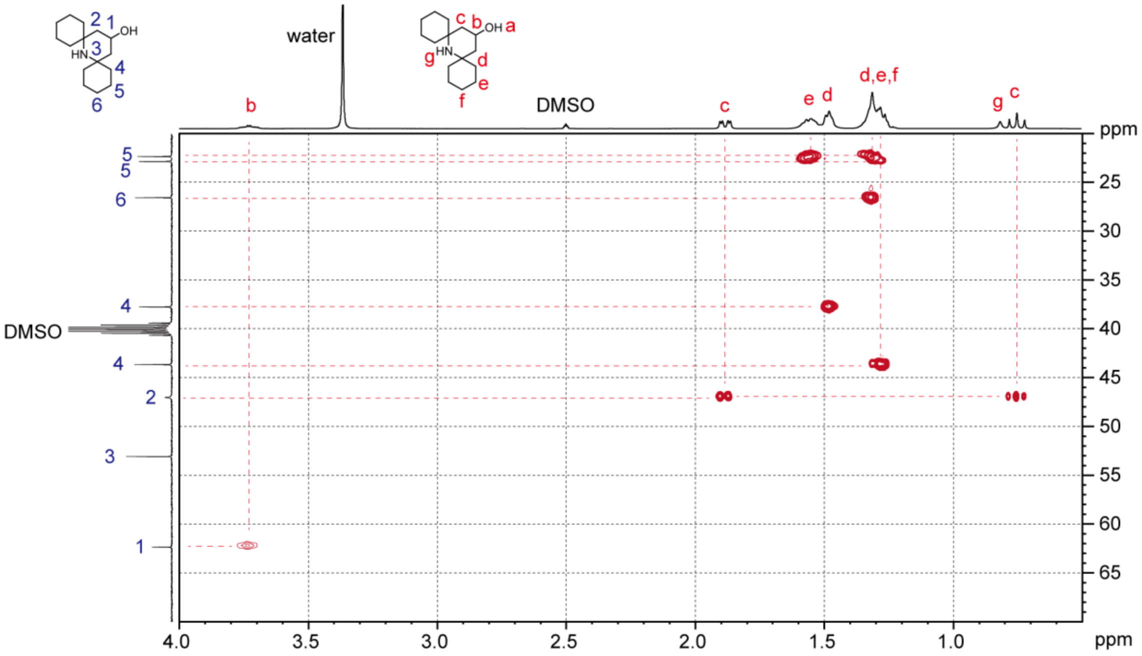
BSCP-OH: Yield: 514 mg (72 %). ^{1}H NMR (400 MHz, DMSO-d_6, δ): 4.31 (d, J = 4.4 Hz, 1H), 3.70-3.62 (m, 1H), 1.82 (dd, J = 10.3, 3.2 Hz, 2H), 1.55-1.45 (m, 4H), 1.48-1.38 (m, 4H), 1.30-1.15 (m, 12H), 0.76 (s, 1H), 0.69 (t, J = 11.8 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6, δ): 62.3, 53.0, 46.9, 37.7, 26.5, 22.8, 22.3. IR (ATR): 3286, 2921, 2848, 2666, 1442, 1357, 1343, 1316, 1304, 1286, 1260, 1206, 1186, 1176, 1155, 1137, 1112, 1088, 1075, 1053, 1027, 1011, 955, 930, 922, 909, 884, 866, 848, 793, 760, 680.



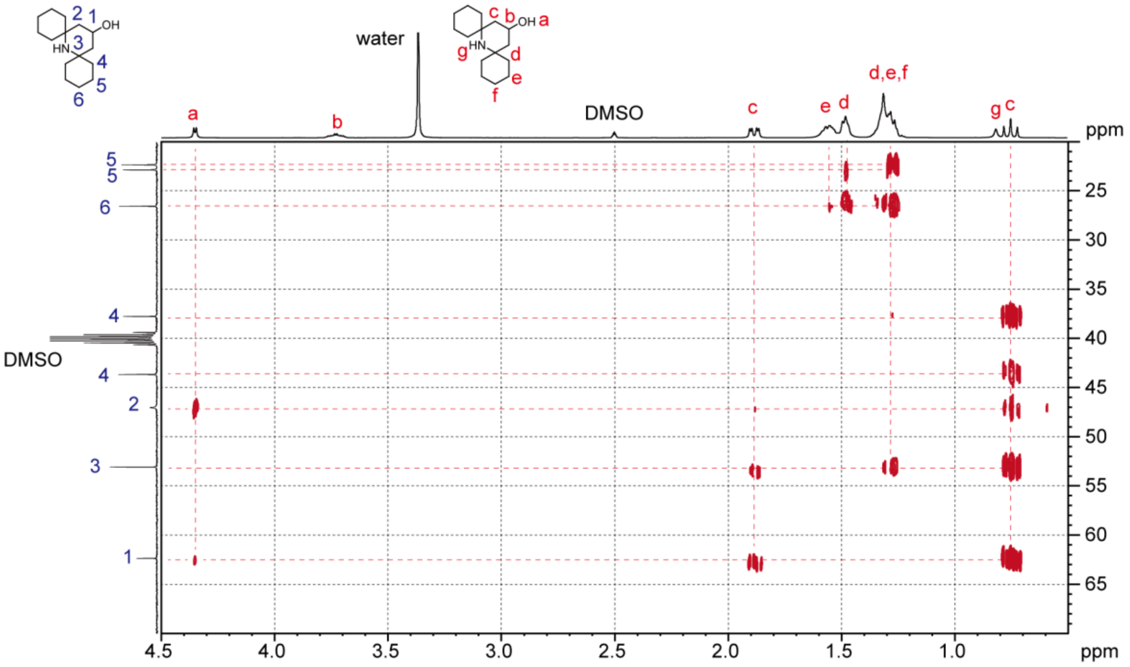
^{1}H NMR spectrum of BSCP-OH



^{13}C NMR spectrum of BSCP-OH

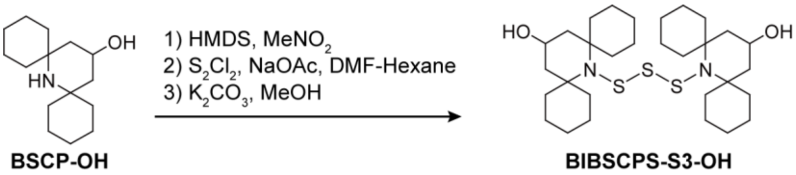


HSQC spectrum of BSCP-OH



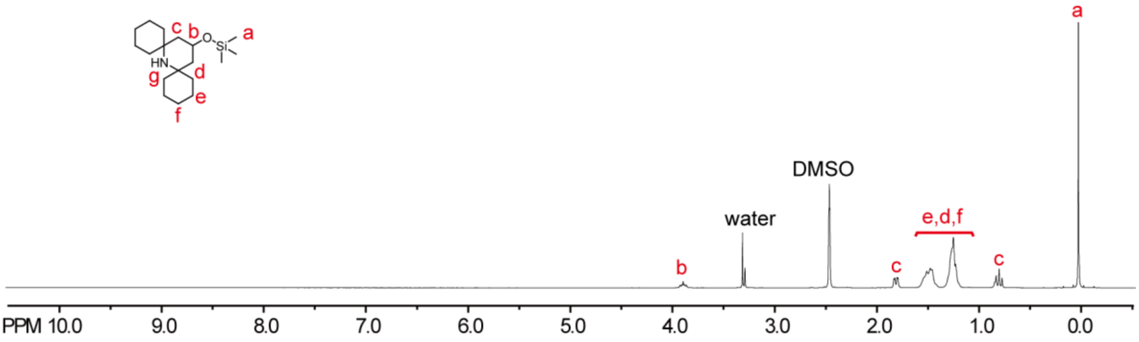
HMBC spectrum of BSCP-OH

1.3.3 BIBSCPS-S3-OH



Into a flask, BSCP-OH (9.49 g, 40 mmol), 1,1,1,3,3,3-hexamethyldisilazane (6.45 g, 40 mmol), and nitromethane (40 mL) were added under argon atmosphere. After the reaction mixture was stirred at 50 °C overnight, the solvent was removed under reduced pressure to give the product, 4-tetramethylsiloxy-2,6-bis(spirocyclohexyl)piperidine (BSCP-OTMS), which was analyzed by ^{1}H NMR and used in the next step without further purification.

BSCP-OTMS: Yield: 11.98 g (96 %). ^{1}H NMR (400 MHz, MeOH-d_4, δ): 3.91 (m, 1H), 1.86 (dd, J = 12.1, 3.5 Hz, 2H), 1.60-1.20 (m, 20H), 1.48-1.38 (m, 4H), 0.90-0.78 (m, 3H), 0.06 (s, 9H).



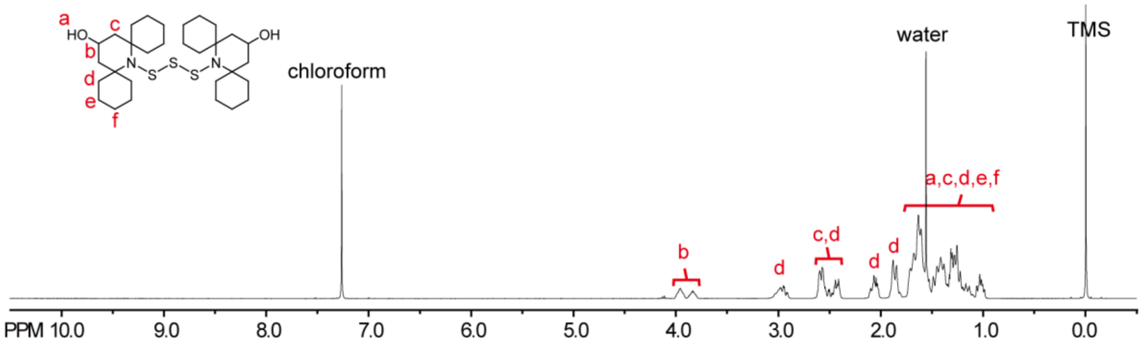
^{1}H NMR spectrum of BSCP-OTMS

BSCP-OTMS (11.98 g, 38.7 mmol), sodium acetate (3.18 g, 38.7 mmol), dry hexane (24.6 mL) and dry DMF (10.6 mL) were added to three-necked flask under argon atmosphere. After the solution was cooled to 0-5 °C, disulfur dichloride (1.14 mL, 14.0 mmol) in dry DMF (8.8 mL) was slowly added and then the resulting solution was stirred for additional 15 min. The solution was poured into ice water and stirred for several minutes. After extraction with chloroform, the organic layer was dried over Na_2SO_4 and the obtained mixture was purified by column chromatography (hexane/chloroform = 1/1, v/v) to mainly afford TMS-protected BIBSCPS-S3-OH (R_f = 0.43, hexane/chloroform =1/1, v/v) as a white solid. Since it seems difficult to completely separate some byproducts by column chromatography due to almost the same R_f values, the objective compound BIBSCPS-S3-OH was purified after deprotection of the TMS groups.

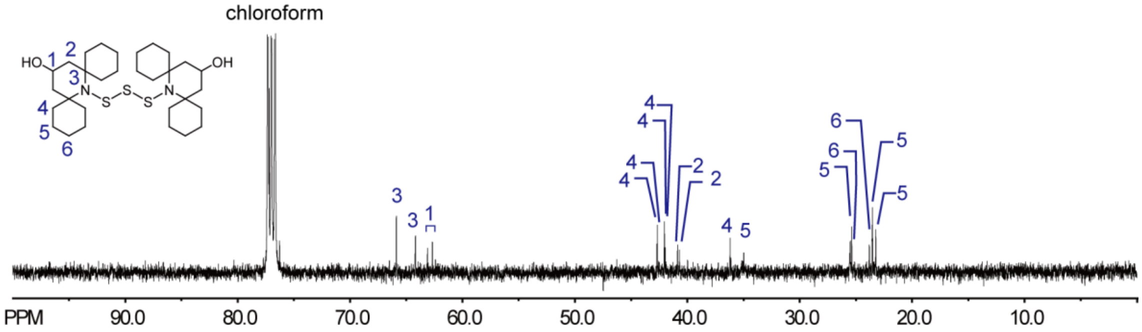
Then, the obtained crude product (1.93 g), K_2CO_3 (746 mg, 5.4 mmol), and MeOH (60 mL) was added into a flask and stirred at room temperature overnight. After the reaction mixture was poured into water, filtered off, and dried under vacuum. The obtained crude product was stirred in ethyl acetate (150 mL) at room temperature for 1h. The insoluble part was separated by filtration and dried under vacuum to afford BIBSCPS-S3-OH as a white solid. Since the soluble part contained BIBSCPS-S3-OH to some extent, this mixture was purified via column chromatography (hexane/ethyl acetate = 3/2, v/v) to afford BIBSCPS-S3-OH.

BIBSCPS-S3-OH: Yield: 1547 mg (7 %). R_f = 0.43 (hexane/chloroform =1/1, v/v), ^{1}H NMR (400 MHz, $CDCl_3$, δ): 4.00-3.78 (m, 2H), 3.07-2.88 (m, 2H), 2.67-2.38 (m, 6H), 2.12-2.01 (m, 2H), 1.86 (d, J = 13.2 Hz, 4H), 1.74-0.98 (m, 36H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 65.8, 64.1, 63.1, 62.6, 42.7, 42.6, 42.1, 42.0, 40.8, 40.7, 36.1, 34.9, 25.4, 25.3, 23.8, 23.5, 23.2. IR (ATR): 3272, 2922, 2850, 1460, 1441, 1357, 1316, 1305, 1266, 1206, 1186, 1176, 1155, 1137, 1089, 1073, 1054, 1045, 1029, 1012, 976, 955, 930, 923, 909, 885, 867, 848, 808, 761, 683, 644. FAB-MS (*m*/*z*): [M+H$^+$] calcd. for

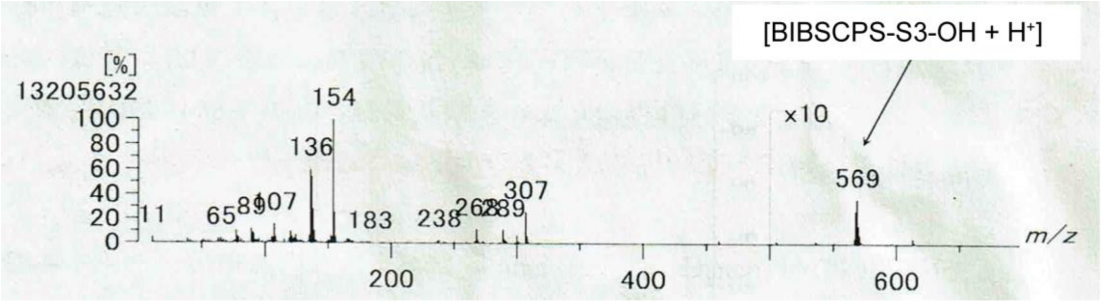
$C_{30}H_{53}N_2O_2S_3$ 569.3269; Found, 569.3259.



^{1}H NMR spectrum of BIBSCPS-S3-OH

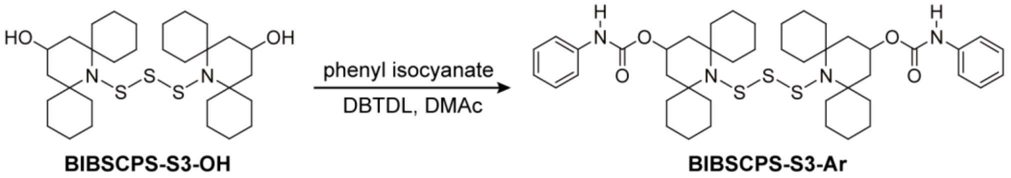


^{13}C NMR spectrum of BIBSCPS-S3-OH



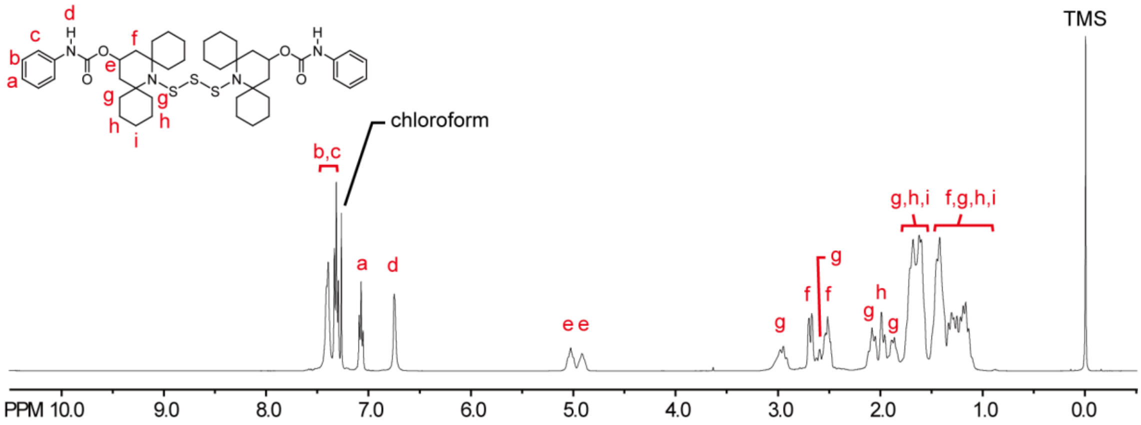
Mass spectrum of BIBSCPS-S3-OH

1.3.4 BIBSCPS-S3-Ar

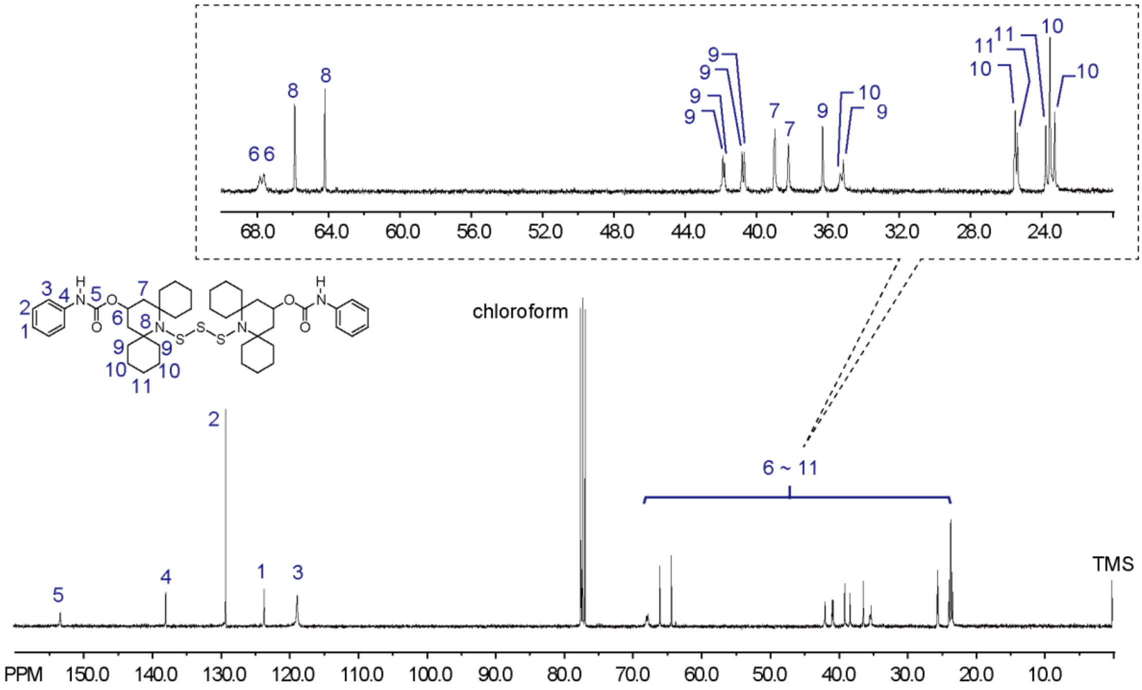


Into a two-necked flask, BIBSCPS-S3-OH (569 mg, 1 mmol) and one drop of di-*n*-butyltin dilaurate (DBTDL) was added and dissolved in dry DMAc (8 mL) under argon atmosphere. Subsequently, phenyl isocyanate (262.1 mg, 2.2 mmol) was added to the solution and the reaction mixture was stirred overnight at room temperature. After pouring water, the obtained precipitate was collected by filtration, extracted with chloroform, dried over with Na_2SO_4, and the obtained mixture was then purified via column chromatography (hexane/ethyl acetate = 4/1, v/v) to give BIBSCPS-S3-Ar as a white solid.

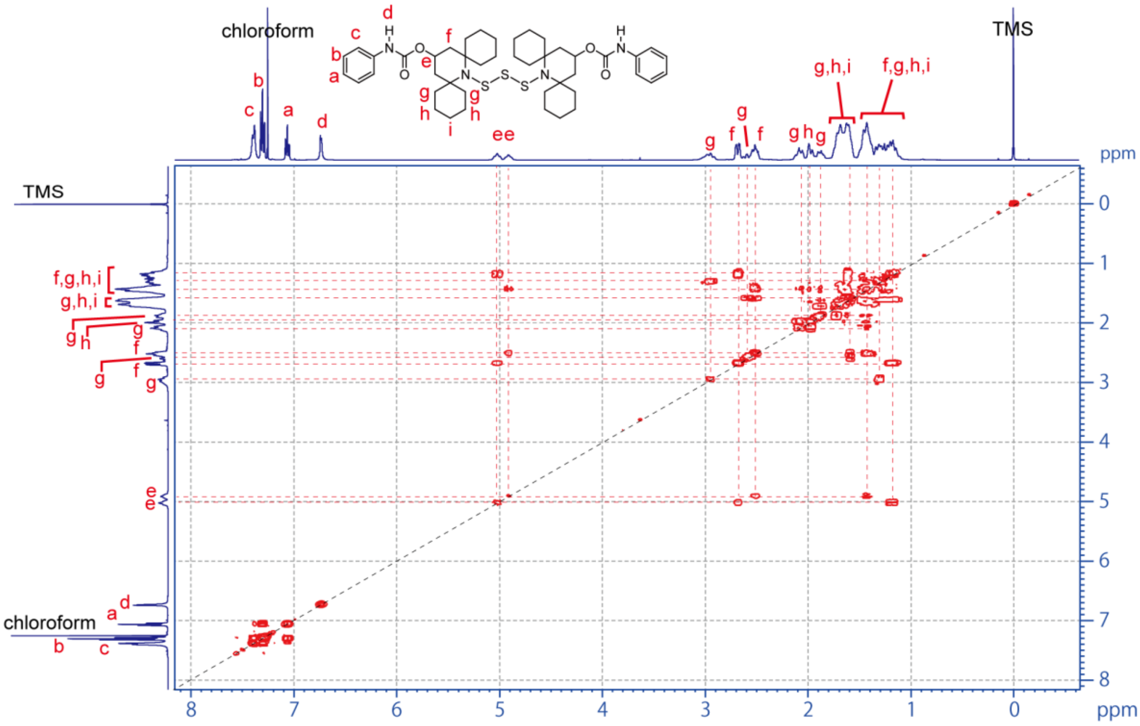
BIBSCPS-S3-Ar: Yield: 618 mg (77 %). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.38 (d, J = 6.4 Hz 4H), 7.29 (t, J = 7.5 Hz, 4H), 7.05 (t, J = 7.3 Hz, 2H), 6.73 (s, 2H), 5.08-4.83 (m, 2H), 3.07-2.88 (m, 2H), 2.67 (dd, J = 13.3, 7.3 Hz, 2H), 2.61-2.45 (m, 4H), 2.10-2.03 (m, 2H), 1.97 (d, J = 12.8 Hz, 2H), 1.91-1.81 (m, 2H), 1.76-1.57 (m,16H), 1.48-1.12(m, 18H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 153.0, 137.6, 128.9, 123.3, 118.4, 67.6, 67.4, 65.7, 64.0, 41.7, 41.6, 40.6, 40.5, 38.8, 38.0, 36.1, 35.1, 34.9, 25.3, 25.2, 23.6, 23.3, 23.1. IR (ATR): 3439, 3352, 2923, 2862, 1715, 1599, 1526, 1500, 1456, 1442, 1405, 1381, 1353, 1341, 1311, 1219, 1171, 1155, 1093, 1052, 1027, 1015, 997, 976, 948, 924, 897, 838, 862, 838, 802, 747, 690, 647, 617.



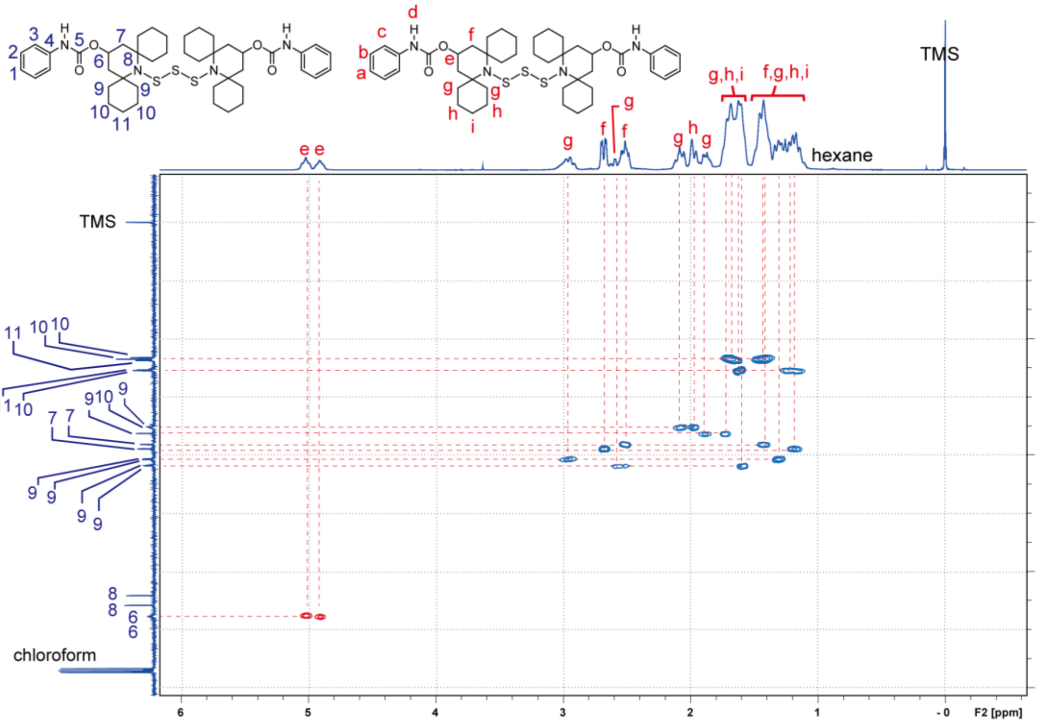
^{1}H NMR spectrum of BIBSCPS-S3-Ar



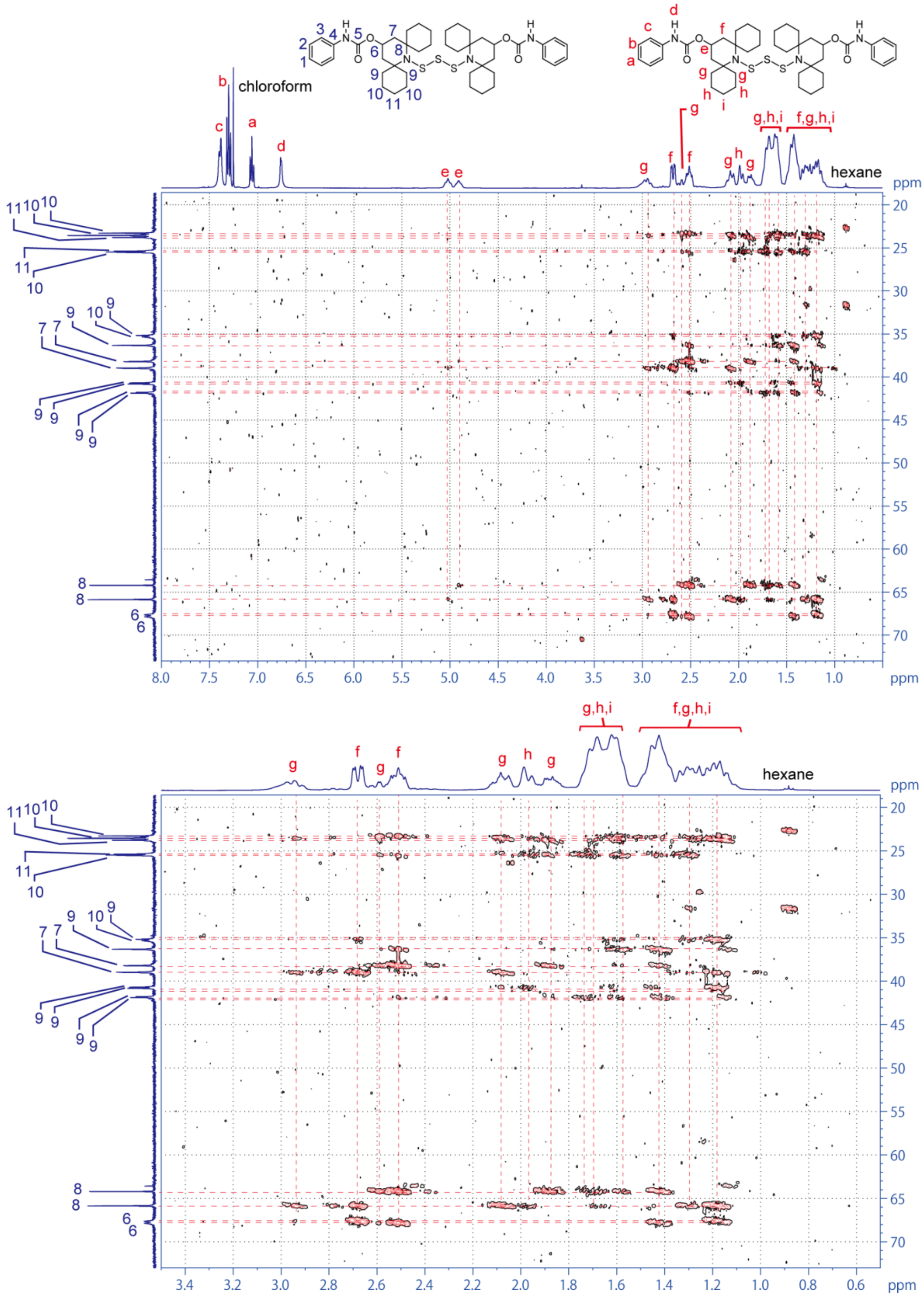
^{13}C NMR spectrum of BIBSCPS-S3-Ar



COSY spectrum of BIBSCPS-S3-Ar

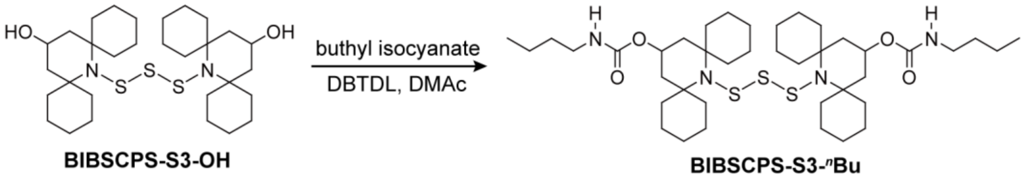


HSQC spectrum of BIBSCPS-S3-Ar

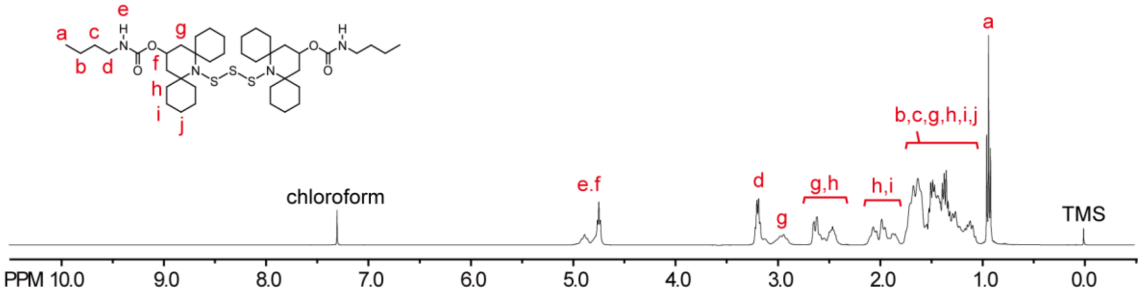


HMBC spectrum of BIBSCPS-S3-Ar

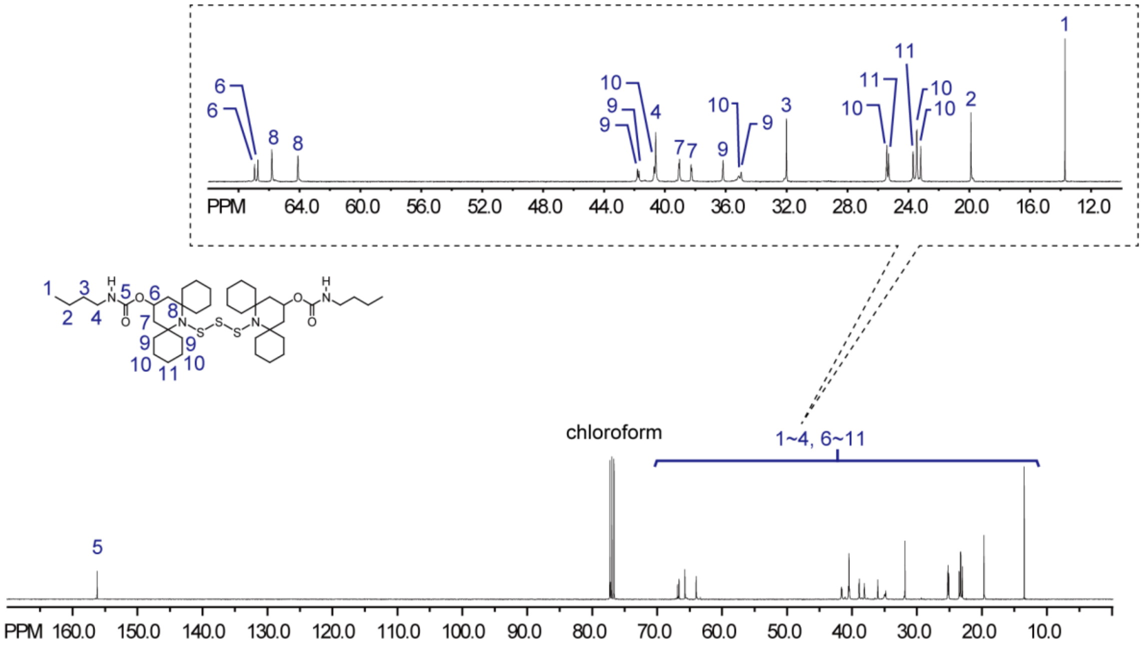
1.3.5 BIBSCPS-S3-^{n}Bu



Into a two-necked flask, BIBSCPS-S3-OH (796 mg, 1.4 mmol), one drop of DBTDL, and dry DMAc (10 mL) was added under argon atmosphere. Then, butyl isocyanate (416 mg, 4.2 mmol) was added into the solution and the reaction mixture was stirred at room temperature overnight. After the resulted solution was poured into water, the white precipitate was collected by filtration and extracted with chloroform. The combined organic layer was washed by water and dried over Na_2SO_4. After the filtrate was condensed under the reduced pressure, BIBSCPS-S3-^{n}Bu was obtained as a white powder via silica gel column chromatography (hexane/ethyl acetate = 3/1, v/v). BIBSCPS-S3-^{n}Bu: Yield: 869 mg (81%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 4.93-4.67 (m, 4H), 4.28-4.21 (br, 4H), 3.55-3.41 (m, 4H), 3.04-2.86 (m, 2H), 2.66-2.39 (m, 6H), 2.12-1.79 (m, 6H), 1.74-1.05 (m, 42H), 0.92 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 156.1, 66.9, 66.7, 65.,8, 64.1, 41.8, 41.6, 40.7, 40.6, 39.0, 38.2, 36.1, 35.1, 34.9, 32.0, 25.4, 25.2, 23.6, 23.4, 23.1, 19.8, 13.7. IR (ATR): 3357, 2922, 2860, 2659, 1718, 1635, 1619, 1249, 1182, 1151, 1093, 1039, 1063, 1012, 982, 948, 923, 892, 863, 846, 808, 777, 719, 665.

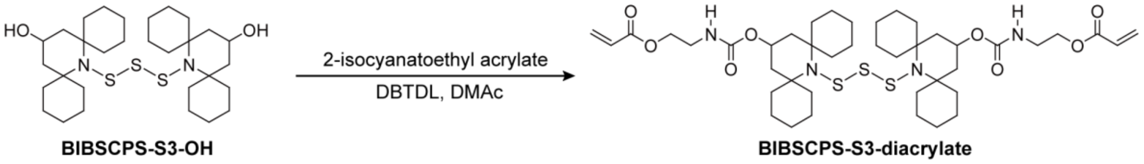


^{1}H NMR spectrum of BIBSCPS-S3-^{n}Bu



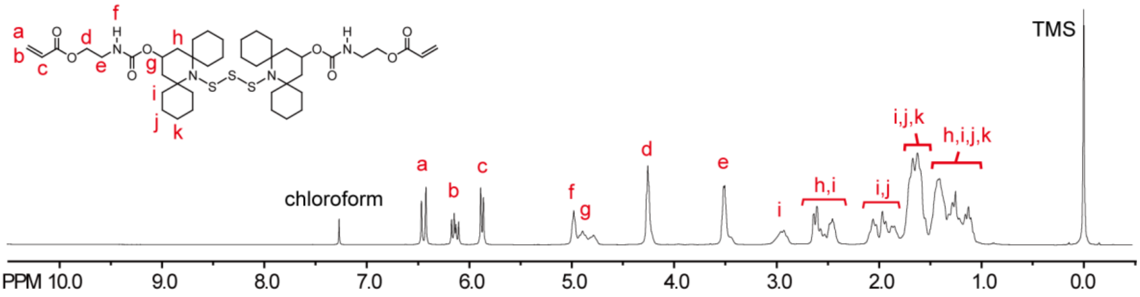
^{13}C NMR spectrum of BIBSCPS-S3-^{n}Bu

1.3.6 BIBSCPS-S3-diacrylate

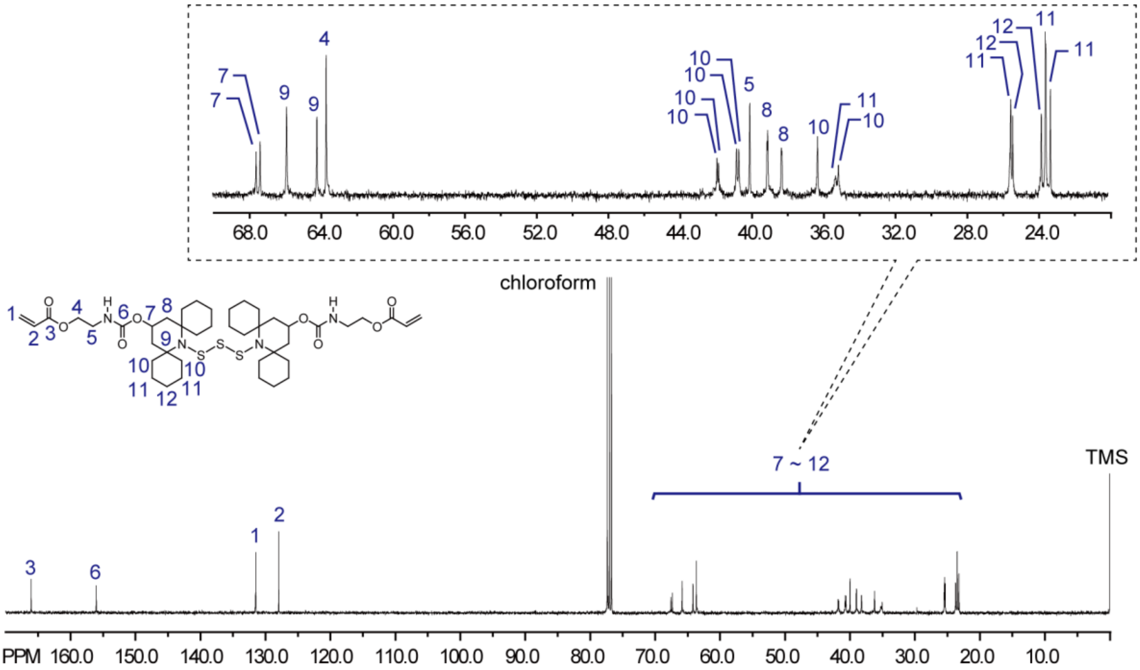


Into a two-necked flask, BIBSCPS-S3-diol (569 mg, 1 mmol) and one drop of DBTDL was added and dissolved in dry DMAc (8 mL) under argon atmosphere. After 2-isocyanatoethyl acrylate (262 mg, 2.2 mmol) was added to the solution, the reaction mixture was stirred at room temperature overnight. The resulted solution was poured into water. The precipitate was collected by filtration and extracted with chloroform. The combined organic layer was washed by water. After drying the organic layer over Na_2SO_4 followed by filtration, the filtrate was condensed under the reduced pressure. Purification by silica gel column chromatography (hexane/ethyl acetate = 2/1, v/v) afforded BIBSCPS-S3-diacrylate as a white powder.

BIBSCPS-S3-diacrylate: Yield: 526 mg (62 %). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 6.44 (d. *J* = 17.2 Hz, 2H), 6.17-6.10 (dd, *J* = 17.2, 10.4 Hz, 2H), 5.87 (d, *J* = 10.4 Hz, 2H), 4.98 (s, 2H), 4.94-4.74 (m, 2H), 4.28-4.21 (br, 4H), 3.55-3.41 (m, 4H), 3.04-2.86 (m, 2H), 2.67-2.41 (m, 6H), 2.12-1.82 (m, 6H), 1.76-1.54 (m, 16H), 1.47-1.08 (m, 18H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 166.0, 155.9, 131.5, 127.8, 67.5, 67.3, 65.8, 64.1, 63.6, 41.8, 41.7, 40.7, 40.5, 39.9, 39.0, 38.9, 25.4, 25.2, 23.6, 23.4, 23.1. IR (ATR): 3357, 2922, 2860, 2659, 1718, 1635, 1619, 1249, 1182, 1151, 1093, 1039, 1063, 1012, 982, 948, 923, 892, 863, 846, 808, 777, 719, 665.

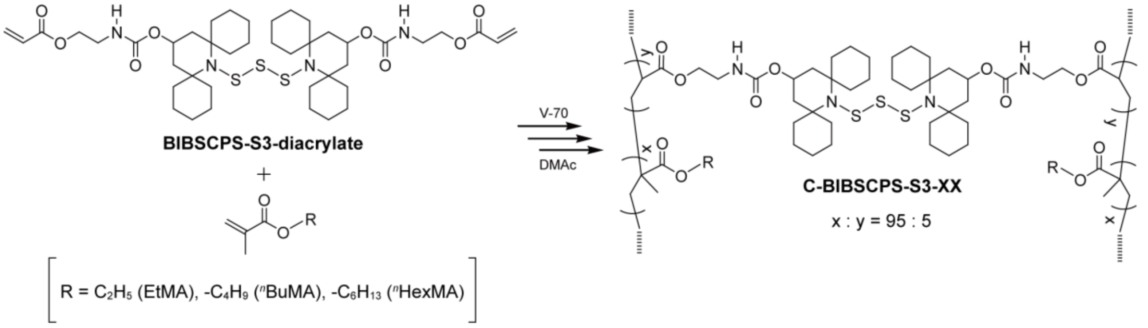


^{1}H NMR spectrum of BIBSCPS-S3-diacrylate



^{13}C NMR spectrum of BIBSCPS-S3-diacrylate

1.3.7 C-BIBSCPS-S3-EtMA, C-BIBSCPS-S3-^{n}BuMA, and C-BIBSCPS-S3-^{n}HexMA

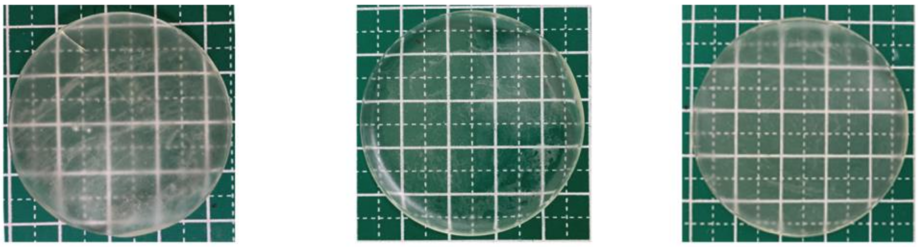


A series of C-BIBSCPS-S3-XX, where XX indicates the monomer (ethyl (EtMA), butyl (^{n}BuMA), or hexyl methacrylate (^{n}HexMA)) for matrix of cross-linked polymer, were prepared by the conventional free radical polymerization. The typical procedure as an example for C-BIBSCPS-S3- ^{n}HexMA was as follows. BIBSCPS-S3-diacrylate (364 mg, 0.55 mmol) and ^{n}HexMA (1787 mg, 10.5 mmol) were dissolved in dry DMAc (2.3 mL) under argon atmosphere and degassed by bubbling with argon for 45 minutes. After 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70, 34.1 mg, 0.11 mmol) was added into the solution, the reaction mixture was stirred at room temperature and bubbled with argon for 10 minutes. Then, the solution was casted via syringe onto a PTFE petri dish in an argon-filled separable flask and was left for 2 days. The obtained film was quenched by exposure to air, separated from dish by immersing to the mixture solution of chloroform and methanol (3/1, v/v). After the film was washed with mixture solution of chloroform and methanol (gradient from 3/1 to 1/3, v/v) for several times, the swelled film was dried on PTFE sheet at room temperature for 6 h. Finally, the objective cross-linked polymer film (C-BIBSCPS-S3-HMA) was obtained, followed by drying in vacuo at 50 °C for 24 h.

C-BIBSCPS-S3-HexMA: Yield: 1763 mg (82%). IR (ATR): 3374, 2955, 2929, 2859, 1724, 1652, 1531, 1467, 1379, 1268, 1239, 1171, 1146, 1065, 1037, 988, 968, 911, 809, 748, 726.

C-BIBSCPS-S3-^{n}BuMA: Yield: 78%. IR (ATR): 3375, 2957, 2930, 2871, 1723, 1638, 1524, 1465, 1450, 1403, 1383, 1343, 1268, 1240, 1144, 1094, 1063, 1039, 1019, 965, 945, 892, 862, 844, 808, 778, 748, 656.

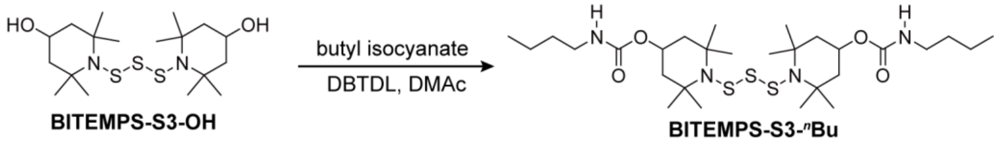
C-BIBSCPS-S3-EtMA: Yield: 72%. IR (ATR): 3377, 2957, 2930, 2871, 1722, 1636, 1519, 1455, 1405, 1386, 1342, 1240, 1143, 1094, 1063, 1039, 1018, 965, 946, 892, 862, 845, 809, 778, 748, 666.



C-BIBSCPS-S3-EtMA C-BIBSCPS-S3-^{n}BuMA C-BIBSCPS-S3-HexMA

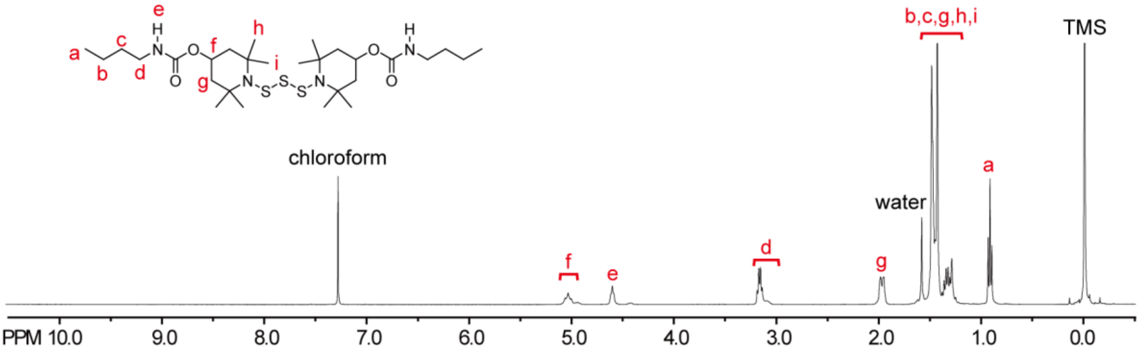
Figure S1 Photos of the obtained C-BIBSCPS-XX films.

1.3.8 BITEMPS-S3-^{n}Bu

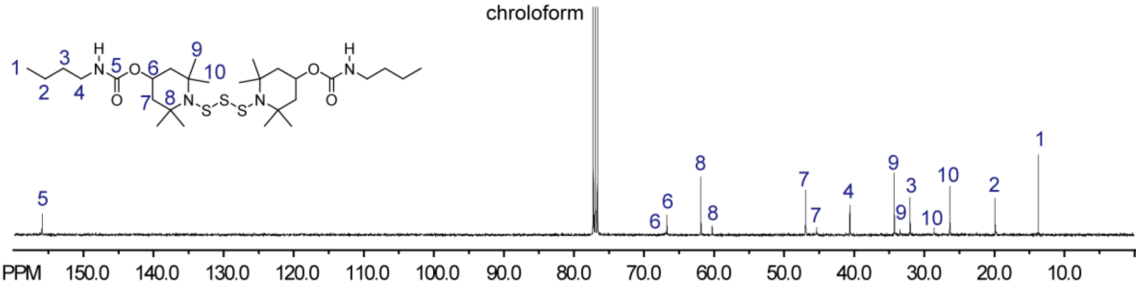


BITEMPS-S3-^{n}Bu was prepared by the same procedure as BIBSCPS-S3-^{n}Bu with BITEMPS-S3-OH (1430 mg, 3.5 mmol), DBTDL (1 drop), butyl isocyanate (763.3 mg, 7.7 mmol), and dry DMAc (20 mL).

BITEMPS-S3-^{n}Bu: Yield: 1572 mg (74 %). ^{1}H NMR (400 MHz, CDCl$_3$, δ): 5.10-4.89 (m, 2H), 4.58 (s, 2H), 3.22-3.08 (m, 4H), 3.03-2.86 (m, 2H), 1.96 (d, J = 11.9 Hz, 4H), 1.52-1.23 (m, 36H), 0.92 (t, J = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, CDCl$_3$, δ): 156.0, 66.9, 66.7, 61.9, 60.2, 46.9, 45.3, 40.5, 34.2, 33.4, 32.0, 28.5, 26.2, 19.8, 13.7. IR (ATR): 3334, 2964, 2931, 2871 1692, 1513, 1460, 1409 1380, 1366, 1312, 1299, 1236, 1197, 1171, 1136, 1112, 1083, 1049, 1010, 987, 937, 898, 841, 776, 738.

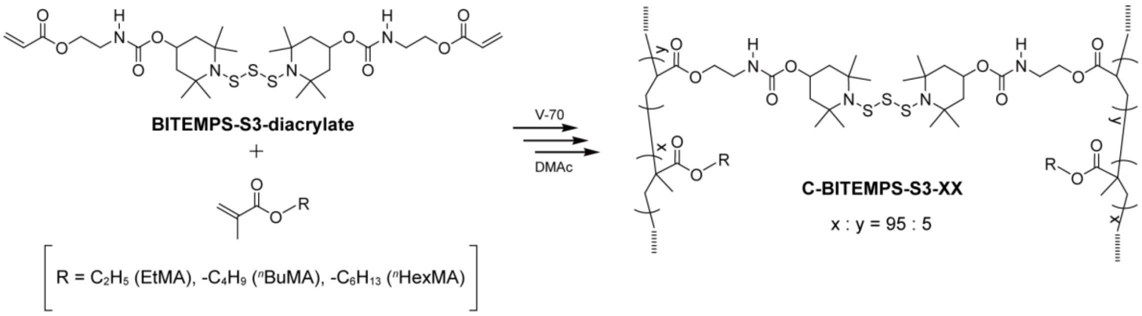


^{1}H NMR spectrum of BITEMPS-S3-^{n}Bu



^{13}C NMR spectrum of BITEMPS-S3-^{n}Bu

1.3.9 C-BITEMPS-S3-XX

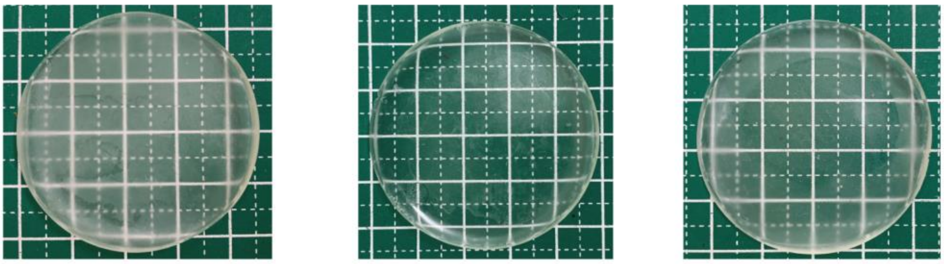


A series of C-BITEMPS-S3-XX, where XX indicates the monomer for matrix of the cross-linked polymer, were synthesized by the same procedure as C-BIBSCPS-S3-XX using BIBSCPS-S3-diacrylate.

C-BITEMPS-S3-^{n}HexMA: Yield: 84%. IR (ATR): 3379, 2955, 2929, 2859, 1724, 1652, 1528, 1467, 1380, 1368, 1268, 1239, 1171, 11146, 1064, 1015, 989, 968, 941, 912, 809, 748, 726, 669.

C-BITEMPS-S3-^{n}BuMA: Yield: 81 %. IR (ATR): 3378, 2981, 2934, 1717, 1636, 1521, 1477, 1447, 1382, 1365, 1235, 1171, 1143, 1062, 1022, 986, 966, 938, 858, 809, 750, 668.

C-BITEMPS-S3-EtMA: Yield: 83%. IR (ATR): 2958, 2933, 2874, 1722, 1524, 1465, 1381, 1367, 1268, 1239, 1170, 1143, 1063, 1020, 965, 943, 881, 843, 809, 748.



C-BITEMPS-S3-EtMA C-BITEMPS-S3-^{n}BuMA C-BITEMPS-S3-HexMA

Figure S2 Photos of the obtained C-BITEMPS-XX films.

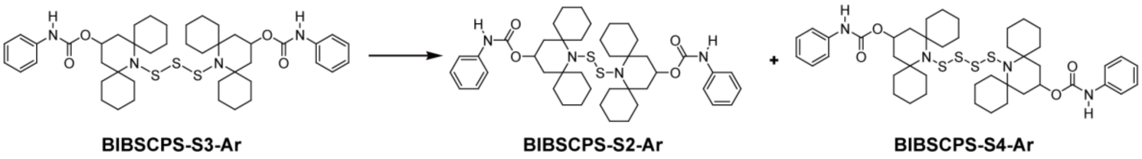
2 X-ray Crystal structure

The single crystal of BIBSCPS-S3-OH was obtained by the recrystallization from chloroform/hexane. Data collection was performed at –160 °C on a Rigaku XtaLaB Synergy-DW dual wavelength X-ray diffractometer with an HPC X-ray detector. The structure was solved by using the OLEX2 software package.[3] Refinements were performed anisotropically for all non-hydrogen atoms by the full-matrix least-squares method. Hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. The severely disordered solvent molecules were removed using the SQUEEZE routine of PLATON software.[4] Crystal data and processing parameters are summarized in Table S1. Deposition Number 2098390 contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

Table S1 X-ray crystallographic details of BIBSCPS-S3-OH

Compound	BIBSCPS-S3-diol
Empirical formula	$C_{30}H_{52}N_2O_2S_3$
Formula weight	568.91
Crystal system	trigonal
Space group	$P3_121$ (No. 152)
a/Å	24.3882(13)
b/Å	24.3882(13)
c/Å	6.6885(3)
α/°	90
β/°	90
γ/°	120
Volume/Å^3	3445.2(4)
Z	3
D_{calc} g/cm^3	0.823
μ/mm^{-1}	1.619
F(000)	930.00
Rflns collected	10229
Data/restraints/ parameters	4162/0/170
R [all data]	0.443
R_1 [$I > 2\sigma(I)$]	0.405
$_{\text{w}}R2$ [all data]	0.1101
GOF on F^2	1.055
ρ_{max}/hole / e Å^{-3}	0.21/-0.25
CCDC No.	2098390

3 Disproportionation reaction of BIBSCPS-S3-Ar



To confirm the disproportionation reaction of the trisulfide linkage of the BIBSCPS-S3 moiety, 500 μL BIBSCPS-S3-Ar solution (0.4M, DMF) was heated at 80 °C for 24 h. Figure S3 shows the mass spectrum of the reaction solution, where it was confirmed that BIBSCPS-S2-Ar (ESI-MS: *m*/*z* for $C_{44}H_{62}N_4O_4S_2Na$ $[M+Na]^+$ calculated: 797.4110, found: 797.4111) and BIBSCPS-S4-Ar (ESI-MS: *m*/*z* for $C_{44}H_{62}N_4O_4S_4Na$ $[M+Na]^+$ calculated: 861.3552, found: 861.3561) were produced.

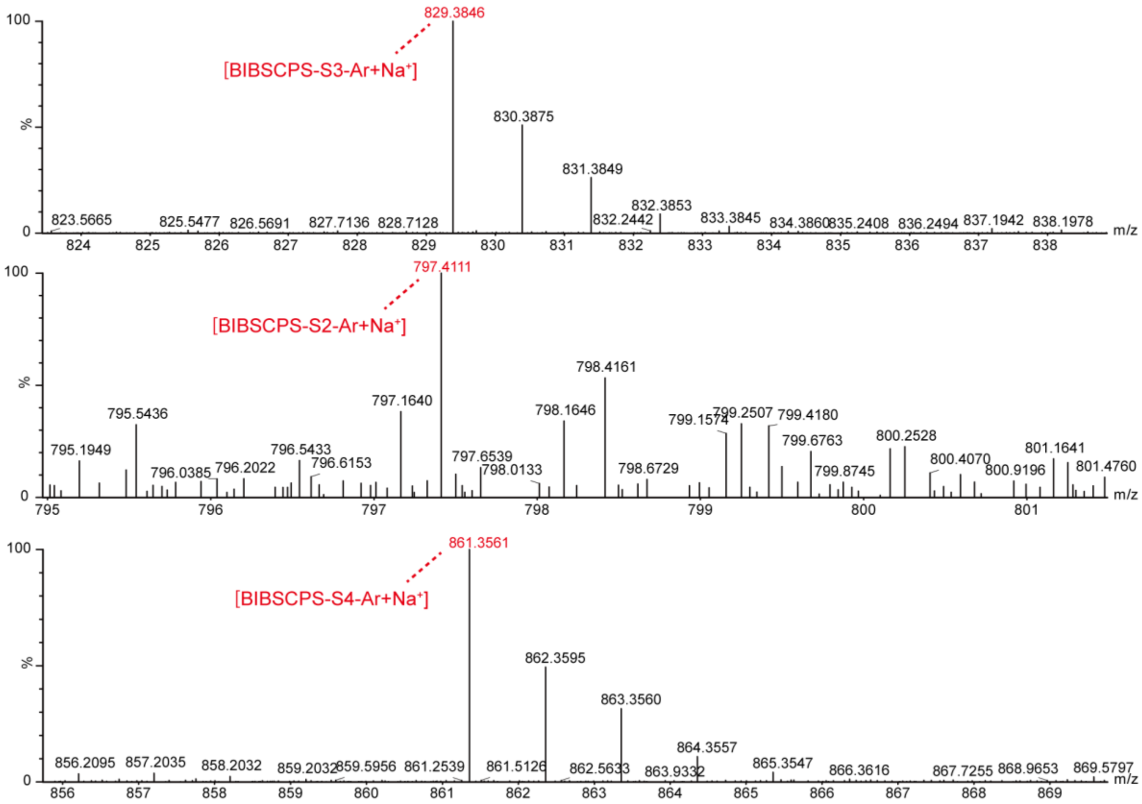


Figure S3 Mass spectrum of a BIBSCPS-S3-Ar solution heated at 80 °C for 24 h (0.4M, DMF solution).

4 Thermal analysis data

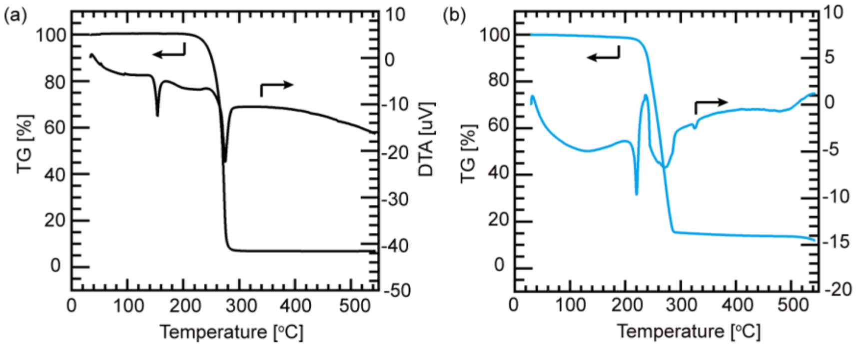


Figure S4 TG and DTA curves of (a) BITEMPS-S3-Ar and (b) BIBSCPS-S3-Ar under a nitrogen atmosphere at a heating rate of 10 °C min^{-1}.

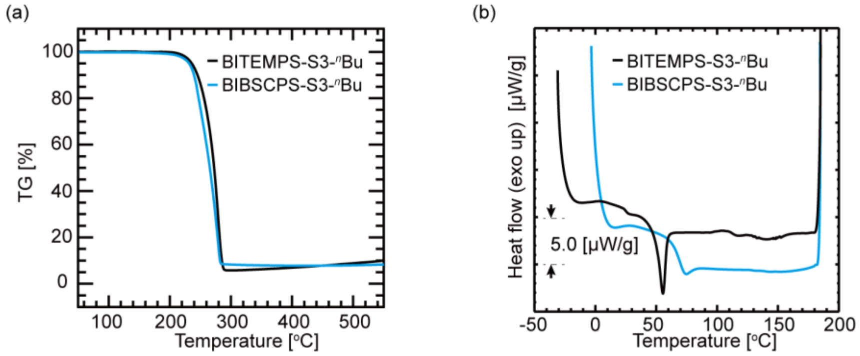


Figure S5 (a) TG and (b) DSC curves of BITEMPS-S3-^{n}Bu and (b) BIBSCPS-S3-^{n}Bu under a nitrogen atmosphere at a heating rate of 10 and 20 °C min^{-1}, respectively.

Table S2 Thermal properties of the model compounds

Sample	T_{d5} [%]	T_m [°C]
BITEMPS-S3-Ar	242.3	153.7
BITEMPS-S3-^{n}Bu	234.2	55.5
BIBSCPS-S3-Ar	232.9	220.4
BIBSCPS-S3-^{n}Bu	229.7	75.0

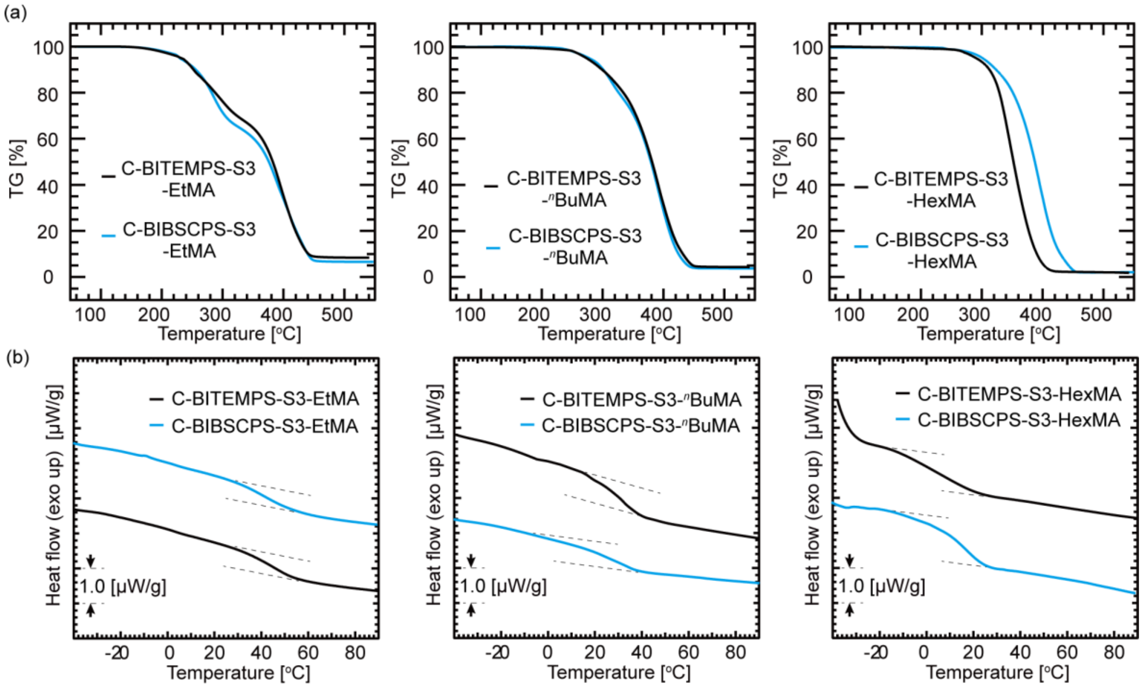


Figure S6 (a) TG and (b) DSC curves of C-BITEMPS-S3-XX and C-BIBSCP-S3-XX under a nitrogen atmosphere at a heating rate of 10 and 20 °C min^{-1}, respectively.

Table S3 Thermal properties of the polymer networks

Sample	T_{d5} [%]	T_g [°C]
C-BITEMPS-S3-EtMA	231.7	43.0
C-BITEMPS-S3-*n*BuMA	271.4	21.9
C-BITEMPS-S3-HexMA	284.1	11.7
C-BIBSCPS-S3-EtMA	233.1	37.5
C-BIBSCPS-S3-*n*BuMA	278.1	20.7
C-BIBSCPS-S3-HexMA	289.1	12.4

5 Stress-relaxation tests

For the tests, rectangular films (ca. 0.8 mm (T) x 4 mm (W) x 20 mm (L)) were prepared. The stress-relaxation behavior was measured at specified temperature (100 to 140 °C) by an instantaneous 3% strain, which was firstly applied after temperature equilibrium in 5 min, and the applied stress decay was monitored, while maintaining a constant strain (3%). The relaxation modulus was normalized by initial value and the monitored time were normalized at t = 0, where the strain reached the target value.

All of the observed σ/σ_0 curves were fitted with Weibul and Kohlrausch-Williams-Watts function (equation 1 in main text) and the average relaxation time ($\langle\tau\rangle$) were calculated from equation 2 in main text. All of the fitting parameters and $\langle\tau\rangle$ were summarized in Table S4.

Table S4 Parameters based on stretched exponential model fitting to stress-relaxation experimental data of C-BITEMPS-S3-XX and C-BIBSCPS-S3-XX.

Sample	Temperature [°C]	τ^{*a} [min]	β^{a} [-]	$\sigma_{\mathrm{perm}}/\sigma_0{}^{a}$ [-]	$\langle\tau\rangle^{b}$ [min]
C-BITEMPS-S3-EtMA	140	1.16	0.61	0.15	1.68
	130	2.17	0.59	0.17	3.30
	120	6.34	0.51	0.19	11.85
	110	87.38	0.48	0.11	182.6
C-BITEMPS-S3-^{n}BuMA	140	1.65	0.51	0.12	3.12
	130	3.46	0.54	0.13	6.07
	120	8.37	0.54	0.21	14.56
	110	72.01	0.63	0.06	100.21
C-BITEMPS-S3-^{n}HexMA	140	1.12	0.51	0.17	2.12
	130	1.90	0.62	0.17	2.74
	120	5.36	0.73	0.19	6.49
	110	15.63	0.55	0.05	26.46
C-BIBSCPS-S3-EtMA	140	1.10	0.55	0.07	2.40
	130	1.58	0.48	0.06	3.35
	120	2.72	0.52	0.14	5.03
	110	6.56	0.55	0.18	12.57
C-BIBSCPS-S3-^{n}BuMA	140	1.11	0.45	0.07	2.69
	130	1.95	0.47	0.09	4.42
	120	3.68	0.50	0.15	7.13
	110	6.85	0.36	0.35	31.8
C-BIBSCPS-S3-^{n}HexMA	140	1.15	0.51	0.02	2.21
	130	2.72	0.61	0.02	3.96
	120	4.94	0.65	0.04	6.68
	110	12.32	0.67	0.07	16.28

[a] τ^*, β, and $\sigma_{\mathrm{perm}}/\sigma_0$ values were estimated from the stress-relaxation data measured at 140 °C using Weibul and Kohlrausch-Williams-Watts function. [b] $\langle\tau\rangle$ was calculated from equation 2 in main text.

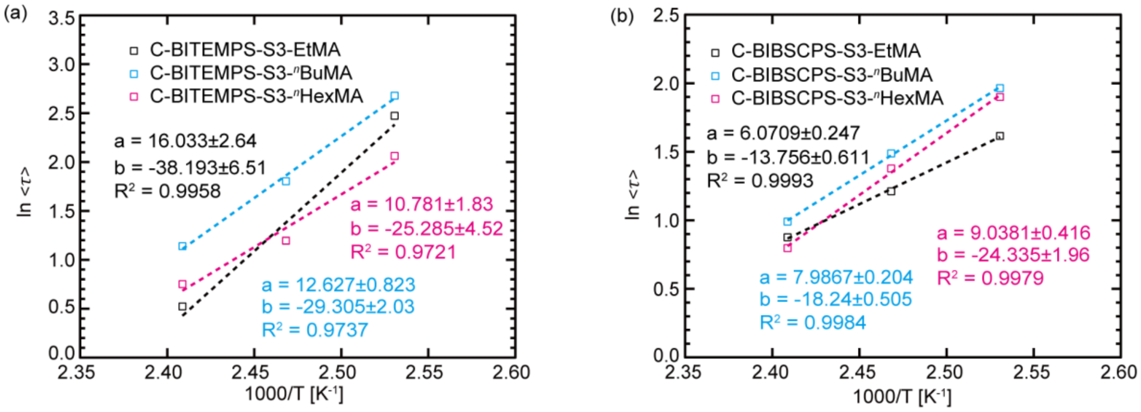


Figure S7 Arrhenius analysis of the stress relaxation associated with average relaxation time for (a) C-BITEMPS-XX and (b) C-BIBSCPS-S3-XX, respectively.

6 Determination of chain-transfer constants

Chain-transfer constants (C_tr) for BITEMPS-S3-^{n}Bu and BIBSCPS-S3-^{n}Bu as chain-transfer agents (CTAs) were determined using the conventional method (i.e. Mayo equation) as follows:

$$\frac{1}{P_\mathrm{n}} = \frac{1}{P_\mathrm{n0}} + C_\mathrm{tr}\left(\frac{[S]}{[M]}\right)$$

where P_n is the number-average degree of polymerization with CTA, P_n0 is the number-average degree of polymerization without CTA, $[S]$ is the molar concentration of the CTA, and $[M]$ is the molar concentration of monomer.

The typical procedure as an example for BITEMPS-S3-^{n}Bu was described as follows. ^{n}HexMA (2179.2 mg, 16.0 mmol), BITEMPS-S3-^{n}Bu (12.1 mg, 0.02 mmol), V-70 (49.3 mg, 0.16 mmol), and DMAc (16.8 mL) were charged into a two-necked flask and subjected to four cycles of freeze-pump-thaw and subsequent refilling with argon. The flask was then thermostated at 30 °C for 2 h. The polymer was isolated from precipitation into methanol and dried under vacuum at room temperature for 24 h. From ^{1}H NMR spectra, the monomer conversion of *n*-hexyl methacrylate was determined to be

8.6%. The monomer: initiator: CTA ratio was set to be 800: 8: 1. The polymerization results are summarized in Table S5.

Table S5 Results of polymerization of various methacrylate monomers with BITEMPS-S3-^{n}Bu or BIBSCPS-S3-^{n}Bu[a]

CTA	Monomer	$([S]/[M]) \times 10^3$	M_n [a] [kDa]	M_w [a] [kDa]	$Đ$ [a] [-]	$\overline{P}_n$ [a] [-]
BITEMPS-S3-^{n}Bu	^{n}HexMA	1.25	44.1	84.7	1.92	258.7
		2.50	28.7	54.6	1.90	168.3
		5.00	18.7	29.4	1.57	109.9
	^{n}BuMA	1.25	44.5	66.3	1.49	312.8
		2.50	34.2	48.4	1.41	240.6
		5.00	20.5	27.9	1.36	144.2
	EtMA	1.25	20.4	40.0	1.96	179.1
		2.50	14.7	25.9	1.76	128.6
		5.00	7.3	12.6	1.72	64.0
BIBSCPS-S3-^{n}Bu	^{n}HexMA	1.25	37.8	62.0	1.63	222.1
		2.50	33.6	53.1	1.58	197.3
		5.00	30.0	47.8	1.59	176.3
	^{n}BuMA	1.25	39.8	60.3	1.51	279.6
		2.50	34.8	49.4	1.41	244.7
		5.00	31.1	44.4	1.43	219.1
	EtMA	1.25	23.2	42.2	1.82	203.3
		2.50	17.2	29.3	1.70	151.2
		5.00	13.9	27.3	1.96	122.2

[a]Polymerization was carried out in DMAc at 30 °C using V-70 as an initiator and the monomer : initiator was 100 : 1. [b]M_n, M_w, $Đ$, and $\overline{P}_n$ were estimated from SEC (PSt, $CHCl_3$).

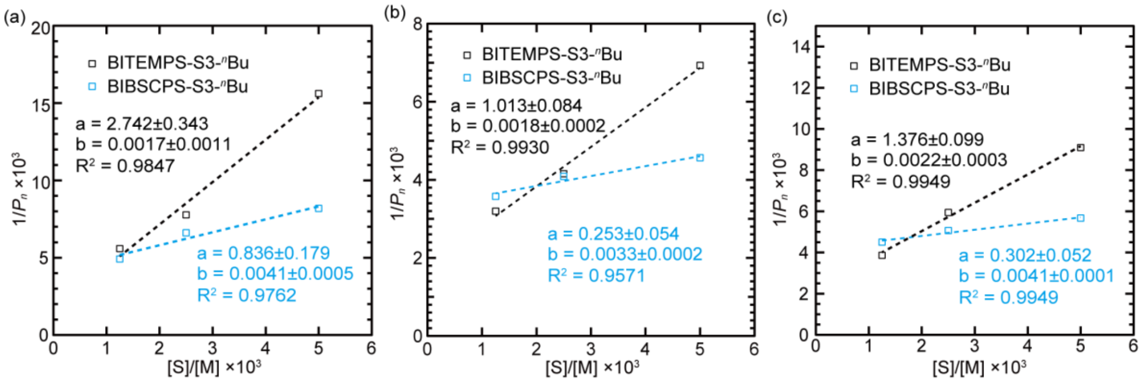


Figure S8 Mayo plots for the polymerization of (a) EtMA, (b) ^{n}BuMA, and (c) ^{n}HexMA in the presence of BITEMPS-S3-^{n}Bu or BIBSCPS-S3-^{n}Bu as a CTA.

7 Cyclic tensile tests

Cyclic tensile tests were performed on INSTRON5582 using dogbone-shaped samples (0.7-1.2 mm (T) x 4 mm (W) x 13 mm (L)) with a strain rate 10 mm/min at room temperature. Prior to cyclic tensile tests, the mechanical properties for C-BITEMPS-S3-^{n}HexMA and C-BIBSCPS-S3-^{n}HexMA were evaluated and summarized in Table S6. Then, the specimens were loaded to different strains from 25 to 75 % toward fracture strain.

Table S6 Mechanical properties of C-BITEMPS-S3-^{n}HexMA and C-BIBSCPS-S3-^{n}HexMA for cyclic tensile tests

Sample	Young's modulus [MPa]	Fracture strain [%]	Maximum stress [MPa]
C-BITEMPS-S3-^{n}HexMA	6.78	271.3	2.68
C-BIBSCPS -S3-^{n}HMA	10.20	312.5	2.72

8 Healing tests

8.1 General procedure of tensile tests

Tensile tests were performed on INSTRON5582 using dogbone-shaped samples (0.7–1.2 mm (T) x 4 mm (W) x 13 mm (L)) prepared with a cutting die with a strain rate 10 mm/min at room temperature.

8.2 Healing tests

The specimens were cut in half and then pressed together tightly at the cut surface. The specimens were sandwiched by two stainless plates pressed by two paper clips. The whole instruments were heated in the thermostatic chamber at different temperatures for 24 h in air. Although disproportionation reaction among cross-linking points would occur during thermal treatment, its mechanical properties were merely affected due to maintaining the same number of cross-linking points. To evaluate mechanical properties of pristine samples, specimens without cutting were similarly treated for each condition. Each result is average from two samples as summarized in Table S7.

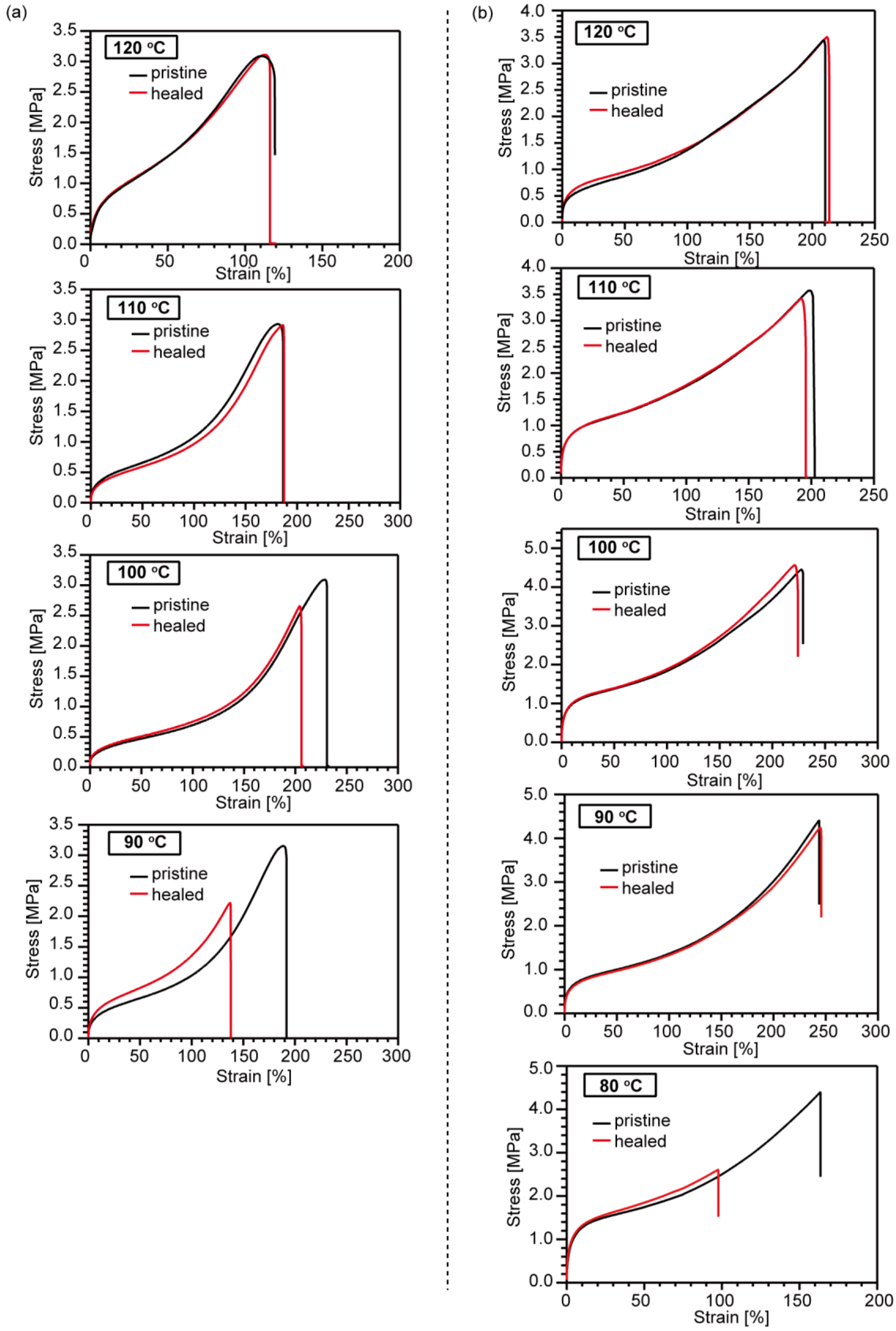


Figure S9 Stress-strain curves of (a) C-BITEMPS-S3-^{n}HexMA and (b)

C-BIBSCPS-S3-^{n}HexMA healed at different temperatures for 24 h.

Table S7 Average mechanical properties of C-BITEMPS-S3-^{n}HexMA and C-BIBSCPS-S3-^{n}HexMA for evaluation of temperature dependence on healability.

Sample	State	Treated temperature [°C]	Treated time [h]	Fracture strain [%]	Maximum stress [MPa]
C-BITEMPS-S3-HexMA	Pristine	120	24	124.1 ± 4.9	3.09 ± 0.02
	Healed	120	24	120.0 ± 1.4	3.10 ± 0.01
	Pristine	110	24	194.8 ± 8.4	3.00 ± 0.06
	Healed	110	24	189.0 ± 1.7	2.96 ± 0.04
	Pristine	100	24	223.3 ± 7.3	3.00 ± 0.09
	Healed	100	24	199.2 ± 6.7	2.65 ± 0.01
	Pristine	90	24	179.4 ± 12.4	2.96 ± 0.20
	Healed	90	24	146.4 ± 8.6	2.30 ± 0.08
C-BIBSCPS-S3-HexMA	Pristine	120	24	225.6 ± 12.0	3.57 ± 0.07
	Healed	120	24	218.8 ± 8.5	3.48 ± 0.03
	Pristine	110	24	214.4 ± 16.6	3.89 ± 0.32
	Healed	110	24	209.6 ± 14.0	3.93 ± 0.50
	Pristine	100	24	245.8 ± 12.5	3.00 ± 0.21
	Healed	100	24	244.0 ± 2.7	3.06 ± 0.01
	Pristine	90	24	231.7 ± 8.5	4.05 ± 0.33
	Healed	90	24	223.6 ± 17.2	3.94 ± 0.38
	Pristine	80	24	159.2 ± 4.2	4.09 ± 0.31
	Healed	80	24	99.8 ± 2.1	2.57 ± 0.03

9 References

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