Supporting Information

Aziridine-Based Organocatalytic Polymerization for Tunable Sulfur Incorporation in Polyureas

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1. General Information

1.1. Materials

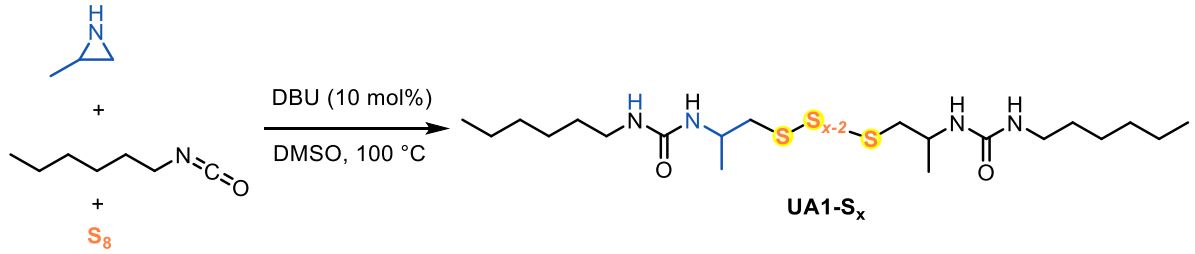
Elemental sulfur (99.95%), sodium sulfide (90%), hexyl isocyanate (98%), hexamethylene diisocyanate (99%), isophorone diisocyanate (99%), tolylene-2,4-diisocyanate (98%), 1,3-bis(isocyanatomethyl)benzene (98%), 4,4'-diphenylmethane diisocyanate (98%), (2,4,6-trioxotriazine-1,3,5(2H,4H,6H)-triyl)tris(hexamethylene) isocyanat (95%), 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD, 97%), phosphazene base *t*-Bu-P_2 solution (~2.0 M in hexane, Sigma-Aldrich), phosphazene base *t*-Bu-P_4 solution (~0.8 M in hexane, Sigma-Aldrich), 1,8-diazabicyclo[5.4.0]-7-undecene (DBU, 99%), *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDETA, 99%), and dichloromethane (DCM) were purchased commercially and used without further purification. Dimethyl sulfoxide (DMSO), *N,N*-dimethylformamide (DMF), and toluene were dried over CaH_2 and distilled before use. Tetrahydrofuran (THF) was dried over 4Å MS before use. 2-Methylaziridine and 2-(phenylmethyl)aziridine were prepared according to reported procedures (*Polym. Chem.*, 2022, **13**, 4324-4332).

1.2. Characterizations

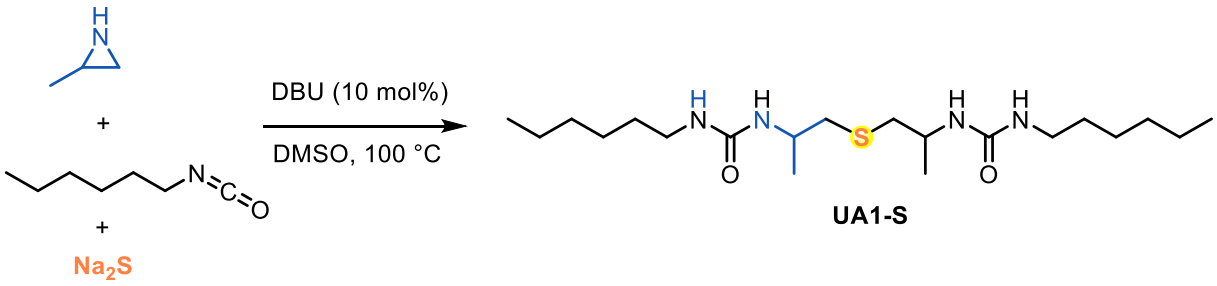
The ^{1}H and ^{13}C NMR spectra were measured on a JNM-ECZ500R/S1 or Bruker AVANCE III 400 or 600 spectrometer at 25 °C using DMSO-d_6 as the solvent. Size exclusion chromatography (SEC) measurements were carried out in DMF with 0.01 M LiBr at 60 °C with the Agilent 1260 Infinity II instrument, equipped with two PLgel 10 μm MIXED-B columns and a differential refractive index (DRI) detector. The system was calibrated with poly(methylmethacrylate) (PMMA) standards at a flow rate of 1.0 mL/min. Thermal stabilities were evaluated by measuring thermogravimetric analysis (TGA) thermograms on an STA 449

F5 Jupite under dry nitrogen at a heating rate of 10 °C/min. Differential scanning calorimetry (DSC) measurements were performed using a Mettler Toledo DSC3 calorimeter. Two scanning cycles of heating-cooling were performed in the temperature range from -50 or 25 to 180 °C with a heating rate of 10 °C/min under nitrogen. FT-IR spectra were obtained on a Thermo-Fisher Nicolet 6700 spectrometer. The XRD pattern was detected by using a TD-3500XRD (Dandong Tongda Technology Co., Ltd, China) under the conditions of 40 kV and 40 mA, in the 2θ range from 5 to 80 °C. Scanning electron microscopy (SEM) was performed on a Hitachi Regulus 8100 scanning electron microscope with an Xplore30 energy dispersive spectroscopy (EDS). Organic elemental analysis (OEA) (Elementar UNICUBE, Germany) was conducted to determine the C, H, N, and S content of the polymers. Tensile stress-strain curves were obtained by using a universal testing machine (Inspekt Table Blue 5KN). Dog-bone samples were used for the test. The crosshead speed was 10 mm/min. The average values with error bars of all mechanical data were obtained after 3 times tests for three samples. Young modulus was measured at 1% strain of the stress-strain curve.

2. Synthetic Procedures

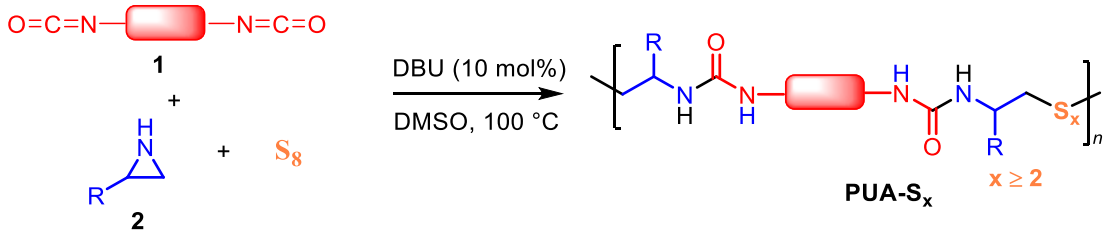


Synthesis of Urea UA1-Sx. A vial was charged with 2-methylaziridine (73 μL, 1.0 mmol, 1.0 equiv.), hexyl isocyanate (146 μL, 1.0 mmol, 1.0 equiv.), and DMSO (1.0 mL) under N_2. After stirring at room temperature for ten minutes, elemental sulfur (160 mg, 5.0 mmol, 5.0 equiv.) and DBU (15 μL, 0.1 mmol, 0.1 equiv.) were added. The vial was sealed and immersed in a preheated oil bath (100 °C). After stirring for 12 h, the mixture was quenched by adding water and then extracted with dichloromethane (DCM). The organic phase was collected, dried over Na_2SO_4, and then concentrated under vacuum to give the desired product **UA1-Sx** as a brown solid in 91% yield. ^{1}H NMR (400 MHz, DMSO-d_6, TMS): δ 5.91-5.73 (4H, m), 3.96-3.87 (2H, m), 3.18-3.03 (4H, m), 2.93-2.98 (4H, m), 1.34-1.21 (16H, m), 1.14-1.07 (6H, m), 0.89-0.84 (6H, m). ^{13}C NMR (125 MHz, DMSO-d_6): δ 157.8, 46.0, 45.1, 39.7, 31.6, 30.5, 26.6, 22.7, 20.5, 14.5.

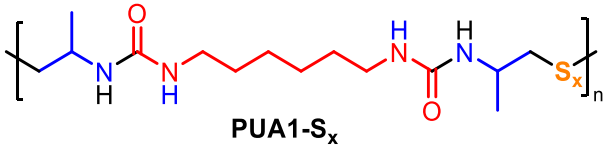


Synthesis of UA1-S. A vial was charged with 2-methylaziridine (73 μL, 1.0 mmol, 1.0 equiv.), hexyl isocyanate (146 μL, 1.0 mmol, 1.0 equiv.), and DMSO (1.0 mL) under N_2. After stirring at room temperature for ten minutes, sodium sulfide (117 mg, 1.5 mmol, 1.5 equiv.) and DBU (15 μL, 0.1 mmol, 0.1 equiv.) were added. The vial was sealed and immersed in a

preheated oil bath (100 °C). After stirring for 12 h, the mixture was quenched by adding water and then extracted with dichloromethane (DCM). The organic phase was collected, dried over Na_2SO_4, and then concentrated under vacuum to give the desired product **UA1-S** as a white solid in 70% yield. ^{1}H NMR (500 MHz, DMSO-d_6, TMS): δ 5.83-5.76 (4H, m), 3.75-3.66 (2H, m), 2.98-2.93 (4H, m), 2.63-2.59 (2H, m), 2.48-2.43 (2H, m), 1.37-1.21 (16H, m), 1.08-1.04 (6H, m), 0.86 (6H, t, J = 7.0 Hz). ^{13}C NMR (125 MHz, DMSO-d_6): δ 157.3, 47.2, 39.3, 35.0, 30.5, 27.2, 21.9, 20.5, 12.0. HRMS (ESI$^+$) calculated for $C_{20}H_{42}N_4O_2S^+$(M^++H): 403.31067, found: 403.30978.



General Procedure for the Synthesis of PUA-S$_x$. A vial was charged with aziridine (2.0 mmol, 2.0 equiv.), diisocyanate (1.0 mmol, 1.0 equiv.), and DMSO (1.0 mL) under a nitrogen atmosphere. Elemental sulfur (2.0 mmol, 2.0 equiv.) and DBU (0.1 mmol, 0.1 equiv.) were then added sequentially. The vial was sealed and placed in a preheated oil bath at 100 °C, stirring for a specific time. Afterward, the mixture was filtered to remove unreacted sulfur and the filtrate was gradually added to a large excess of methanol (~200 mL). The precipitate was collected by centrifugation and dried under vacuum, yielding the desired polysulfide **PUA-S$_x$**.



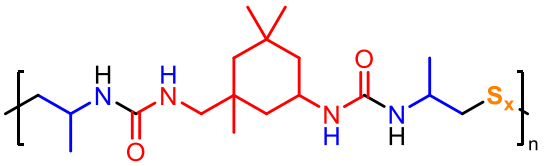
PUA1-S$_x$:1a/2a/S$_8$

brown solid; 91% yield; $M_{n,SEC}$ = 16.2 kDa, $Đ$ = 2.92; T_g = 82°C, $T_{d,5\%}$ = 233 °C.

FT-IR (neat): 3321, 2930, 2854, 1618, 1560, 1253, 630 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6, TMS): δ 5.95-5.77 (4H, m) , 3.89-3.77 (2H, m), 2.99-2.94 (4H, m), 2.92-2.66 (4H, m),1.41-1.28 (4H, m), 1.27-1.19 (4H, m), 1.13-1.05 (6H, m).

^{13}C NMR (125 MHz, DMSO-d_6): δ 157.9, 45.9, 45.0, 40.9, 39.7, 30.6, 26.7, 20.8, 20.4.



PUA2-S$_x$

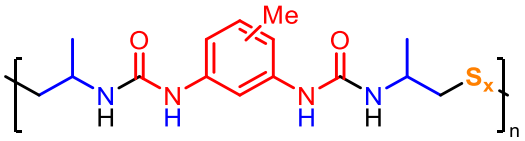
PUA2-S$_x$: 1b/2a/S$_8$

brown solid; 88% yield; $M_{n,SEC}$ = 5.6 kDa, $Đ$ = 2.09, $T_{d,5\%}$ = 182 °C.

FT-IR (neat): 3342, 2966, 2926, 1633, 1558, 1243, 624 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6, TMS): δ 5.90-5.56 (4H, m), 3.91-3.56 (3H, m), 3.13-2.63 (6H, m), 1.60-0.75 (21H, m).

^{13}C NMR (150 MHz, DMSO-d_6): δ 157.6, 156.6, 53.2, 46.9, 46.4, 45.4, 44.4, 42.2, 36.0, 34.9, 31.4, 29.8, 27.5, 23.1, 19.8.



PUA3-S$_x$

PUA3-S$_x$: 1c/2a/S$_8$

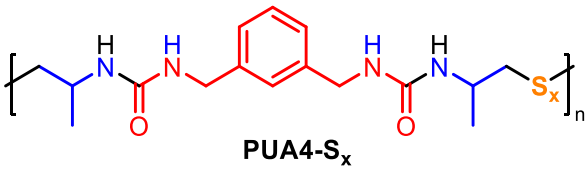
brown solid; 97% yield; $M_{n,SEC}$ = 8.2 kDa, $Đ$ = 1.46; $T_{d,5\%}$ = 236 °C.

FT-IR (neat): 3321, 2973, 2925, 1651, 1539, 1226, 624, 459 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6, TMS): δ 8.40-8.33 (1H, m), 7.84-7.46 (2H, m), 7.15-6.91 (2H, m), 6.72-6.55 (1H, m), 6.20-6.00 (1H, m), 3.95-3.94 (2H, m), 3.13-2.86 (4H, m), 2.19-1.95

(3H, m), 1.24-1.09 (6H, m).

^{13}C NMR (150 MHz, DMSO-d_6): δ 154.4, 152.7, 138.3, 138.0, 129.8, 119.3, 111.5, 109.9, 45.1, 44.6, 44.4, 44.2, 19.9, 19.7, 17.1.



PUA4-S$_x$

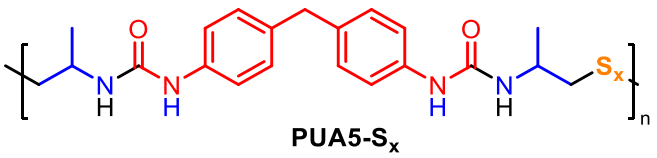
PUA4-S$_x$: 1d/2a/S$_8$

Brown solid; 75% yield; $M_{n,SEC}$ = 12.4 kDa, $Đ$ = 2.35; T_g = 72 °C, $T_{d,5\%}$ = 189 °C.

FT-IR (neat): 3321, 2969, 2925, 1627,1556, 1244, 1019, 618 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6, TMS): δ 7.23-7.08 (4H, m), 6.42-5.98 (4H, m), 4.30-4.04 (4H, m), 4.01-2.31 (2H, m), 3.25-2.63 (4H, m), 1.27-0.99 (6H, m).

^{13}C NMR (150 MHz, DMSO-d_6): δ 158.8, 157.9, 141.2, 128.7, 126.2, 125.8, 66.4, 65.6, 47.5, 47.4, 46.1, 45.9, 45.2, 43.3, 40.9, 21.5, 20.7, 20.4, 18.9.



PUA5-S$_x$

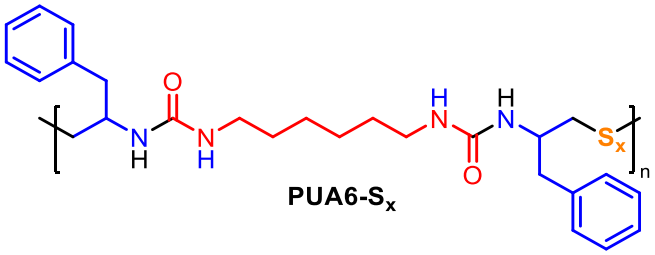
PUA5-S$_x$: 1e/2a/S$_8$

Brown solid; 93% yield; $M_{n,SEC}$ = 14.7 kDa, $Đ$ = 1.87; $T_{d,5\%}$ = 216 °C.

FT-IR (neat): 3321, 2973, 2926, 1539, 1509, 1232, 636, 512 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6, TMS): δ 8.58-8.28 (2H, m), 7.34-7.25 (4H, m), 7.10-7.01 (4H, m), 6.30-6.10 (2H, m), 4.03-3.90 (2H, m), 3.79-3.73 (2H, m), 3.24-2.81 (4H, m), 1.32-1.08 (6H, m).

^{13}C NMR (125 MHz, DMSO-d_6): δ 155.1, 138.7, 134.8, 129.3, 118.8, 118.4, 45.0, 40.9, 39.7, 20.6, 20.4.



PUA6-S_x

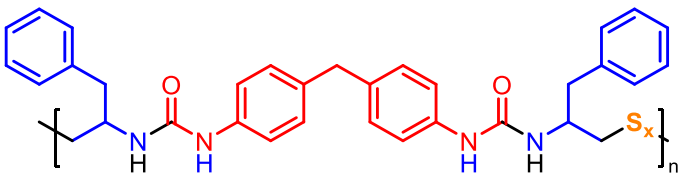
PUA6-S_x: 1a/2b/S_8

Brown solid; 77% yield; $M_{n,SEC}$ = 15.5 kDa, $Đ$ = 4.33; T_g = 48 °C, $T_{d,5\%}$ = 205 °C.

FT-IR (neat): 3321, 2931, 2861, 1633, 1562, 1249, 1025, 701, 618, 506 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6, TMS): δ 7.28-7.13 (10H, m), 5.98-5.74 (4H, m), 4.10-4.00 (2H, m), 3.14-2.60 (12H, m), 1.29-1.17 (8H, m).

^{13}C NMR (150 MHz, DMSO-d_6): δ 158.2, 157.7, 138.8, 129.6, 128.7, 126.6, 50.7, 44.3, 40.9 30.4, 26.6.



PUA7-S_x

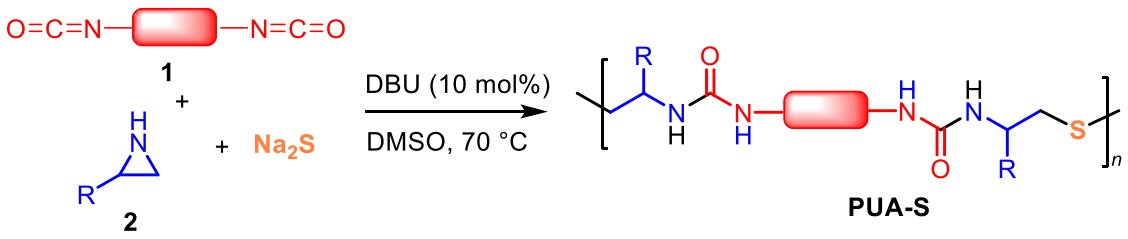
PUA7-S_x: 1e/2b/S_8

Brown solid; 73% yield; $M_{n,SEC}$ = 13.1 kDa, $Đ$ = 2.57; T_m = 62 °C, $T_{d,5\%}$ = 223 °C.

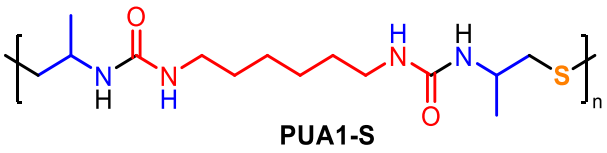
FT-IR (neat): 3321, 3026, 2908, 1545, 1509, 1238, 701, 512 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6, TMS): δ 8.53-8.29 (2H, m), 7.31-6.95 (18H, m), 6.15-6.09 (2H, m), 4.19-4.07 (2H, m), 3.81-3.69 (2H, m), 3.08-2.64 (8H, m).

^{13}C NMR (150 MHz, DMSO-d_6): δ 153.6, 150.0, 138.1, 138.0, 137.5 134.9 133.7, 129.1 128.6, 128.1, 125.5 118.2 117.3 52.4 43.4, 40.9.



General Procedure for the Synthesis of PUA-S. A vial was charged with aziridine (2.0 mmol, 2.0 equiv.), diisocyanate (1.0 mmol, 1.0 equiv.), and DMSO (1.0 mL) under a nitrogen atmosphere. Sodium sulfide (3.0 mmol, 3.0 equiv.) and DBU (0.1 mmol, 0.1 equiv.) were then added sequentially. The vial was sealed and placed in a preheated oil bath at 70 °C, stirring for a specific time. Afterward, the mixture was filtered to remove inorganic salts and the filtrate was gradually added to a large excess of methanol (~200 mL). The precipitate was collected by centrifugation and dried under vacuum, yielding the desired poly(urea thioether) **PUA-S**.



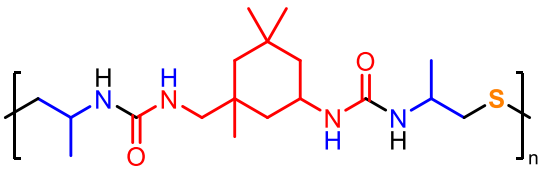
PUA1-S: 1a/2a/Na_2S

White solid; 77% yield; $M_{n,SEC}$ = 10.9 kDa, $Đ$ = 2.54; T_g = 87 °C, $T_{d,5\%}$= 260 °C.

FT-IR (neat): 3321, 2926, 2861, 1609, 1562, 1255, 624 cm^{-1}.

^1H NMR (500 MHz, DMSO-d_6, TMS): δ 5.85-5.79 (4H, m), 3.71-3.69 (2H, m), 2.97-2.93 (4H, m), 2.64-2.58 (2H, m), 2.48-2.43 (2H, m), 1.33-1.22 (8H, m), 1.07-1.05 (6H, m).

^{13}C NMR (125 MHz, DMSO-d_6): δ 158.0, 45.7, 39.7, 30.6, 26.7, 20.6.



PUA2-S

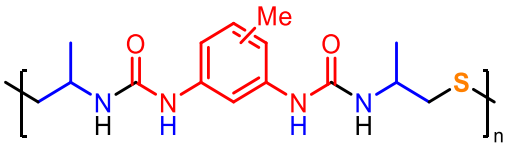
PUA2-S: 1b/2a/Na_2S

White solid; 69% yield; $M_{n,SEC}$ = 16.6 kDa, $Đ$ = 2.05; $T_{d,5\%}$ = 230 °C.

FT-IR (neat): 3333, 2961, 2920, 1633, 1556, 1084, 618, 470 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6, TMS): δ 5.95-5.68 (4H, m), 3.70 (3H, s), 2.82-2.59 (4H, m), 2.47-2.38 (2H, m), 1.07-0.70 (21H, m).

^{13}C NMR (150 MHz, DMSO-d_6): δ 158.7, 157.2, 54.1, 47.5, 46.8, 45.0, 42.7, 40.9, 35.5, 32.0, 31.9, 30.9, 28.1, 23.7, 20.6.



PUA3-S

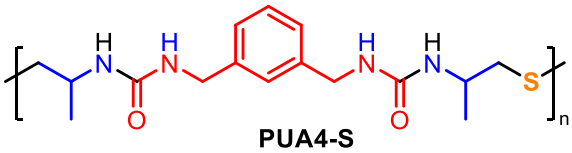
PUA3-S: 1c/2a/Na_2S

White solid; 83% yield; $M_{n,SEC}$ = 15.3 kDa, $Đ$ = 1.53; $T_{d,5\%}$ = 224 °C.

FT-IR (neat): 3315, 2967, 2926, 1645, 1539, 1238, 960, 630, 494, 459 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6, TMS): δ 8.34 (1H, s), 7.85-7.54 (2H, m), 7.12-6.89 (2H, m), 6.62 (1H, s), 6.00-5.98 (1H, m),3.82-3.78 (2H, m), 2.69-2.57 (4H, m), 2.16-2.06 (3H, m), 1.22-1.04 (6H, m).

^{13}C NMR (125 MHz, DMSO-d_6): δ 155.1, 139.0, 138.6, 130.5, 119.8, 112.0, 110.4, 45.64, 20.6, 17.8.



PUA4-S

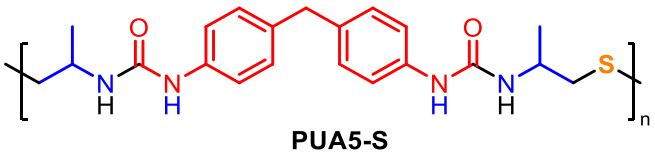
PUA4-S: 1d/2a/Na_2S

White solid; 89% yield; $M_{n,SEC}$ = 28.3 kDa, $Đ$ = 1.75; T_g = 113 °C, $T_{d,5\%}$ = 248 °C.

FT-IR (neat): 3315, 2867, 2931, 1556, 1403, 1244, 618 cm^{-1}.

^1H NMR (500 MHz, DMSO-d_6, TMS): δ 7.23-7.06 (4H, m), 6.41-6.29 (2H, m), 5.96-5.93 (2H, m), 4.20-4.09 (4H, m), 3.79-3.73 (2H, m), 2.68-2.59 (2H, m), 2.48-2.40 (2H, m), 1.16-0.96 (6H, m).

^{13}C NMR (150 MHz, DMSO-d_6): δ 162.5, 143.8, 129.0, 126.2, 125.7, 47.2, 43.7, 40.5, 20.6.



PUA5-S

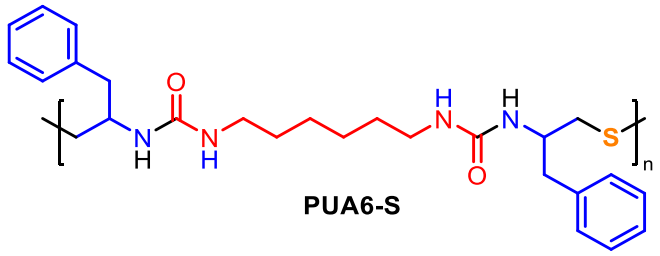
PUA5-S: 1e/2a/Na_2S

White solid; 72% yield; $M_{n,SEC}$ = 14.3 kDa, $Đ$ = 1.95; $T_{d,5\%}$ = 277 °C.

FT-IR (neat): 3303, 2967, 2926, 1550, 1509, 1232, 624, 512 cm^{-1}.

^1H NMR (500 MHz, DMSO-d_6, TMS): δ 8.33-8.32 (2H, m), 7.28-7.20 (4H, m), 7.03-6.99 (4H, m), 6.10-6.07 (2H, m), 3.84-3.64 (4H, m), 2.71-2.56 (4H, m), 1.20-1.05 (6H, m).

^{13}C NMR (125 MHz, DMSO-d_6): δ 155.1, 138.8, 134.8, 129.3, 118.8, 45.5, 20.5.



PUA6-S

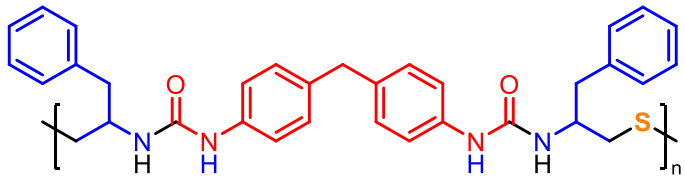
PUA6-S: 1a/2b/Na_2S

White solid; 62% yield; $M_{n,SEC}$ = 5.6 kDa, $Đ$ = 1.57; T_g = 61 °C, $T_{d,5\%}$ = 229 °C.

FT-IR (neat): 3327, 2931, 2861, 1562, 1409, 1008, 624, 494 cm^{-1}.

^1H NMR (500 MHz, DMSO-d_6, TMS): δ 7.30-7.16(10H, m), 5.86-5.76 (4H, m), 3.87-3.85 (2H, m), 2.95-2.63 (12H, m), 1.28-1.16 (8H, m).

^{13}C NMR (150 MHz, DMSO-d_6): δ 156.4, 140.3, 130.9, 128.6, 124.6, 58.1, 40.5, 37.8, 30.4, 25.8.



PUA7-S

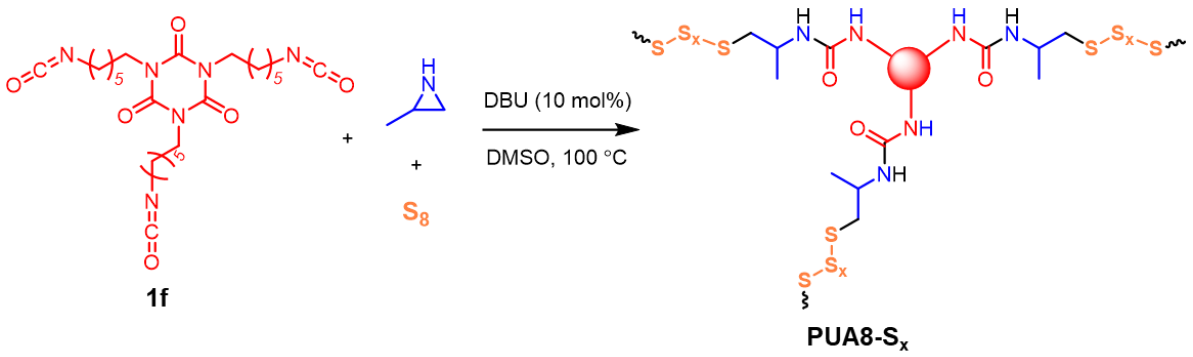
PUA7-S: 1e/2b/Na_2S

White solid; 61% yield; $M_{n,SEC}$ = 9.4 kDa, $Đ$ = 2.04; T_g = 150 °C, $T_{d,5\%}$ = 242 °C.

FT-IR (neat): 3321, 3032, 2920, 1539, 1509, 1232, 695, 506 cm^{-1}.

^1H NMR (500 MHz, DMSO-d_6, TMS): δ 8.68-8.34 (2H, m), 7.32-6.99 (18H, m), 6.22-6.08 (2H, m), 4.00-3.68 (4H, m), 2.94-2.62 (8H, m).

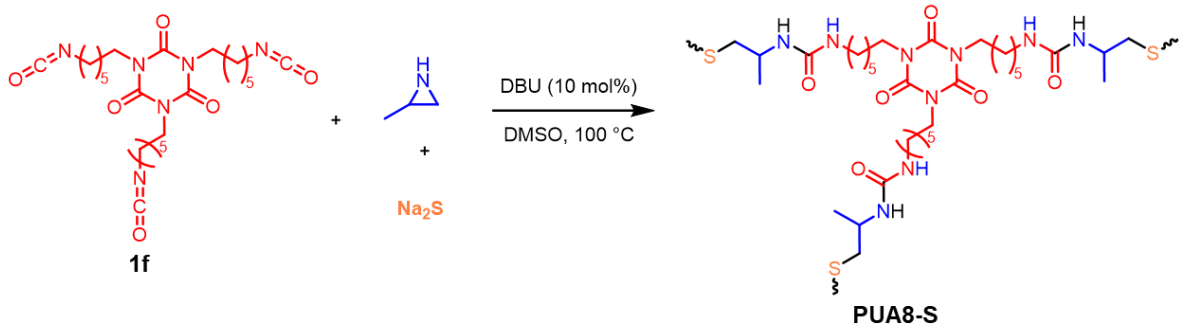
^{13}C NMR (150 MHz, DMSO-d_6): δ 156.1, 139.0, 130.0, 129.3, 129.2, 128.2, 126.6, 120.3, 118.2, 51.5, 40.9, 40.5, 37.4.



Procedure for the Synthesis of Polyurea Vitrimer. In a vessel, isocyanate **1f** (1.51 g, 3 mmol, 1.0 equiv.), 2-methylaziridine (0.65 mL, 9.0 mmol, 3.0 equiv.), and DMSO (3.0 mL) were added. The mixture was stirred for 5-10 minutes. Elemental sulfur (0.29 g, 9.0 mmol, 3.0 equiv.) and DBU (45 μL,0.3 mmol, 0.1 equiv.) were then added to the reaction mixture. The reaction was heated at 100 °C and stirred for approximately 1 hour until the mixture formed a gel. The gel was transferred to a petri dish and dried under vacuum at 100 °C in an oven until completely dry.

Procedure for the Preparation of Dog-bone-shaped Samples. The solid material obtained from the previous step was pulverized to a uniform powder. The resulting granules were then placed into a mold and hot-pressed at 10 MPa and 140 °C for 5-10 minutes to form dog-bone-shaped samples. The mold used for this process was designed according to ISO 37:2005/3 standards and made of stainless steel with a Teflon coating to prevent sticking during pressing. Hot-pressing was conducted using a hydraulic lamination hot press (Dongguan Zhenggong Electromechanical Equipment Technology Co., Ltd.) at 110 °C and 10 MPa.

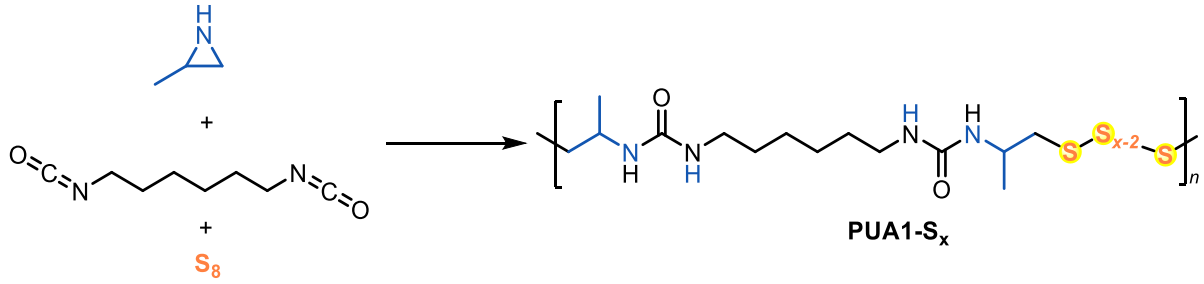
After tensile tests, the dog-bone-shaped samples were re-pulverized and re-pressed at 140 °C for further testing.



Procedure for the Synthesis of Poly(urea thioether) PUA8-S. In a vessel, isocyanate **1f** (0.31 g, 0.6 mmol, 1.0 equiv.), 2-methylaziridine (0.13 mL, 1.8 mmol, 3.0 equiv.), and DMSO (0.6 mL) were added. The mixture was stirred for 5-10 minutes. Sodium sulfide (0.21 g, 2.7 mmol, 4.5 equiv.) and DBU (9 μL, 0.06 mmol, 0.1 equiv.) were then introduced, and the reaction was carried out at 70 °C with stirring for 4 hours. The resulting gel was transferred to a petri dish and dried in a vacuum oven at 100 °C. After drying, a significant amount of residual sodium sulfide was observed in the sample. To remove the remaining sodium sulfide, the sample was treated with water under ultrasonic conditions, effectively removing most of the residual sodium sulfide. The sample was then re-dried in a vacuum oven at 100 °C.

3. Supporting Tables and Figures

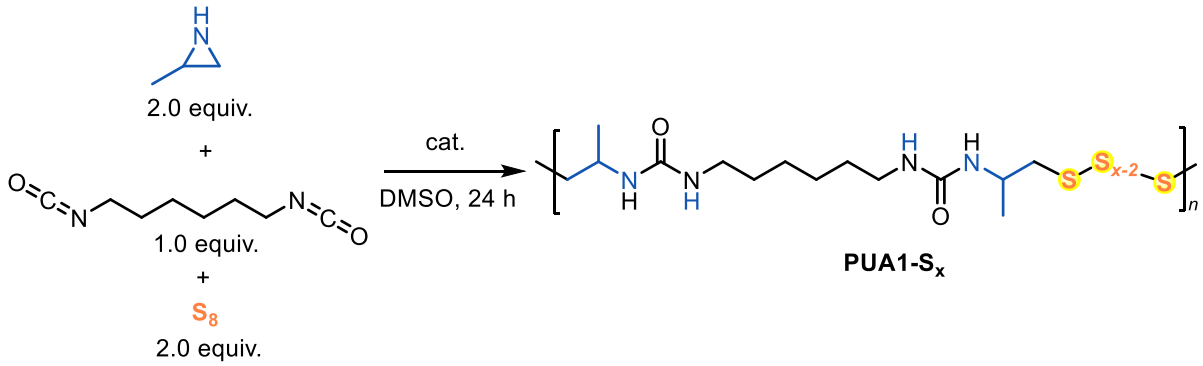
Table S1. Polymerization of 2-methylaziridine, hexamethylene diisocyanate, and elemental sulfur.



entry	temp. (°C)	solvent	cat. (10 mol%)	$[HDI]_0:[MAz]_0:[S_8]_0$	time (h)	M_n[a] (Da)	$Đ$[a]
1	80	DMSO	MTBD	1:2:4	36	3270	1.20
2	80	DMSO	*t*-BuP$_2$	1:2:4	48	3090	1.27
3	80	DMSO	*t*-BuP$_4$	1:2:4	38	3410	1.40
4	80	DMF	*t*-BuP$_4$	1:2:4	24	2880	1.44
5	80	toluene	*t*-BuP$_4$	1:2:4	24	3450	1.50
6	60	THF	*t*-BuP$_4$	1:2:4	24	2110	1.51
7	100	DMSO	*t*-BuP$_4$	1:2:4	24	3450	1.40
8	100	DSMO	*t*-BuP$_4$	1:2:2	24	6050	2.08
9	100	DMSO	*t*-BuP$_4$	1:2:8	24	3250	1.32

[a]Determined by SEC in DMF at 60 °C (PMMA calibration).

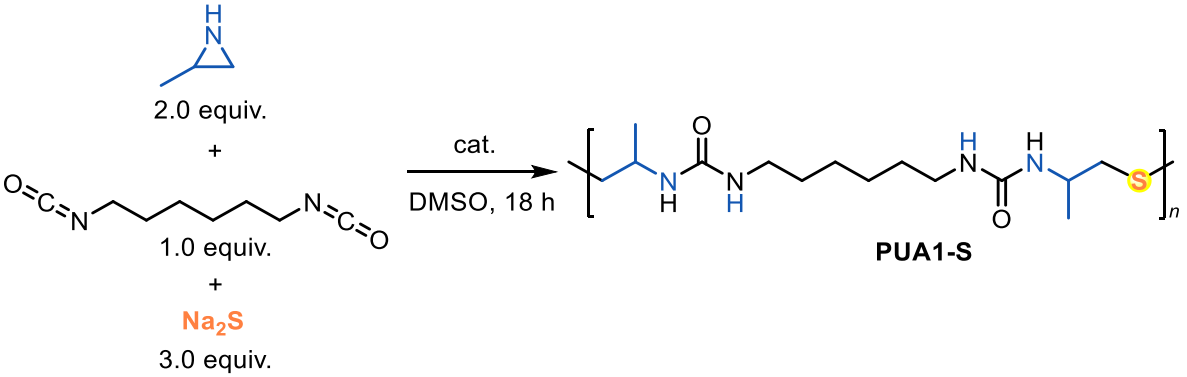
Table S2. Polymerization of 2-methylaziridine, hexamethylene diisocyanate, and elemental sulfur in DMSO.



entry[a]	temp. (°C)	cat. (10 mol%)	M_n[b] (Da)	$Đ$[b]
1	100	*t*-BuP$_4$	6050	2.08
2	100	DBU	16220	2.92
3	100	PMDETA	6970	2.74
4	100	*t*-BuP$_2$	16130	2.89
5	100	MTBD	14150	2.57
6[c]	100	DBU	10340	1.87
7	80	DBU	4480	1.64
8[d]	100	DBU	12180	2.16
9	40	DBU	< 2000	-
10[e]	100	DBU	4970	1.80

[a]Reaction conditions: 2-methylaziridine (0.2 mmol, 2.0 equiv.), hexamethylene diisocyanate (0.1 mmol, 1.0 equiv), S_8 (0.2 mmol, 2.0 equiv.), DBU (10 mol%), DMSO, 24 h. [b]Determined by SEC in DMF at 60 °C (PMMA calibration). [c]Hexamethylene diisocyanate was scaled up to 0.5 mmol. [d]The mixture of 2-methylaziridine (2.0 equiv.) and hexamethylene diisocyanate (1.0 equiv.) was stirred for 10 minutes at room temperature in DMSO. Water (10.0 equiv.) was then added, followed by elemental sulfur (2.0 equiv.) and DBU (10 mol%). [e]DBU (5 mol%).

Table S3. Screening of polymerization conditions for aziridine, isocyanate, and sodium sulfide.



entry[a]	temp.(°C)	cat.	M_n[b] (Da)	$Đ$[b]
1	100	DBU	6440	1.87
2	70	DBU	10880	2.54
3	40	DBU	8610	2.00
4[c]	70	-	-	-
5[d]	70	DBU	4130	1.98

[a]Reaction conditions: 2-methylaziridine (0.2 mmol, 2.0 equiv.), hexamethylene diisocyanate (0.1 mmol, 1.0 equiv), Na_2S (0.3 mmol, 3.0 equiv.), DBU (10 mol%), DMSO, 18 h. [b]Determined by SEC in DMF at 60 °C (PMMA calibration). [c]No polymerization was observed when the reaction was carried out without the addition of a catalyst. [d]DBU (5 mol%).

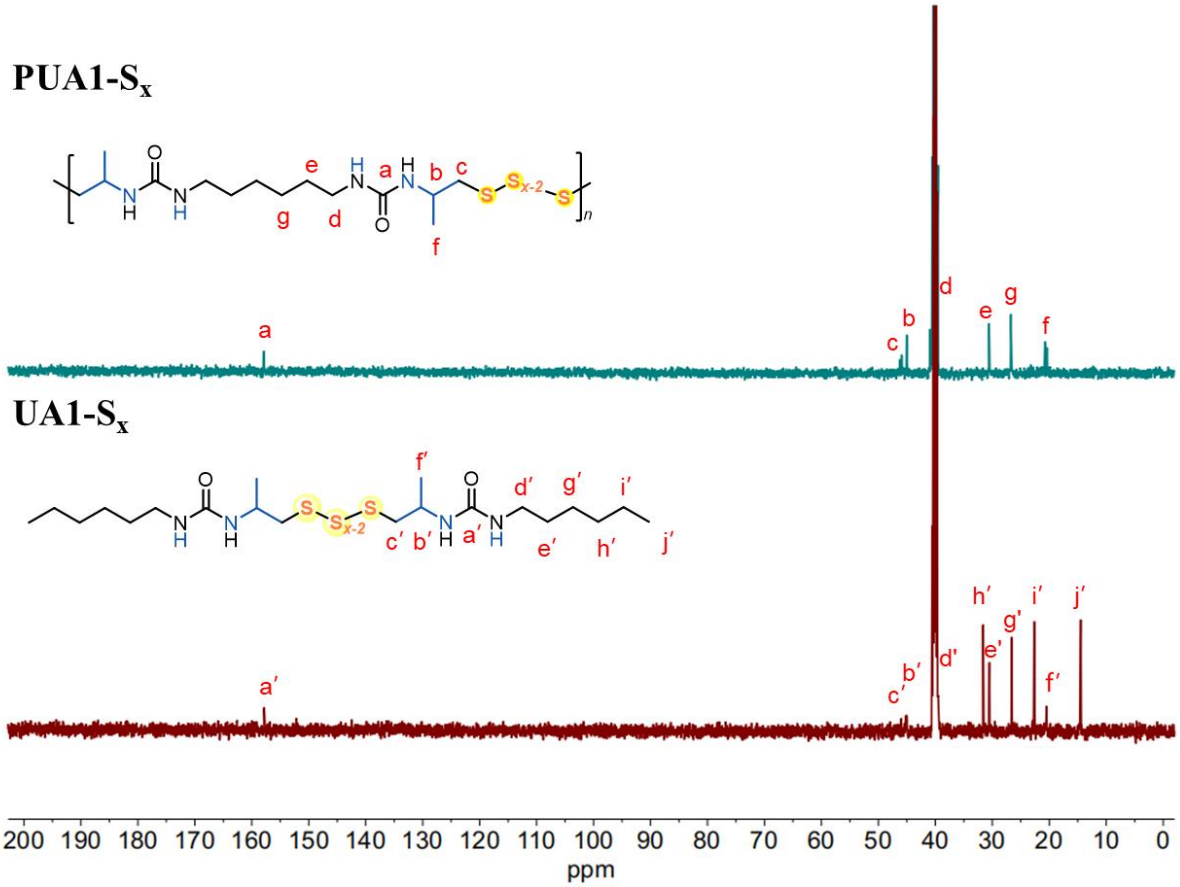


Fig. S1. ^{13}C NMR (DMSO-d_6) spectra of **PUA1-S$_x$** and **UA1-S$_x$**.

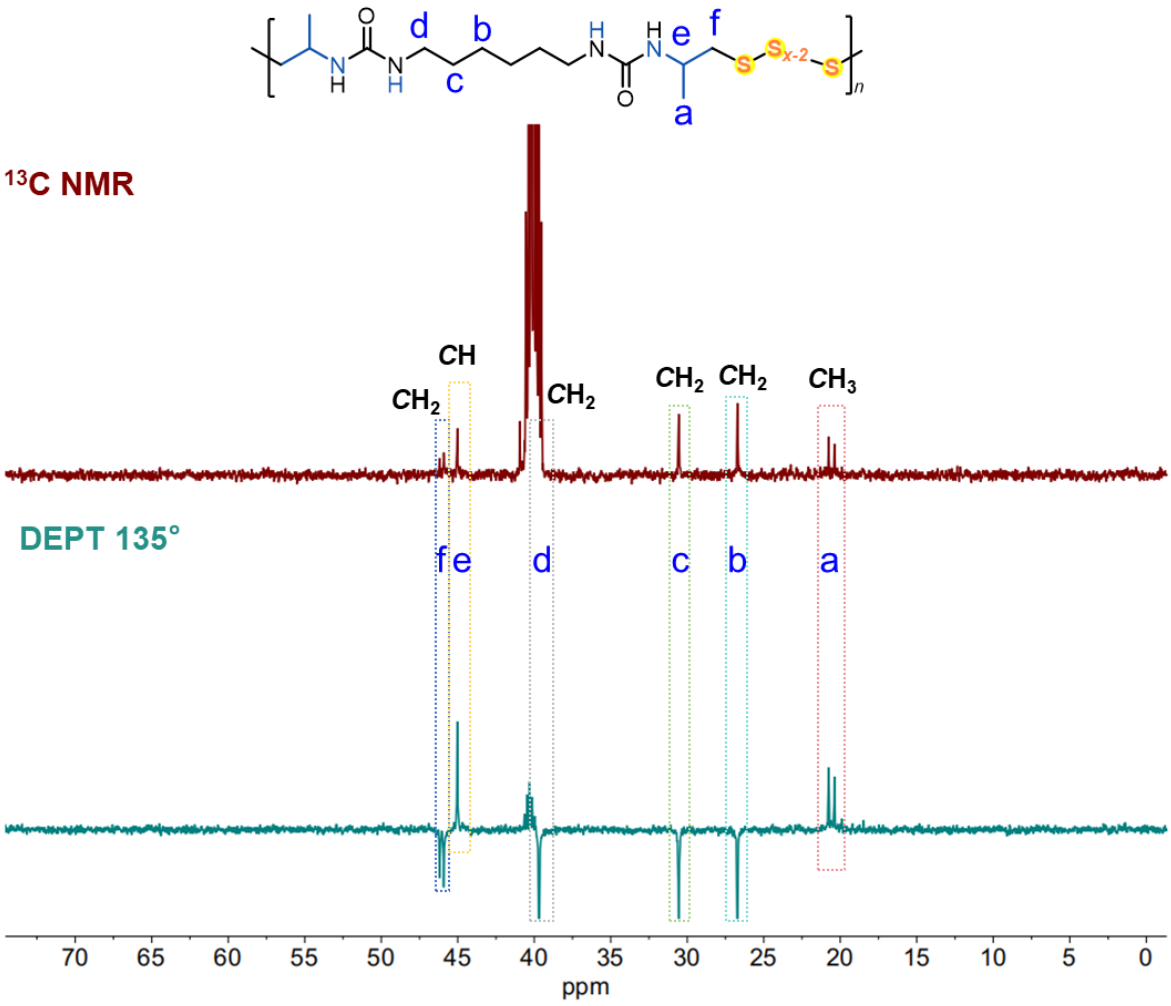


Fig. S2. ^{13}C NMR (DMSO-d_6) and DEPT 135° spectra of **PUA1-S$_x$**.

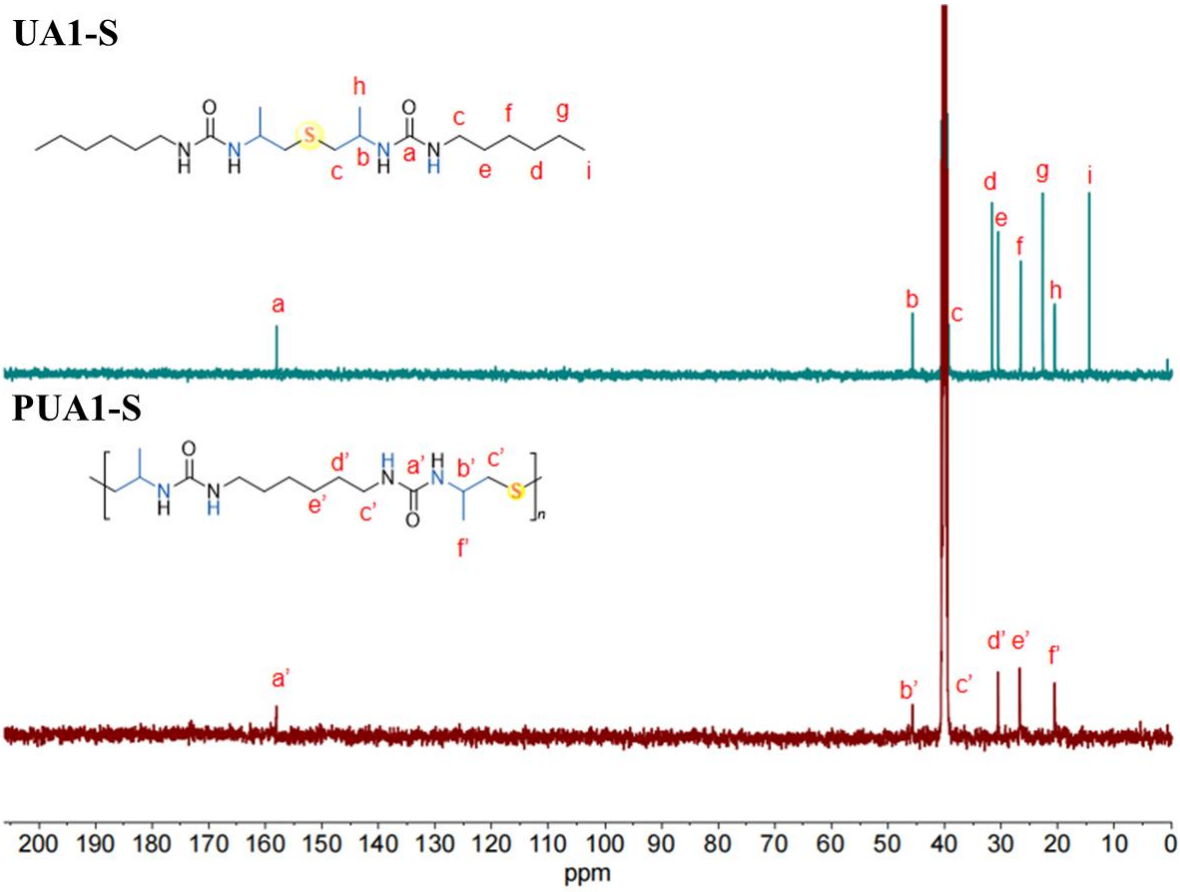


Fig. S3. ^{13}C NMR (DMSO-d_6) spectra of **UA1-S** and **PUA1-S**.

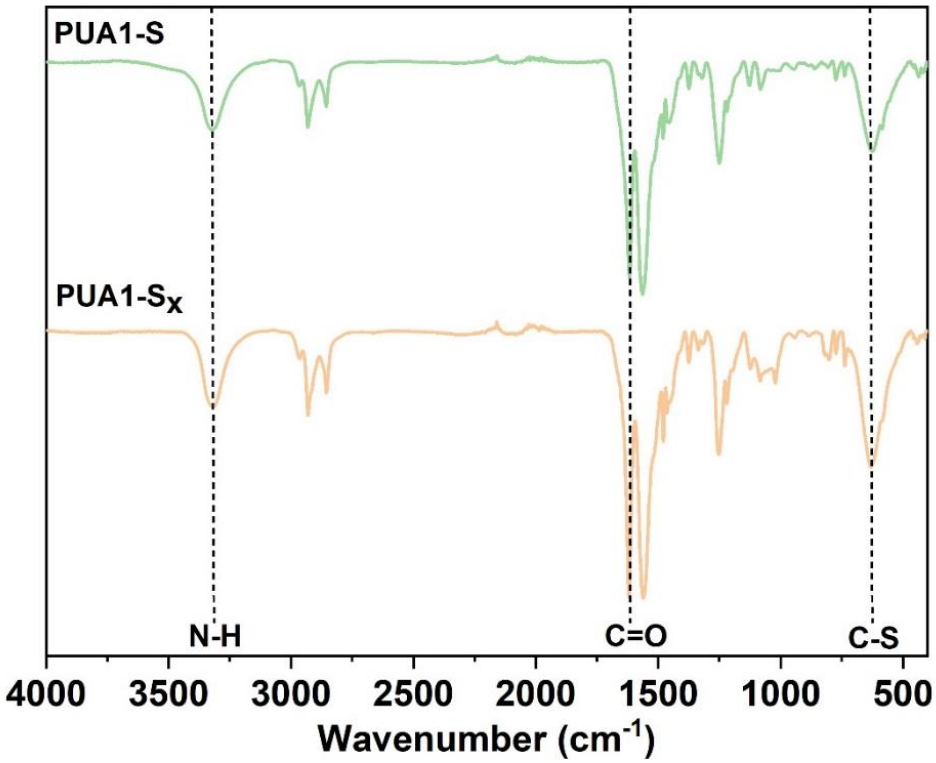


Fig. S4. FT-IR spectra of **PUA1-S$_x$** and **PUA1-S**.

Table S4. Organic element analysis (OEA) of **PUA-S$_x$**.

polymer	feeding ratio (wt%)				test result 1st (wt%)				test result 2nd (wt%)			
	C	N	H	S	C	N	H	S	C	N	H	S
PUA1-S$_x$	49.7	15.5	8.4	17.7	47.5	14.9	7.5	19.6	47.4	15.1	6.7	19.2
PUA2-S$_x$	53.7	13.9	8.5	15.9	49.4	12.3	7.5	15.9	49.3	12.6	7.9	16.5
PUA3-S$_x$	50.8	15.8	6.3	18.1	48.9	14.5	6.8	17.1	48.9	14.7	6.8	17.6
PUA4-S$_x$	52.2	15.2	6.6	17.4	49.5	13.5	6.1	18.9	49.4	13.4	6.1	18.8
PUA5-S$_x$	58.6	13.0	6.1	14.9	58.9	12.0	6.4	16.3	56.8	11.9	6.6	16.5
PUA6-S$_x$	56.0	13.1	8.5	15.0	57.8	10.5	7.7	16.5	57.3	10.5	8.2	16.8
PUA7-S$_x$	62.4	11.2	7.3	12.8	63.2	8.7	6.1	14.6	63.3	8.8	6.2	14.7

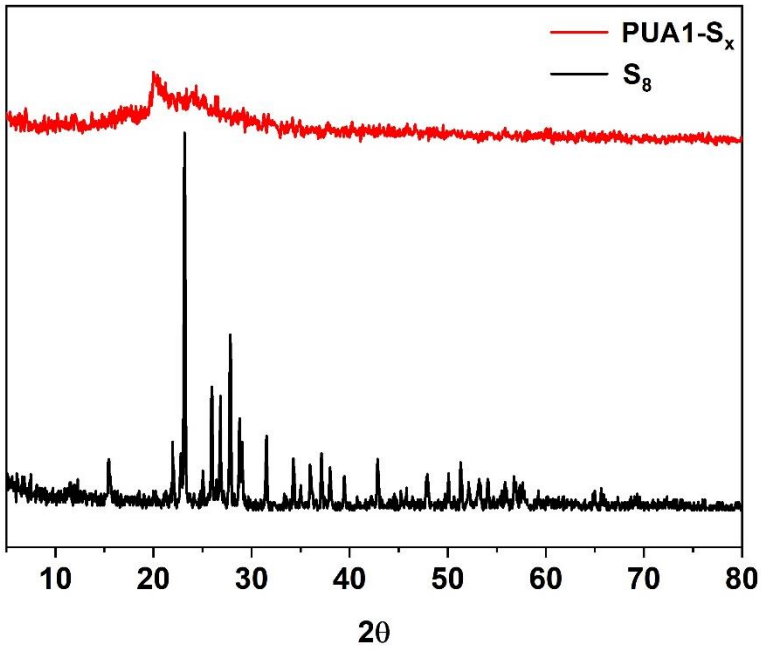


Fig. S5. XRD curves of **PUA1-S$_x$** and **S$_8$**.

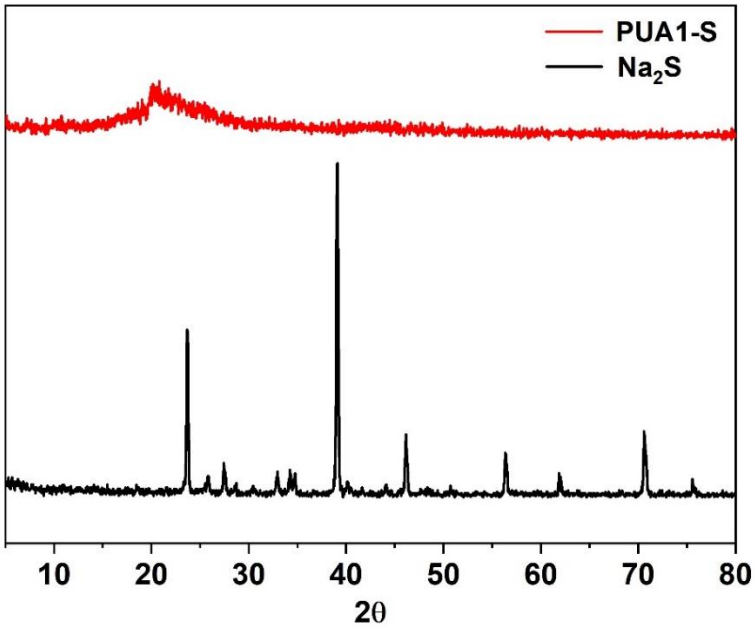


Fig. S6. XRD curves of **PUA1-S** and **Na$_2$S**.

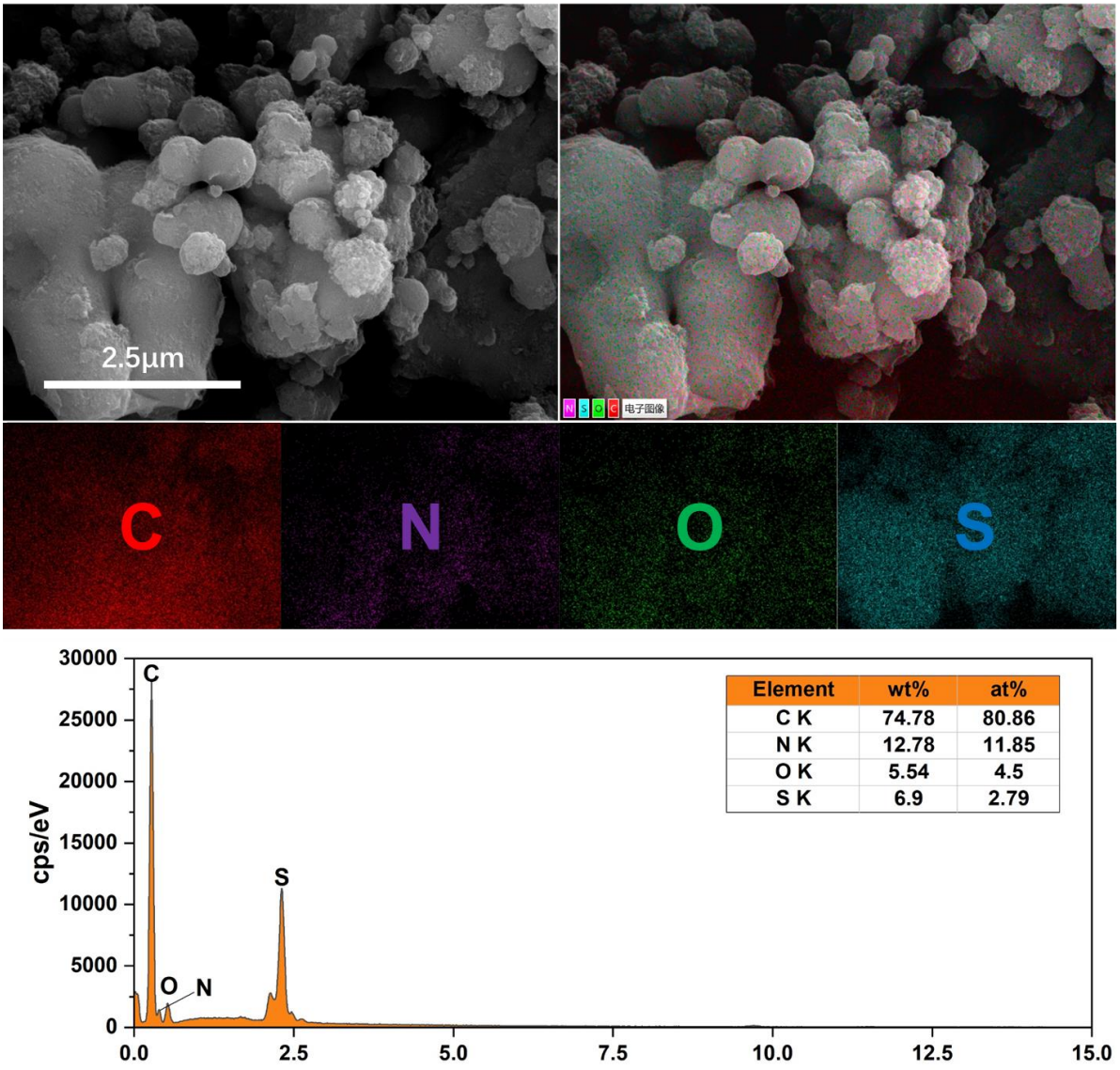


Fig. S7. SEM-EDS analysis and mapping images of **PUA5-S$_x$**.

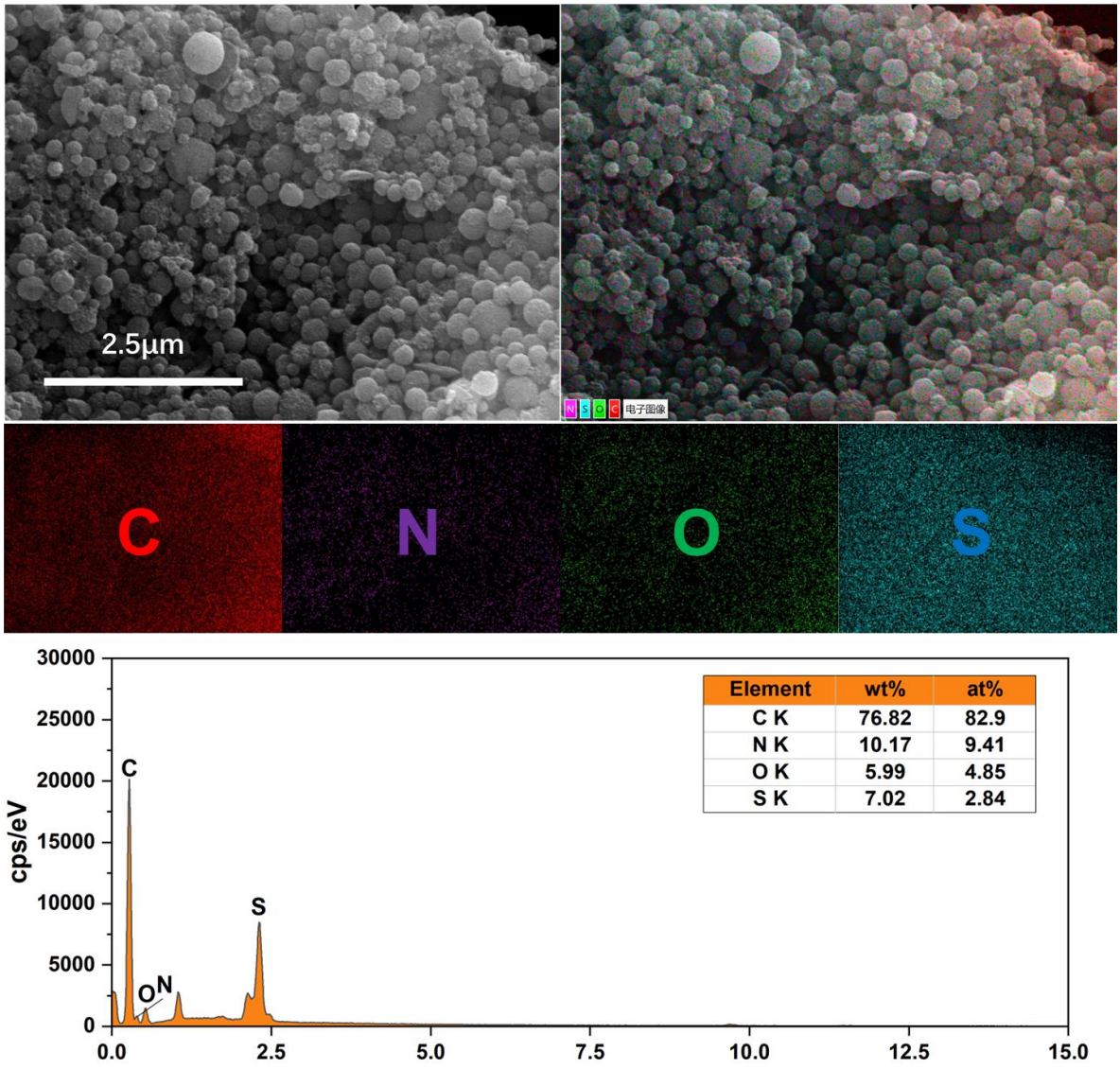


Fig. S8. SEM-EDS analysis and mapping images of P**UA5-S**.

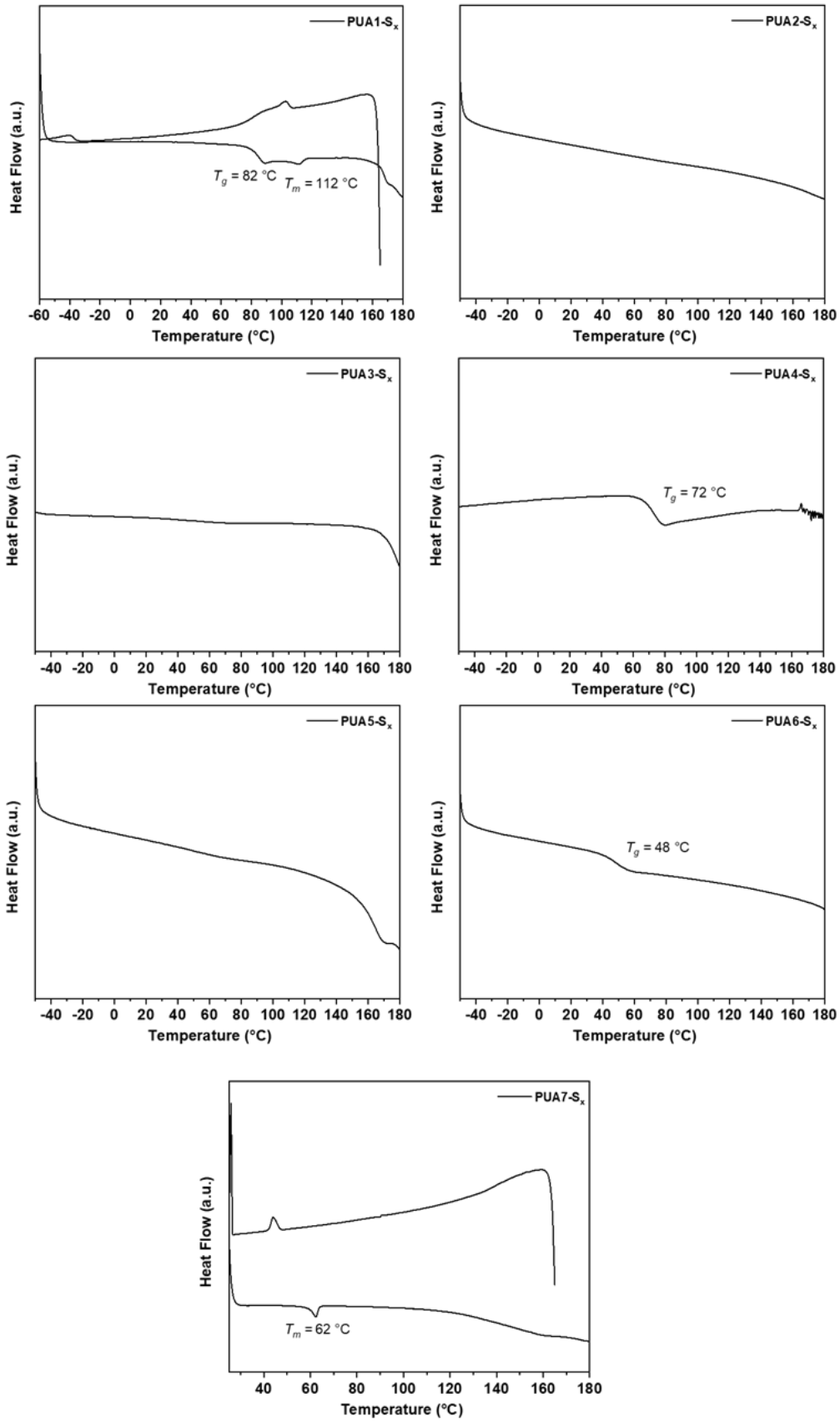


Fig. S9. DSC curves of **PUA1-S$_x$** to **PUA7-S$_x$**.

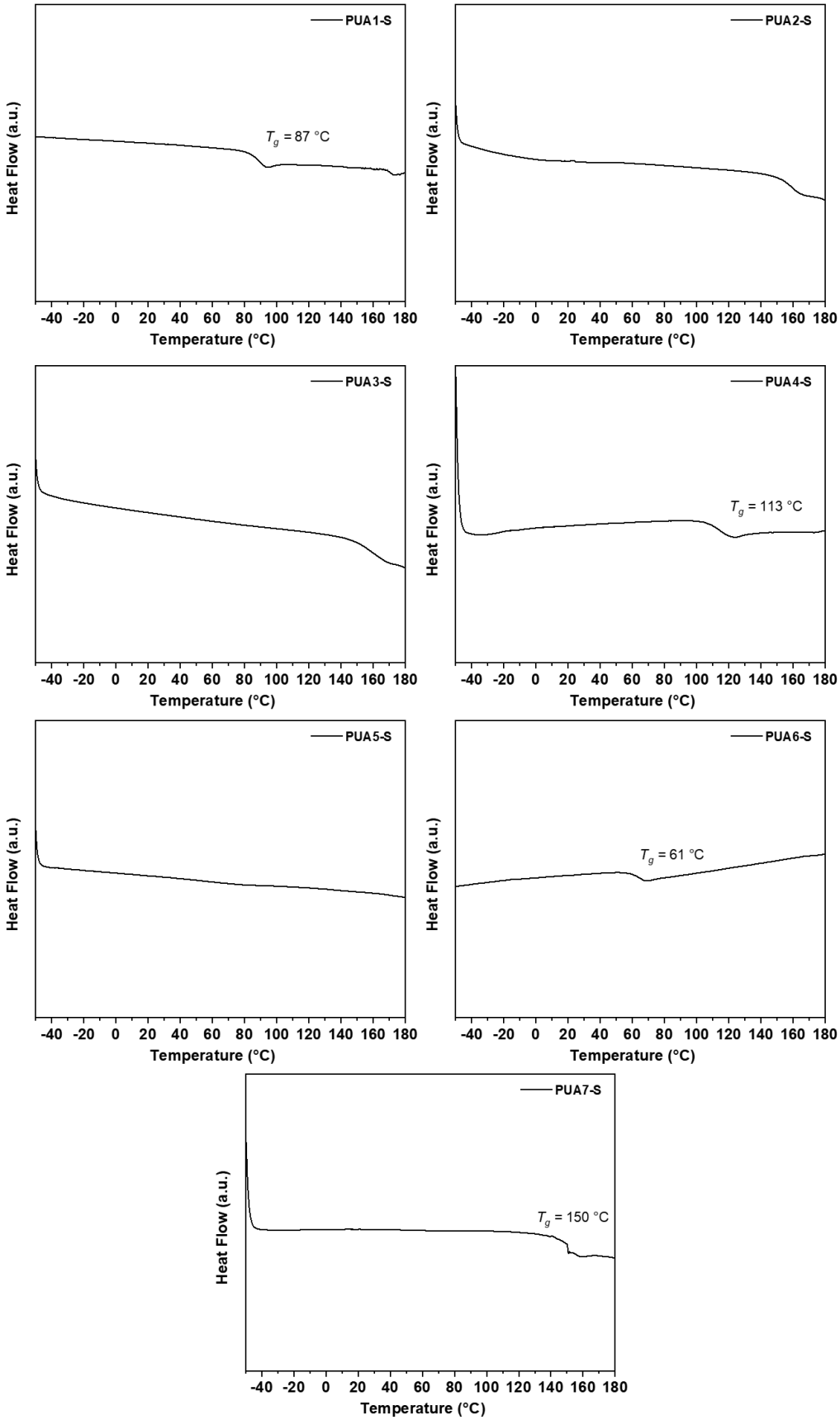


Fig. S10. DSC curves (2[ed] run (heating), 10 °C/min) of **PUA1-S** to **PUA7-S**.

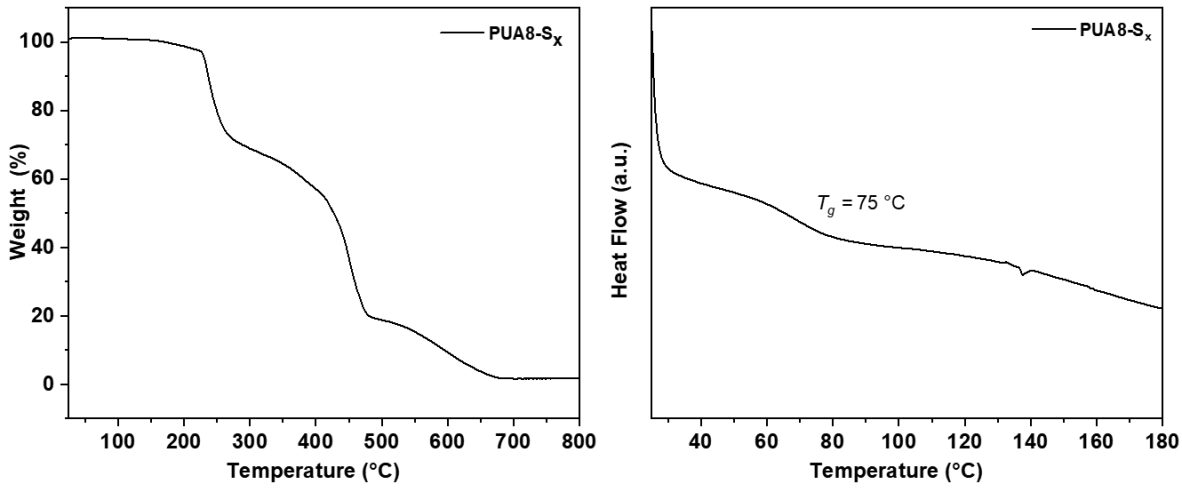


Fig. S11. TG and DSC curves of cross-linked **PUA8-S$_x$**.

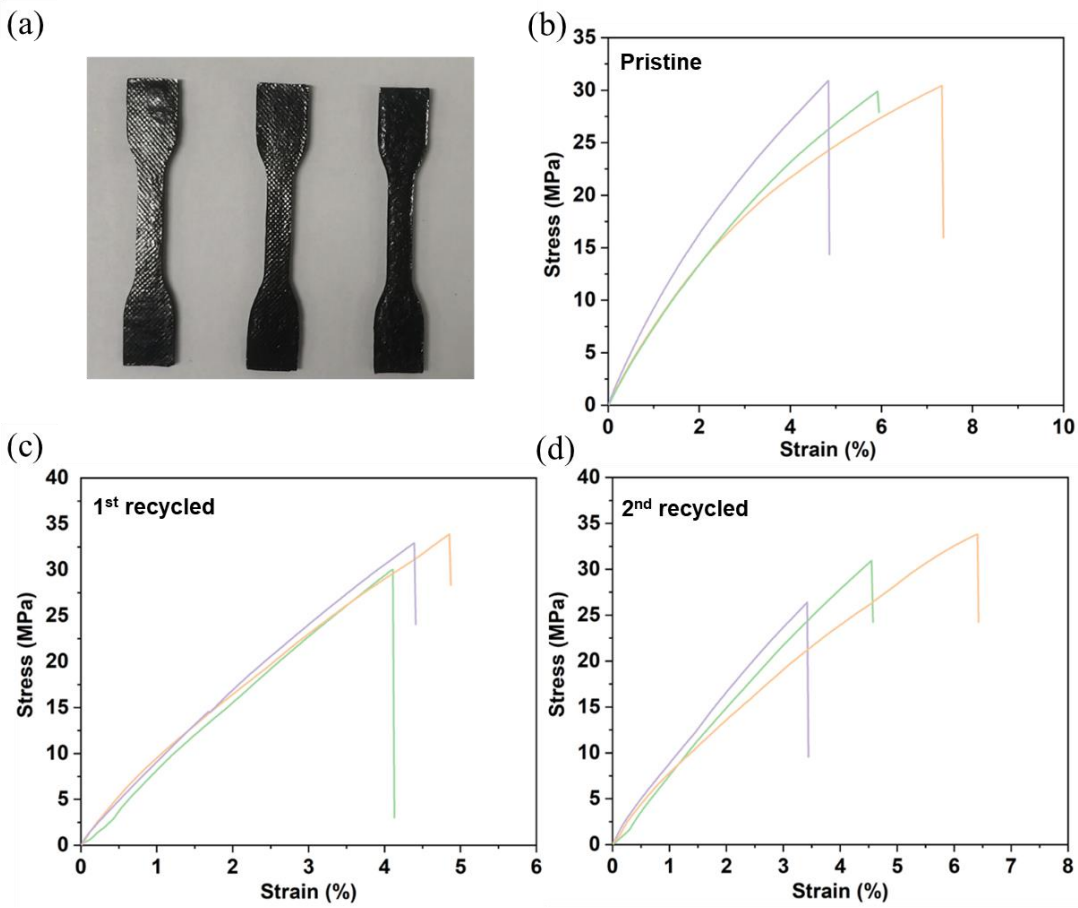


Fig. S12. (a) Photos of the dog-bone-shaped vitrimer samples. Stress-strain curves of (b) pristine, (c) first-recycled, and (d) second-recycled **PUA8-S$_x$**.

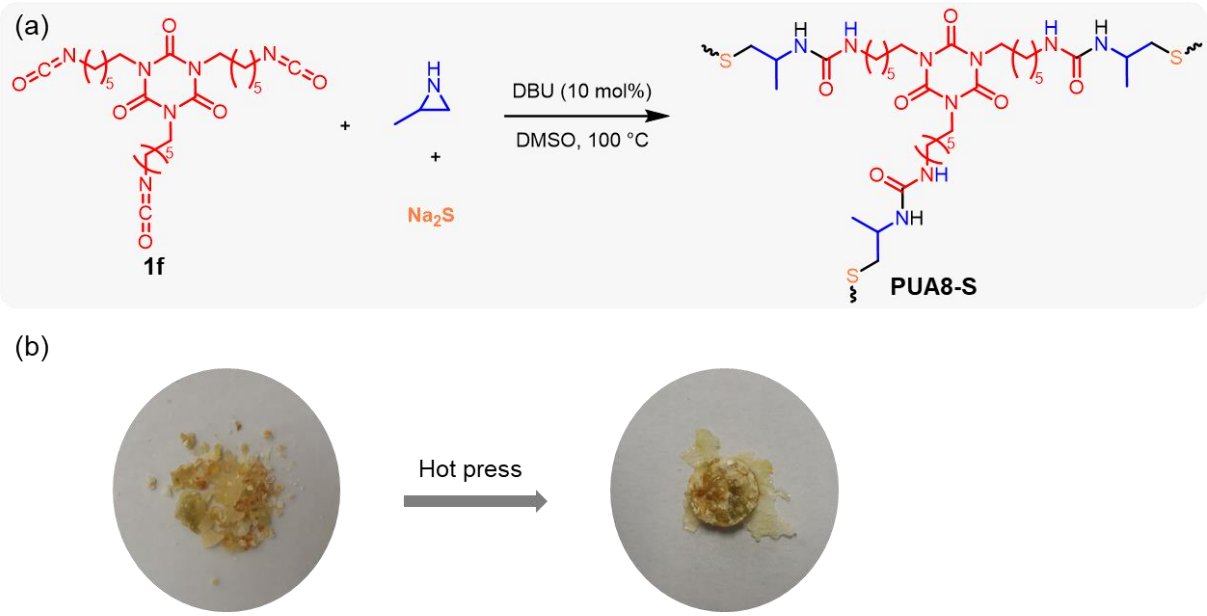
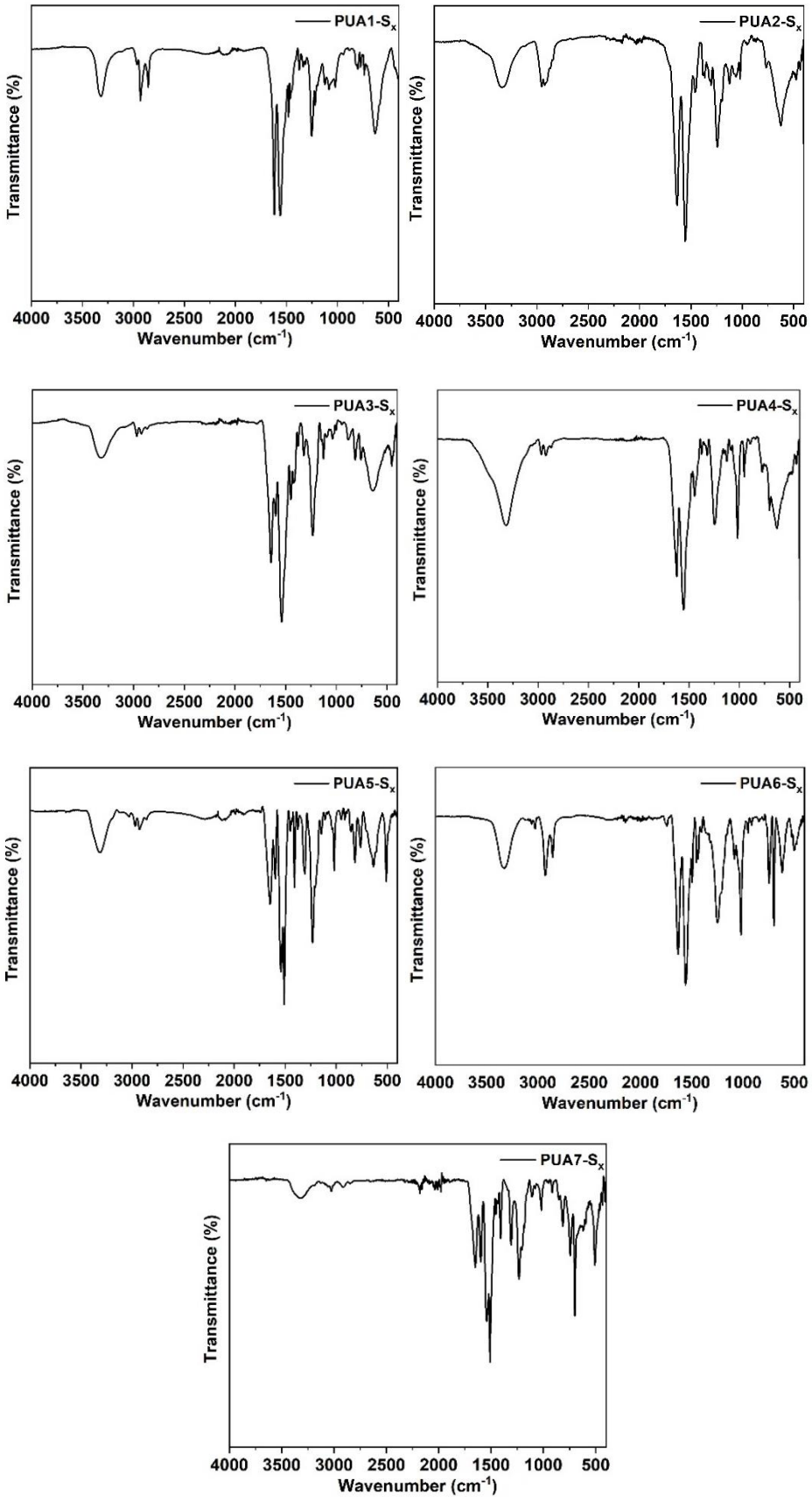
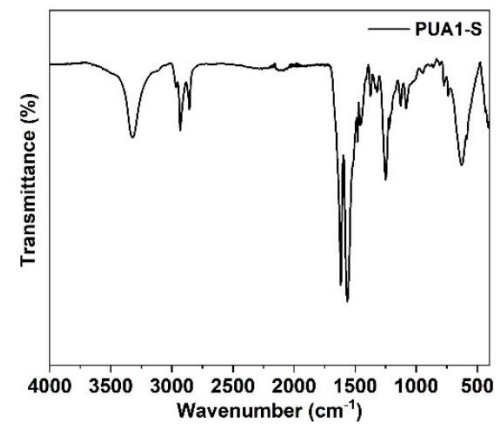
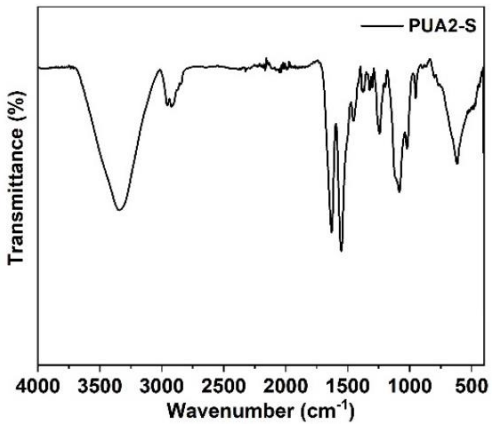


Fig. S13. (a) Synthesis of polyurea vitrimer **PUA8-S**. (b) Failure of reprocessing for **PUA8-S**.

4. Spectroscopic FT-IR and NMR Data




PUA1-S
Transmittance (%)
4000 3500 3000 2500 2000 1500 1000 500
Wavenumber (cm-1)


PUA2-S
Transmittance (%)
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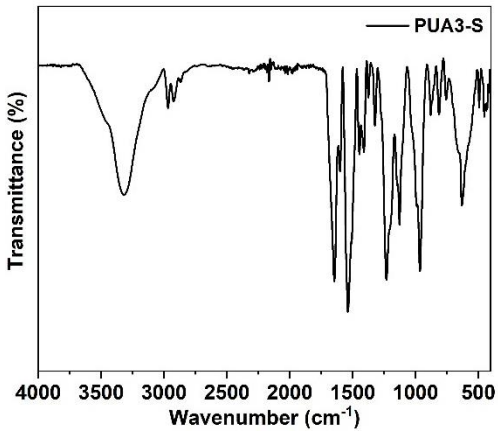
Wavenumber (cm-1)


PUA3-S
Transmittance (%)
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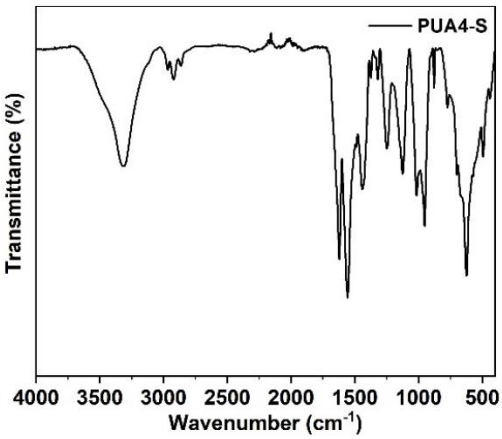
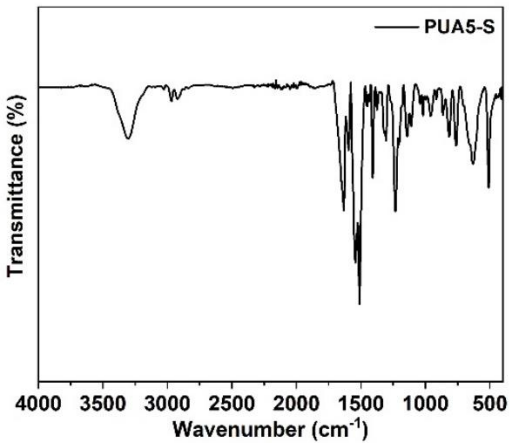
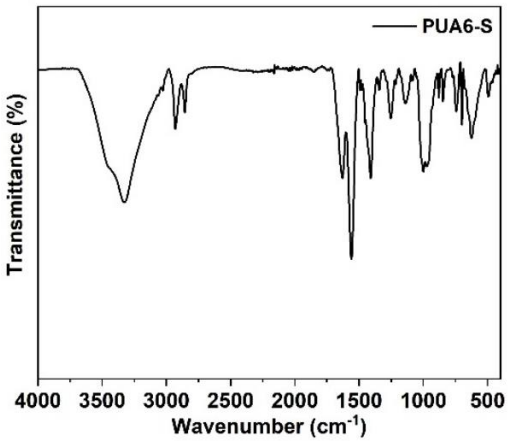
Wavenumber (cm-1)


PUA4-S
Transmittance (%)
4000 3500 3000 2500 2000 1500 1000 500
Wavenumber (cm-1)


PUA5-S
Transmittance (%)
4000 3500 3000 2500 2000 1500 1000 500
Wavenumber (cm-1)


PUA6-S
Transmittance (%)
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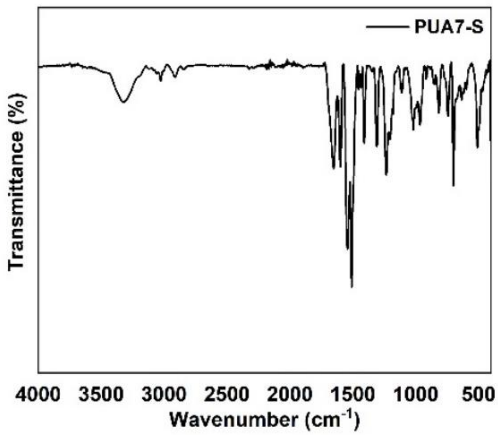
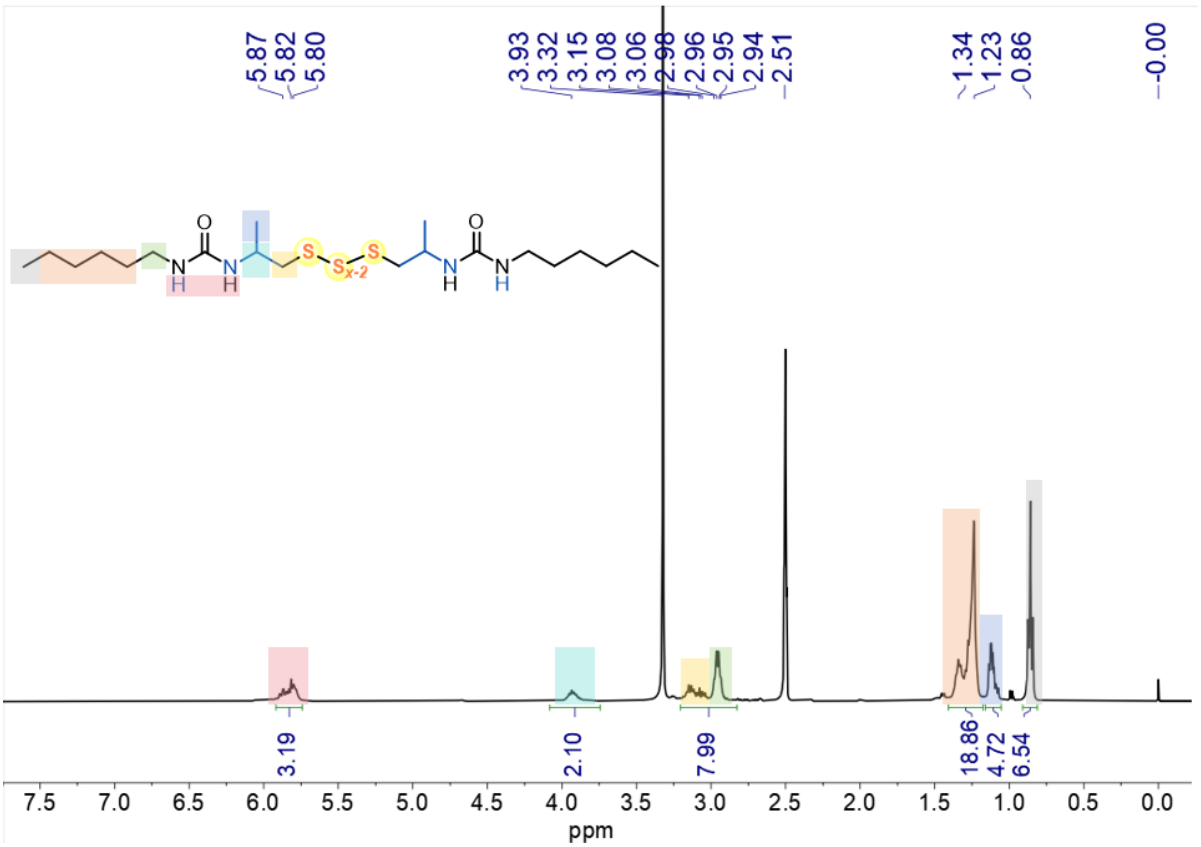
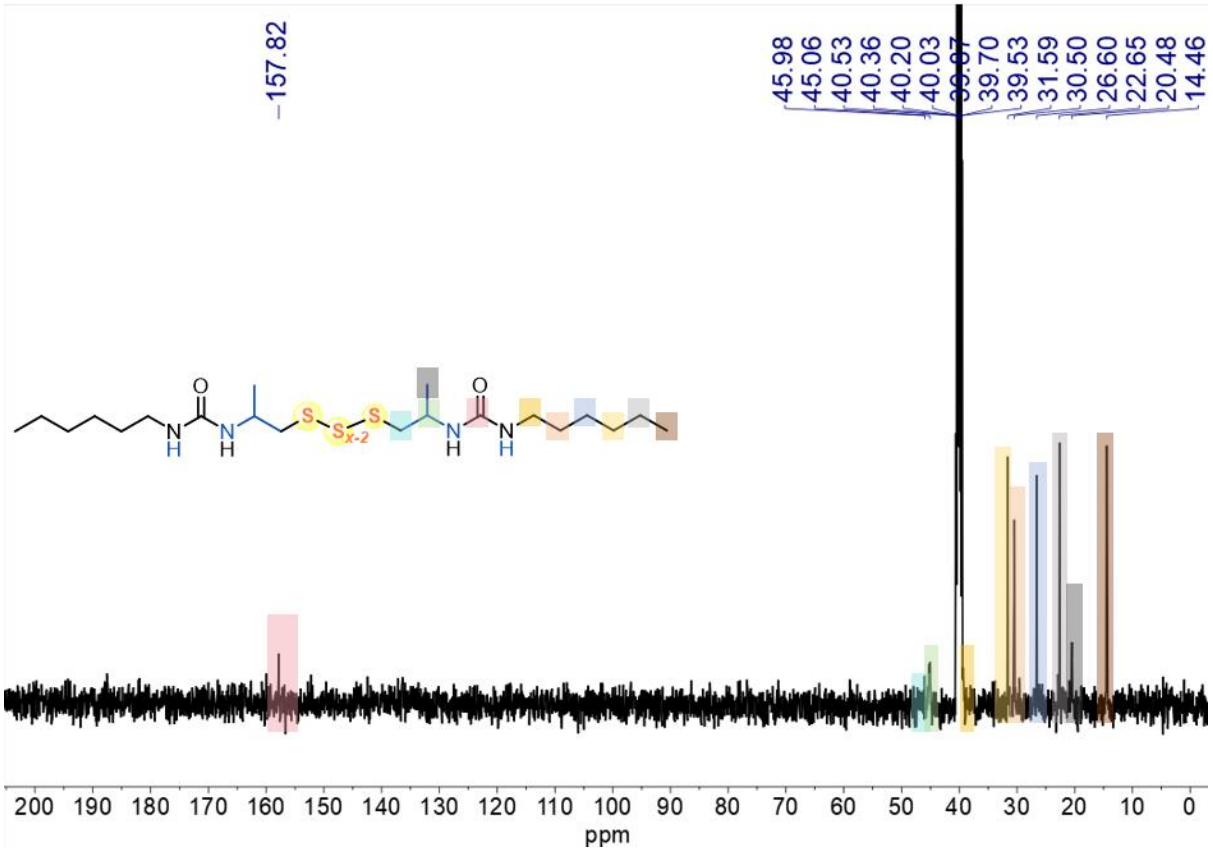
Wavenumber (cm-1)


PUA7-S
Transmittance (%)
4000 3500 3000 2500 2000 1500 1000 500
Wavenumber (cm-1)


5.87
5.82
5.80
3.93
3.32
3.15
3.08
3.06
2.98
2.96
2.95
2.94
2.51
1.34
1.23
0.86
-0.00
3.19
2.10
7.99
18.86
4.72
6.54
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm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45.98
45.06
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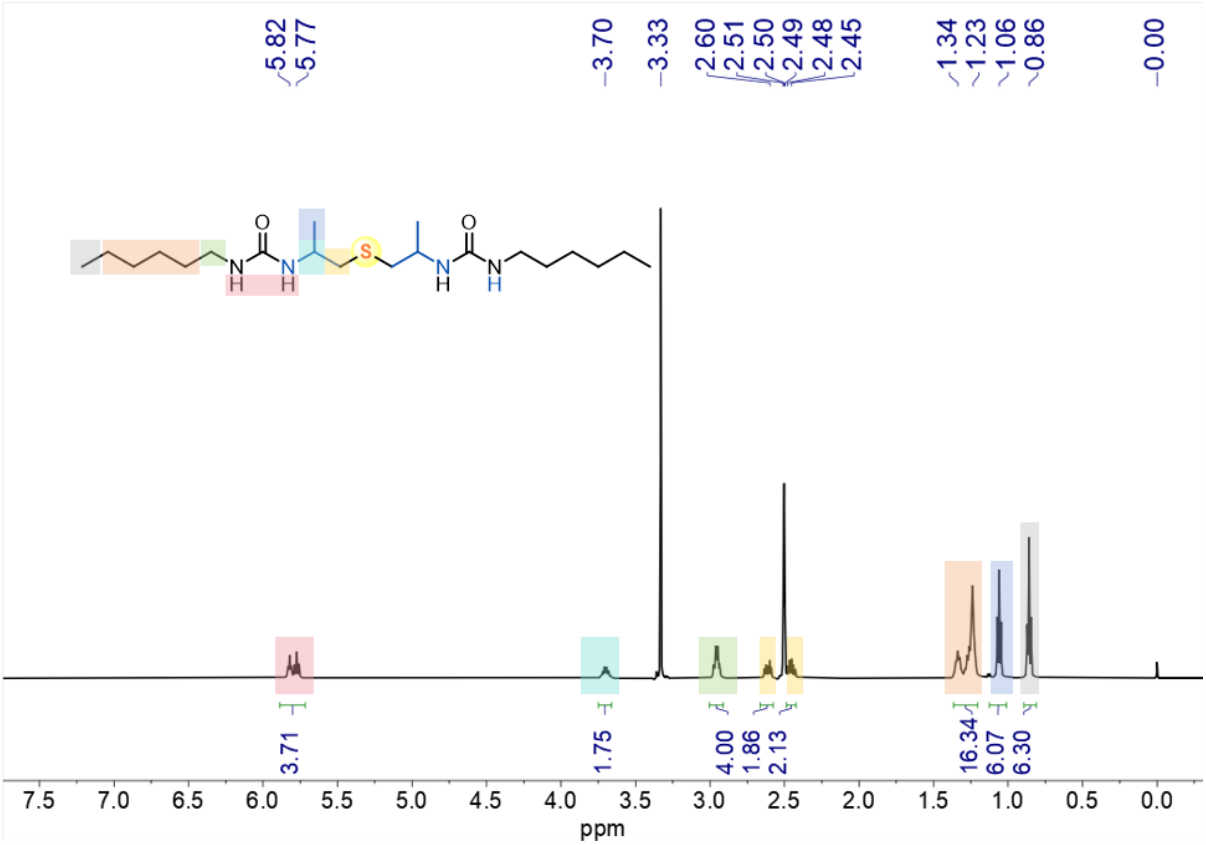
40.36
40.20
40.03
39.70
39.53
31.59
30.50
26.60
22.65
20.48
14.46
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


5.82
5.77
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3.33
2.60
2.51
2.50
2.49
2.48
2.45
1.34
1.23
1.06
0.86
0.00
3.71
1.75
4.00
1.86
2.13
16.34
6.07
6.30
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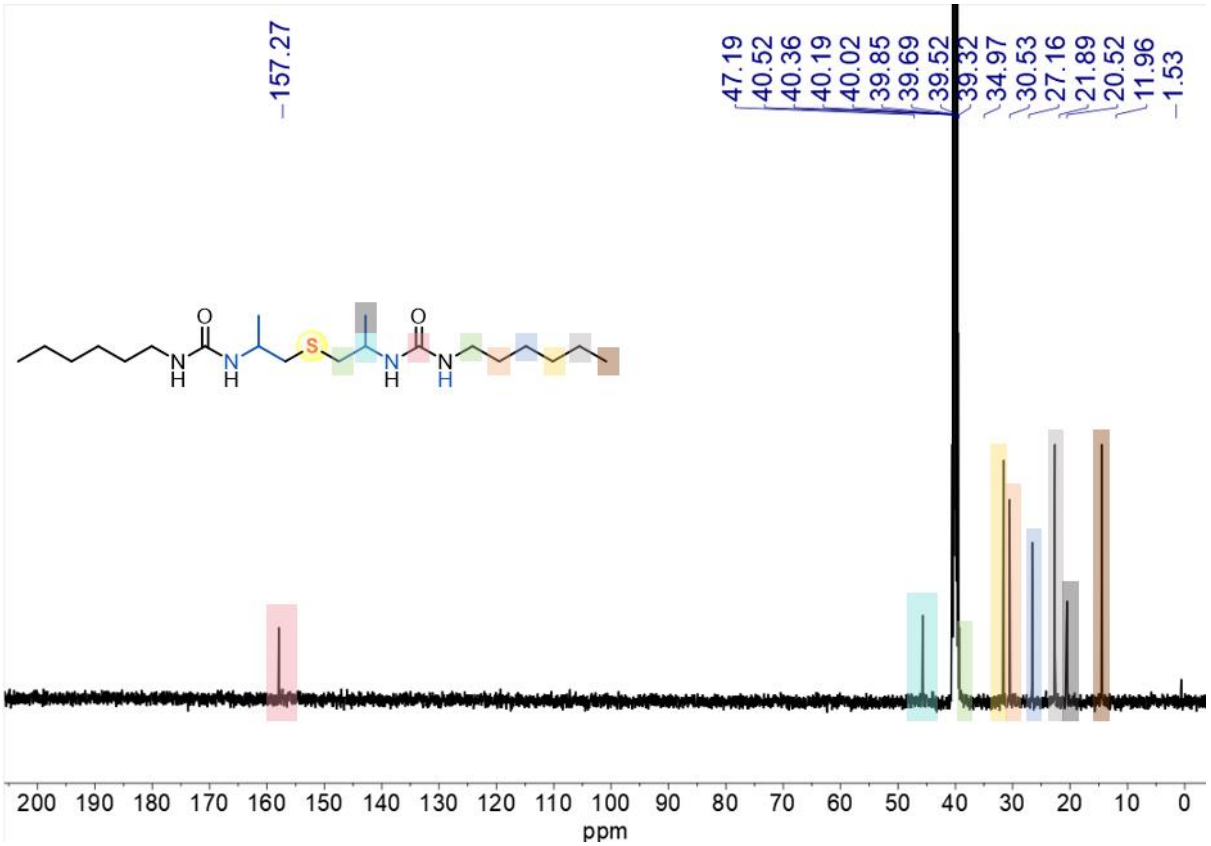
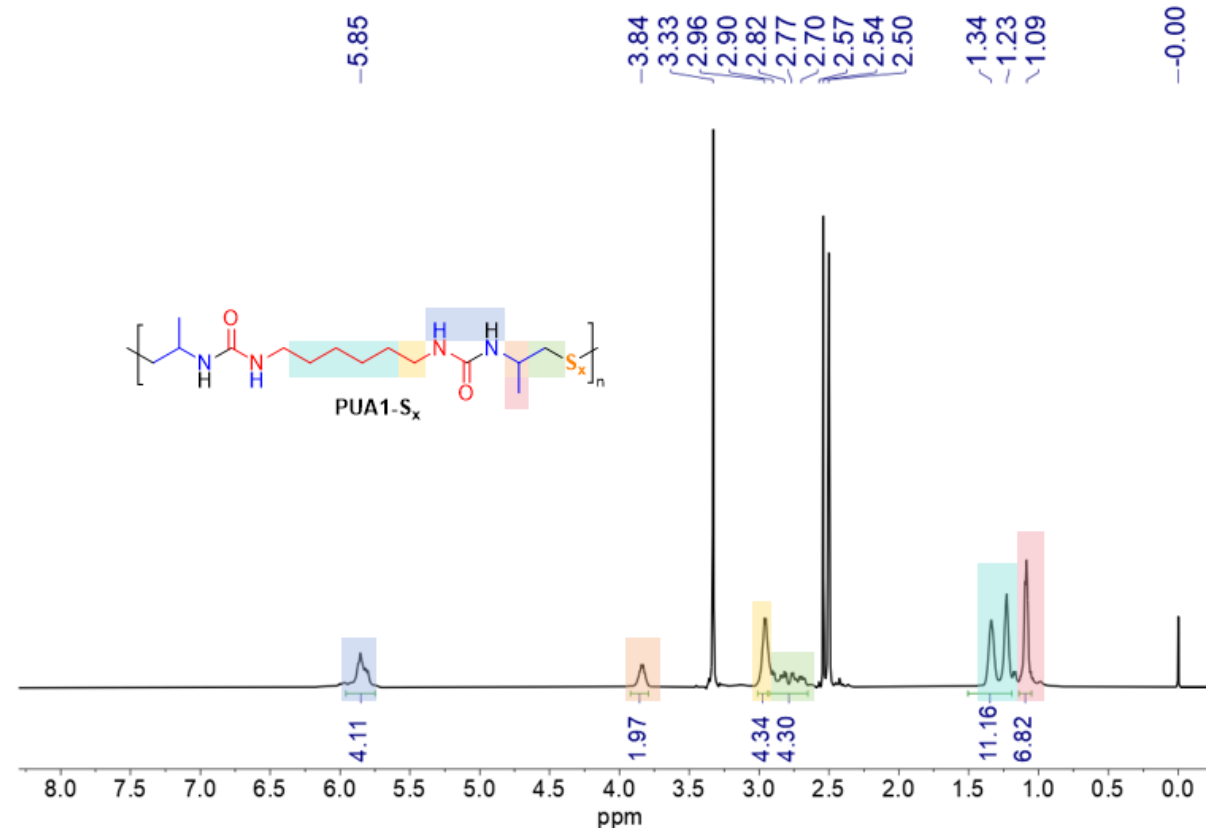
ppm


157.27
47.19
40.52
40.36
40.19
40.02
39.85
39.69
39.52
39.32
34.97
30.53
27.16
21.89
20.52
11.96
1.53
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm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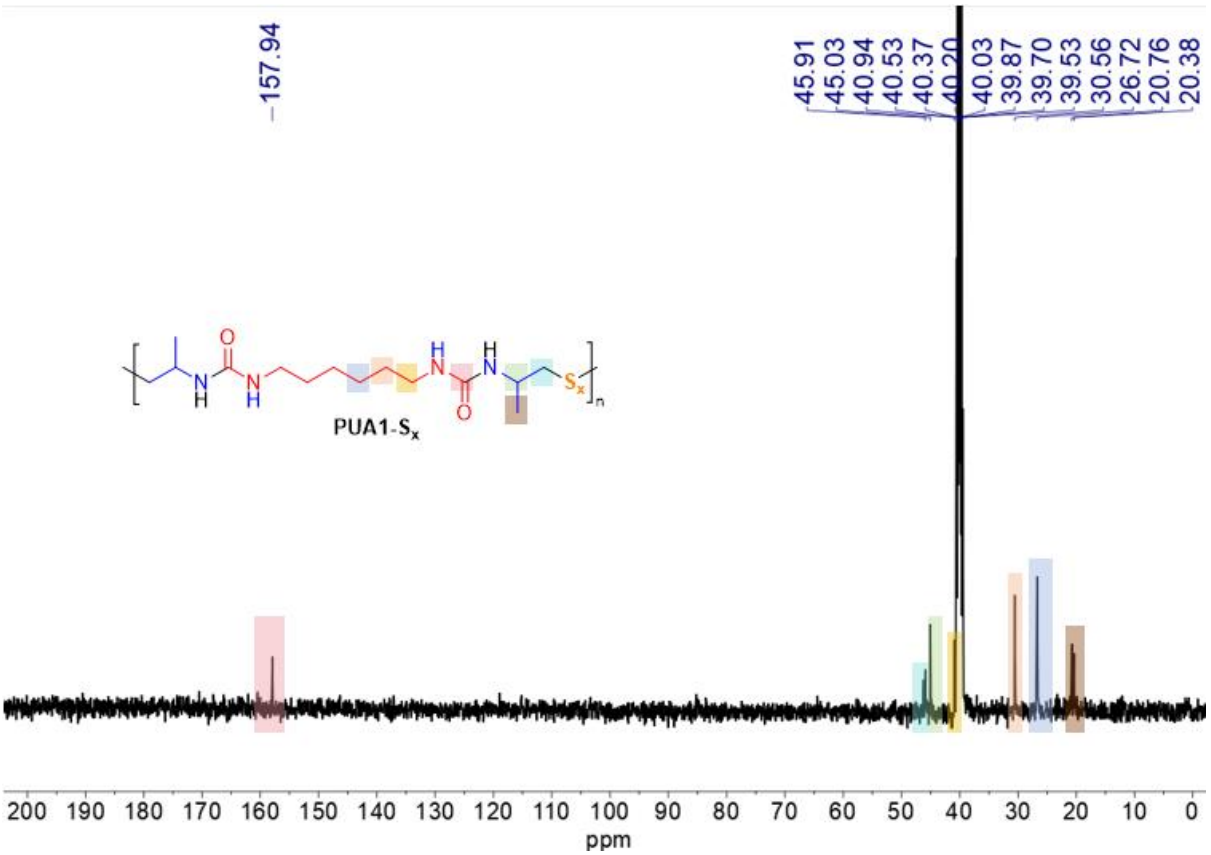
3.84
3.33
2.96
2.90
2.82
2.77
2.70
2.57
2.54
2.50
1.34
1.23
1.09
0.00
PUA1-Sx
4.11
1.97
4.34
4.30
11.16
6.82
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm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45.91
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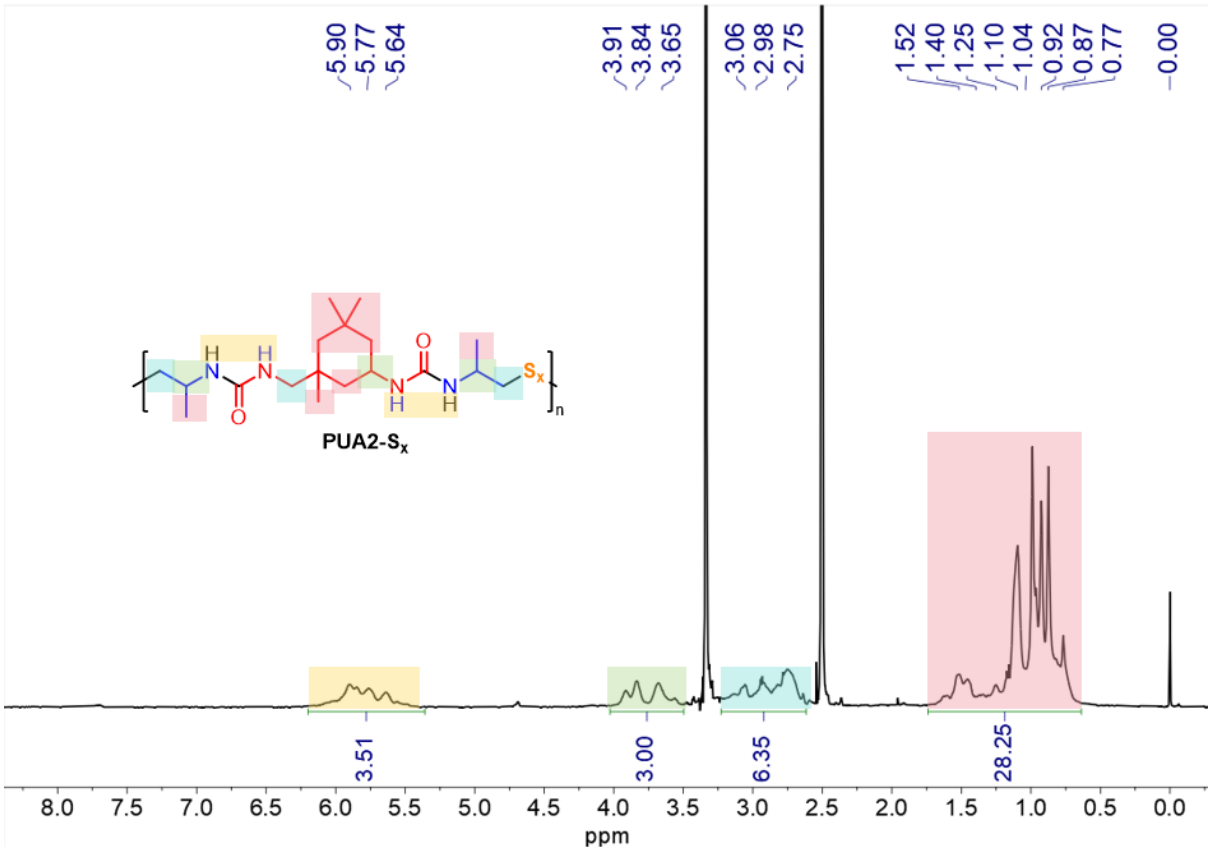
40.94
40.53
40.37
40.20
40.03
39.87
39.70
39.53
30.56
26.72
20.76
20.38
PUA1-Sx
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm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5.77
5.64
3.91
3.84
3.65
3.06
2.98
2.75
1.52
1.40
1.25
1.10
1.04
0.92
0.87
0.77
0.00
PUA2-Sx
3.51
3.00
6.35
28.25
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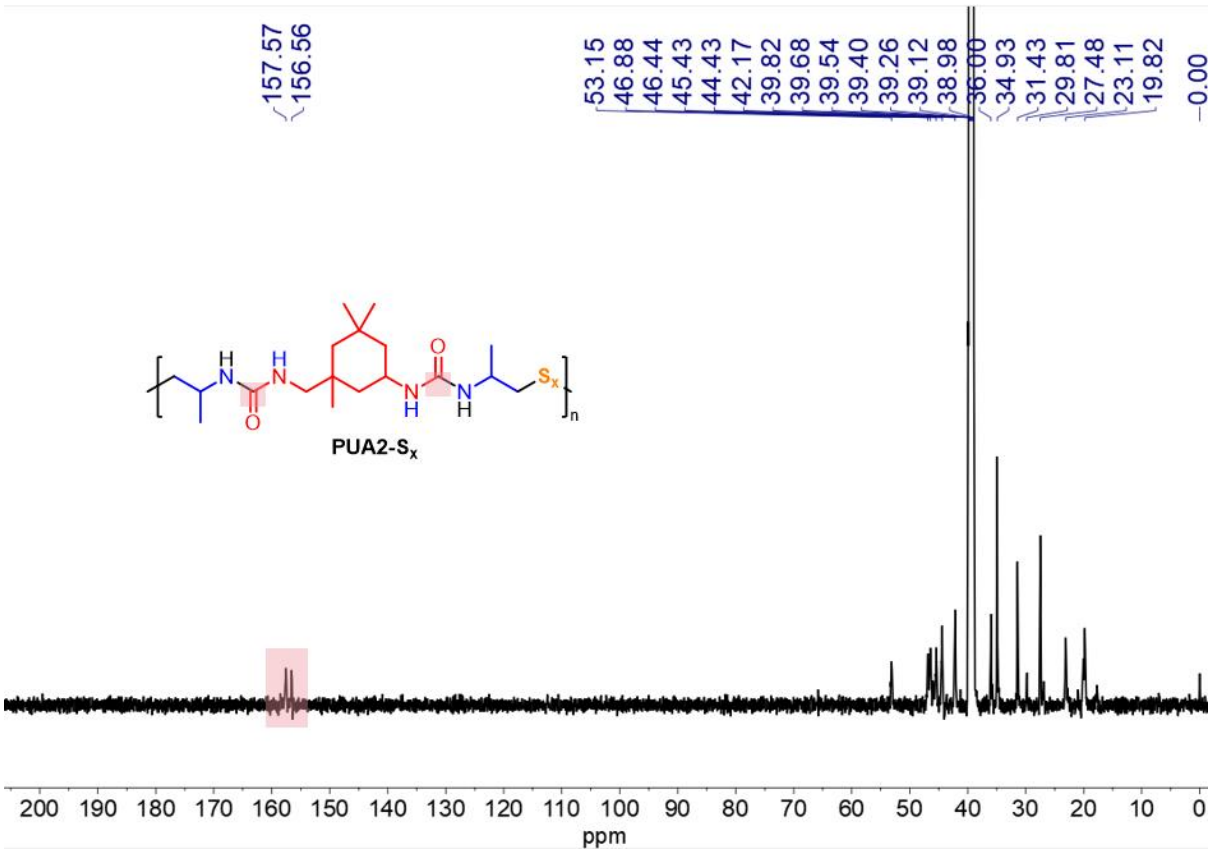
ppm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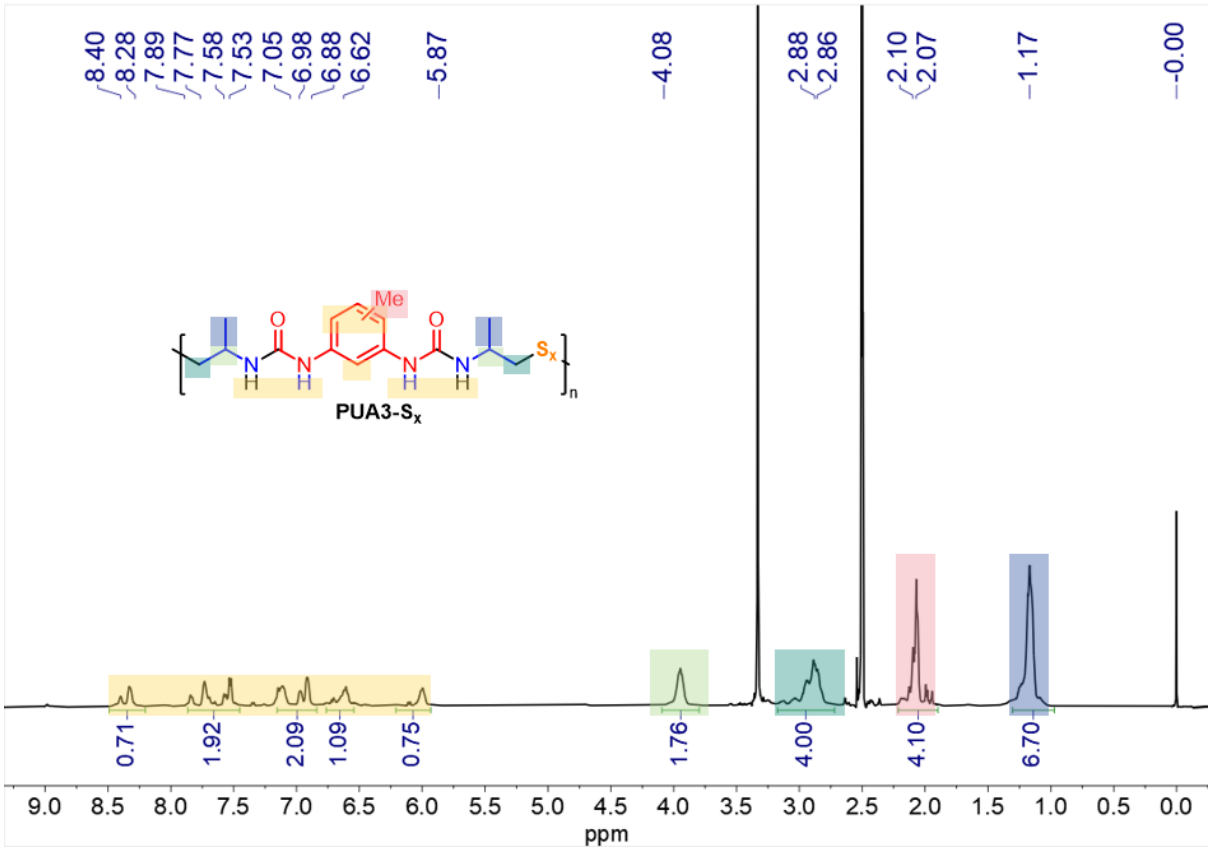
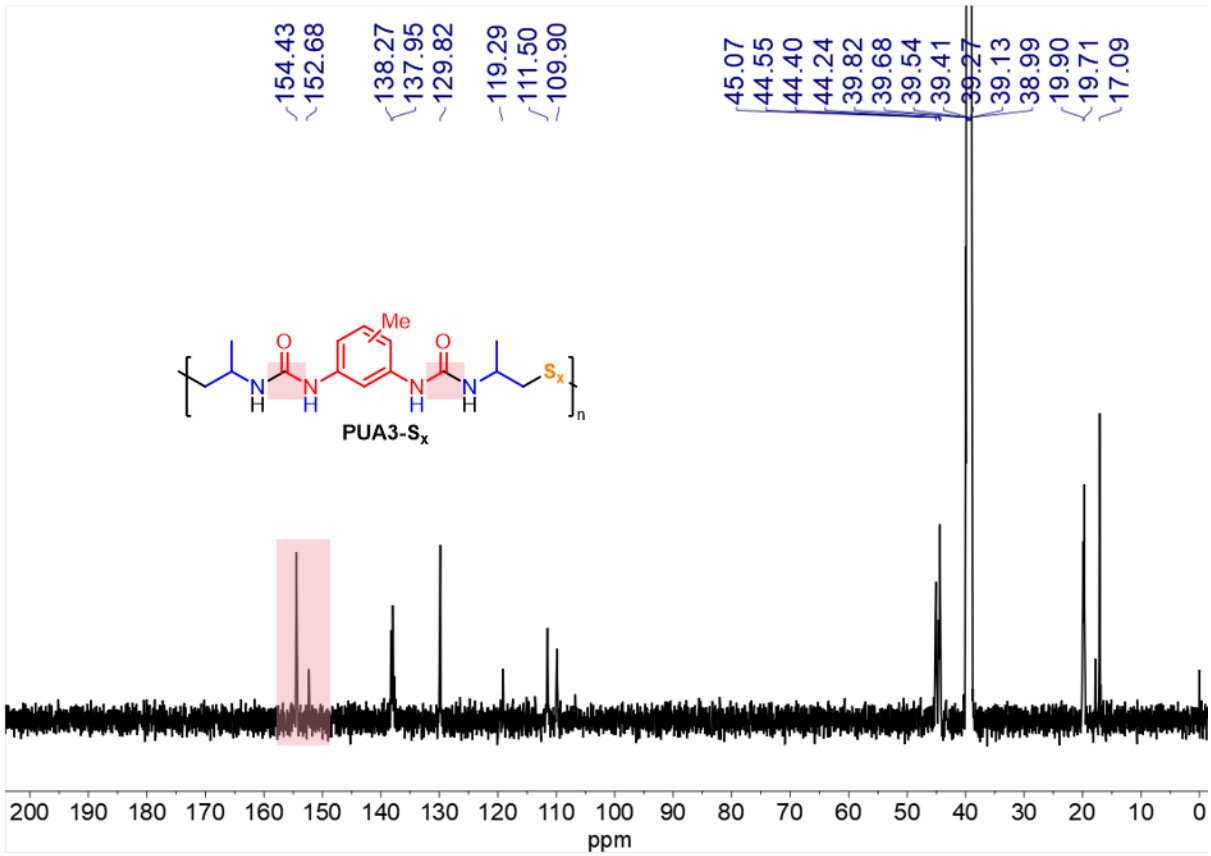
156.56
53.15
46.88
46.44
45.43
44.43
42.17
39.82
39.68
39.54
39.40
39.26
39.12
38.98
36.00
34.93
31.43
29.81
27.48
23.11
19.82
0.00
PUA2-Sx
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


8.40
8.28
7.89
7.77
7.58
7.53
7.05
6.98
6.88
6.62
5.87
4.08
2.88
2.86
2.10
2.07
1.17
-0.00
Me
PUA3-Sx
0.71
1.92
2.09
1.09
0.75
1.76
4.00
4.10
6.70
ppm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152.68
138.27
137.95
129.82
119.29
111.50
109.90
45.07
44.55
44.40
44.24
39.82
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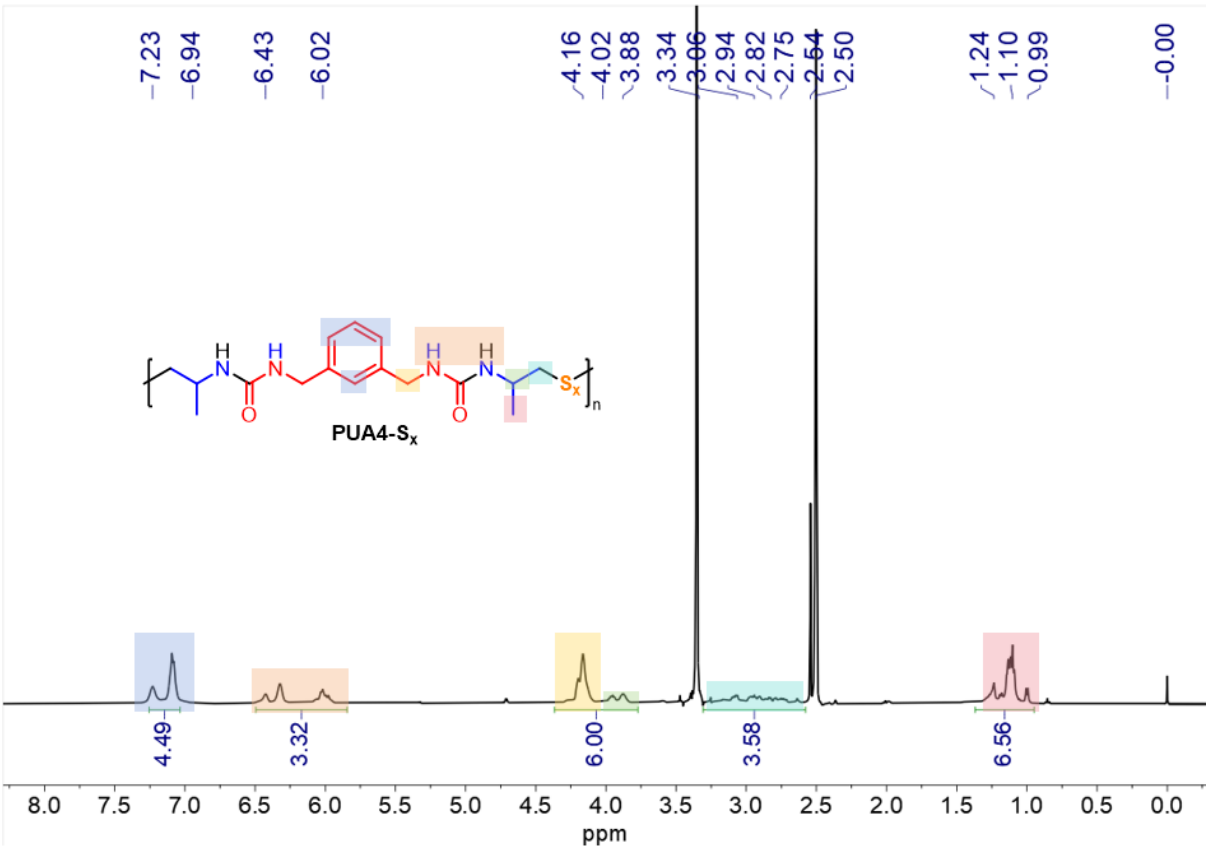
39.41
39.27
39.13
38.99
19.90
19.71
17.09
Me
PUA3-Sx
ppm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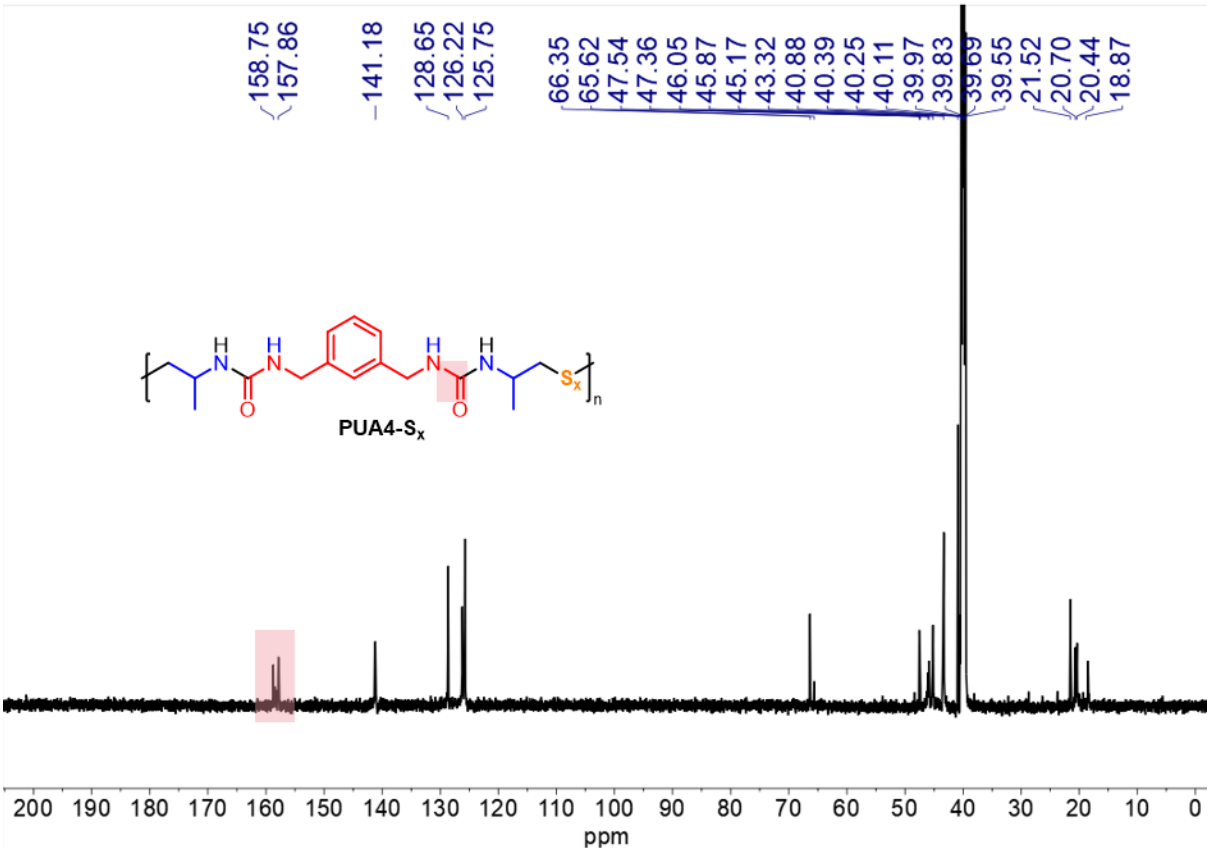
6.94
6.43
6.02
4.16
4.02
3.88
3.34
3.06
2.94
2.82
2.75
2.64
2.50
1.24
1.10
0.99
-0.00
PUA4-Sx
4.49
3.32
6.00
3.58
6.56
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm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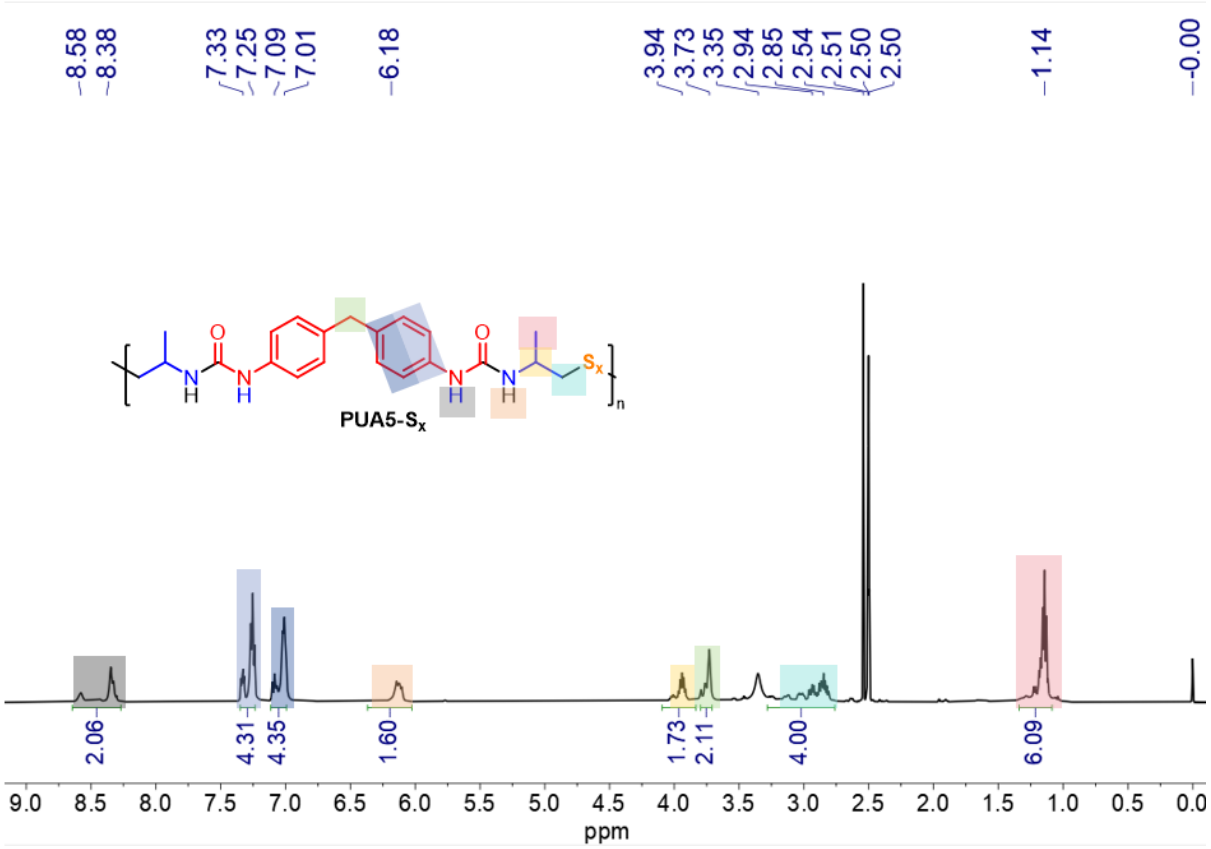
157.86
141.18
128.65
126.22
125.75
66.35
65.62
47.54
47.36
46.05
45.87
45.17
43.32
40.88
40.39
40.25
40.11
39.97
39.83
39.69
39.55
21.52
20.70
20.44
18.87
PUA4-Sx
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm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8.38
7.33
7.25
7.09
7.01
6.18
3.94
3.73
3.35
2.94
2.85
2.54
2.51
2.50
2.50
1.14
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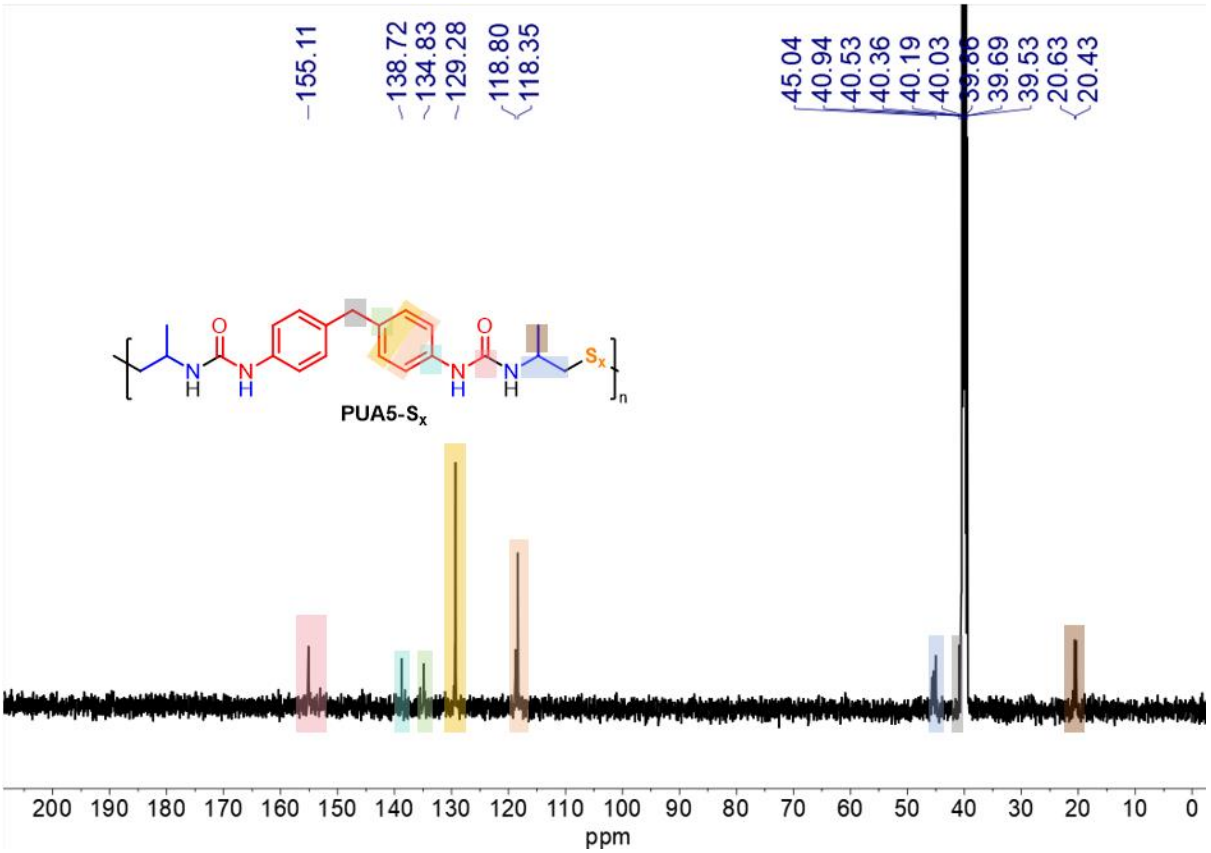
PUA5-Sx
2.06
4.31
4.35
1.60
1.73
2.11
4.00
6.09
ppm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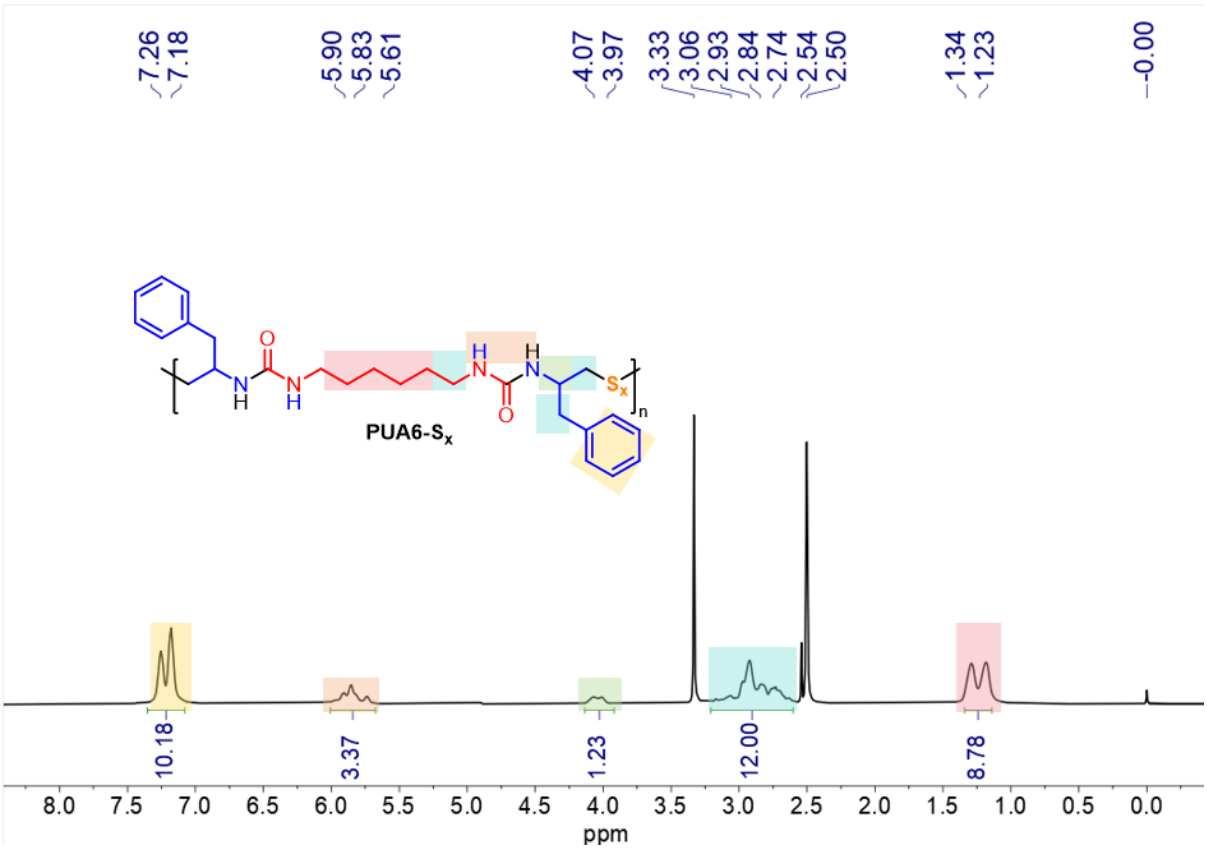
138.72
134.83
129.28
118.80
118.35
45.04
40.94
40.53
40.36
40.19
40.03
39.86
39.69
39.53
20.63
20.43
PUA5-Sx
ppm


7.26
7.18
5.90
5.83
5.61
4.07
3.97
3.33
3.06
2.93
2.84
2.74
2.54
2.50
1.34
1.23
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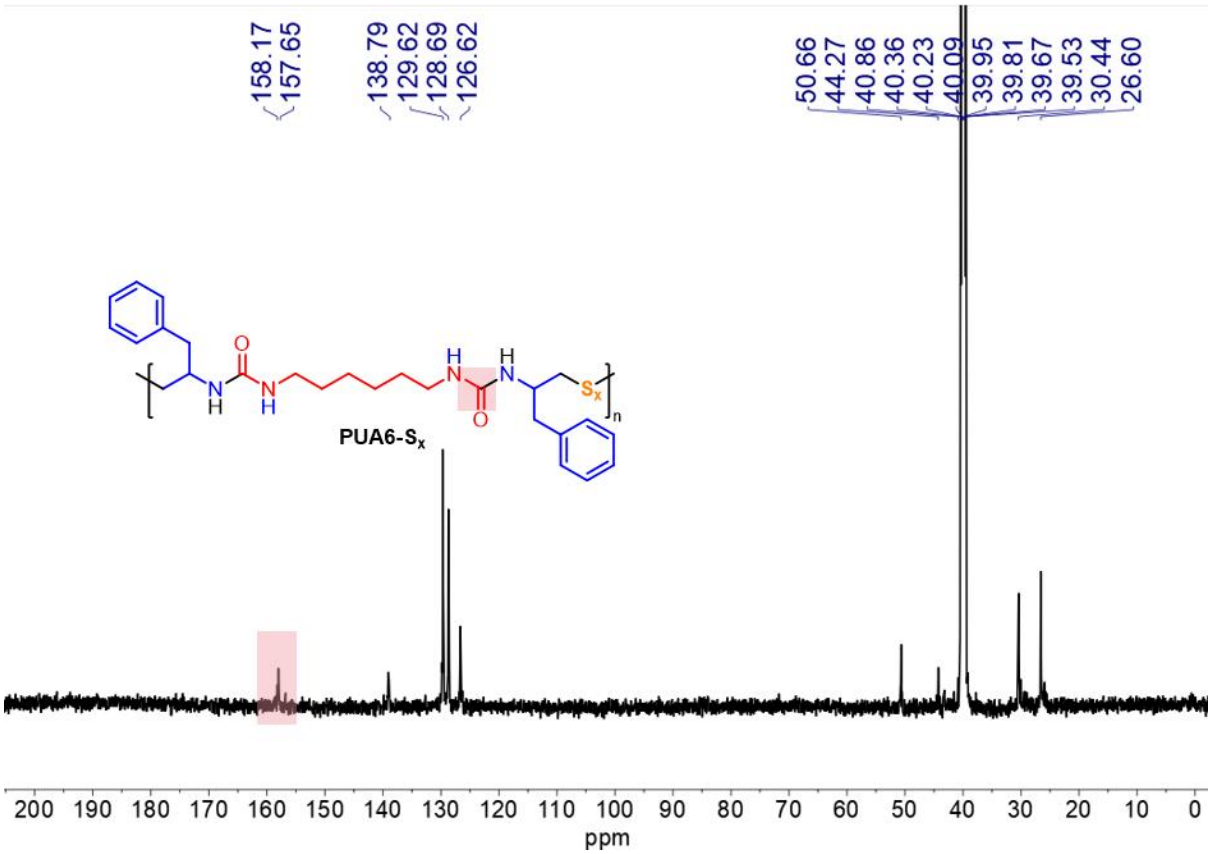
PUA6-Sx
10.18
3.37
1.23
12.00
8.78
ppm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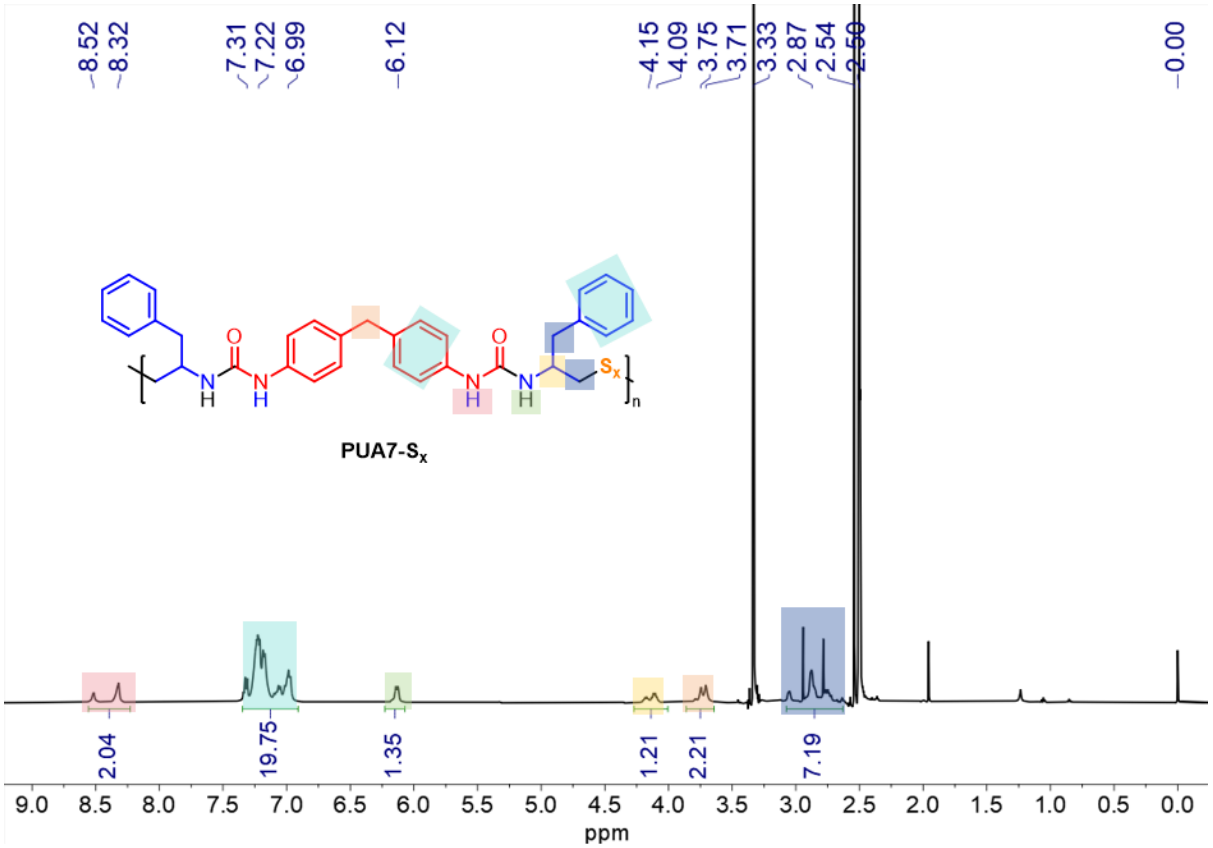
129.62
128.69
126.62
50.66
44.27
40.86
40.36
40.23
40.09
39.95
39.81
39.67
39.53
30.44
26.60
PUA6-Sx
ppm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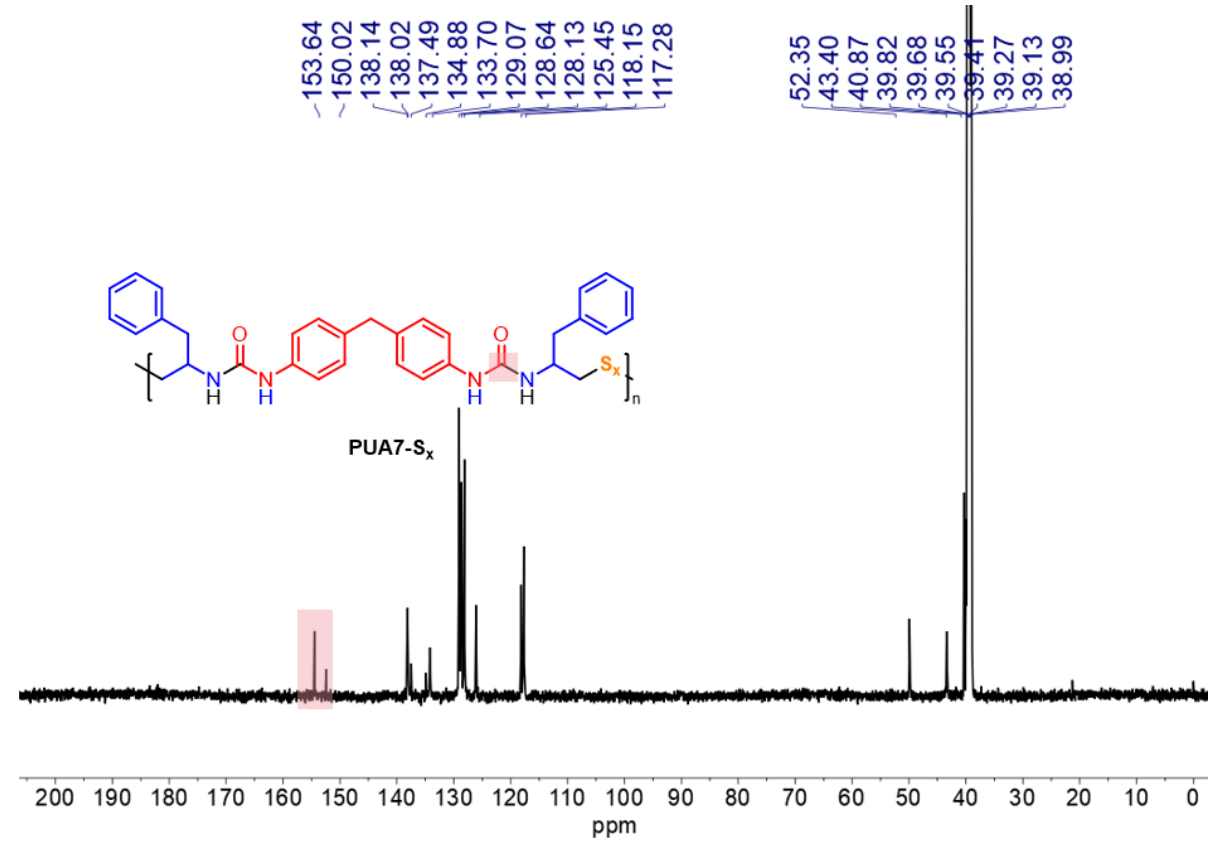
8.32
7.31
7.22
6.99
6.12
4.15
4.09
3.75
3.71
3.33
2.87
2.54
2.50
0.00
PUA7-Sx
2.04
19.75
1.35
1.21
2.21
7.19
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm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150.02
138.14
138.02
137.49
134.88
133.70
129.07
128.64
128.13
125.45
118.15
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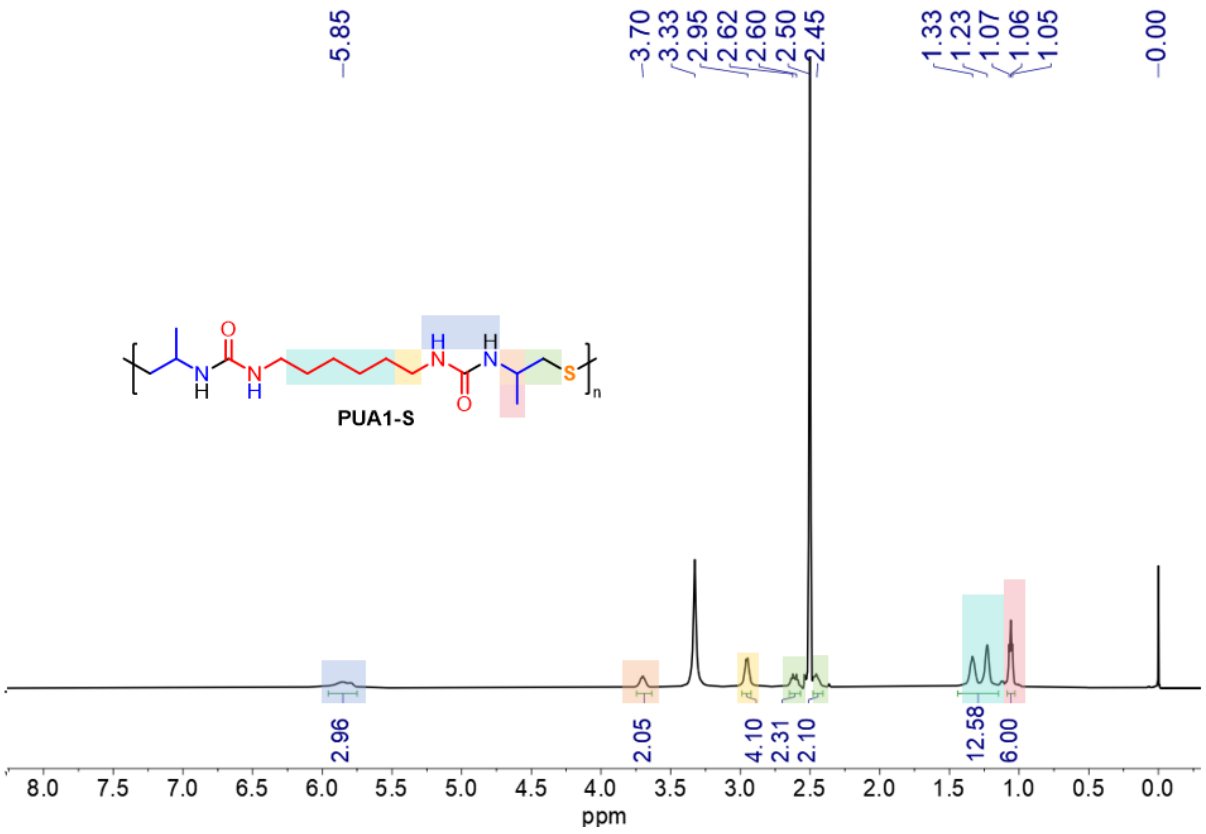
52.35
43.40
40.87
39.82
39.68
39.55
39.41
39.27
39.13
38.99
PUA7-Sx
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm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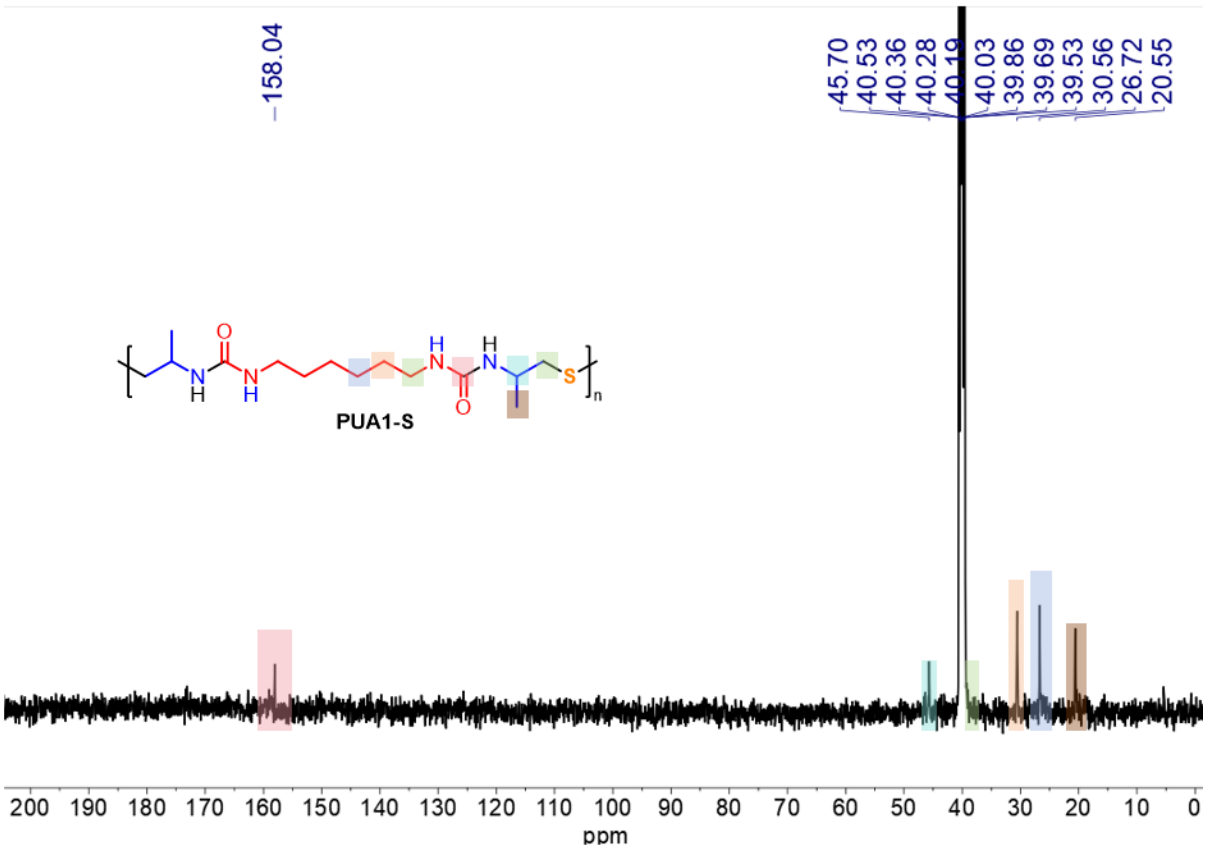
3.70
3.33
2.95
2.62
2.60
2.50
2.45
1.33
1.23
1.07
1.06
1.05
0.00
PUA1-S
2.96
2.05
4.10
2.31
2.10
12.58
6.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm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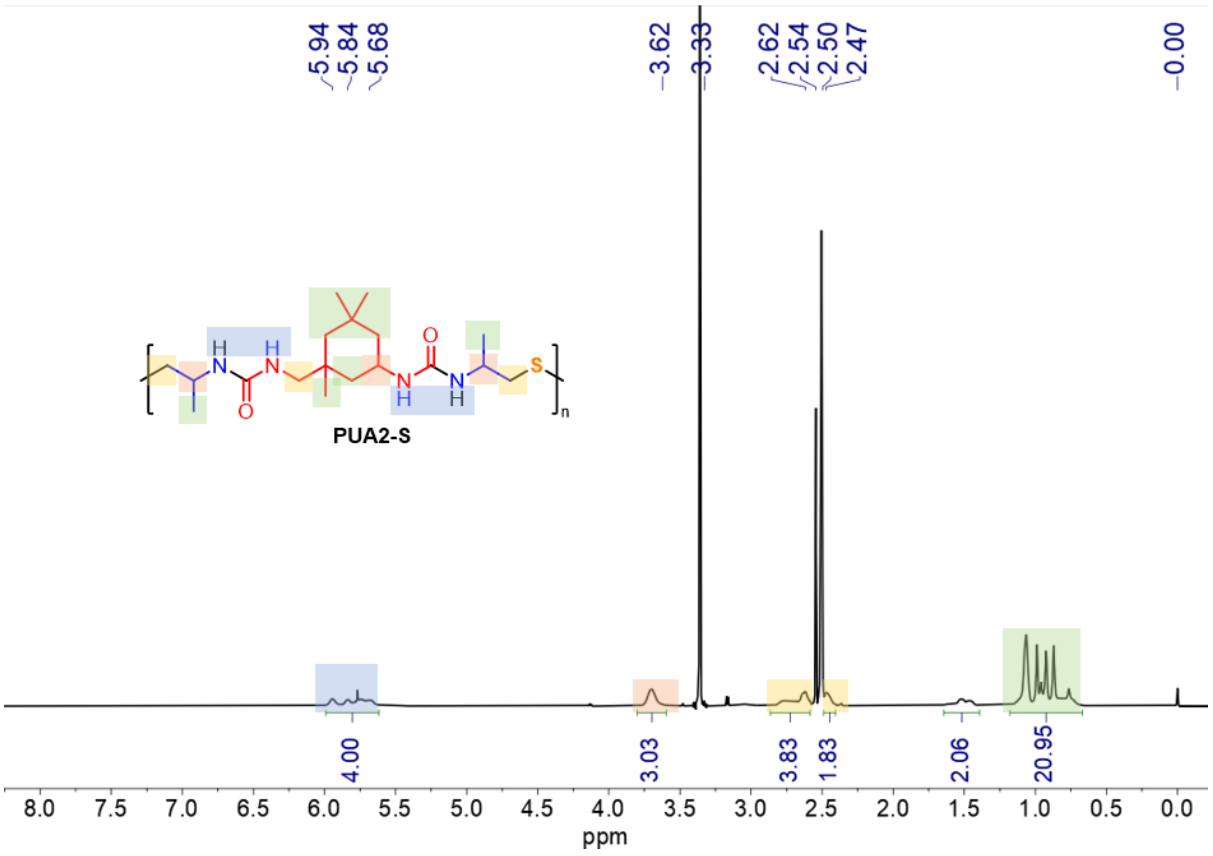
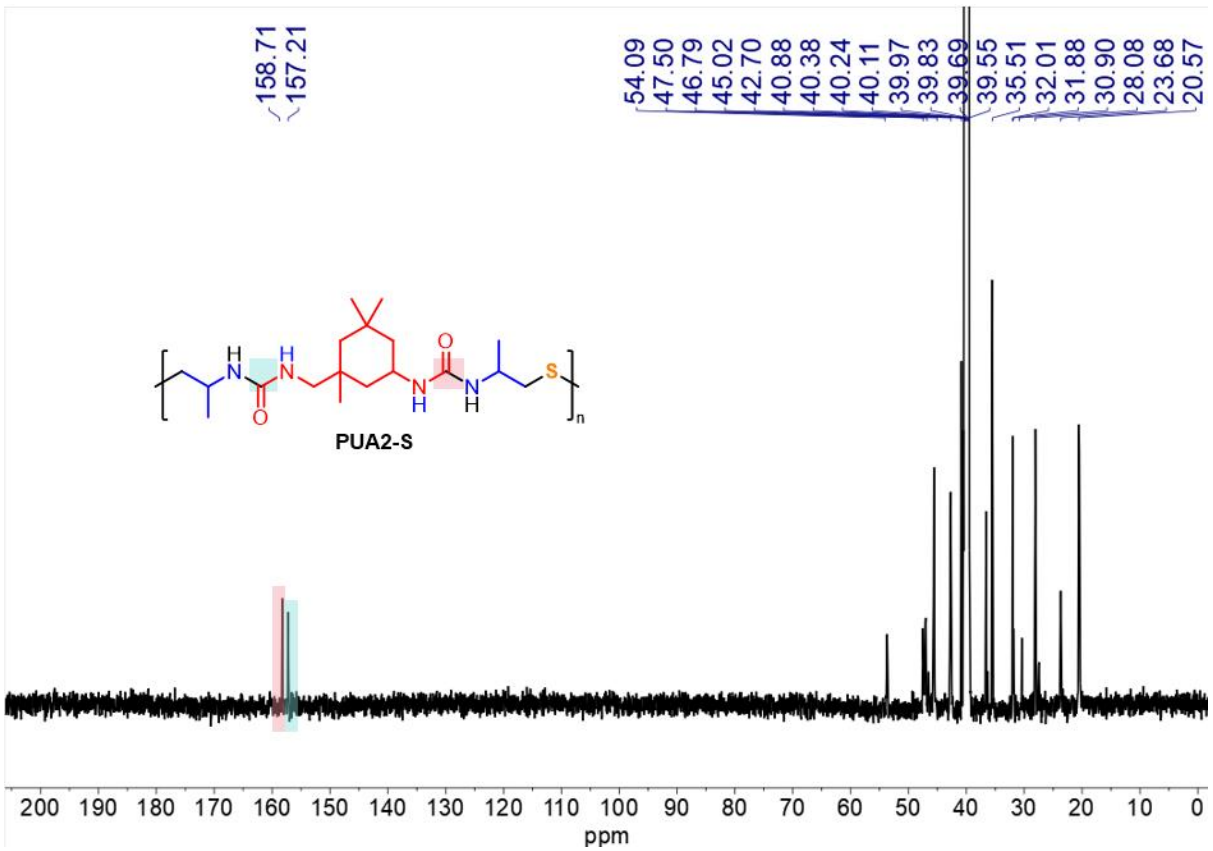
45.70
40.53
40.36
40.28
40.19
40.03
39.86
39.69
39.53
30.56
26.72
20.55
PUA1-S
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


5.94
5.84
5.68
3.62
3.33
2.62
2.54
2.50
2.47
0.00
PUA2-S
4.00
3.03
3.83
1.83
2.06
20.95
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm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157.21
54.09
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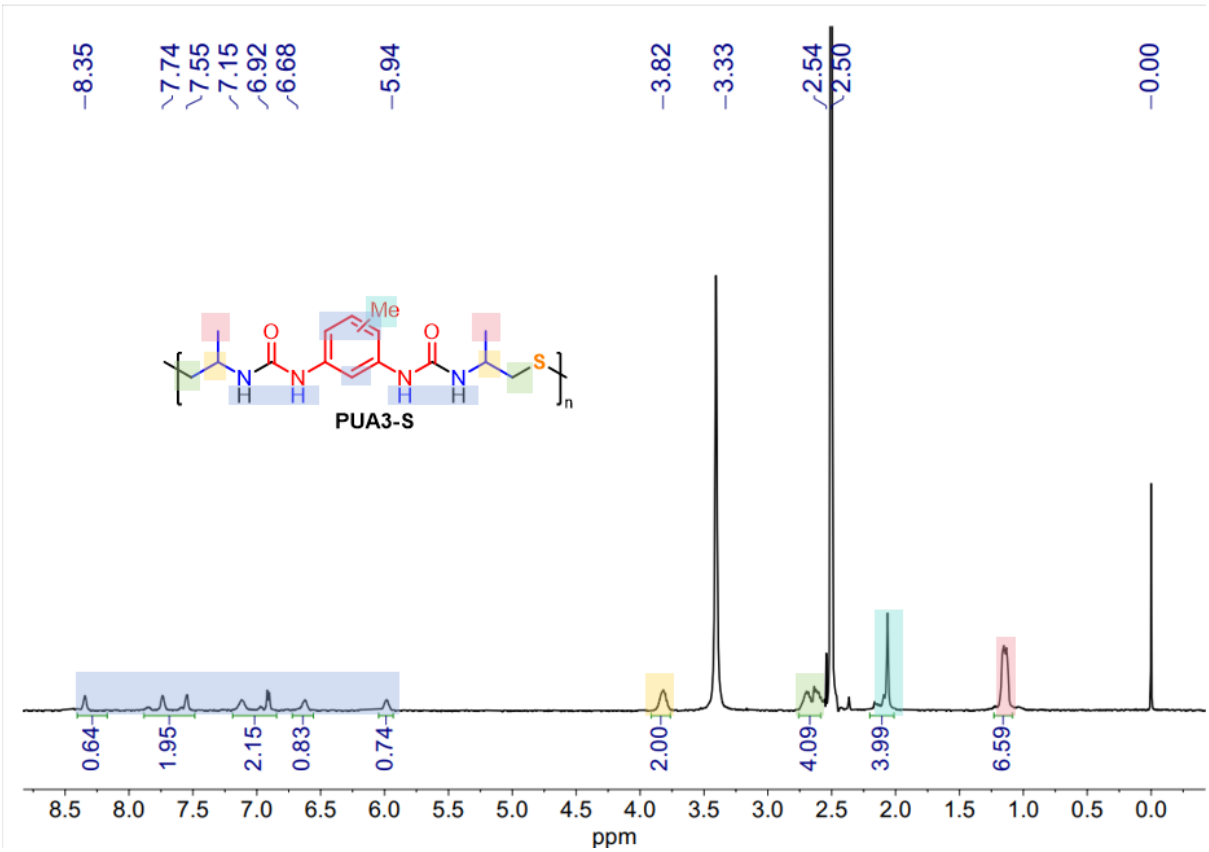
46.79
45.02
42.70
40.88
40.38
40.24
40.11
39.97
39.83
39.69
39.55
35.51
32.01
31.88
30.90
28.08
23.68
20.57
PUA2-S
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm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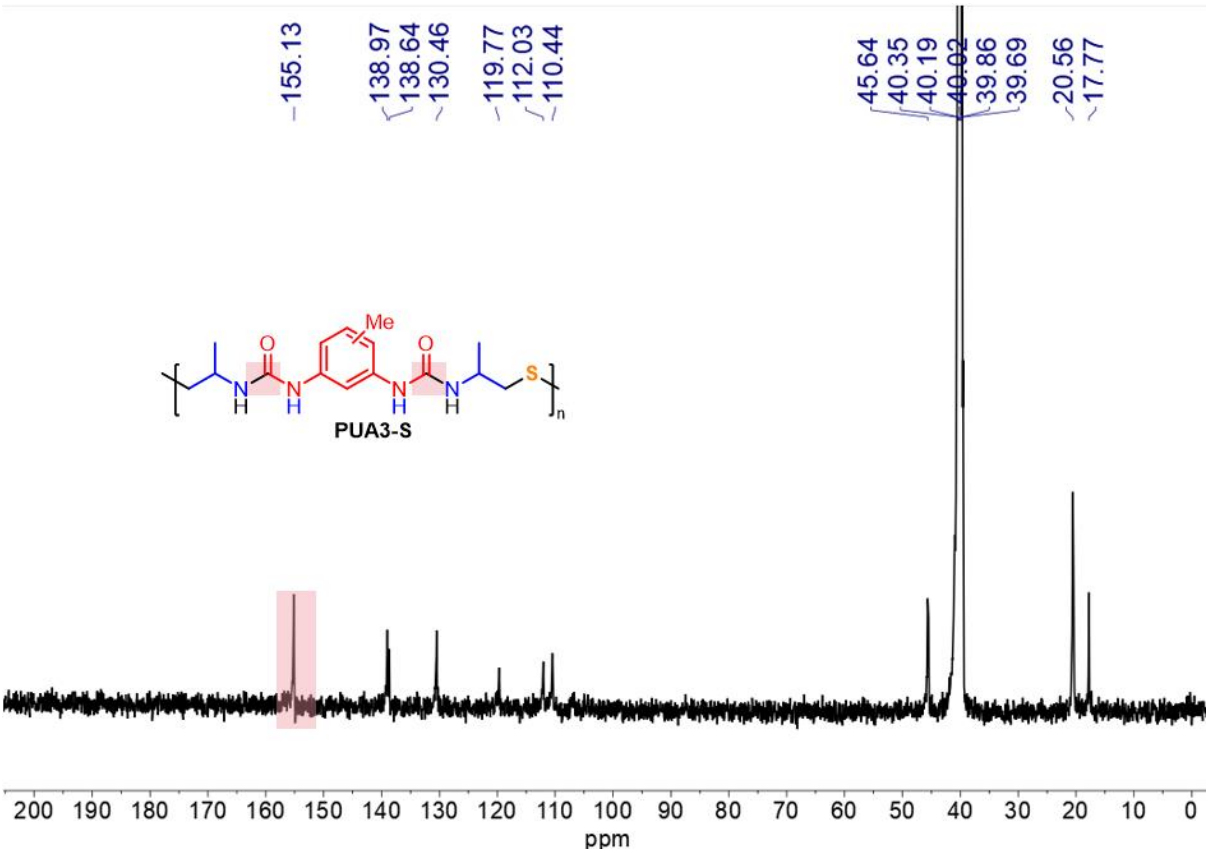
7.55
7.15
6.92
6.68
5.94
3.82
3.33
2.54
2.50
0.00
Me
PUA3-S
0.64
1.95
2.15
0.83
0.74
2.00
4.09
3.99
6.59
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm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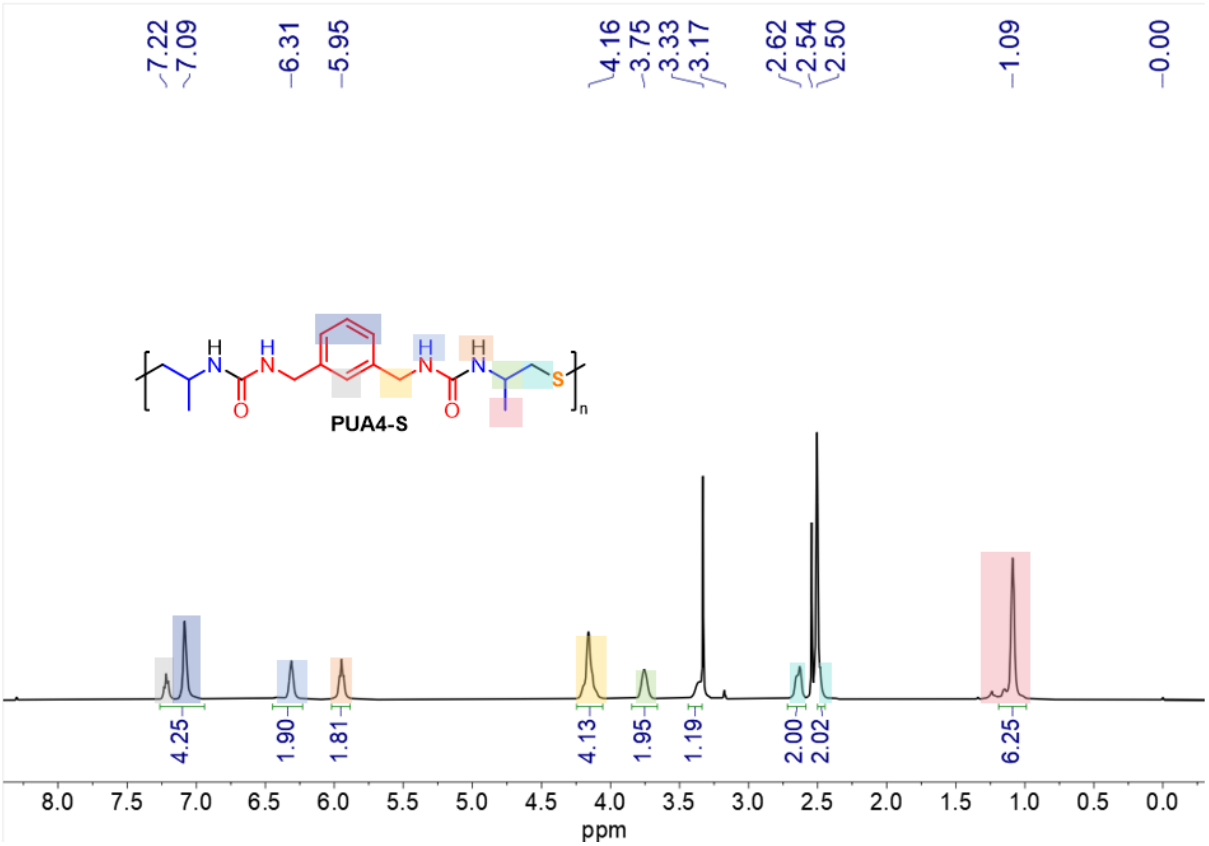
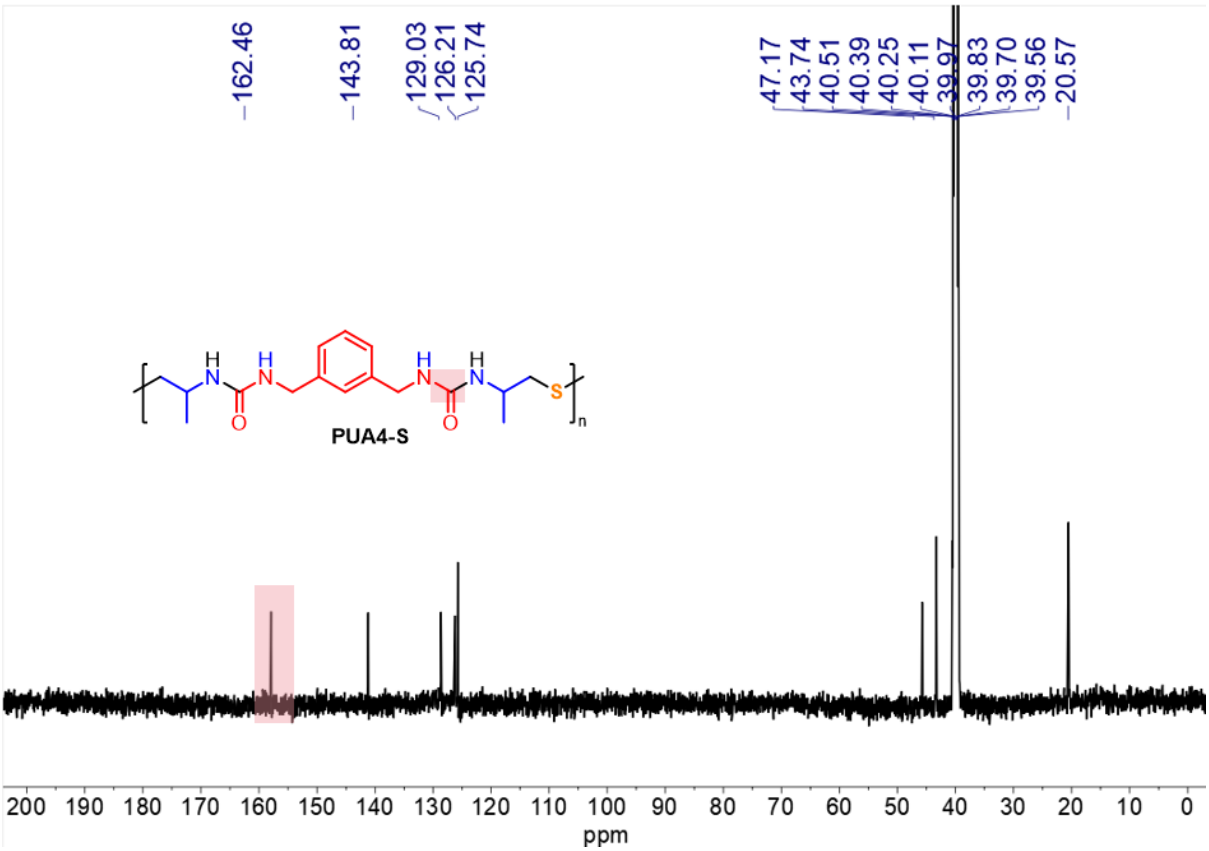
138.64
130.46
119.77
112.03
110.44
45.64
40.35
40.19
40.02
39.86
39.69
20.56
17.77
Me
PUA3-S
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


7.22
7.09
6.31
5.95
4.16
3.75
3.33
3.17
2.62
2.54
2.50
1.09
0.00
PUA4-S
4.25
1.90
1.81
4.13
1.95
1.19
2.00
2.02
6.25
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm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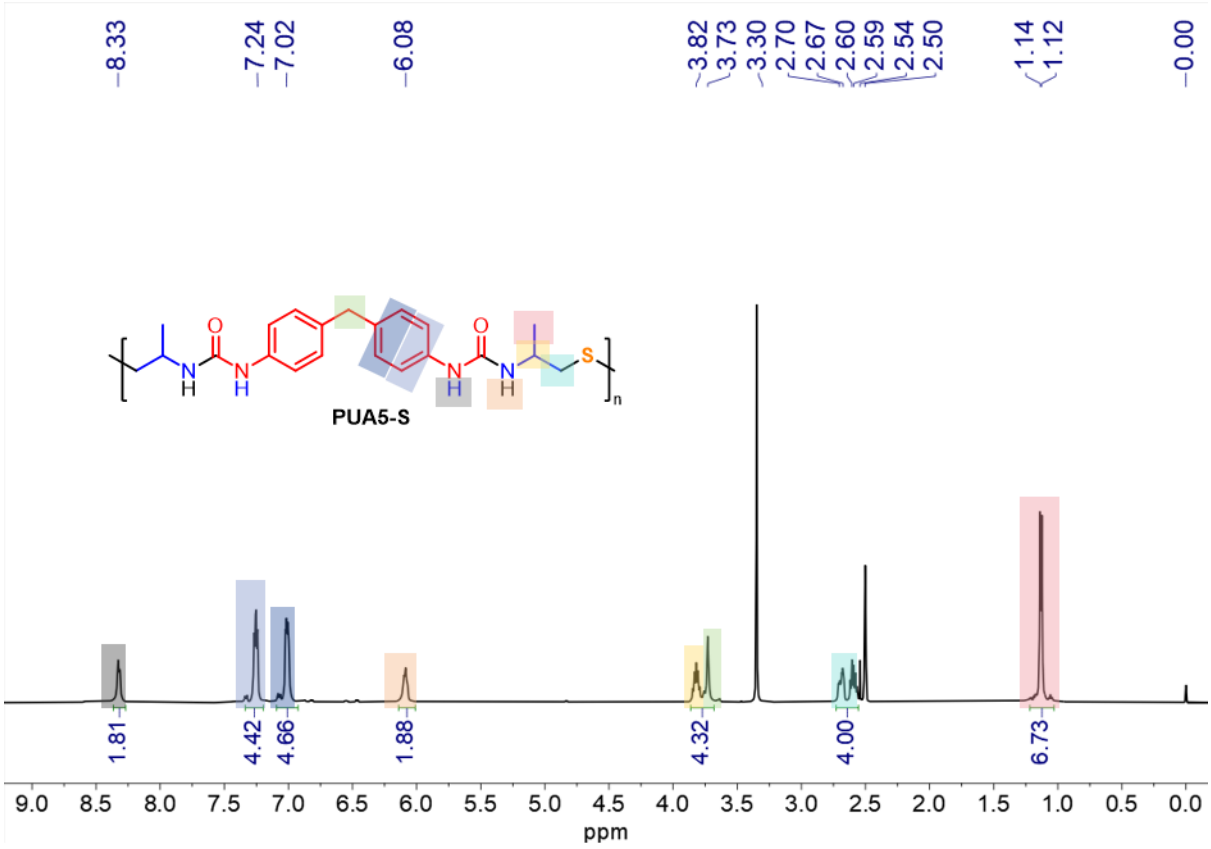
143.81
129.03
126.21
125.74
47.17
43.74
40.51
40.39
40.25
40.11
39.97
39.83
39.70
39.56
20.57
PUA4-S
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm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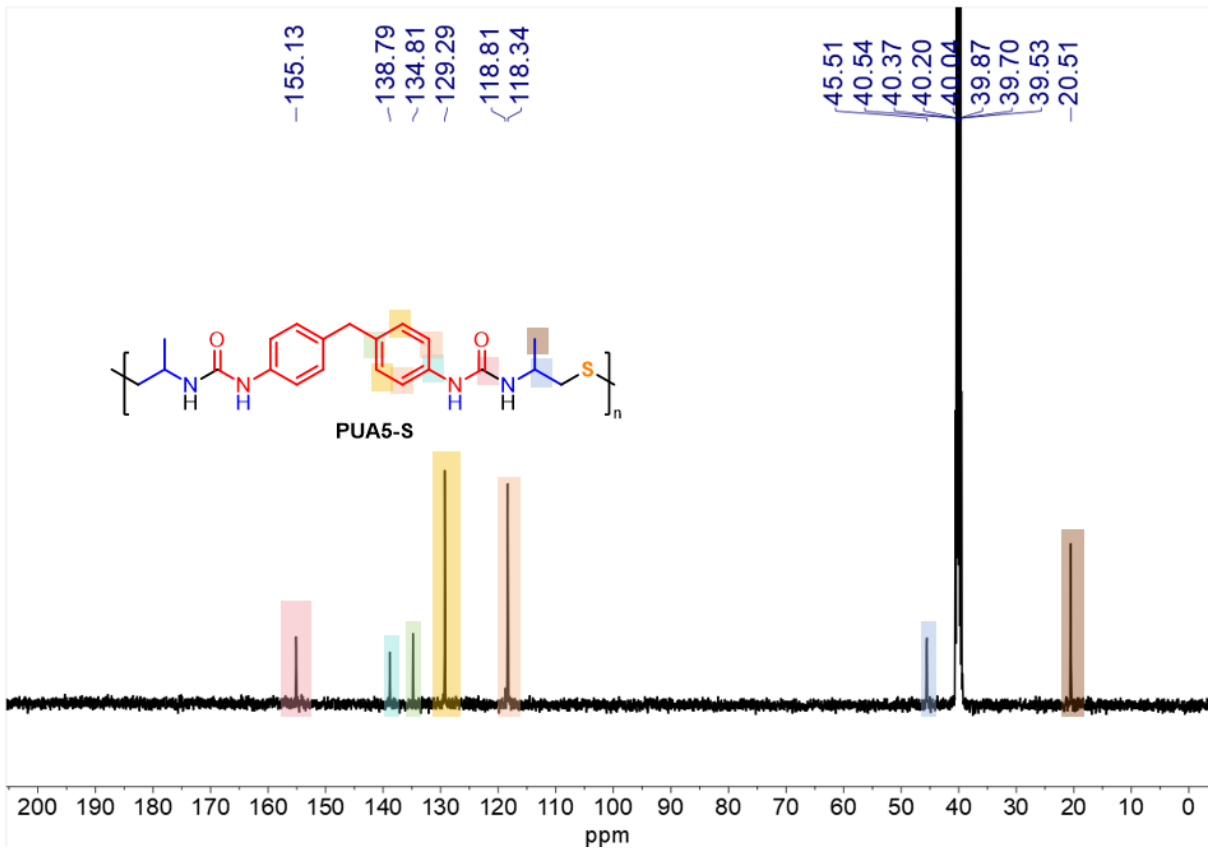
7.24
7.02
6.08
3.82
3.73
3.30
2.70
2.67
2.60
2.59
2.54
2.50
1.14
1.12
0.00
PUA5-S
1.81
4.42
4.66
1.88
4.32
4.00
6.73
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm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138.79
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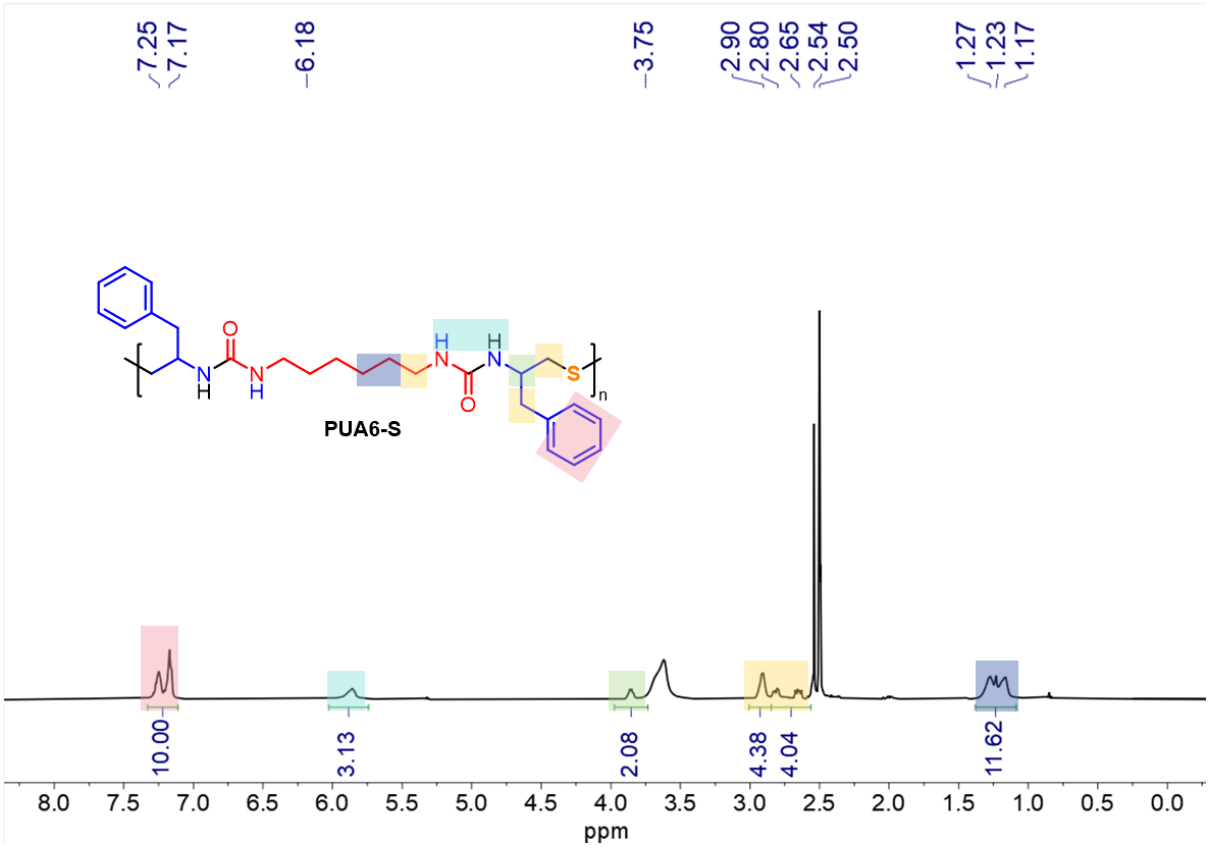
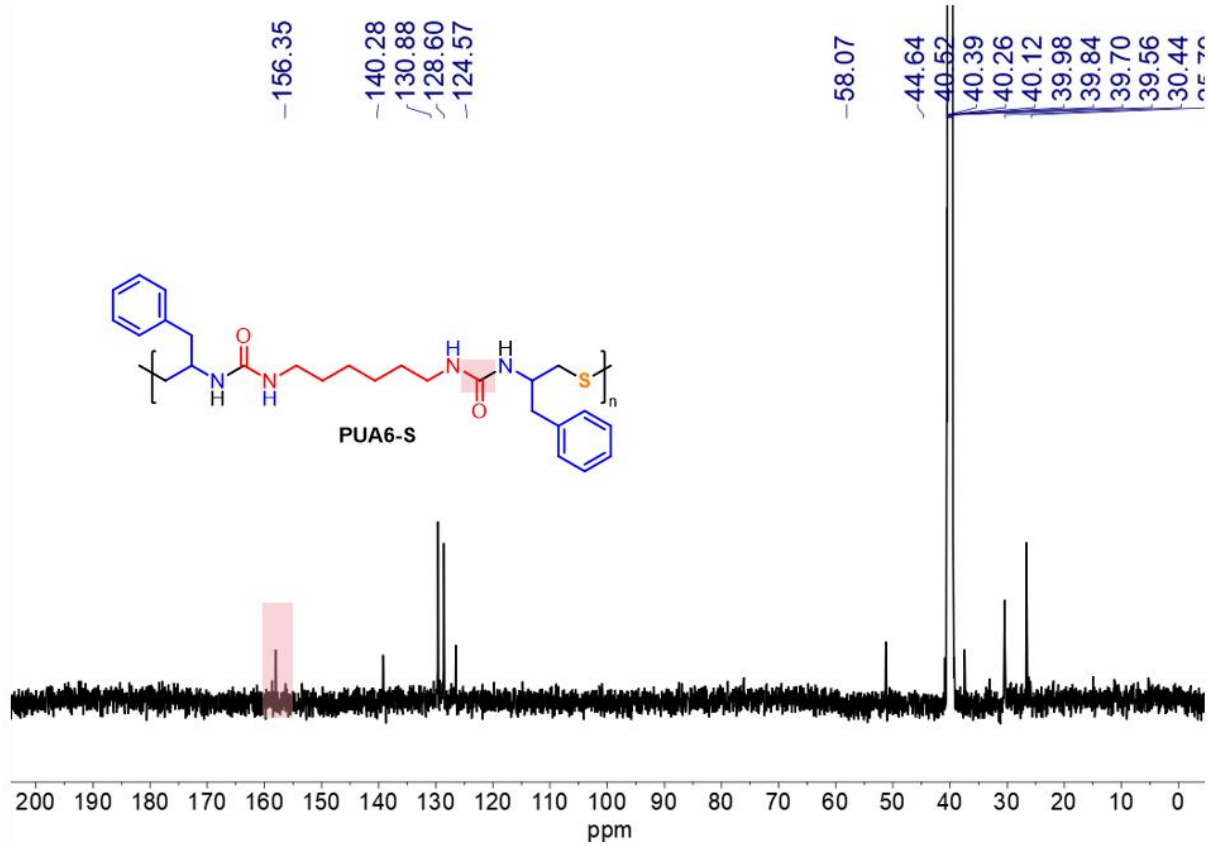
129.29
118.81
118.34
45.51
40.54
40.37
40.20
40.04
39.87
39.70
39.53
20.51
PUA5-S
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


7.25
7.17
6.18
3.75
2.90
2.80
2.65
2.54
2.50
1.27
1.23
1.17
PUA6-S
10.00
3.13
2.08
4.38
4.04
11.62
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm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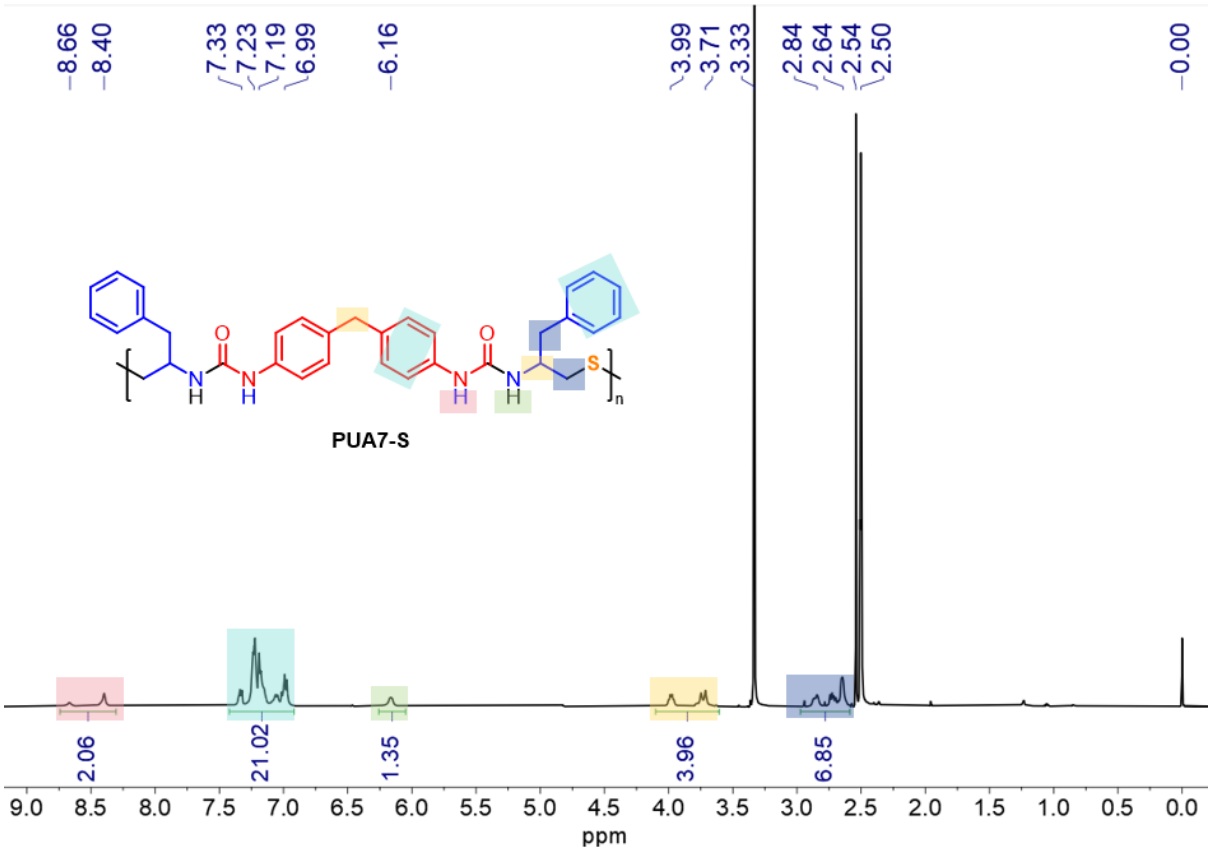
128.60
124.57
58.07
44.64
40.52
40.39
40.26
40.12
39.98
39.84
39.70
39.56
30.44
PUA6-S
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm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7.23
7.19
6.99
6.16
3.99
3.71
3.33
2.84
2.64
2.54
2.50
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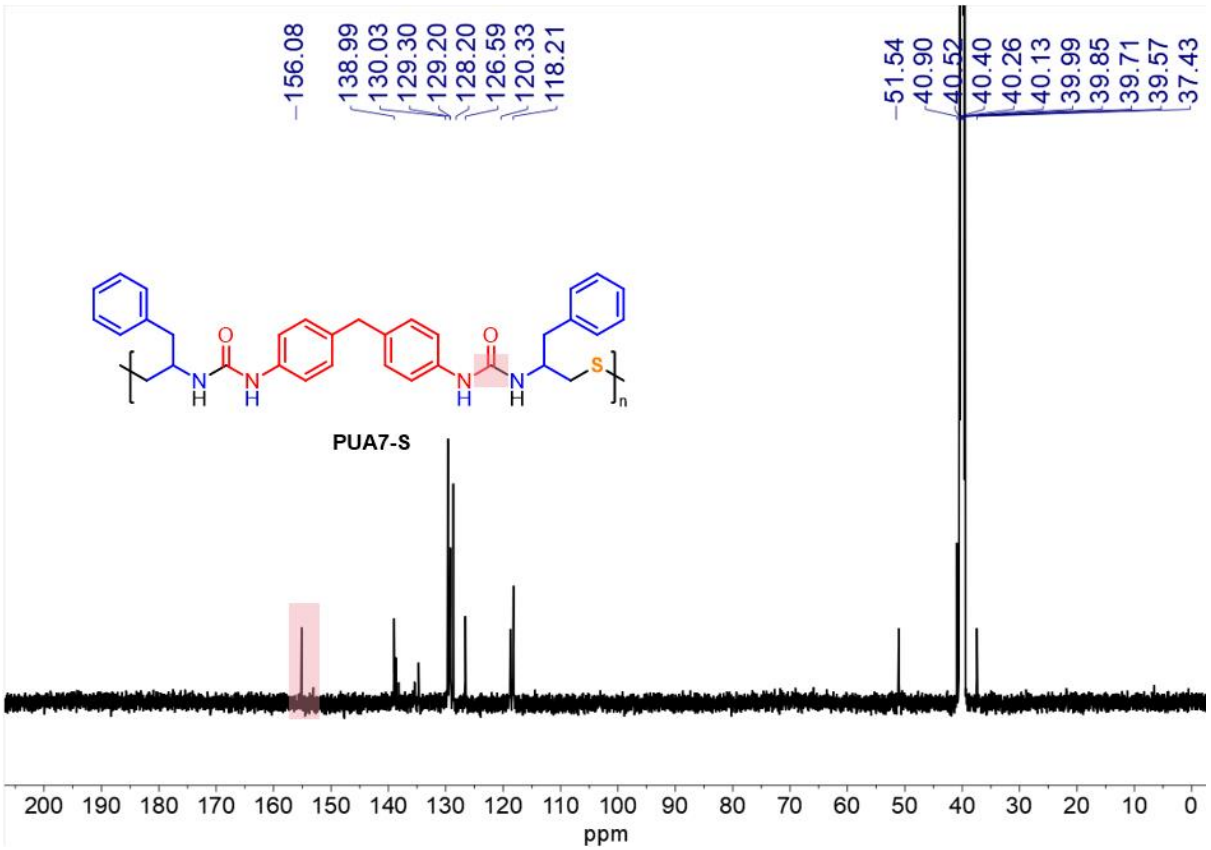
PUA7-S
2.06
21.02
1.35
3.96
6.85
ppm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129.30
129.20
128.20
126.59
120.33
118.21
51.54
40.90
40.52
40.40
40.26
40.13
39.99
39.85
39.71
39.57
37.43
PUA7-S
ppm