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Supramolecular sulfur-containing polymers with hydrogen bonding

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Supramolecular sulfur-containing polymers with hydrogen bonding

Although sulfur-containing polymers have been realized by various methods such as copolymerization and reverse vulcanization, there are few reports on the synthesis of supramolecular sulfur-containing polymers in which a supramolecular polymer is fused with a sulfur-containing polymer. Herein, we prepare a supramolecular sulfur-containig polymer by introducing a 2-ureido-4[1*H*]pyrimidinone (UPy) unit at both ends of linear sulfur and connecting between the UPys via hydrogen bonding.

Keywords: sulfur-containing polymer, sulfur, supramolecular polymer, hydrogen bonding

1. Introduction

Sulfur is an abundant resource. Sulfur-containing polymers have attracted attention as a alternatives to carbon polymers fabricated from exhaustible petroleum resources.[1-4] Additionally, sulfur-containing polymers exhibit various properties not observed in carbon polymers such as transparency and capacitance. Hence, sulfur-containing polymers have potential in lenses and lithium-ion batteries.[5-7]

Although polysulfide polymers can be prepared by simply heating sulfur (S_8),[8,9] the obtained polysulfide polymers are unstable. They are prone to depolymerization during the cooling process and exhibit a low solubility in common organic solvents. To overcome these problems, a radical copolymerization method and a polycondensation method have been developed.[10,11] The resultant sulfur-containing polymers are soluble in common organic solvents. For example, a sulfur-containing polymer obtained by copolymerization of S_8 and styrene acquired the solubility derived from polystyrene and were dissolved in chloroform ($CHCl_3$), tetrahydrofuran (THF), and dimethyl sulfoxide (DMSO). In addition, to overcoming the shortcomings of sulfur-containing polymers, these methods realize sulfur-containing polymers with functional properties such as self-healing.[12-16] Recently, an inverse vulcanization method in which di-vinyl and tri-vinyl monomer and sulfur are copolymerized has been reported.[17] The obtained sulfur-containing polymers were stable for a long time at r.t. in air and high capacitance and repeatable charge/discharge performance. Thus, they have potential as positive electrode materials in lithium-ion batteries. Due to these these diverse demands and requirements for functional sulfur-containing polymer materials, polymer chemistry approaches such as a copolymerization method and an inverse vulcanization technique have been developed as method for producing polysulfide polymers. Various demands and requirements for polysulfide polymers in the recent years have prompted the development of new methodologies for obtaining polysulfide polymers.

In this research, we report a new methodology to synthesize a polysulfide polymer via a supramolecular chemistry approach. For this purpose, we focused on supramolecular polymers, which were prepared by connecting monomers with each other through non-covalent bonds.[18-21] Unlike ordinary polymers formed from covalent bonds, supramolecular polymers exhibit reversible formation and dissociation. Consequently, they are suitable for a wide range of applications, including self-healing materials, stimuli-responsive materials, and catalysts.[22-26] Supramolecular formation of sulfur-containing polymers may give functional supramolecular sulfur-containing polymers.[27,28] Herein, we prepare a sulfur-containing organic compound with hydrogen bonding unit, 2-ureido-4[1*H*]pyrimidinone (UPy), at both ends to give a main-chain type supramolecular sulfur-containing polymers (poly(LS-UPy)) (Fig. 1).

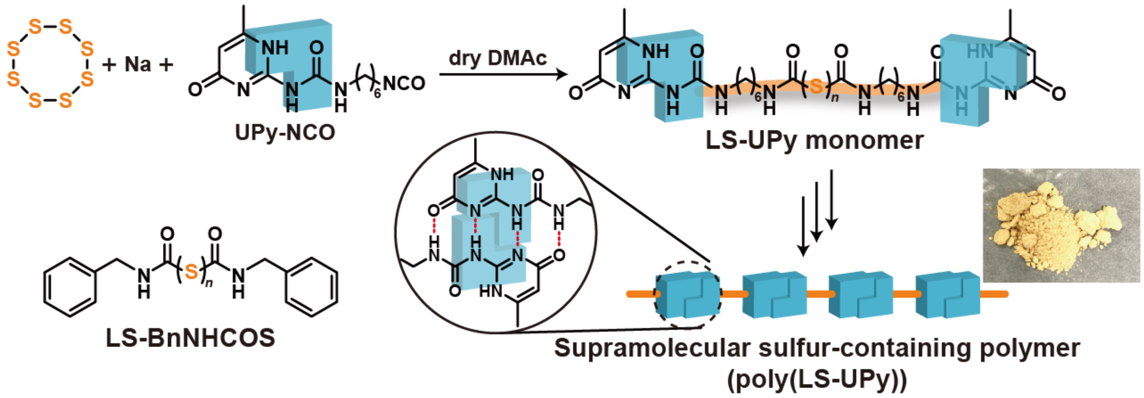

Figure 1. (a) Preparation of supramolecular sulfur-containing polymers with hydrogen bonding units (poly(LS-UPy)) and chemical structure of a reference compound (LS-BnNHCOS). The inserted photograph is poly(LS-UPy).

2. Results and Discussion

Figure 1 outlines the synthesis of the LS-UPy monomer. S_8, sodium metal (Na), and 2-(6-isocyanatohexylaminocarbonylamino)-6-methyl-4[1*H*]-pyrimidinone (UPy-NCO)[29] were stirred in dry *N*,*N*-dimethylacetamide (DMAc) at 70 °C under a N_2 atmosphere. Then the resultant precipitate was collected by filtration and washed with water and $CHCl_3$ to remove residual reagents. In the ^{1}H NMR spectrum of the obtained sample, the signal of methylene protons (A, B, and C in Fig. 2) near the isocyanate groups shifted. In addition, there are no diffraction peaks for S_8 in the X-ray powder diffraction (XRD) measurement of the obtained sample (Figures S1), suggesting there are no raw materials left in the obtained sample. Elemental analysis was conducted to investigate the chain length (n) of linear sulfur in the LS-UPy, which was 2.1. These results confirm the preparation of the LS-UPy monomer.

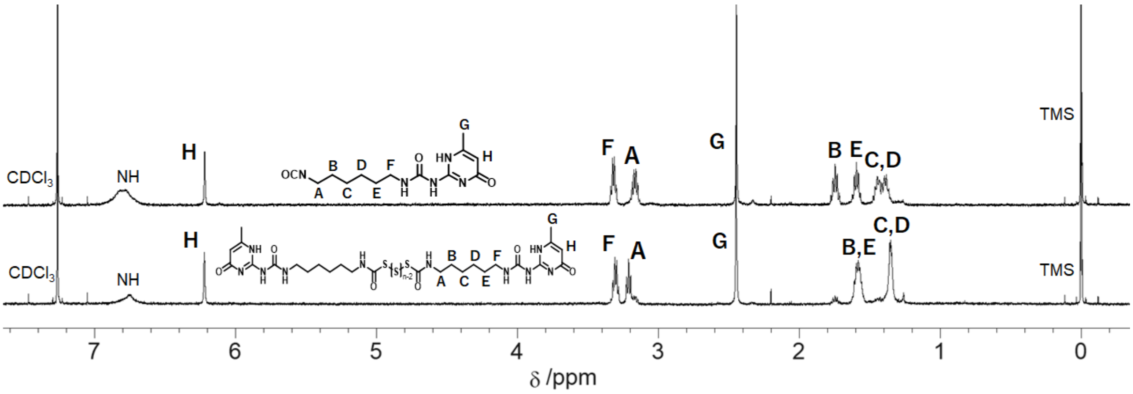

Figure 2. ^{1}H NMR spectra of UPy-NCO (a) and LS-UPy (b) in $CDCl_3$/TFA-*d* (3.6 wt%) at r.t.

We performed FT-IR and solid-state ^{1}H NMR spectroscopic analyses to investigate the formation of hydrogen bonds between the UPy units in the poly(LS-UPy). The FT-IR spectrum contained peaks derived from the NH stretching vibration bands at 3145 cm^{-1} and 3220 cm^{-1} (Fig. 3a). These observations are consistent with the previous report[30] in which quadruple hydrogen bonds appeared between UPy units. In addition, the solid-state ^{1}H NMR spectrum showed three amide proton peaks (δ = 12.2 ppm, 13.5 ppm, and 14.6 ppm) ascribed to hydrogen bonding (Fig. 3b).[30] These results indicate that hydrogen bonding links the LS-UPy monomers.

In order to investigate the molecular weight of poly(LS-UPy), we attempted to perform gel permeation chromatography (GPC) measurements, however, the GPC measurements were unsuccessful because poly(LS-UPy) did not dissolve in $CHCl_3$ due to the hydrogen bonding between the UPy units. However, when trifluoroacetic acid (TFA), a hydrogen bonding inhibitor, was added to Poly(LS-UPy) in $CHCl_3$, poly(LS-UPy) immediately dissolved. Thus, the degree of polymerization (DP) of poly(LS-UPy) was calculated through end-group analysis by ^{1}H NMR using a mixed solvent of $CDCl_3$/TFA-*d*. The peaks at 3.16 and 1.74 ppm were ascribed to $H_{A'}$ and $H_{B'}$ of the end group of poly(LS-UPy), respectively (Fig. 4). Because $H_{A'}$ overlapped with H_A, the ratio of $H_{B'}$ and H_B was used to determine the DP of poly(LS-UPy). DP of the poly(LS-UPy) was about 10. We also investigated the DP value using a diffusion-ordered ^1H NMR (DOSY NMR) measurement in a mixed solvent of $CDCl_3$/TFA-*d*. The diffusion coefficient (*D*) value of poly(LS-UPy) dissolved in 1.4 wt% TFA in $CDCl_3$ (5.1×10^{-11} $m^2 \cdot s^{-1}$) (Fig. 5a) was smaller than that of poly(LS-UPy) dissolved in 10 wt% TFA in $CDCl_3$ (6.4×10^{-11} $m^2 \cdot s^{-1}$) (Fig. 5b). In the case of LS-BnNHCOS, which lacked UPy unit and had only only a urethane bond, the value of *D* remained constant as the TFA concentration changed (Figs. 5c and 5d). The DP of the poly(LS-UPy) decreased upon the addition of TFA. The hydrodynamic radius (r_H) of the poly(LS-UPy) was determined using the Stokes-Einstein equation.[31] The r_H value of the poly(LS-UPy) in 1.4 wt% TFA in $CDCl_3$ was 9.1 nm. The size of the LS-UPy monomer calculated using MM2 was 0.80 nm, suggesting that the DP of poly(LS-UPy) was about 11. These results are almost same as the DP calculated from the end-group analysis via ^1H NMR (DP = 10), showing that poly(LS-UPy) is a supramolecular sulfur-containing polymer with molecular weight of 7,000 linked by hydrogen bonding between the UPy units.

Since poly(LS-UPy) was disassembled by addition of TFA, poly(LS-UPy) should form again by removal of TFA. We remove TFA and performed DOSY NMR measurement. poly(LS-UPy) with high r_H was observed (Figs. 6a and S4), which was similar to poly(LS-UPy) before disassembly. This result indicates that poly(LS-UPy) formed again. These results show that poly(LS-UPy) can be freely disassembled and re-assembled in response to stimuli (Fig. 6b).

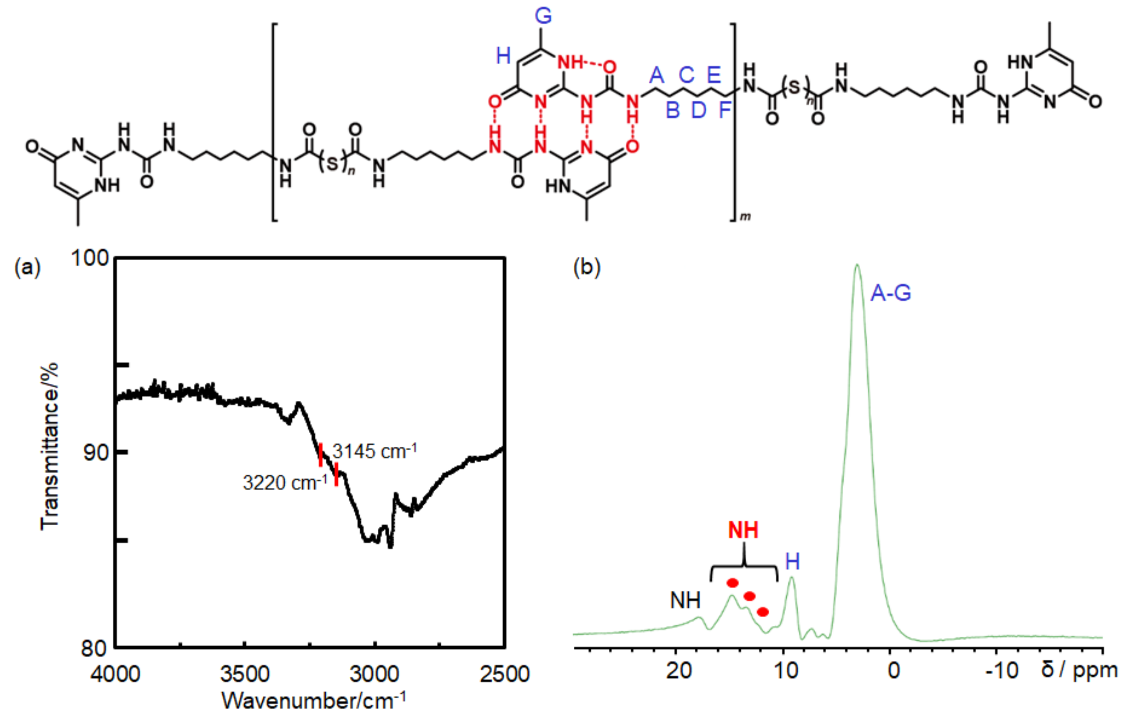

Figure 3. (a) FT-IR and (b) solid-state ^{1}H NMR spectra of poly(LS-UPy).

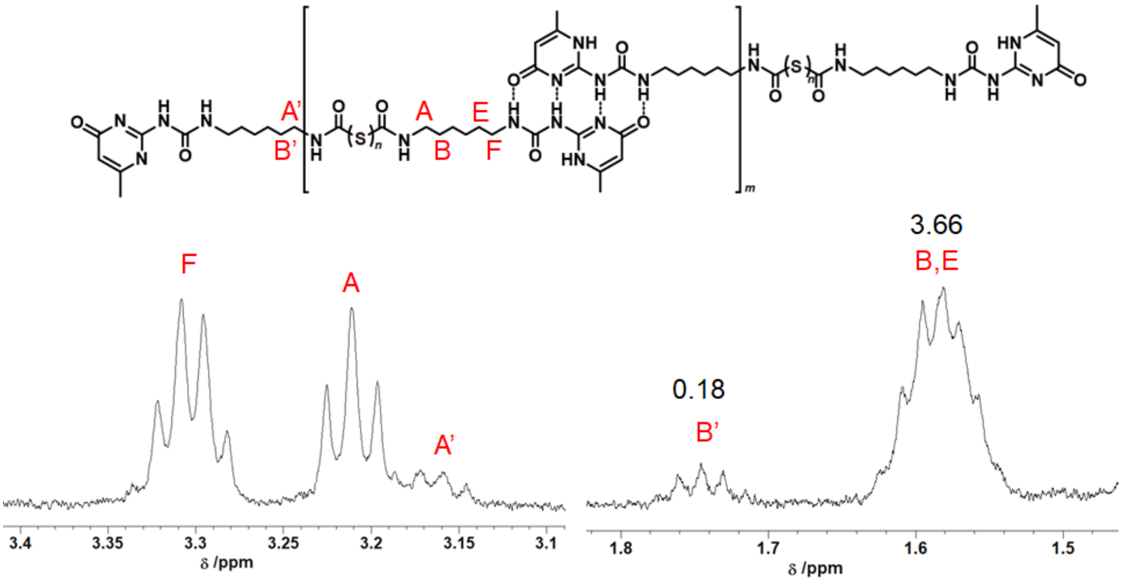

Figure 4. ^{1}H NMR spectrum of LS-UPy in $CDCl_3$/TFA-*d* (1.6 wt%) at r.t.

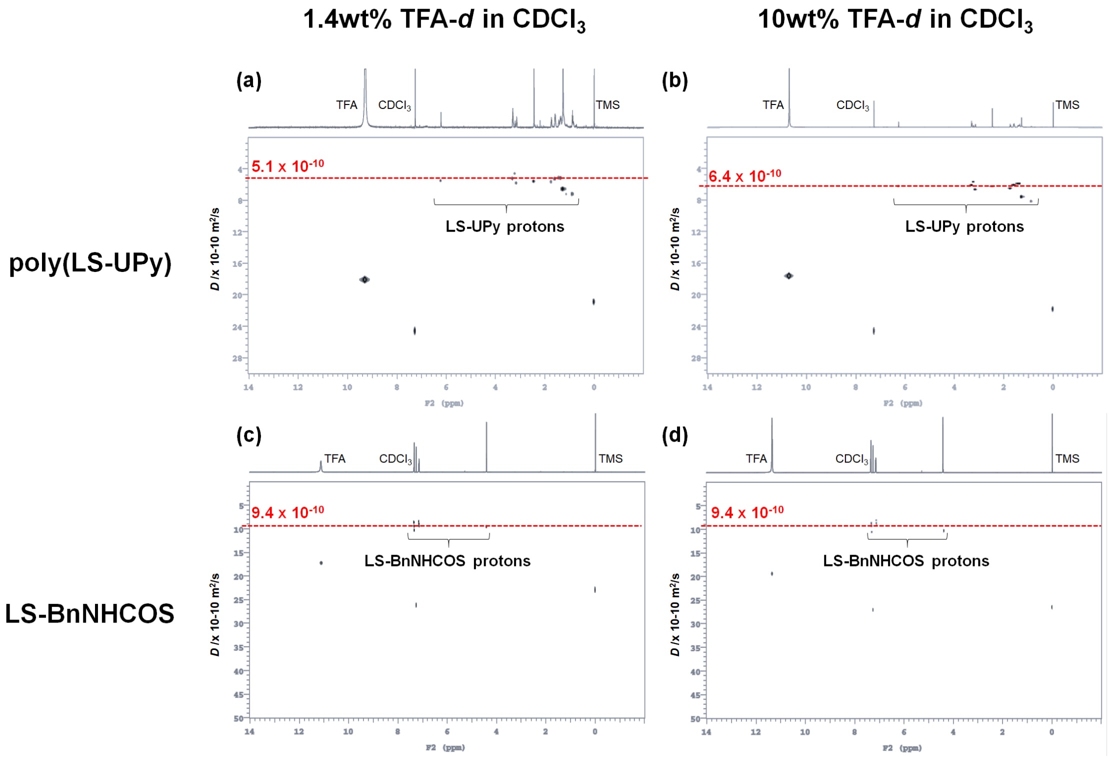

Figure 5. DOSY NMR spectra (600 MHz CDCl$_3$/TFA-*d*, r.t.) of poly(LS-UPy) (a and b) and LS-BnNHCOS (c and d) in 1.4 wt% (a and c) and 10 wt% (b and d) TFA-*d* in CDCl$_3$.

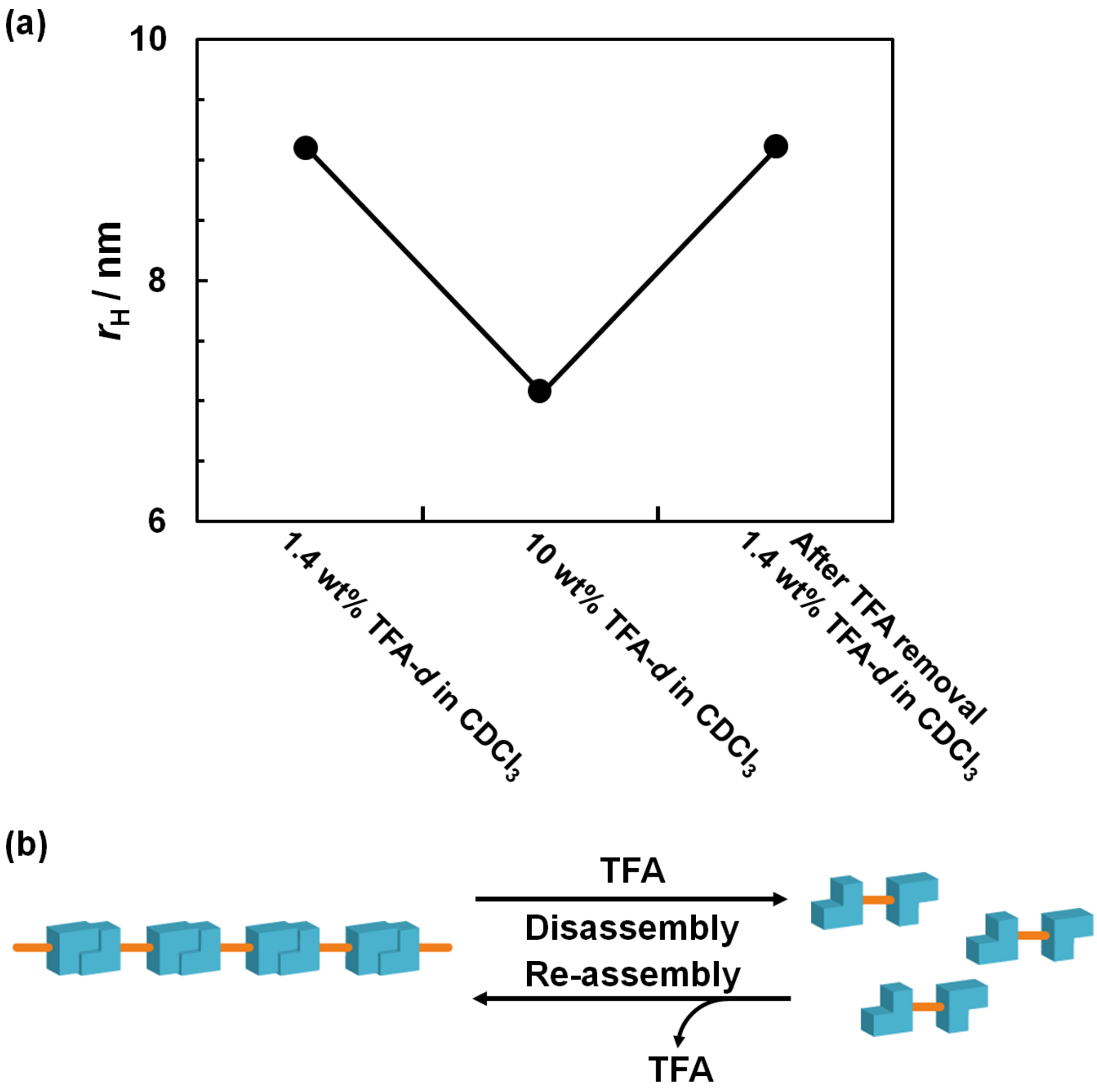

Figure 6. (a) Hydrodynamic radius (r_H) of poly(LS-UPy) in 1.4 wt% and 10 wt% TFA-*d* in $CDCl_3$ and dissolved again in 1.4 wt% TFA-*d* in $CDCl_3$ after removal of TFA. (b) Schematic image of disassembly and re-assembly of poly(LS-UPy).

3. Conclusions

A novel supramolecular sulfur-containing polymer was synthesized by introducing a UPy unit at both ends of linear sulfur-containing compound and linking the UPy units via hydrogen bonding. Disassembly and re-assembly of the supramolecular sulfur-containing polymer were controlled by dissociation and re-formation of UPy units with the addition and removal of TFA, respectively. The methods presented here should help develop sulfur-containing polymers, which have potential as chemo-responsive materials in the future.

4. Experimental Section

4.1 Materials

All of the reagents and chemicals were obtained from commercial sources, unless otherwise noted. Sulfur was purified by recrystallization from carbon disulfide.

4.2 Measurements

The NMR spectra were acquired using JEOL JNM-ECS 400, 500, and 600 (for DOSY) MHz NMR spectrometers. Chemical shifts in the ^1H and ^{13}C spectra were referenced to tetramethylsilane (TMS) ($\delta = 0.00$ ppm) and CHCl3 ($\delta = 77.0$ ppm) respectively. Solid-state NMR spectra were recorded using a JEOL JNM-ECZ600R spectrometer (600 MHz). The solid-state NMR experiments were carried out using a commercial JEOL 1.0 mm magic-angle-spinning (MAS) probe with a spinning frequency of 1000 kHz. The solid-state ^1H MAS NMR spectra were recorded with a single pulse excitation, a 90° pulse length of 1.0 μs, and a recycle delay of 5.0 s. All spectra were referenced to solid glycine and were collected at r. t. Fourier transform infrared (FT-IR) spectra were recorded with a JASCO FT/IR 6100 spectrophotometer. The X-ray powder diffraction (XRD) data were collected using a Rigaku MiniFlex600 diffractometer employing CuKα radiation and samples were measured by using flat-bed sample holder. Gel permeation chromatography (GPC) measurements were performed with in $CHCl_3$ at 40 ºC with polystyrene columns [TSKgel GMHHR-M × 2; flow rate = 1.0 mL/min] connected to a Tosoh DP-8020 pump, a CO-8020 column oven, a UV-8020 ultraviolet detector, and an RI-8020 refractive-index detector.

4.3 Preparation of UPy-NCO

UPy-NCO was synthesized as reported before with the following procedure[29]: 2-ureido-4-[1H]pyrimidinone (UPy, 5.0 g, 40 mmol) was reacted with hexamethylene diisocyanate (47 g, 0.28 mol) at 100 °C for 16 h under the protection of nitrogen. After hexane was added, the resulting precipitate was filtered and washed with hexane for three times. The white powder was dried under reduced pressure to give the UPy-NCO (yield 89%).

^{1}H NMR δ (400 MHz, $CDCl_3$, TMS)/ppm = 13.14 (s, -CCH$_3$N*H*C-, 1H), 11.89 (s, -CN*H*CO-, 1H), 10.21 (t, -CH$_2$N*H*CON*H*-, 1H), 5.84 (s, -CCH$_3$C*H*CO-, 1H), 3.29 (m, -NHC*H*$_2$CH$_2$- and –C*H*$_2$NCO, 4H), 2.25 (s, -CCH$_3$, 3H), 1.65 (m, -NHCH$_2$C*H*$_2$- and -C*H*$_2$CH$_2$NCO, 4H), 1.43 (m, -C*H*$_2$C*H*$_2$CH$_2$CH$_2$NCO, 4H).

4.4 Preparation of monomer (LS-UPy monomer)

S_8 (0.38 mg, 1.5 mmol) and Na (83 mg, 3.6 mmol) were added to dry DMAc (30 mL) and stirred at 70 °C for 24 h under a N_2 atmosphere. UPy-NCO (0.94 g, 3.2 mmol) was added to the solution and stirred at 70°C for 24 h under a N_2 atmosphere. Afterward, the solution was cooled to r.t. The resultant precipitate was collected by filtration. Then it was rinsed with water and $CHCl_3$ four times to remove the residual sulfur, Na, and UPy-NCO. The obtained solid was dried under reduced pressure to give the LS-UPy monomer (yield 40%).

^{1}H NMR δ (400 MHz, $CDCl_3$/TFA-*d*, TMS)/ppm = 13.02 (brs, -CCH$_3$N*H*C-, 2H), 11.84 (brs, -CN*H*CO-, 2H), 10.18 (brs, -CH$_2$N*H*CON*H*-, 2H), 9.28 (brs, -C*N*HC-, 2H), 6.76 (brs, -CH$_2$*N*HCOS-, 2H), 6.22 (s, -CC*H*C-, 2H), 3.36 (m, -NHC*H*$_2$CH$_2$-, 4H), 3.21 (m, -

SCONHCH_2CH$_2$-, 4H), 2.43 (s, -CCH$_3$, 6H), 1.61 (m, -CH$_2$CH_2CH$_2$CH$_2$CH_2CH$_2$-, 8H) 1.38 (m, -CH$_2$CH$_2$CH_2C H_2CH$_2$CH$_2$-, 8H). Anal. Calcd. for C26H40N10O6S2.1: C 47.65, H 6.15, N 21.37, Found: C 47.60, H 6.91, N 21.99.

4.5 Preparation of comparison sample (LS-BnNHCOS)

S_8 (0.12 mg, 0.46 mmol) and sodium sulfate pentahydrate (0.17 mg, 1.0 mmol) were stirred in H_2O (5.0 mL) at r.t. for 24 h. The resultant solution was freeze-dried. The dried sample and benzyl isocyanate (0.12 mg, 1.1 mmol) were stirred in dry DMF (5.0 mL) at r.t. for 12 h under a N_2 atmosphere. The liquid phase was removed, and the obtained solid was purified by silica-gel column chromatography ($R_f = 0.74$, CH_2Cl_2/MeOH = 90:10) to give LS-BnNHCOS (yield 40%).

^{1}H NMR δ (500 MHz, $CDCl_3$, TMS)/ppm = 7.42-7.29 (m, C$_6$$H_6$-, 12H), 4.78 & 4.86 (s, -NHCH_2C$_6$H$_6$, 4H). Anal. Calcd. for C16H16N2S: C 63.98, H 5.37, N 9.33, S 10.37, Found: C 64.40, H 4.77, N 9.31, S 11.3.

4.6 Calculation of the hydrodynamic radius from diffusion coefficient

The hydrodynamic radius (r_H) of each sample was calculated from the Stokes-Einstein relationship for a sphere with stick boundary conditions:

$$r_H = \frac{k_B T}{6\pi\eta D}$$

where k_B, T, η, and D are Boltzmann's constant, temperature (297 K), the solvent viscosity, and the diffusion coefficient, respectively.

4.7 Disassembly and re-assembly of poly(LS-UPy)

Poly(LS-UPy) (1.0 mg) was stirred in 10 wt% TFA-*d* in $CDCl_3$ (1.0 mL) at r.t. for 24 h to decompose poly(LS-UPy). After removing the solvent, the obtained sample was dissolved in 1.4 wt% TFA-*d* in $CDCl_3$ (1.0 mL). The solution was stirred at r.t. for 24 h.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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