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Effects of 2,5-furanylene sulfides in polymer main chains on polymer physical properties

Abu Bin Ihsan [1] · Yasuhiro Tawara[2] · Shinya Goto[2] · Hirokazu Kobayashi[3] · Kiyotaka Nakajima [3] ·
Atsushi Fukuoka [3] · Yasuhito Koyama [1]

Abstract

We developed 2,5-furanylene sulfide-containing polymers bearing different spacers as repeating units and evaluated the interactions between the furanylene sulfide units in the polymers. The treatment of 2,5-dichlorofuran derivatives with dithiolates at 200 °C promotes polycondensation via nucleophilic aromatic substitution to give the corresponding furanylene sulfide-containing polymers. Tensile measurements and spectral analyses demonstrate that the furanylene sulfide moieties form remarkably stable π–π stacking structures based on the enhanced dipole moment induced by sulfur linkages. When the polymer has a long spacer between repeating furanylene sulfide units, the polymer behaves as a chemically stable network polymer comprised of π–π stacking structures as cross-linking units.

Introduction

The introduction of aryl sulfide linkages endows polymers with unique properties such as high thermal stability, high tensile strength, high refractive index, and low solubility in organic solvents [1–5]. These properties originate not only from the characteristics of the sulfur atom itself but also from C−S bonds and further interactions between sulfide-containing aromatic units. Poly(phenylene sulfide) (PPS), a representative member of aryl sulfide-containing high performance polymers, occupies an important position in engineering plastics [6]. It has been reported that the alternation of the phenylene spacer to other aromatics changes the polymer properties [7–9].

Furan is a heteroaromatic compound and can be prepared from biomass in the form of renewable and nonedible carbohydrates [10–12]. We have reported the catalytic production of furan derivatives from naturally abundant polysaccharides [13–22]. Furan derivatives have been regarded as a biosourced alternative to petroleum-dependent aromatics. Recently, furan-based polymers analogous to poly(ethylene terephthalate) and bisphenol A-based epoxy resins have been developed [23–26]. It was revealed that the furan-based polymers exhibit improved thermal stability and glassy modulus relative to their phenylic analogs.

On the basis of this background, we planned the development of 2,5-furanylene sulfide-containing polymers. We expected that the introduction of sulfide linkages to the 2 and 5 positions of furan would improve the weak dipole moment of unsubstituted native furan and facilitate interchain interactions to afford favorable material properties. We herein describe the effects of 2,5-furanylene sulfide in polymer main chains on the physical properties of the polymers. The furan-based polymers were prepared by the polycondensation of a 2,5-dichlorofuran derivative with three types of dithiolates in N-methyl-2-pyrrolidone (NMP) via a nucleophilic aromatic substitution (S_NAr) reaction [27–29]. The polymerization proceeded smoothly at 200 °C without any additive. By conducting tensile measurements

✉ Yasuhito Koyama
  ykoyama@pu-toyama.ac.jp

1   Department of Pharmaceutical Engineering, Faculty of Engineering, Toyama Prefectural University, 5180 Kurokawa, Imizu, Toyama 939-0398, Japan

2   Material Engineering, R&D Division, DENSO Corporation, 1-1 Syowa-chou, Kariya, Aichi 448-8661, Japan

3   Institute for Catalysis, Hokkaido University, N21 W10, Kita-ku, Sapporo 001-0021, Japan

and spectral analyses at various temperatures, it was found that the polymers exhibit remarkably strong interactions between the furan units. The results indicate that the interaction is attributed to the π-π stacking structures between the furan units with enhanced dipole moments induced by sulfur linkages.

Experimental

Materials

3-Furaldehyde (Sigma Aldrich, Darmstadt, Germany), hexylamine (Tokyo Chemical Industry Co., Ltd., Tokyo, Japan), sodium borohydride (Tokyo Chemical Industry Co., Ltd., Tokyo, Japan), acetic anhydride (Kanto Chemical Co., Ltd., Tokyo, Japan), triethylamine (Nacalai Tesque, Inc., Kyoto, Japan), 4-dimethylaminopyridine (DMAP, Tokyo Chemical Industry Co., Ltd., Tokyo, Japan), N-chlorosuccinimide (NCS, Sigma Aldrich, Darmstadt, Germany), sodium bicarbonate (Wako Pure Chemical Industry, Co., Ltd., Osaka, Japan), N-methylpyrrolidone (NMP, Tokyo Chemical Industry Co., Ltd., Tokyo, Japan), 4,4'-thiobisbenzenethiol (Tokyo Chemical Industry Co., Ltd., Tokyo, Japan), 1,10-decanedithiol (Tokyo Chemical Industry Co., Ltd., Tokyo, Japan), 1,3-propanedithiol (Tokyo Chemical Industry Co., Ltd., Tokyo, Japan), sodium sulfide (Tokyo Chemical Industry Co., Ltd., Tokyo, Japan), potassium carbonate (Wako Pure Chemical Industry, Co., Ltd., Osaka, Japan), and Me_3OBF_4 (Tokyo Chemical Industry Co., Ltd., Tokyo, Japan) were used without further purification. Quinoline (Kanto Chemical Co., Ltd., Tokyo, Japan) was dried over KOH pellets before use.

Measurements

^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on JEOL JNM-ESC400 (JEOL, Tokyo, Japan) and Bruker AVANCE II 400 (Bruker, Fällanden, Switzerland) spectrometers using $CDCl_3$ and DMSO-d_6 as solvents; measurements were calibrated using residual undeuterated solvent and tetramethylsilane as the internal standards. Diffusion-ordered NMR spectroscopy (DOSY) measurements were carried out using 2.0 mg of the test compound in 600 μL of DMSO-d_6 to estimate the diffusion coefficients. DOSY spectra were recorded on a Bruker AVANCE II 400 spectrometer to estimate the M_w values of the polymers [30–32]. All experiments were performed without spinning to avoid convection. The standard Bruker pulse program, ledbpgp2s, employing simulated echo and longitudinal eddy delay with bipolar gradients and two spoil gradients, was utilized. The obtained DOSY spectra were processed by Topspin 3.2 software. Diffusion coefficients

of a chosen narrow chemical shift in the spectra of the compounds were extracted by using Dynamics center software (ver. 2.4.8, Bruker). Size exclusion column chromatography (SEC) analyses were carried out using a chromatographic system consisting of a LC-20AT pump with a SPD-20A UV detector, an RID-20A RI detector (Shimadzu Co. Ltd., Kyoto, Japan), and two consecutive linear polystyrene gel columns (Tosoh TSKgel GMHHR-H and TSKgel G3000HHR) at room temperature using polystyrene standards in $CHCl_3$ or dextran standards in DMSO at a flow rate of 1.0 mL/min. FT-IR spectra were obtained using KBr pellets and a Nexus 870 spectrometer (Thermo Fisher Scientific Inc., Waltham, MA, USA). FT-IR spectra were obtained via an attenuated total reflection (ATR) method using a Perkin Elmer spectrum 100 spectrometer (Perkin Elmer, Shelton, USA). The tensile measurement of **Poly-2** was performed by an EZ-SX (Shimadzu Co. Ltd., Kyoto, Japan). The rectangular specimens were 4.1 mm in width and 0.3 mm in thickness, and the distance between clamps was 0.85 mm. The stretching velocity was 10 mm/min. The temperature dependence of the absorbance of **Poly-3** was estimated by UV spectra using a JASCO V-630 spectrophotometer connected to a JASCO CTU-100 circulating thermoset unit (JASCO Co. Ltd., Tokyo, Japan). Differential scanning calorimetry (DSC) analyses were carried out on a DSC-60 plus instrument (Shimadzu Co. Ltd., Kyoto, Japan) under an N_2 atmosphere (flow rate: 50 mL/min. Elemental analyses were carried out at the Center for Instrumental Analysis, Hokkaido University by request. The amounts of carbon (C), hydrogen (H), and nitrogen (N) in percent weight of the polymer were determined by the differential thermal conductivity method using a CHN Corder MT-6 (Yanaco) analyzer. Sulfur (S) was quantified by the flask combustion method using a Dionex DX-500 ion chromatograph. Halogens (Br/Cl) were quantified by ion chromatography using a Dionex ICS-1600 ion chromatograph (Thermo Fisher Scientific Inc., Waltham, MA, USA).

Synthesis of 2,5-dichlorofuran derivative 4

To a solution of 3-furaldehyde **1** (1.75 g, 0.018 mol) in CH_2Cl_2 (40 mL) was added hexylamine (2.42 mL, 0.018 mmol) at room temperature. After stirring for 21 h, the mixture was dried over $MgSO_4$, filtered, and concentrated in vacuo to give an imine, **2**, as a crude material. The crude material was used in the next reaction without further purification.

The crude imine **2** was dissolved in MeOH (30 mL). To this solution, $NaBH_4$ (689 mg, 0.018 mol) was added portionwise at room temperature. The mixture was stirred for 1 h at a constant temperature and then evaporated in vacuo to give a sec-amine. This product was used in the next reaction without further purification.

To a mixture of the crude product in $CHCl_3$ (20 mL) was added Et_3N (37.9 mL, 0.273 mol), DMAP (223 mg, 1.82 mmol), and Ac_2O (25.8 mL, 0.273 mmol) at room temperature. The reaction mixture was stirred for 1 d and quenched by pouring into sat. aq. $NaHCO_3$. The products were extracted with AcOEt. The combined organic layer was washed with sat. aq. $NaHCO_3$, dried over $MgSO_4$, filtered, and concentrated in vacuo to give a quantitative yield of amide **3** (4.60 g) in three steps. The crude product was used in the next reaction without further purification.

The crude amide **3** (1.21 g, 5.41 mmol) was dissolved in DMF (20 mL). To the mixture was added $NaHCO_3$ (910 mg, 10.8 mmol) and NCS (1.59 g, 11.9 mmol) at room temperature. The mixture was warmed to 130 °C, stirred for 5 h, and cooled to room temperature. The reaction was quenched by the addition of AcOEt and water. The layers were separated. The aqueous layer was extracted with AcOEt. The combined organic layer was washed with water (×2) and brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The obtained crude material was purified by florisil column chromatography (eluent: hexane-$CHCl_3$ (1:1) → $CHCl_3$) to afford 2,5-dichlorofuran derivative **4** (964 mg, 61% overall yield in four steps) as a yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 6.43 (s, furan), 6.26 (s, furan), 6.12 (s, furan), 4.35 (s, CH_2), 4.29 (s, CH_2), 4.22 (s, CH_2), 3.29 (brd, CH_2), 3.18 (brd, CH_2), 2.15 (s, Ac), 2.13 (s, Ac), 2.11 (s, Ac), 1.59–1.50 (m, CH_2), 1.32–1.25 (m, CH_2), 0.91–0.85 (m, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ 170.5 (C=O), 170.4 (C=O), 169.9 (C=O), 142.2, 141.7, 135.7, 135.0, 132.2, 119.3, 118.4, 116.3, 113.3, 111.6, 110.0, 108.3, 48.3, 48.1, 45.5, 42.8, 38.8, 38.6, 31.4, 31.3, 29.6, 28.33, 28.28, 27.2, 26.5, 26.4, 22.47, 22.43, 21.8, 21.3, 21.2, 13.92, 13.87 ppm; IR (KBr) υ 2959, 2930, 2858, 1654, 1603, 1513, 1420, 1368, 1257, 1207, 1158, 1088, 1043, 944, 725 cm^{-1}; MALDI−TOF MS: 292.09 calculated for $C_{13}H_{20}Cl_2NO_2{}^+[M + H^+]$, 292.05 found.

Synthesis of unit model 6 A mixture of 2,5-dibromofuran (100 mg, 0.443 mmol), toluenethiol (110 mg, 0.885 mmol), Na_2CO_3 (46.9 mg, 0.443 mmol) and quinoline (0.44 mL) was heated at 200 °C for 2 h under a nitrogen atmosphere. The mixture was cooled to room temperature and quenched by the addition of MeOH and water. The products were extracted with $CHCl_3$. The combined organic layer was dried over $MgSO_4$, filtered, and concentrated in vacuo. The obtained crude material was purified by silica gel column chromatography (eluent: hexane → hexane-$CHCl_3$ (3:1)) and subsequent preparative thin layer silica gel column chromatography (eluent: hexane-$CHCl_3$ (10:1)) to give **4** (5.6 mg), an orange oil, as an analytical pure sample; ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 7.14 (d, $J = 5.2$ Hz, 2 H, Ar), 7.06 (d, $J = 5.2$ Hz, 2 H, Ar), 6.67 (s, 2 H, furan), 2.30 (s, 6 H, Me) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ

148.0, 137.1, 131.8, 130.0, 129.1, 120.1, 21.2 ppm; IR (KBr) υ 3136, 3022, 2918, 1491, 1452, 1399, 1377, 1263, 1211, 1179, 1143, 1114, 1086, 1066, 1019, 1010, 936, 838, 738, 664 cm^{-1}.

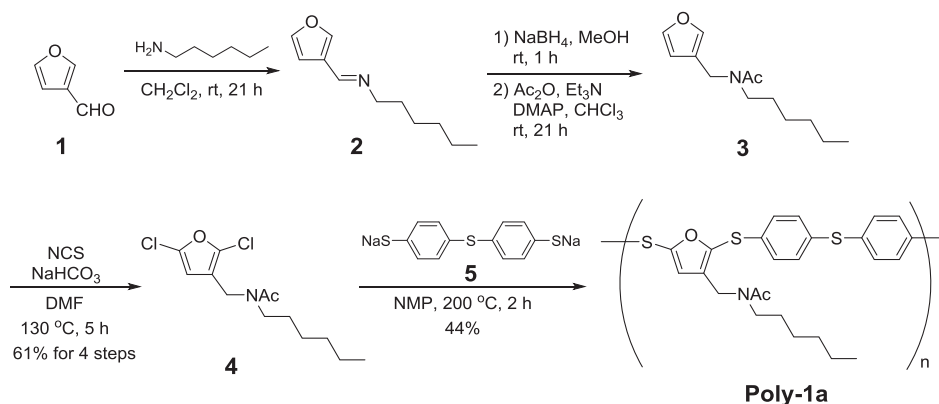## Typical procedure for the polycondensation of 4 with dithiolate

Synthesis of **Poly-1b**

A mixture of **4** (136.3 mg, 0.466 mmol), 4,4'-thio-bisbenzenethiol (116.8 mg, 0.466 mmol), and K_2CO_3 (132.2 mg, 0.956 mmol) in NMP (1.0 mL) was sonicated, and the atmosphere was replaced with Ar. The mixture was heated to 200 °C, stirred for 2 h, and cooled to room temperature. The reaction was quenched by the addition of water. The products were extracted with $CHCl_3$, dried over $MgSO_4$, filtered, and concentrated in vacuo to give a crude material (256.4 mg). The crude product was dissolved in a small amount of $CHCl_3$ and then reprecipitated with hexane to give a black solid. The solid product was collected by filtration and dried in vacuo overnight to give **Poly-1b** (174.8 mg, 80%) as a black solid: M_w 9,700 Da (estimated by DOSY); M_w/M_n 1.4 (estimated by SEC on the basis of dextran standards); T_g 51.6 °C (estimated by DSC); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 7.42–7.02 (m, Ar), 6.80 (brd, furan), 4.49–4.30 (m, CH_2), 3.22 (brd, CH_2), 3.08 (brd, CH_2), 2.09 (s, Ac), 1.46 (brd, CH_2), 1.26–1.20(m, CH_2), 0.85 (brd, CH_2) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ 170.7, 147.5, 146.7, 143.9, 134.2, 131.8, 129.8, 128.6, 128.0, 127.8, 121.6, 119.4, 113.7, 48.4, 45.7, 43.9, 40.3, 40.1, 31.5, 28.6, 26.5, 22.7, 22.1, 21.5, 14.1 ppm; IR (ATR) υ 2926, 2855, 1643, 1573, 1473, 1416, 1389, 1256, 1182, 1093, 1074, 1010, 941, 808, 742 cm^{-1}.

Poly-2 (144.2 mg, 73%) as a black solid: M_w 2,900 Da for the DMSO-d_6-soluble component (estimated by DOSY); M_w/M_n 1.8 (estimated by SEC on the basis of dextran standards); T_g 7.6 °C (estimated by DSC); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 6.44 (brd, furan), 6.32 (brd, furan), 4.35 (s, CH_2), 4.26 (s, CH_2), 3.32 (brd, CH_2), 3.17 (brd, CH_2), 2.15 (s, Ac), 2.11 (s, Ac), 1.44-1.20 (m), 0.89 (brd) ppm; IR (ATR) υ 2924, 2853, 1677, 1649, 1453, 1302, 1260, 1197, 1012, 856, 714 cm^{-1}.

Poly-3 (103.2 mg, 68%) as a black solid: M_w 3,400 Da (estimated by DOSY); M_w/M_n 1.7 (estimated by SEC on the basis of dextran standards); T_g 22.8 °C (estimated by DSC); ^{1}H NMR (400 MHz, $CDCl_3$, 295 K) δ 4.96 (brd), 1.80 (s, Ac), 1.68 (brd), 1.25 (brd), 0.87 (brd) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ 180.4, 171.7, 170.8, 146.1–122.0 (brd), 50.0, 31.6, 30.8, 29.7, 29.5, 28.7, 28.2, 27.3, 26.6, 25.7, 24.5, 22.7, 21.5, 21.1, 17.8, 14.1 ppm; IR (ATR) υ 2957, 2928, 2858, 1629, 1564, 1403, 1342, 1206, 1131, 1048, 1010, 922, 831 cm^{-1}.

Scheme 1 Synthesis of monomer **4** and polycondensation of **4** with **5**

Typical procedure for the methylation of Poly-2

To a suspension of **Poly-2** (10.0 mg, 0.023 mmol per a repeating unit) in CH_2Cl_2 (1.0 mL) was added Me_3OBF_4 (34.7 mg, 0.235 mmol) at room temperature. After stirring for 17.5 h at a constant temperature, toluene (1.0 mL) was added to the mixture. The reaction mixture was heated at 100 °C to remove CH_2Cl_2, and the suspension was further stirred for 2.5 h at the same temperature. The obtained black solid was collected by filtration, washed with toluene and CH_2Cl_2 and dried in vacuo to give a quantitative yield of methylated **Poly-2** (17 mg): M_w 3,500 Da (estimated by DOSY); ^{1}H NMR (400 MHz, DMSO-d_6, 298 K) δ 7.22–6.96 (furan), 3.61–3.50 (brd, CH_2), 3.25–3.16 (brd, CH_2), 2.85–2.84 (Me), 1.90 (s, Ac), 1.77–0.83 (brd) ppm; IR (ATR) υ 3566, 3340, 1634, 1428, 1036, 936 cm^{-1}.

Results and discussion

Scheme 1 shows the synthesis of monomer **4**. For the spectroscopic evaluation of polymer properties, we prepared furan-based polymers with good solubility. Thus, we introduced a flexible pendant group to the furan monomer before the polymerization. 3-Furaldehyde (**1**) was selected as the starting compound. Aldehyde **1** was treated with hexylamine in CH_2Cl_2 to give an imine, **2**, with a long alkylene group. The reduction of imine **2** was followed by acetylation to give **3**. Regioselective chlorination of **3** was performed by N-chlorosuccinimide (NCS) in the presence of $NaHCO_3$ in DMF at 130 °C to produce 2,5-dichlorofuran derivative **4** in 61% overall yield in four steps. It was found that florisil column chromatography was essential for the purification of **4**, while typical silica gel column chromatography facilitated the hydrolysis of **4**, suggesting the remarkably higher activity of **4** with nucleophiles. Although we also attempted the preparation of a 2,5-dibromofuran derivative corresponding to **4**, we could not isolate the compound due to the high water sensitivity.

The obtained monomer **4** was polycondensed with freshly prepared bis(sodium thiolate) **5** in NMP at 200 °C. After stirring for 2 h, the reaction mixture became a black solution, which was cooled to room temperature and quenched by the addition of water. The products were extracted with $CHCl_3$. The combined organic layer was dried over $MgSO_4$, filtered, and concentrated in vacuo to give black solid. Reprecipitation using a small amount of $CHCl_3$ in hexane afforded **Poly-1a** with a 44% yield. The results clearly indicate the high polymerizability of 2,5-dichlorofuran compared with that obtained with conventional dichlorobenzene as the monomer of PPS. We also found that the neutral dithiol performed efficiently as the coupling partner of **4** in the presence of K_2CO_3 to give **Poly-1b** at an 80% yield (Scheme 2 and Table 1, entry 1).

As expected, **Poly-1b** showed good solubility in a variety of organic solvents. The structure of **Poly-1b** was confirmed by IR and ^{1}H NMR spectroscopic analysis (Figure S6 and Fig. 1). In the IR spectrum [see Supporting Information], strong peaks clearly support the presence of amide carbonyl groups (1650 cm^{-1}) and the furan skeleton (1400 and 1000 cm^{-1}) in the polymer. Figure 1 shows the ^{1}H NMR spectra of **4**, **Poly-1b**, and unit model (**6**) [see Supporting Information]. In the ^{1}H NMR spectrum of **4** (Fig. 1a), the signals from protons that are adjacent to the amide moiety appear as splitted signals, which indicates that the cis-trans rotamers of the N,N-disubstituted amide bond and the atropisomers are caused by steric repulsion between the substituted furan and the amide sp^2 plane. In the ^{1}H NMR spectrum of **Poly-1b** (Fig. 1b), the chemical shifts of all aliphatic signals agree with those of **4**. The appearance of aromatic signals suggests the incorporation of aromatic spacer structures that originated from the dithiol coupling partner. The chemical shifts are also in good agreement with those of unit model **6**. These results strongly support the formation of the **Poly-1b** structure.

According to the literature [30–32], the weight-average molecular weight (M_w) of **Poly-1b** was estimated by the diffusion coefficient obtained from diffusion-ordered NMR

Scheme 2 Synthesis of polymers
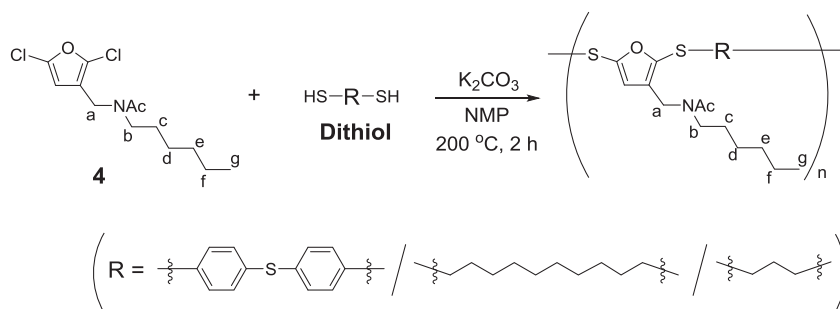
Table 1 Results of polycondensations[a]

Entry	Dithiol	Yield (%)[b]	M_w (kDa)[c]	M_w/M_n[d]	Polymer
1	4,4′-thiobisbenzenethiol	80	9.7	1.4	**Poly-1b**
2	1,10-decanedithiol	73	2.9[e]	1.8	**Poly-2**
3	1,3-propanedithiol	68	3.4	1.7	**Poly-3**
4	Na₂S	–[f]	–	–	**Poly-4**

[a]The reaction was performed by using **4** (0.47 mmol) and dithiol (0.47 mmol) in the presence of K_2CO_3 (0.96 mmol) in NMP (1.0 mL) at 200 °C for 2 h

[b]Hexane-insoluble part

[c]Weight-average molecular weight (M_w) values were estimated by DOSY spectra on the basis of dextran standards

[d]Polydispersity indices (M_w/M_n) were estimated by SEC using DMSO as an eluent on the basis of dextran standards

[e]DMSO-soluble part

[f]No reaction

spectroscopy (DOSY) in DMSO-d_6 on the basis of dextran standards and determined to be 9.7 kDa [see Supporting Information]. The polydispersity index (M_w/M_n) was estimated to be 1.4 by size exclusion column chromatography (SEC) using DMSO as the eluent. SEC was not reliable for estimating the molecular weight of **Poly-1b**, even when using the same solvent and standards as those of DOSY. The SEC profile of **Poly-1b** produced a peak that appeared at an early retention time that corresponded closely to a monomer [see Supporting Information], probably due to the strong interaction between **Poly-1b** and the column stationary phase, leading to an underestimation of molecular weight. We also investigated the versatility of spacer moieties (R), and the results are summarized in Scheme 2. We found that aliphatic dithiols also reacted with **4** to give the corresponding polymers, **Poly-2** and **Poly-3** (Table 1, entries 2 and 3), while there was no reaction with Na₂S (Table 1, entry 4). We also attempted to prepare poly(furanylene sulfide) (PFS), an analog of PPS. The synthesis of PFS was conducted using an unsubstituted 2,5-dihalofuran and Na₂S in an autoclave [33], and the results are

summarized in Tables S1 and S2 [see Supporting Information]. We began the polymerization using commercially available 2,5-dibromofuran in NMP (Table S1, entry 1). By structural analysis of the products, it was found that the MeOH-insoluble component included a large quantity of bromine and that the MeOH-soluble component was contaminated with 2-bromofuran as a side product. Thus, we used quinoline as a solvent to suppress radical-mediated hydrogen abstraction as an undesirable side reaction (Table S1, entry 2), assuming that the polymerization of 2,5-dibromofuran with Na₂S would proceed via a radical nucleophilic aromatic substitution ($S_{RN}1$) mechanism [34]. However, we did not obtain the desired polymer. On the other hand, the polymerization of 2,5-dichlorofuran with Na₂S in NMP afforded the corresponding polymer (Table S1, entry 3), which was revealed by elemental analysis (Table S2), while the polymerization of 2,5-dichlorofuran in quinoline was ineffective (Table S1, entry 4). Based on these results, it was expected that the combination of 2,5-dichlorofuran and NMP would facilitate an S_NAr reaction rather than an $S_{RN}1$ mechanism, which could play an important role in the synthesis of 2,5-furanylene sulfide-containing polymers.

Poly-2 had limited solubility in various organic solvents such as hexane, MeOH, CHCl₃, THF, DMF, and DMSO, as **Poly-2** has not only pendant groups but also flexible long alkylene spacers. During the purification process, **Poly-2** spontaneously formed a self-standing film as shown in Fig. 2. The IR spectrum of **Poly-2** strongly suggests the formation of a 2,5-furanylene sulfide-containing polymer (Figure S8) [see Supporting Information], because the characteristic peaks of carbonyl groups and the furan skeleton appear at positions similar to those of **Poly-1b**. The ¹H NMR spectrum of the CDCl₃-soluble component of **Poly-2** after extensive sonication also provided structural evidence for **Poly-2** (Figure S7) [see Supporting Information].

Since **Poly-2** resembled an elastic polymer to the touch, we measured the stress-strain curve of **Poly-2** at room temperature to determine the strength and toughness of the polymer film (Fig. 3a). Figure 3a shows the high fracture stress (σ) and strain (ε) values, which reached 1.5 MPa and 1000%, respectively. From the tensile stress-strain curve,

Fig. 1 ^{1}H NMR spectra of (a) 4, (b) Poly-1b, and (c) unit model (6) (400 MHz, CDCl$_3$, 298 K)
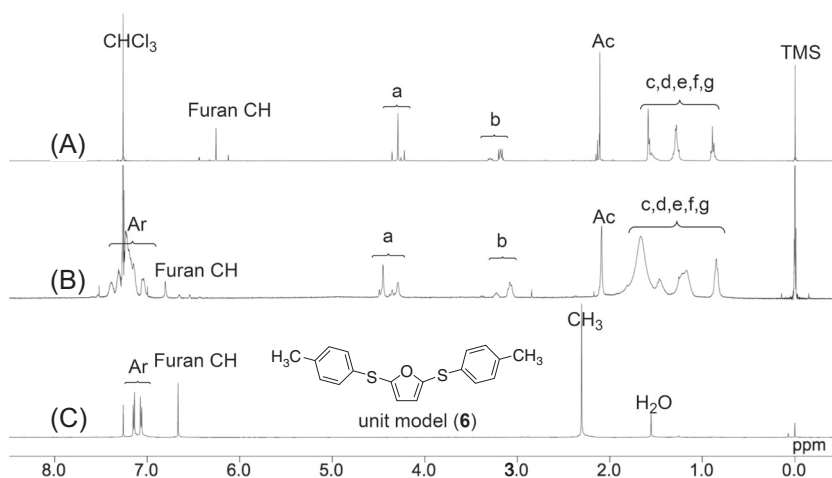
Fig. 2 Photographs of (a) Poly-1b, (b) Poly-2, and (c) Poly-3
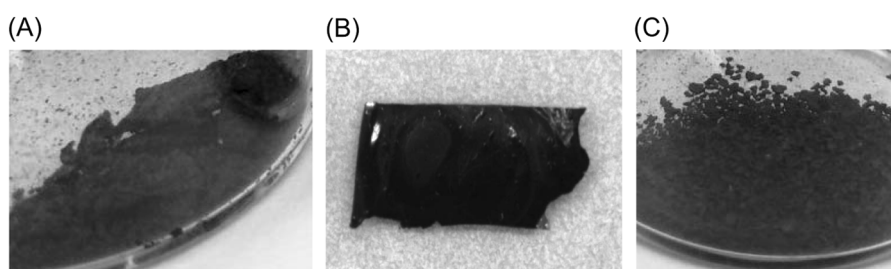

we found a clear yield point (σ_y: 0.6 MPa, ε_y: 75%), which is indicative of a tough material. The elastic modulus (E) was found to be 2.7 MPa. The work of extension to fracture (W_{ext}), a parameter characterizing the work required to fracture the sample, was calculated from the area under the tensile stress-strain curves until sample failure. The W_{ext} value (6.6 MJ/m^3) is comparable to that of natural rubber (10 MJ/m^3) as a typical elastomer [35], suggesting that Poly-2 contains cross-linking points as a result of interchain interactions between the furan units as hard segments. The distinct yielding observed beyond a certain strain could originate from the internal disruption of the interactions. An interchain interaction was also confirmed by the tendency observed in the Mooney–Rivlin profile (Fig. 3b), where the reduced stress ($\sigma^* = \sigma /(\lambda - \lambda^{-2})$) is plotted as a function of $1/\lambda$. Here, $\lambda = \varepsilon + 1$ is the stretch ratio. At large values of $1/\lambda$, the plot has a positive slope, indicating the occurrence of strain softening. On the other hand, the negative slope at lower $1/\lambda$ values indicates strain hardening, which can be evidence of the existence of strong interactions that do not break within the observation time scale and produce the finite extensibility of polymer chains.

Poly-3 showed good solubility in various organic solvents in spite the structural similarity to Poly-2. The IR spectrum of Poly-3 supports the proposed polymer structure (Figure S10) [see Supporting Information]. On the other hand, the ^{1}H NMR spectrum of Poly-3 was found to be very broad at various temperatures (Fig. 4). Several proton signals, such as a furan methyne signal, were lacking in the spectra. The signal intensity of methylene protons at low temperature gradually decreased as the solution was heated to a higher temperature. When the temperature was decreased to room temperature, the peak returned to the original broad signal. We found that the signal disappeared at approximately 60 °C, indicating that Poly-3 undergoes dynamic and reversible structural changes on an NMR time scale. The dynamic behavior and the proximity of asymmetric furan moieties arranged in noncontrolled directions could cause several signals to disappear. The effects of amide rotamers on the broadening can be ruled out, because the ^{1}H NMR spectra of both Poly-1b and Poly-2 with same amide groups showed relatively sharp signals.

To clarify the equilibrium chemical species in the CDCl$_3$ solution of Poly-3, we measured the UV-vis spectra of Poly-3 in CHCl$_3$ at various temperatures (Fig. 5). The spectra include long wavelength absorptions up to approximately 700 nm, indicating the existence of intramolecular charge transfer, such as the π-π stacking of furan skeletons. Since the spectra include an isosbestic point at 280 nm (Figures S24, S27, and S30) [see Supporting Information], it was revealed that two types of chemical species are included in the equilibrium. As the temperature increased, hyperchromism was observed at 250–280 nm (Fig. 5a), while the transition at 370–450 nm indicated

Fig. 3 a Stress-strain curve and (**b**) Mooney–Rivlin profile of **Poly-2**
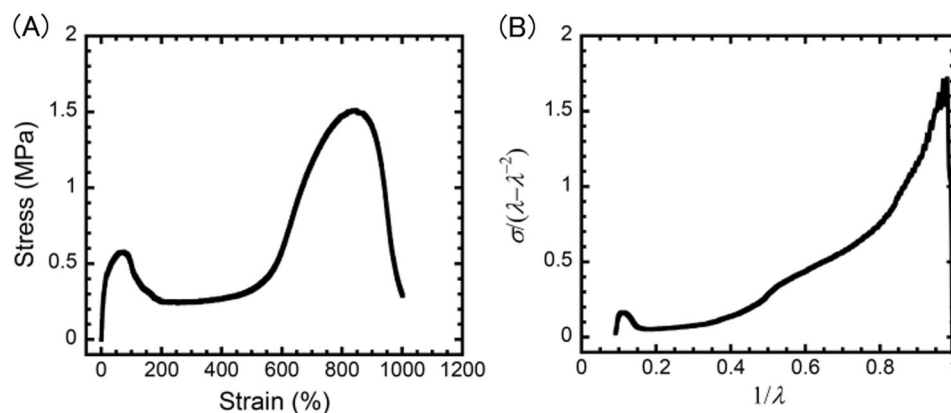
Fig. 4 ^{1}H NMR spectra of **Poly-3** at various temperatures (400 MHz, CDCl$_3$)
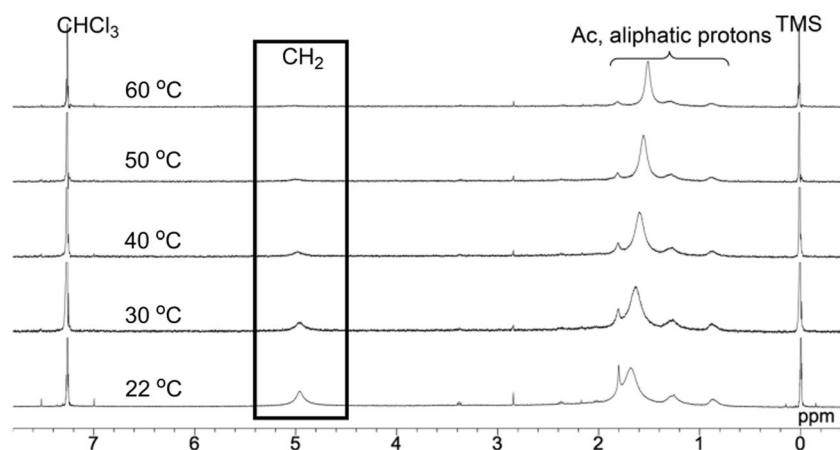

hypochromism (Fig. 5b). The thermochromism was fully reversible. Based on the plots of the temperature dependency of the molar absorbance (Figs. 5c, d), we observed the opposite trend at 260 and 405 nm, and both plots include an inflection point. These results indicate the following: (i) **Poly-3** has π-stacked furan moieties at low temperature. (ii) The short spacers in **Poly-3** facilitates intrachain interactions between the furan units. In **Poly-2**, with long spacers, the interchain interactions of furan moieties would become dominant and could function as a physical cross-linking point [36]. The low solubility of **Poly-2** is consistent with this inherent property of cross-linked polymers. (iii) Upon heating, **Poly-3** undergoes a globule to coil transition, i.e., an entropy-driven conformational change to adopt an extended polymer chain along with the dissociation of π-stacked furan units [37].

Considering two chemical species such as π-stacked and free furans, the enthalpy (ΔH) and entropy (ΔS) terms were obtained by the following equation: $\ln K_a = -\Delta H/RT + \Delta S/R$ (Fig. 6) [38, 39]. The plots are nonlinear and include an inflection point at approximately 22 °C. The inflection region includes no apparent change in association constant (K_a) between the two chemical species. The inflection temperature is similar to the glass transition temperature (T_g) observed in DSC measurements (Figure S34, T_g of **Poly-3**: 22.8 °C) [see Supporting Information]. Therefore, we conclude that **Poly-3** transitions from a solid to a glassy state, even in solution where thermal energy is consumed by the latent heat of phase transition without a change in K_a. We divided the plots into approximate low- and high-temperature areas and estimated the slopes and intercepts for each approximated line. As a result, the entropy term ($T\Delta S$), rather than the enthalpy term (ΔH), was observed to be dominant in these systems. The ΔH in the low-temperature region is 32.4 kJ. mol^{-1}, which is less than that in the high-temperature region (55.5 kJ.mol^{-1}). Considering the signal transition in the full scale of UV-vis spectra, we conclude that the first relaxation at low temperature is attributed to the glass transition of flexible alkylene moieties, while the second relaxation at high temperature comes from the dissociation of the π-π stacking structures of furan units. The numerical magnitude of ΔH for the dissociation of π-stacking is much higher than those of typical aromatic compounds [40, 41] and is comparable with the dissociation energy of several covalent bonds [42]. The stable π-stacking of furan units can be attributed to the enhanced dipole moment induced by sulfide linkages. The

Fig. 5 UV-vis spectra of **Poly-3** at various temperatures (100 μM per repeating unit, CHCl₃) in a range of (**a**) 250–320 nm and (**b**) 370–450 nm and temperature dependencies of molar absorbance at (**c**) 260 nm and (**d**) 405 nm
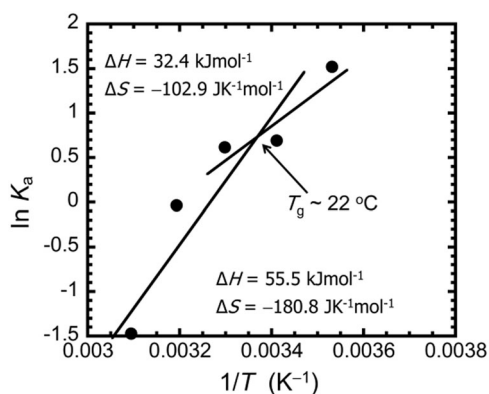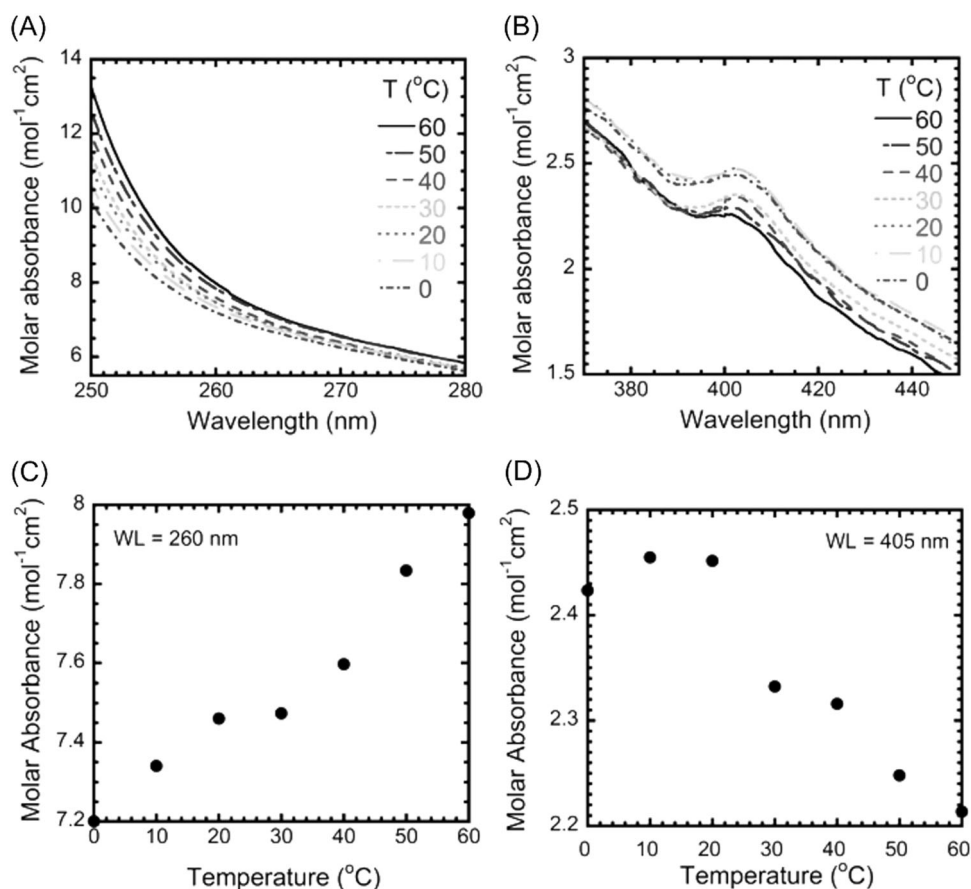
Fig. 6 van't Hoff plots based on the UV absorption of **Poly-3** at 260 nm at various temperatures

strong π-stacking interaction observed in the tensile test of **Poly-2** is in good agreement with the ΔH of **Poly-3**.

To further reveal the physical cross-link of **Poly-2**, we also performed the *S*-methylation of **Poly-2** with the Meerwein reagent (Me₃OBF₄) according to the literature with a slight modification (Scheme 3) [43]. Treatment of **Poly-2** with Me₃OBF₄ at 100 °C afforded the corresponding *S*-methylated polymer in a quantitative yield. The obtained polymer was soluble in DMSO-*d₆*, probably due to the change of steric and electronic factors around the furanylene moieties. Thus, we estimated the M_w of the polymer to be 3500 Da by using the DOSY measurement [see Supporting Information], indicating that the M_w order of virgin **Poly-2** would be similar to those of **Poly-1b** and **Poly-3**. These results could also provide evidence that the cross-links of **Poly-2** are not covalent, but rather physical cross-links that are based on interactions of the 2,5-furanylene sulfide moieties.

Conclusions

In conclusion, we developed 2,5-furanylene sulfide-containing polymers. From the spectral analyses and tensile tests, we found that the furanylene sulfide moieties form thermally favorable π-π stacking structures. The numerical value of the association enthalpy is quite large and is comparable to the dissociation energy of several covalent bonds. In a similar manner, we also attempted the preparation of poly(furanylene sulfide) analogs of PPS. The present study provides new insight for the creation of furan-based high performance polymers. A rational control of the dipole moment of the furan unit might provide interesting functions for furan as a biosourced alternate.

Scheme 3 Methylation of **Poly-2**
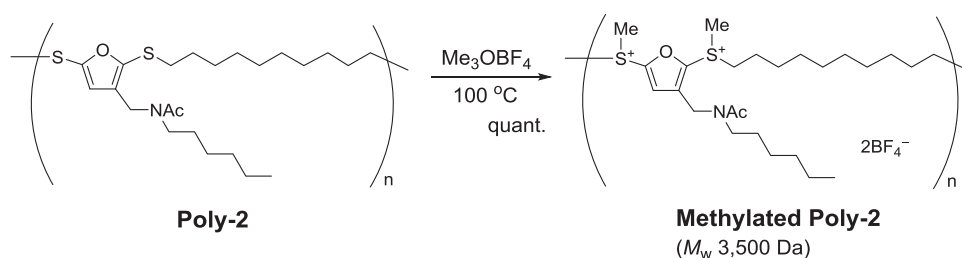
Poly-2

Methylated Poly-2
(M_w 3,500 Da)

Acknowledgements

Compliance with ethical standards

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