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Novel Electron-Donating Quinonoid Compounds: 2,5-Bis(4′,5′-dimethyl-1′,3′-dithiolan-2′-ylidene)- and 2,5-Bis(1′,3′-dithian-2′-ylidene)-2,5-dihydrothiophenes. Synthesis and Polymerization in the Presence of Oxygen

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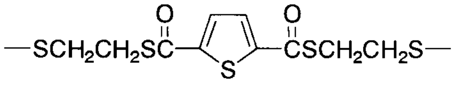
ABSTRACT: Two novel electron-donating quinonoid compounds, 2,5-bis(4′,5′-dimethyl-1′,3′-dithiolan-2′-ylidene)-2,5-dihydrothiophene (**1b**) and 2,5-bis(1′,3′-dithian-2′-ylidene)-2,5-dihydrothiophene (**1c**), were synthesized successfully. The homopolymerizations of **1b** and **1c** took place only in the presence of oxygen to give the corresponding polymers composed of three different structural units. The ratios of the structural units in the polymers were significantly dependent on the polarity of the solvents used for the polymerizations. On the basis of NMR analysis of the resulting polymers and of the reaction products of **1b** and **1c** with water, a possible polymerization mechanism via a radical-cation intermediate was proposed.

Introduction

Previously, we prepared 2,5-bis(1′,3′-dithiolan-2′-ylidene)-2,5-dihydrothiophene (**1a**)[1] as an isolable and polymerizable electron-donating quinonoid compounds based on 2,5-dimethylene-2,5-dihydrothiophene and investigated its polymerization behavior. It has dithioacetal rings at the exocyclic positions that are capable of ring-opening polymerization, and its polymerization takes place only in the presence of oxygen to give polymers composed of three different structural units, one bearing two thioester groups obtained by ring-opening (A), a second bearing one thioester group from ring-opening and one cyclic dithioacetal ring obtained without ring-opening (B), and a third bearing two cyclic dithioacetal rings obtained with no ring-opening (C).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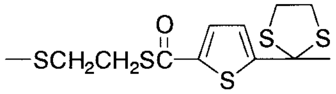
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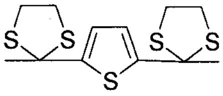
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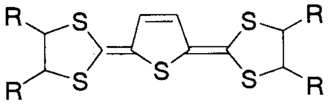
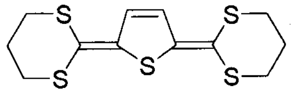
The relatively poor solubility of **1a** and its polymer toward conventional solvents prevented a detailed investigation of the polymerization of **1a**. Further investigation of derivatives of **1** with higher solubilities was desired to study the mechanism of formation of the three different structural units. 2,5-Bis(4′,5′-dimethyl-1′,3′-dithiolan-2′-ylidene)-2,5-dihydrothiophene (**1b**) is one candidate with improved solubility because the methyl groups on the 4 and 5 positions of the dithiolane rings should improve the solubility of the quinonoid compound and its polymer because of the lack of planarity. It is well-known that the ring size of the cyclic compound can also affect ring-opening polymerizability,[2−4] and 2,5-bis(1′,3′-dithian-2′-ylidene)-2,5-dihydrothiophene (**1c**) was synthesized as an electron-donating quinonoid compound with a six-membered ring containing 1,3-dithiane units.

In this work, the syntheses of **1b** and **1c** and their polymerizations in the presence of oxygen are described.


1a: R = H
1b: R = Me


1c

Experimental Section

Materials. 2,5-Thiophenedicarbaldehyde (**2**) was prepared according to the method reported by Ferigna et al.[5] 2,5-Bis(1′,3′-dithiolan-2′-ylidene)-2,5-dihydrothiophene (**1a**) was prepared according to the procedure reported previously.[1] *p*-Chloranil (Wako Pure Chemicals Ltd.) was purified by recrystallization from benzene. Chloroform, dichloromethane, 1,2-dichloroethane, benzene, hexane, diethyl ether, and chlorobenzene were refluxed over calcium hydride for 12 h and then distilled. Thiophene (TCI Co.), 2,3-butanedithiol (TCI Co.), 1,3-propanedithiol (TCI Co.), trityl tetrafluoroborate (Aldrich Co.), boron trifluoride diethyl etherate (Aldrich Co.), butyllithium (1.6 M solution in hexane, Aldrich Co.), *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA, Aldrich Co.), and tetrabutylammonium perchlorate (Aldrich Co.) were used without further purification.

Monomer Synthesis. 2,5-Bis(4′,5′-dimethyl-1′,3′-dithiolan-2′-yl)thiophene (3). 2,5-Thiophenedicarbaldehyde (**2**) (1.5 g, 11 mmol) and 2,3-butanedithiol (2.5 g, 21 mmol) were dissolved in 30 mL of chloroform, the resulting solution was

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cooled to 0 °C, and 1 mL of boron trifluoride diethyl etherate was added. Stirring was continued for 1 h. The reaction mixture was washed three times with 20 mL of saturated aqueous sodium bicarbonate, dried over anhydrous magnesium sulfate, and filtered. The filtrate was placed under reduced pressure to remove solvents and give a brown, viscous oil, which was then dissolved in a small amount of benzene. The resulting solution was passed through a silica gel column using a mixture of benzene and hexane as the eluent. A yellow elution band was collected and then placed under reduced pressure to remove solvents and give 3.6 g (99% yield) of **3** as an orange, viscous oil: IR (KBr) ν_{C-H} 2928, ν_{C-H} 2880, $\nu_{C=C}$ 1520, ν_{C-S} 808 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.82 (m, 2H, thiophene ring), 5.88, 5.80, 5.76 (s, 2H, >CH−), 3.98, 3.81, 3.48 (m, 4H, dithiolane ring), 1.46 (m, 12H, Me); ^{13}C NMR ($CDCl_3$) δ 148.75, 148.52, 148.37, 147.37, 147.17, 147.02, 145.10, 144.87, 144.69 (3 position in thiophene ring), 125.30, 125.25, 125.14, 124.78, 124.67, 124.36, 124.27 (2 position in thiophene ring), 57.81, 55.81, 54.30, 53.73 (−CH<), 50.42, 49.09, 47.98 (−*C*HMe−), 18.17, 17.38, 16.80, 15.78 (−Me). Anal. Calcd. for $C_{14}H_{20}S_5$: C, 48.23; H, 5.78; S, 45.99. Found: C, 48.10; H, 5.80; S, 46.10.

2,5-Bis(1′,3′-dithian-2′-yl)thiophene (4). **4** was synthesized as white needles in 98% yield from the reaction of **2** with 1,3-propanedithiol in a process similar to that for **3**, followed by recrystallization from hexane: mp 146−147 °C; IR (KBr) ν_{C-H} 2862, $\nu_{C=C}$ 1439, ν_{C-S} 823 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.01 (s, 2H, thiophene ring), 5.30 (s, 2H, −CH−), 2.97−2.91 (m, 8H, $-SCH_2-$), 2.19−1.90 (m, 4H, $-CH_2-$); ^{13}C NMR ($CDCl_3$) δ 142.91 (3 position in thiophene ring), 125.98 (2 position in thiophene ring), 44.49 (CH), 30.51 (CH_2), 24.96 (CH_2). Anal. Calcd. for $C_{12}H_{16}S_5$: C, 45.00; H, 5.04; S, 49.96. Found: C, 45.08; H, 5.10; S, 49.82.

2,5-Bis(4′,5′-dimethyl-1′,3′-dithiolan-2′-ylidene)-2,5-dihydrothiophene (1b). **3** (2.7 g, 7.6 mmol) and trityl tetrafluoroborate (3.3 g, 10.0 mmol) were dissolved in 40 mL of dichloromethane, and the solution was stirred for 3 h at room temperature. The reaction mixture was placed under reduced pressure to remove solvents and give a black, viscous oil. The oil was washed well with diethyl ether to remove triphenylmethane and unreacted **3** and was then dried under reduced pressure. The residual brown powder was dissolved in 50 mL of dichloromethane, the mixture was cooled to 0 °C under nitrogen, and then 10 mL of dichloromethane containing triethylamine (1.5 g, 14.8 mmol) was added dropwise. After being stirred for 1 h, the reaction mixture was placed under reduced pressure to remove solvents and give brown solids, which were then dissolved in a small amount of dichloromethane. The resulting solution was passed through a silica gel column using dichloromethane as the eluent. A red elution band was collected, concentrated to 100 mL without heating, added to a large amount of hexane (600 mL), and then cooled to −30 °C to obtain 1.0 g (39% yield) of **1b** as yellow needles: mp 147−148 °C; IR (KBr) ν_{C-H} 2926, ν_{C-H} 2878, $\nu_{C=C}$ 1520, ν_{C-S} 831 cm^{-1}; UV−vis ($CHCl_3$) 261($\epsilon = 1.1 \times 10^4$), 420 ($\epsilon = 3.4 \times 10^4$) nm; ^{1}H NMR ($CDCl_3$) δ 6.40 (s, 2H, dihydrothiophene), 3.98−3.65 (m, 4H, dithiolane ring), 1.42 (m, 12H, Me); ^{13}C NMR ($CDCl_3$) δ 129.38 (═C<), 128.48 (dihydrothiophene), 127.60 (dihydrothiophene), 56.39, 55.80, 53.71, 53.19 (CH), 18.73 (CH_3), 15.47 (CH_3). Anal. Calcd. for $C_{14}H_{18}S_5$: C, 48.51; H, 5.23; S, 46.26. Found: C, 48.40; H, 5.13; S, 46.47.

2,5-Bis(1′,3′-dithian-2′-ylidene)-2,5-dihydrothiophene (1c). **1c** was synthesized as yellow needles in 22% yield in a process similar to that for **1b**: mp 133−135 °C; IR (KBr) ν_{C-H} 3032, ν_{C-H} 2856, $\nu_{C=C}$ 1464, ν_{C-S} 808 cm^{-1}; UV−vis ($CHCl_3$) 435 ($\epsilon = 3.8 \times 10^4$) nm; ^{1}H NMR ($CDCl_3$) δ 7.00 (s, 2H, dihydrothiophene), 3.02−2.88 (m, 8H, $-SCH_2-$), 2.26−2.17 (m, 4H, $-CH_2-$); ^{13}C NMR ($CDCl_3$) δ 144.19 (═C<), 129.83 (dihydrothiophene), 115.49 (dihydrothiophene), 30.71 (SCH_2), 24.80 (CH_2). Anal. Calcd. for $C_{12}H_{14}S_5$: C, 45.28; H, 4.45; S, 50.27. Found: C, 45.12; H, 4.50; S, 50.38.

Model Compounds. 2-[2′-Mercapto-1′,2′-(dimethyl)ethylthiocarbonyl]-5-(4′,5′-dimethyl-1′,3′-dithiolan-2′-yl)thiophene (5). **1b** (200 mg, 0.576 mmol) was dissolved in 30 mL of chloroform, 20 mL of a 5% HCl/methanol solution was added, and the solution was refluxed for 5 h. The reaction mixture was cooled to room temperature and then neutralized with saturated aqueous sodium bicarbonate (about 10 mL). The resulting solution was extracted three times with 10 mL of chloroform, and the combined extracts dried over anhydrous magnesium sulfate and filtered. The filtrate was placed under reduced pressure to remove solvents and give a yellow-orange, viscous oil. This oil was dissolved in a small amount of dichloromethane, and the solution was passed through a silica gel column using dichloromethane as the eluent. The second yellow elution band was collected and then placed under reduced pressure to remove dichloromethane and give 86 mg (41% yield) of **5** as a pale yellow, viscous oil: IR (NaCl) ν_{C-H} 3036, ν_{C-H} 2930, ν_{SH} 2530, $\nu_{C=O}$ 1601, $\nu_{C(=O)S}$ 1189, ν_{C-S} 826 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.61−7.57 (m, 1H, thiophene ring), 7.04−7.00 (m, 1H, thiophene ring), 5.85, 5.76, 5.71 (s, 1H, −CH<), 3.98 (m, 1H, −C(═O)SC*H*Me−), 3.98, 3.83, 3.52 (m, 2H, dithiolane ring), 3.32 (m, 1H, −C*H*MeSH), 1.67 (d, J = 7.26 Hz, 1H, SH), 1.49−1.34 (m, 12H, Me); ^{13}C NMR ($CDCl_3$) δ 183.83 (−C(═O)S−), 157.81 (thiophene ring), 141.20 (thiophene ring), 131.12 (thiophene ring), 125.59 (thiophene ring), 58.29 (−C(═O)S*C*H−), 55.76, 54.88, 53.84 (−CH<), 49.61, 48.59, 47.31, 46.86 (dithiolane ring), 40.92 (−*C*HMeSH), 22.71 (−CH*Me*SH), 18.17, 17.04, 16.73, 16.40 (Me in dithiolane ring), 15.74 (−C(═O)*C*HMe−). Anal. Calcd. for $C_{14}H_{20}OS_5$: C, 46.11; H, 5.53; O, 4.39; S, 43.97. Found: C, 46.23; H, 5.55; O, 4.31; S, 43.91.

2,5-Bis[2′-mercapto-1′,2′-(dimethyl)ethylthiocarbonyl]thiophene (6). **1b** (100 mg, 0.288 mmol), 3.0 mL of chloroform as the solvent, and one drop of water were placed in a glass ampule into which oxygen gas was bubbled for 15 s. The ampule was then sealed and placed in a bath thermostated at 60 °C for 48 h. The ampule was opened, and the reaction mixture was placed under reduced pressure to remove solvents and give an orange, viscous oil, which was dissolved in a small amount of a 1:1 mixture of benzene and hexane. The resulting solution was passed through a silica gel column using a 1:1 mixture of benzene and hexane as the eluent. The second yellow elution band was collected and then placed under reduced pressure to remove dichloromethane and give 28 mg (26% yield) of **6** as a pale yellow, viscous oil: IR (KBr) ν_{C-H} 3044, ν_{C-H} 2928, 2884, ν_{SH} 2538, $\nu_{C=O}$ 1620, $\nu_{C(=O)S}$ 1167, ν_{C-S} 843 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.71 (s, 2H, thiophene ring), 4.09−3.97 (m, 2H, −C(═O)SC*H*Me−), 3.36−3.27 (m, 2H, −C*H*MeSH), 1.69 (d, J = 7.25 Hz, 2H, −SH), 1.50−1.40 (m, 12H, −Me); ^{13}C NMR ($CDCl_3$) δ 183.43 (−C(═O)S−), 146.68 (thiophene ring), 130.46 (thiophene ring), 47.55 (−C(═O)-S*C*HMe−), 40.72 (−*C*HMe−SH), 22.75 (−CH*Me*−SH), 16.41 (−C(═O)SCH*Me*−). Anal. Calcd. For $C_{14}H_{20}O_2S_5$: C, 44.17; H, 5.30; O, 8.41; S, 42.12. Found: C, 44.21; H, 5.36; O, 8.21; S, 42.22.

2-[3′-(Mercaptopropylthio)carbonyl]-5-(1′,3′-dithian-2′-yl)thiophene (7). **7** was synthesized as a pale yellow, viscous oil (95 mg, 89% yield) from **1c** in a process similar to that for **5**: IR (NaCl) ν_{C-H} 3036, ν_{C-H} 2868, ν_{SH} 2530, $\nu_{C=O}$ 1606, $\nu_{C=c}$ 1497, $\nu_{C(=O)S}$ 1190, ν_{C-S} 828 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.65 (d, J = 3.96 Hz, 1H, thiophene ring), 7.19 (d, J = 3.96 Hz, 1H, thiophene ring), 5.29 (s, 1H, −CH<), 3.17 (t, J = 7.10 Hz, 2H, $-C(=O)SC\mathit{H}_2CH_2CH_2SH$), 2.96−2.91 (m, 4H, $-SCH_2-$ in dithiane ring), 2.62 (dd, J = 6.92, 8.25 Hz, 2H, $-C(=O)SCH_2$-$CH_2C\mathit{H}_2SH$), 2.21−1.91 (m, 4H, $-SCH_2C\mathit{H}_2CH_2S-$), 1.44 (t, J = 8.2 Hz, 1H, −SH); ^{13}C NMR ($CDCl_3$) δ 183.04 (C(═O)S−), 151.21 (thiophene ring), 141.11 (thiophene ring), 130.67 (thiophene ring), 126.97 (thiophene ring), 43.61 (−CH<), 33.34 (CH_2 in dithiane ring), 29.63 ($-C(=O)S-CH_2\mathit{C}H_2CH_2SH$), 27.21 ($-C(=O)S-\mathit{C}H_2CH_2CH_2SH$), 24.57 ($-SCH_2-$ in dithiane ring), 23.09 ($-C(=O)S-CH_2CH_2\mathit{C}H_2SH$). Anal. Calcd. for $C_{12}H_{16}OS_5$: C, 42.85; H, 4.81; O, 4.76; S, 47.5. Found: C, 42.91; H, 4.83; O, 4.82; S, 47.44.

2,5-Bis[3′-(mercaptopropylthio)carbonyl]thiophene (8). **8** was synthesized as a pale yellow, viscous oil (45 mg, 21% yield) from **1c** in a process similar to that for **7**, followed by preparative thin-layer chromatography treatment: IR (KBr) ν_{C-H} 3034, ν_{C-H} 2898, 2884, ν_{SH} 2530, $\nu_{C=O}$ 1613, $\nu_{C(=O)S}$ 1188, ν_{C-S} 820 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.71 (s, 2H, thiophene ring), 3.22 (m, 4H, $-C(=O)S-CH_2CH_2CH_2SH$), 2.63 (m, 4H, $-C(=O)S-CH_2CH_2CH_2SH$), 2.17−1.95 (m, 4H, $-C(=O)S-CH_2CH_2CH_2SH$), 1.43 (m, 2H, $-SH$); ^{13}C NMR ($CDCl_3$) δ 183.88 ($-C(=O)S-$), 146.54 (thiophene ring), 130.42 (thiophene ring), 33.41 ($-C(=O)S-CH_2CH_2CH_2SH$), 27.82 ($-C(=O)S-CH_2CH_2CH_2SH$), 23.34 ($-C(=O)S-CH_2CH_2CH_2SH$). Anal. Calcd. For $C_{12}H_{16}O_2S_5$: C, 40.91; H, 4.59; O, 9.08; S, 45.42. Found: C, 40.86; H, 4.62; O, 9.12; S, 45.40.

Polymerization Procedure. Given amounts of **1b** or **1c** and solvent (benzene, chloroform, 1,2-dichloroethane, or chlorobenzene) were placed in a glass ampule, into which oxygen gas was bubbled for 15 s. Alternatively, the solution was degassed by the freeze−thaw method (repeated three times). The ampule was sealed and placed in a bath thermostated at a given temperature for the time of polymerization and then opened. The reaction mixture was poured into an excess of hexane to precipitate the product, which was purified by three or more cycles of redissolution and reprecipitation. Chloroform and hexane were used as the solvent and precipitant, respectively. The product obtained was dried under reduced pressure at room temperature until a constant weight was obtained.

Measurements. All melting points were obtained with a Yanaco MP-53 melting point apparatus. Elemental analyses were performed on a Yanaco CHN Corder MT-3 instrument. The number-average molecular weights, M_n, of the polymers were estimated on a gel permeation chromatograph (GPC, Tosoh HLC-803D) with a series of Tosoh TSK-gel G2000H, G2500H, G3500H, and G4000H columns, calibrated with polystyrene standards, with tetrahydrofuran as the eluent. ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-EX 270 FT NMR spectrometer using chloroform-*d* with tetramethylsilane as the internal standard. Infrared spectra were obtained on KBr pellets with a JASCO IR-700 spectrometer.

The absorption spectra of the charge-transfer transition for the **1a**−*p*-chloranil (CA), **1b**−CA, and **1c**−CA systems were measured in chloroform at room temperature using a UVIDEC-430B spectrometer. The concentrations of the solutions employed were $[\mathbf{1a}] = [\mathbf{1b}] = [\mathbf{1c}] = [\mathrm{CA}] = 1.0 \times 10^{-3}$ mol/L.

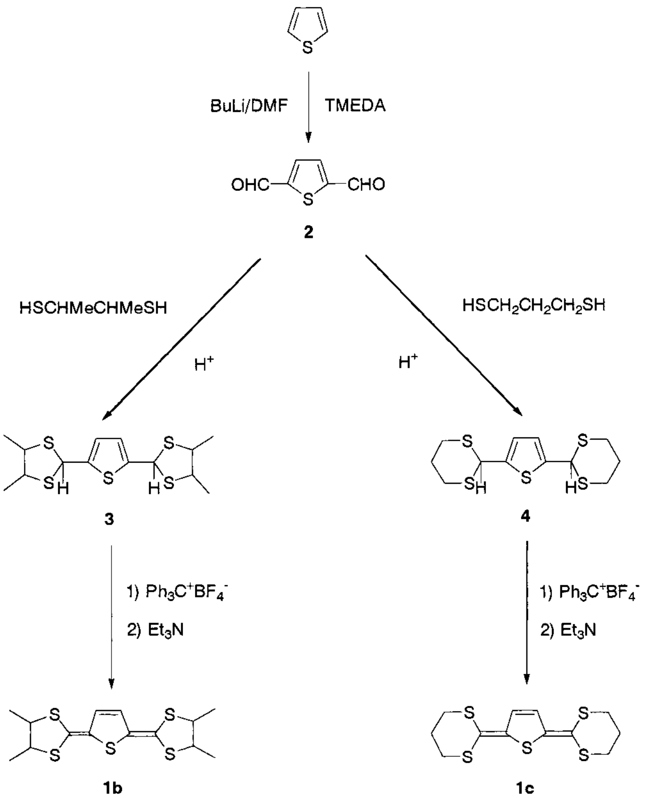
The reduction potentials of monomers **1a**, **1b**, and **1c** were measured on a Yanaco VMA-010 cyclic voltammetric analyzer at room temperature at a scanning rate of 100 mV/s using dichloromethane containing tetrabutylammonium perchlorate (0.1 mol/L) as the supporting electrolyte, with Ag/AgCl, glassy carbon, and platinum wire used as the reference, working, and counter electrodes, respectively.

Results and Discussion

Monomer Synthesis. 2,5-Bis(4′,5′-dimethyl-1′,3′-dithiolan-2′-ylidene)-2,5-dihydrothiophene (**1b**) and 2,5-bis(1′,3′-dithian-2′-ylidene)-2,5-dihydrothiophene (**1c**) were successfully prepared according to Scheme 1.

2,5-Thiophenedicarbardehyde (**2**), prepared by the Vilsmeier reaction of thiophene with *N*,*N*-dimethylformamide (DMF) according to the method reported by Ferigna et al.,[5] reacted with 2,3-butanedithiol or 1,3-propanedithiol in the presence of boron trifluoride diethyl etherate to give 2,5-bis(4′,5′-dimethyl-1′,3′-dithiolan-2′-yl)thiophene (**3**) and 2,5-bis(1′,3′-dithian-2′-yl)thiophene (**4**) as orange, viscous oils in quantitative yields. Reactions of the dithioacetals **3** and **4** with trityl tetrafluoroborate in dichloromethane, followed by deprotonation with triethylamine, afforded **1b** and **1c** as yellow needles in 39 and 22% yield, respectively. We tried to isolate and purify the tetrafluoroborate salts of the dithioacetals **3** and **4**, but all attempts failed because of rapid decomposition; therefore, the deprotonation was performed without purification of these salts. The total yield over four steps from thiophene was 32% for **1b** and 19% for **1c**. Both **1b** and **1c** were air-sensitive, the yellow needles changing to brown solids on standing under air for 1 week, and were therefore stored at −30 °C under nitrogen. The chemical structures of **1b** and **1c** were confirmed by IR, ^1H and ^{13}C NMR, and UV−vis spectroscopies and by elemental analysis. To compare the solubilities of **1b** and **1c** with that of **1a**, the solubility limits in 10 mL of chloroform at 25 °C were estimated and found to be 400 mg/10 mL for **1b** and **1c** and 100 mg/10 mL for **1a**, indicating that the introduction of methyl groups on the dithiolane rings and the six-membered rings should improve the solubility of the electron-donating quinonoid compounds based on 2,5-dimethylene-2,5-dihydrothiophene.

Scheme 1



Electron-Donating Properties. The electron-donating properties of **1a**, **1b**, and **1c** were estimated, both from the value of the first oxidation potential, E_1 (measured by cyclic voltammetry), and from the absorption maximum position of the charge-transfer peak for the interactions of **1a**−**c** with CA. The E_1 value of **1c** was measured to be −1.78 V, but the values of **1a** and **1b** could not be obtained because they were below the limit potential of −2.00 V. This indicates that both **1a** and **1b** are stronger electron donors than **1c**. The measurements of the charge-transfer transition bands for the **1a**−CA, **1b**−CA, and **1c**−CA systems were carried out in chloroform at room temperature. The difference spectrum for the **1c**−CA system did not show an absorption maximum, whereas the corresponding spectra for the **1a**−CA and **1b**−CA systems showed absorption maxima at 544 and 550 nm, respectively. This confirms that both **1a** and **1b** are stronger electron donors than **1c**, corresponding well with the results obtained by the CV measurement. Also, **1b** is a stronger electron donor than **1a**, because of the methyl groups on the 1,3-dithiolane rings. Thus, the electron-donating abilities of **1a**, **1b**, and **1c** decrease in the order **1b** > **1a** > **1c**.

Polymerizations of 1b and Characterization of Its Polymer. The polymerizations of **1b** were carried

Table 1. Polymerization of 1b under Various Conditions and Various Mole Fractions of Structural Units in Polymers[a]

run	**1b** (mg)	[**1b**] (mol/L)	temp (°C)	O_2	solvent, vol (mL)	yield (mg)	M_n	structural unit α	β	γ
1	100.7	0.029	60	absence	$CHCl_3$, 10	0	–	–	–	–
2	101.7	0.029	60	presence	$CHCl_3$, 10	7.8	4000	0.30	0.54	0.16
3	101.0	0.058	60	presence	$CHCl_3$, 10	43.8	4800	0.38	0.48	0.14
4	101.9	0.113	60	presence	$CHCl_3$, 2.5	104.6	5100	0.38	0.50	0.12
5	100.8	0.112	0	presence	$CHCl_3$, 2.5	0	–	–	–	–
6	100.4	0.112	40	presence	$CHCl_3$, 2.5	73.0	5300	0.37	0.54	0.09
7	98.8	0.110	90	presence	C_6H_5Cl, 2.5	65.1	5500	0.67	0.33	0.00
8	101.9	0.112	60	presence	C_6H_6, 2.5	91.4	6700	0.43	0.42	0.15
9	97.7	0.108	60	presence	C_6H_5Cl, 2.5	66.8	5600	0.52	0.41	0.07
10	99.0	0.110	60	presence	$ClCH_2CH_2Cl$, 2.5	97.2	8000	0.55	0.41	0.04

[a] Reaction time = 24 h.

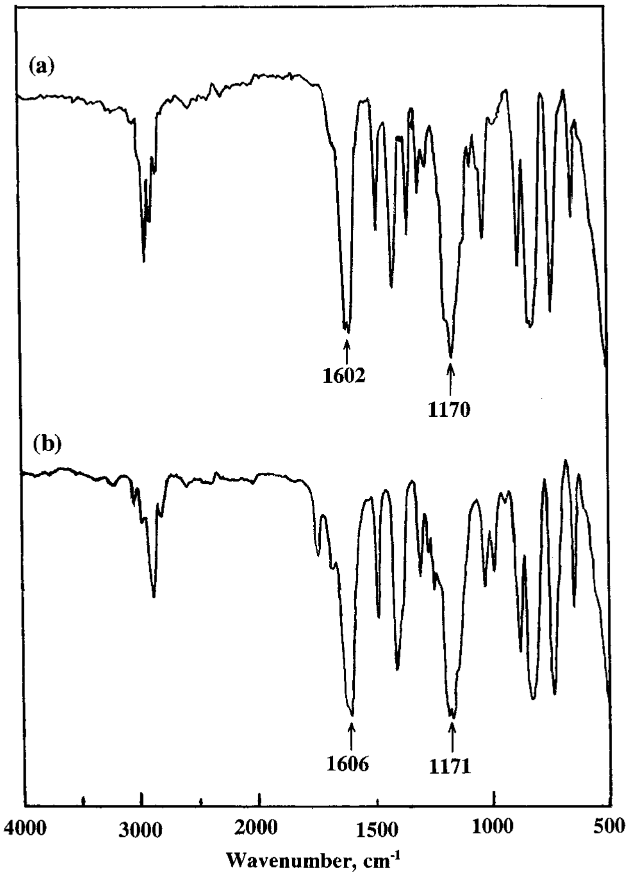
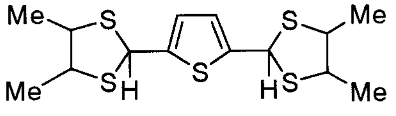


Figure 1. IR spectra (KBr) of the polymers obtained (a) in the polymerization of **1b** (run 4 in Table 1) and (b) in the polymerization of **1c** (run 4 in Table 2).

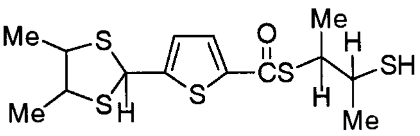
out in benzene, chloroform, 1,2-dichloroethane, and chlorobenzene at 0, 40, 60, and 90 °C in the presence and absence of oxygen at monomer concentrations of 0.029, 0.058, and 0.11 mol/L. All of these polymerizations proceeded homogeneously. The results are summarized in Table 1.

All products obtained were pale yellow powders with number-average molecular weights of 4000–8000 that were soluble in chloroform, dichloromethane, and acetone but insoluble in hexane and isopropyl ether. The polymerizations took place only in the presence of oxygen (as confirmed by runs 1 and 2), similarly to the polymerizations of **1a** reported previously.[1] The polymer yields and the number-average molecular weights of the polymers increased with increasing **1b** monomer concentrations (runs 2–4). The effect of the temperature of the polymerization of **1b** in the presence of oxygen was also investigated (runs 5–7). At 0 °C, no polymerization took place, and **1b** was recovered quantitatively. Above 40 °C, polymers were obtained, indicating that a temperature above 40 °C is required for initiation. However, at temperatures as high as 90 °C, the polymer yield decreased, probably because of the decomposition of the polymers as described below. The polymerization at 60 °C was also investigated in the various solvents (runs 4 and 8–10). The polymer yields and the number-average molecular weights of the polymers varied with solvent used, indicating a strong solvent effect on this polymerization.

The structure of the polymer obtained from **1b** was evaluated by comparing the NMR and IR spectra of the polymer with those of model compounds **3**, **5**, and **6**. Compound **3** was obtained during monomer preparation, and the latter two were prepared by reactions of monomer **1b** with hydrochloric acid and water, respectively.



3



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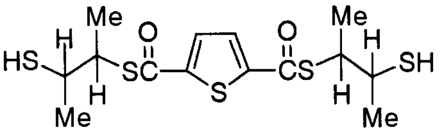
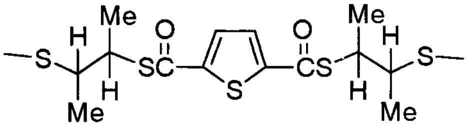


6

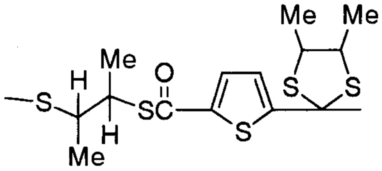
In the IR spectrum of the polymer obtained in run 4 (Figure 1a), new peaks were observed at 1602 and 1170 cm^{-1} that were assigned to the C=O and C–S stretching vibrations of the thioester group, respectively, in good agreement with those of **5** (1601 and 1189 cm^{-1}) and **6** (1620 and 1167 cm^{-1}). Moreover, in the ^{13}C NMR spectrum, the peak due to the C=S unit of the dithioester group (expected in the ring-opening unit of the dithioacetal ring, generally appearing at 220–240 ppm[6]) was not observed. Instead, a peak due to the C=O unit of the thioester group was observed at 183.4 ppm, in good agreement with the corresponding peaks of **5** (183.83

ppm) and **6** (183.43 ppm). Moreover, the peak due to the quarternary carbon of the dithiolane rings was observed at around 74 ppm. These results strongly support the production of thioester groups during the ring-opening polymerization of **1b** and of cyclic dithioacetal rings without ring-opening. The polymers obtained in runs 2, 3, and 6−10 also had IR and ^{13}C NMR spectra similar to those for run 4.

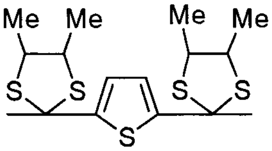
The ^{1}H NMR spectrum of the polymer obtained in run 4 is shown in Figure 2, where each peak was assigned to protons of the three different structural units (α, *β*, and *γ*) and to the terminal unit illustrated in the figure on the basis of the ^{1}H NMR spectra of **3**, **5**, and **6**. Peaks at 7.72 (thiophene ring), 4.20 (−C(=O)S−C*H*MeCHMeS−), 3.50−2.90 (−C(=O)S−CHMeC*H*MeS−), and 1.60−1.20 (Me) ppm were assigned to protons of the α unit; peaks at 7.60 (thiophene ring), 7.35 (thiophene ring), 4.20 (−C(=O)S−C*H*MeCHMeS−), 4.30−3.60 (methine proton in dithiolane ring), 3.50−2.90 (−C(=O)S−CHMeC*H*MeS−), and 1.60−1.2 (Me) ppm were for the *β* unit; peaks at 7.10 (thiophene ring), 4.30−3.60 (methine proton in dithiolane ring), and 1.60−1.20 (Me) ppm were for the *γ* unit; and a peak at 1.70 ppm was the thiol proton on the terminal end bearing S-2-mercapto-1,2-dimethylethyl carbothioate.



α unit



β unit



γ unit

It is concluded, therefore, that the polymers are composed of three different structural units similarly to the polymers obtained by the polymerizations of **1a** in the presence of oxygen. The ratios of the three structural units were determined from the peak area ratios of the protons on the thiophene ring in each unit. Unfortunately, the ratios could not be calculated on the basis of the peaks due to the methine protons appearing at 4.40−2.90 ppm because of peak overlap. The results are summarized in Table 1. The sum of the relative numbers of α and *β* units is much larger than the relative number of *γ* units at both 40 and 60 °C, indicating that the polymerizations of **1b** in oxygen give polymers containing large amounts ring-opened units. The ratios of the three units were almost the same at 40 and 60 °C (runs 3, 4, and 6). For example, the composition of the polymer obtained in run 4 was estimated to be five α units, seven *β* units, and two *γ* units from the ratios of the structural units and the number-average molecular weight of the polymer. On the other hand, the polymer obtained at 90 °C (run 7) contained no *γ* units, and the α unit content was relatively high, despite the fact that the polymer yield was somewhat lower, suggesting that thermal decomposition might have been taking place. To examine the possibility of decomposition further, the following experiment was conducted: 57 mg of the polymer (run 4, with a M_n of 5100 and an $\alpha/\beta/\gamma$ ratio of 0.38/0.50/0.12) was dissolved in 2.5 mL of chlorobenzene and heated at 90 °C in a sealed ampule for 24 h. The reaction product was precipitated by pouring the mixture into a large amount of hexane. The polymer was dried under reduced pressure to give 41 mg (72% yield) of recovered material, which had a M_n of 4300 and an $\alpha/\beta/\gamma$ ratio of 0.49/0.51/0.0. The lower molecular weight and the absence of *γ* units indicate that thermal decomposition takes place at temperatures as high as 90 °C. Thus, the low polymer yield at 90 °C is due to thermal decomposition competing with polymer formation. Moreover, the facts that the polymer obtained at 90 °C (run 7) contained no *γ* units and the isolated polymer heated at 90 °C showed a disappearance of the *γ* units and an increase in the α units indicate that the decomposition of the polymers occurs at the *β* units and/or the *γ* units. Plausible mechanisms for this decomposition are shown in Scheme 2.

On heating, the heterolytic cleavage of the sulfur−carbon bond between the 1,2-dimethyl-2-thioethyl S-thioester group in the α and *β* units and the dithioacetal ring group in the *β* and *γ* units occurs and generates a thiolate anion and a dithioacetal carbocation, the former of which forms a thiol by proton abstraction and the latter of which reacts with the very small amount of water in the system to form a 2-mercapto-1,2-dimethylethyl S-thioester unit through ring-opening. The formation of the 2-mercapto-1,2-dimethylethyl S-thioester from the dithioacetal rings would convert both the *γ* unit to the *β* unit and a *β* unit into an α unit.

The $\alpha/\beta/\gamma$ ratios in the polymers varied depending on solvents used for the polymerization (runs 4 and 8−10). The dielectric constants of benzene, chloroform, chlorobenzene, and 1,2-dichloroethane are reported to be 2.27, 4.81, 5.62, and 10.37, respectively, at 25 °C.[7] The *γ* unit in the polymers tends to decrease with increasing polarity of the solvents. As shown in Scheme 2, the formation of the thiolate anion and the dithioacetal carbocation by heterolytic cleavage is considered to be the initial step in decomposition of the polymer. The higher the polarity of the solvent, the more it can stabilize the generated ionic species by solvation, resulting in the promotion of heterolytic cleavage. It is likely, therefore, that the polymerization in highly polar solvents would afford the polymers with fewer *γ* units.

Polymerizations of 1c and Characterization of Its Polymer. The polymerizations of **1c** were carried out in benzene, chloroform, and 1,2-dichloroethane at 40, 60, and 80 °C in the presence and absence of oxygen at a monomer concentration of 0.12 mol/L. All polymerizations proceeded homogeneously. The results are summarized in Table 2.

As in the polymerizations of **1b**, the polymerizations of **1c** took place only in the presence of oxygen to give pale yellow powders, that were soluble in chloroform, dichloromethane, and acetone but insoluble in hexane and isopropyl ether. The polymer yields and the number-

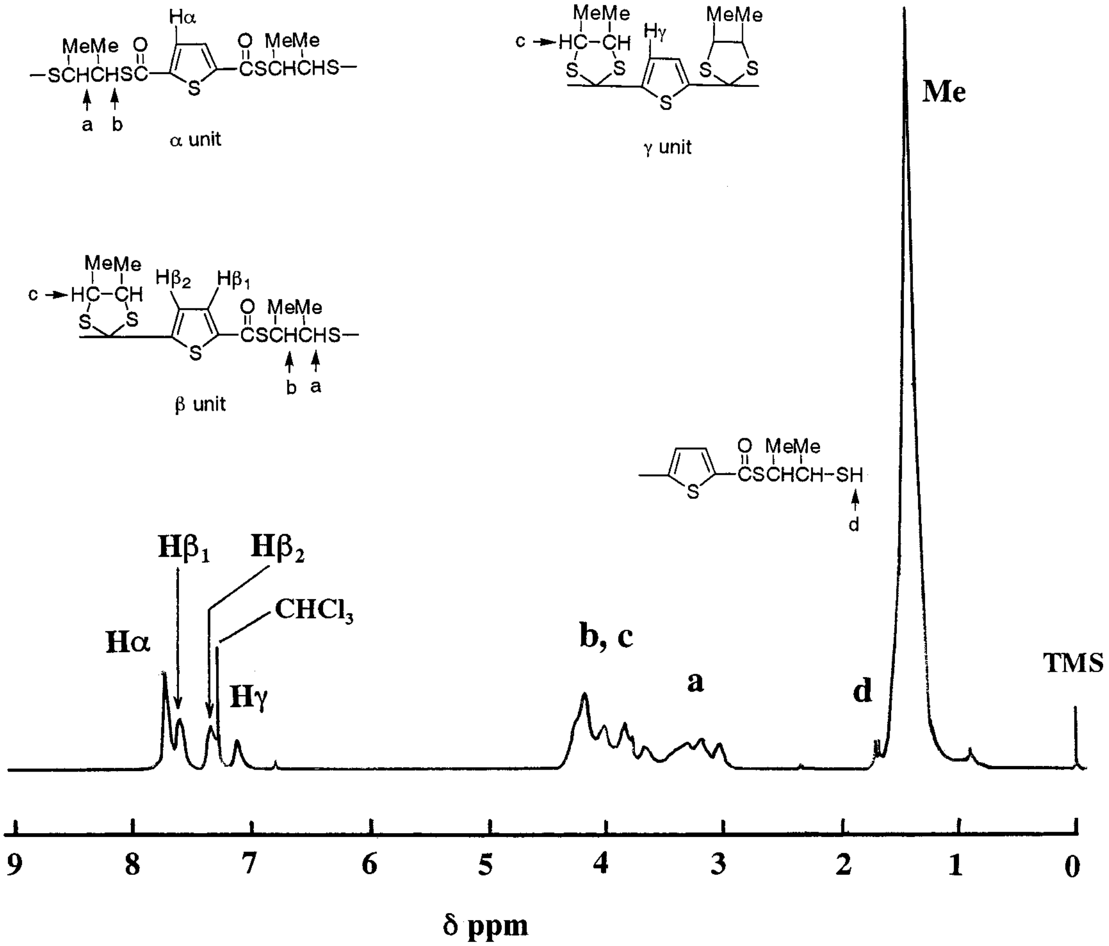


Figure 2. ^{1}H NMR spectrum of the polymer obtained in the polymerization of **1b** (run 4 in Table 1) in chloroform-*d*.

Scheme 2

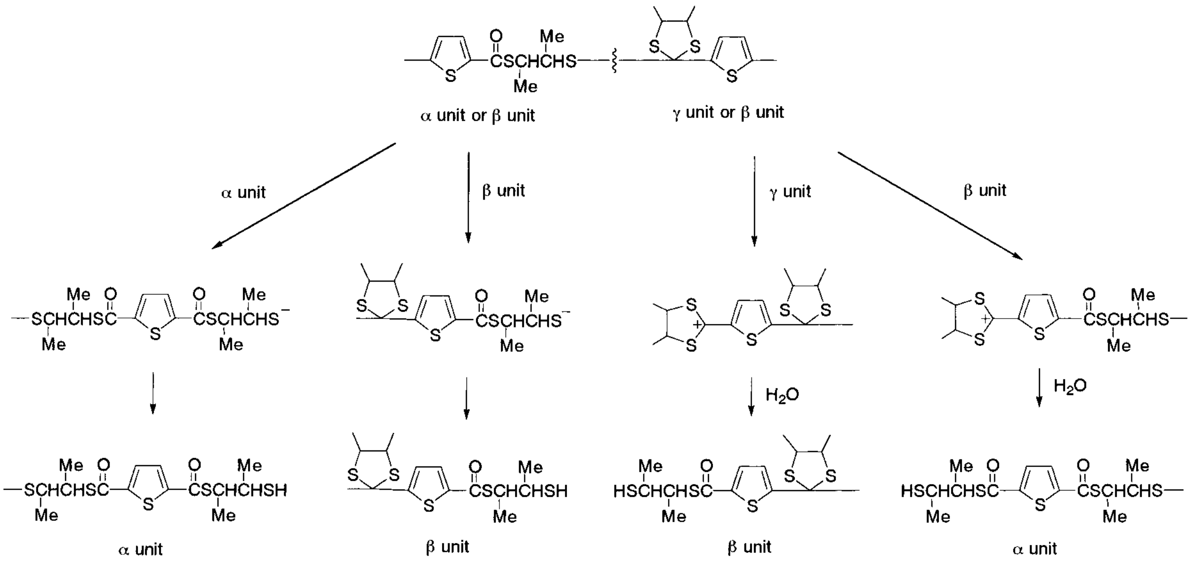


Table 2. Polymerization of 1c under Various Conditions and Various Mole Fractions of Structural Units in Polymers[a]

run	1c (mg)	[1c] (mol/L)	temp (°C)	O$_2$	solvent, vol (mL)	yield (mg)	M_n	structural unit α	structural unit *β*	structural unit *γ*
1	97.9	0.118	60	absence	CHCl$_3$, 2.5	0	–	–	–	–
2	99.9	0.121	60	presence	CHCl$_3$, 2.5	64.0	2200	0.34	0.53	0.13
3	100.2	0.121	60	presence	C$_6$H$_6$, 2.5	35.5	1600	0.33	0.44	0.23
4	100.0	0.121	60	presence	ClCH$_2$CH$_2$Cl, 2.5	51.5	5800	0.41	0.52	0.07
5	100.1	0.121	40	presence	ClCH$_2$CH$_2$Cl, 2.5	23.6	1400	0.33	0.49	0.18
6	100.0	0.121	80	presence	ClCH$_2$CH$_2$Cl, 2.5	82.5	2300	0.46	0.52	0.02

[a] Reaction time = 24 h.

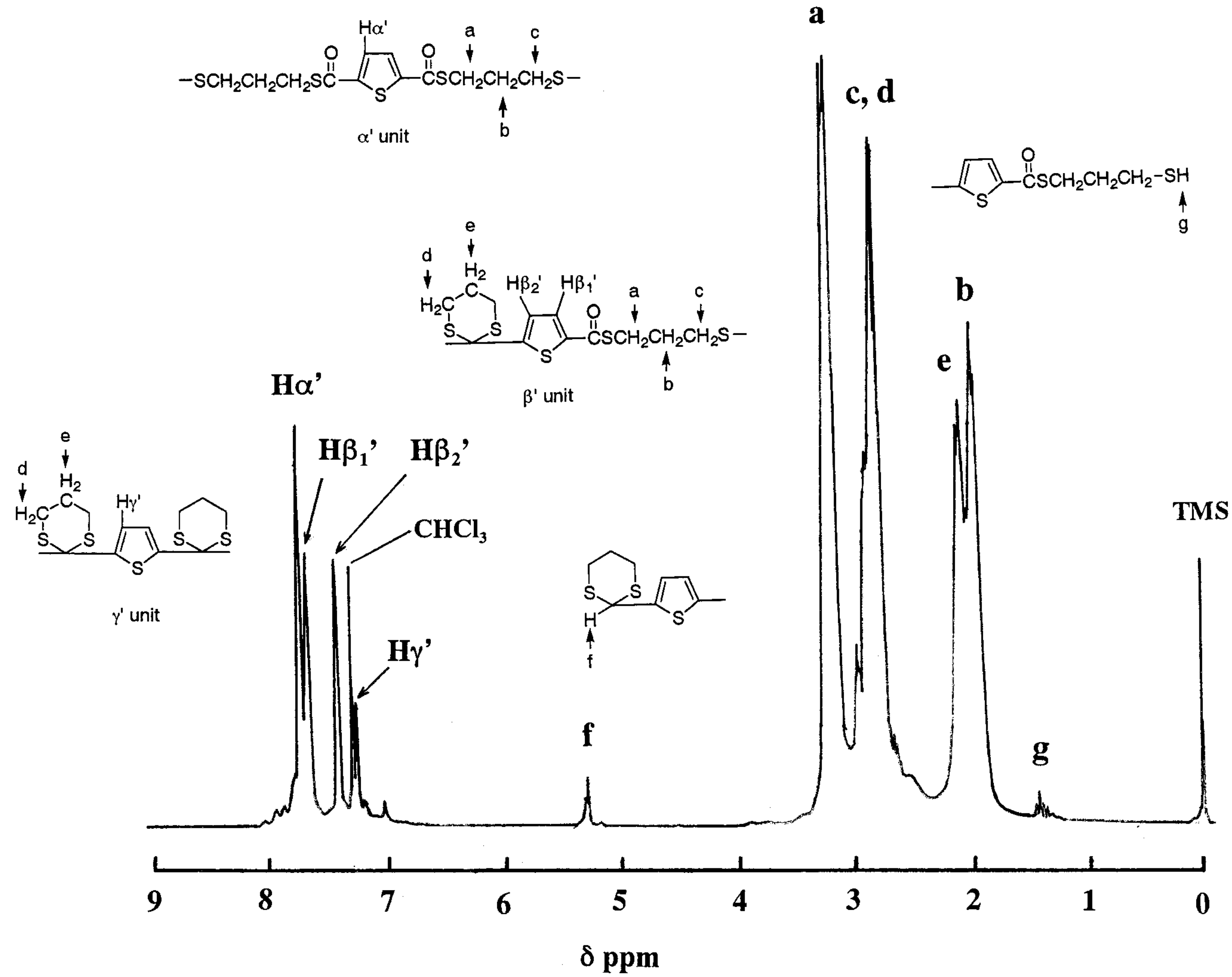
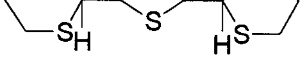


Figure 3. ^{1}H NMR spectrum of the polymer obtained in the polymerization of **1c** (run 4 in Table 2) in chloroform-*d*.

average molecular weights varied appreciably depending on solvent and temperature, probably again because of decomposition of the polymers, as mentioned above.

The structure of the polymer obtained from **1c** was evaluated by comparing the NMR and IR spectra of the polymer with those of model compounds **4**, **7**, and **8**. Compound **4** was obtained during monomer preparation, and the latter two were prepared by reaction of monomer **1c** with hydrochloric acid and water, respectively.



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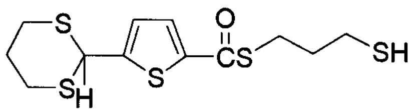

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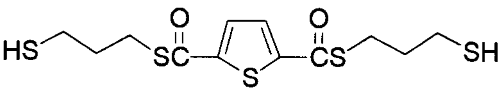

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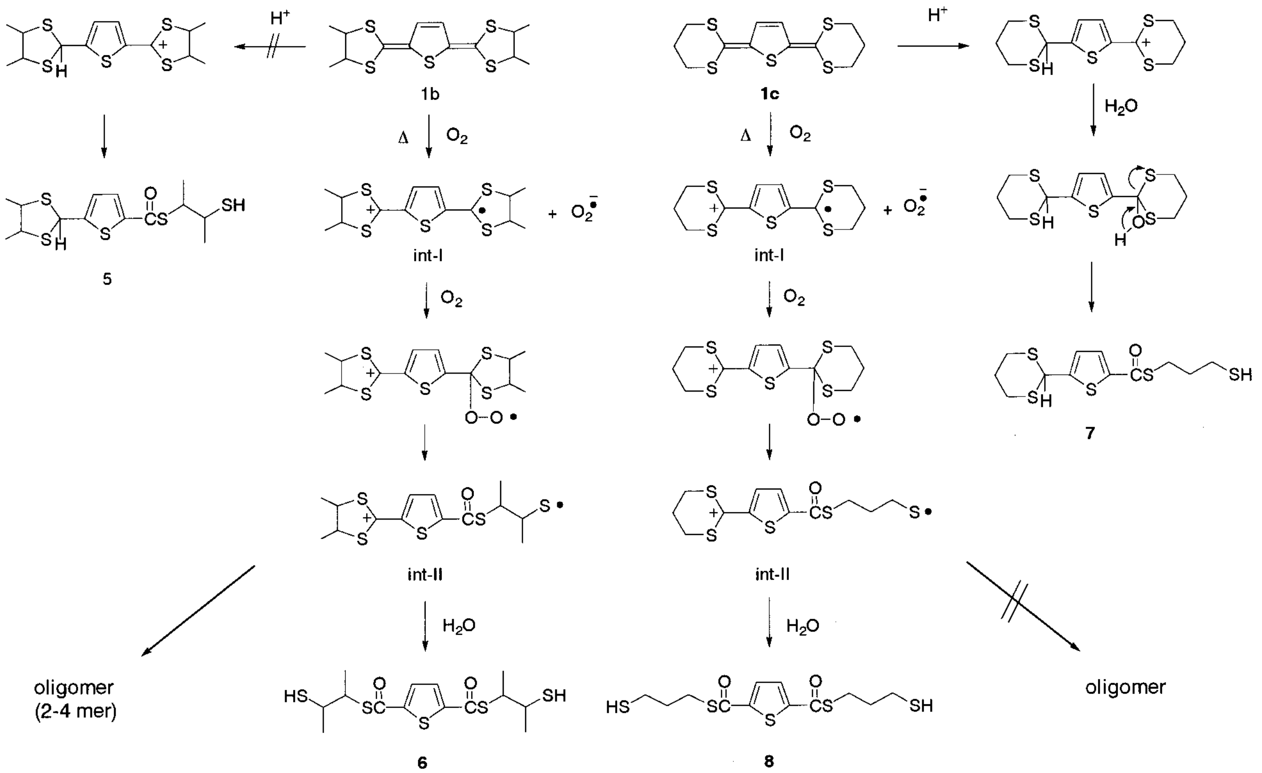
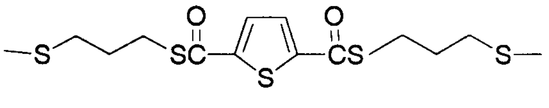
In the IR spectrum of the polymer obtained in run 4 (Figure 1b), new peaks were observed at 1606 and 1171 cm^{-1} that were assigned to the C=O and C−S stretching vibrations, respectively, of the thioester group, in good agreement with the peaks of **7** (1606 and 1190 cm^{-1}) and **8** (1613 and 1188 cm^{-1}). In the ^{13}C NMR spectrum, the peak due to the C=S unit of the dithioester group was not observed. Instead, a peak due to the C=O unit of the thioester group was observed at 183.5 ppm, in good agreement with the corresponding peaks of **7** (183.04 ppm) and **8** (183.88 ppm). These results strongly support the existence of the thioester group in this polymer. Also, the peak due to the quarternary carbons of the dithiane rings was observed at around 73 ppm. The polymers obtained in runs 2, 3, 5, and 6 had IR and ^{13}C NMR spectra similar to those for run 4. The ^{1}H NMR spectrum of the polymer obtained in run 4 is shown in Figure 3, with all peaks assigned to the protons of the three different structural units (α′, *β*′, and *γ*′) and to the terminal unit on the basis of the ^{1}H NMR spectra of **4**, **7**, and **8**. Peaks at 7.70 (thiophene ring), 3.30−3.00 ($-C(=O)S-CH_2CH_2CH_2S-$), 3.00−2.60 ($-C(=O)S-CH_2CH_2CH_2S-$), and 2.20−2.00 ($-C(=O)S-CH_2CH_2CH_2S-$) ppm were assigned to protons of the α′ unit; peaks at 7.60 (thiophene ring), 7.35 (thiophene ring), 3.30−3.00 ($-C(=O)S-CH_2CH_2CH_2S-$), 3.00−2.60 ($-C(=O)S-CH_2CH_2CH_2S-$ and $-SCH_2CH_2CH_2S-$ in dithiane ring), 2.20−2.00 ($-C(=O)S-CH_2CH_2CH_2S-$), and 2.00−

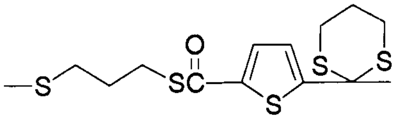
Scheme 3



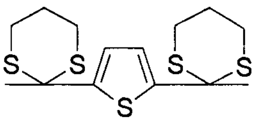
1.80 ($-\mathrm{SC}H_2\mathrm{CH_2C}H_2\mathrm{S}-$ in dithiane ring) ppm were for the β' unit; peaks at 7.20 (thiophene ring), 3.00−2.60 ($-\mathrm{SCH_2C}H_2\mathrm{CH_2S}-$ in dithiane ring), and 2.00−1.80 ($-\mathrm{SC}H_2\mathrm{CH_2C}H_2\mathrm{S}-$ in dithiane ring) ppm were for the γ' unit; a peak at 5.30 ppm was the methine proton of a 1,3-dithiane ring at the terminal end; and a peak at 1.40 ppm was the thiol proton of S-3-mercaptopropyl carbothioate at the terminal end.



α' unit



β' unit



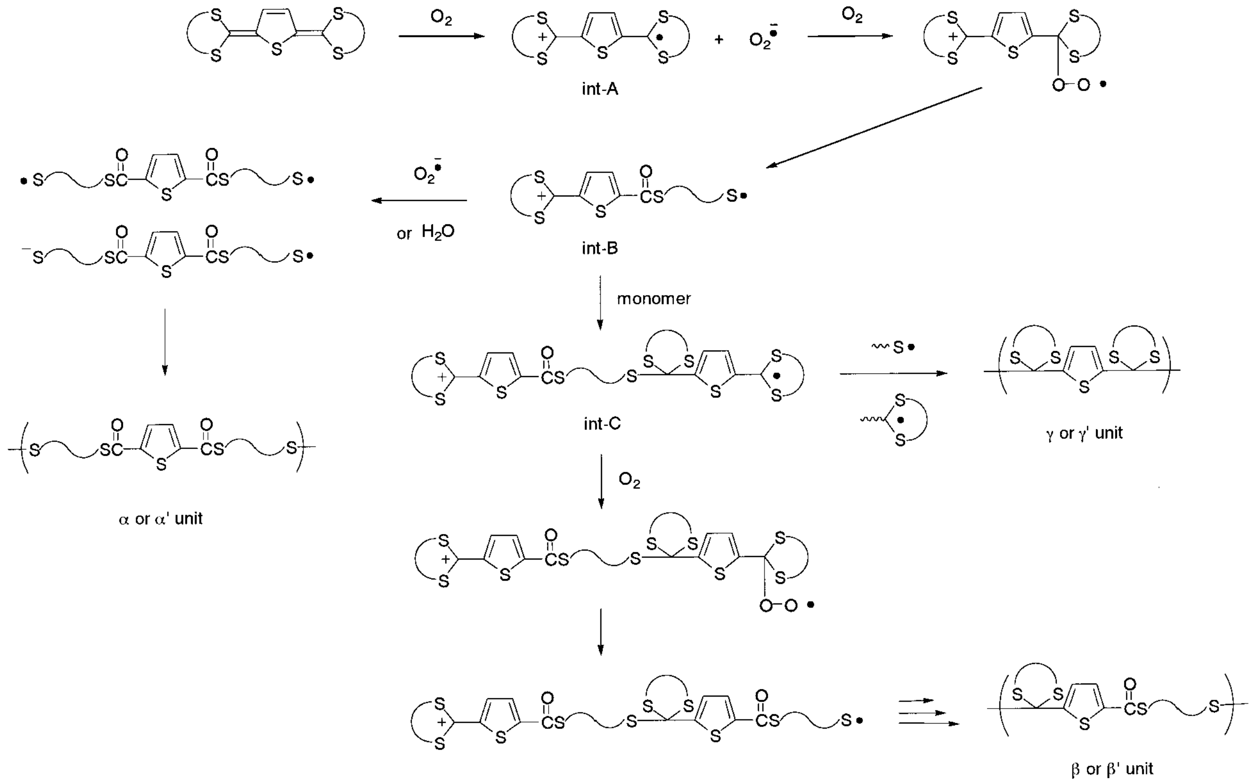
γ' unit

It is concluded, therefore, that these polymers are also composed of the three different structural units as are the polymers obtained by the polymerizations of **1a** and **1b** in the presence of oxygen. The ratios between the structural units were determined from the peak area ratios of the protons on the thiophene ring in each unit and are summarized in Table 2. Similar temperature and solvent dependences were observed for the polymerizations of **1c**, which is indicative of the occurrence of the decomposition as shown in Scheme 2.

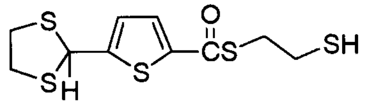
Reactions of 1b and 1c with Water. It has been suggested that water might participate in a ring-opening of the dithioacetal moiety, as shown in Scheme 2, for the decomposition of the polymers. To investigate the influence of water on the polymerization, the reactions of **1b** and **1c** in the presence of a large amount of water were carried out at 60 °C for 48 h in the presence and absence of oxygen. For **1b**, 100 mg of **1b** was dissolved in 3 mL of chloroform, and one drop of water (about 10 mg) was added. No reaction took place in the absence of oxygen, and **1b** was recovered quantitatively. In the presence of oxygen, 72 mg of a brown, viscous oil was obtained as the reaction product, which consisted of a mixture of **6** (28 mg) and oligomers (2−4-mers, 44 mg). For **1c**, 100 mg of **1c** was dissolved in 5 mL of chloroform, and one drop of water (about 10 mg) was added. No reaction took place in the absence of oxygen, and **1c** was recovered quantitatively. In the presence of oxygen, 58 mg of a yellow, viscous oil was obtained as the reaction product, consisting of a mixture of **7** and **8**. The **7**/**8** ratio was evaluated from the peak area ratios between the thiophene ring protons (7.65 and 7.19 ppm) for **7** and the corresponding protons (7.71 ppm) for **8** and found to be 76/24 by weight. This indicates that a large amount of water in the system might prevent the polymerizations of **1b** and **1c** but also might promote a ring-opening of the dithioacetal moiety. Plausible mechanisms for product formation are shown in Scheme 3.

As both **1b** and **1c** are strong electron donors, they should interact with oxygen as a weak electron acceptor.[8] On heating, one-electron-transfer reactions from **1b** and **1c** to oxygen could take place to give the corresponding radical-cation intermediates I (int-**I**), which would react with excess oxygen at their radical sides to form radical-cation intermediates II (int-**II**) through ring-opening. Int-**II** from **1b** would react with the water present in large amounts at its cation site to afford **6** and simultaneously oligomers through a cou-

Scheme 4



pling reaction. Meanwhile, int-**II** from **1c** would react with water to afford only **8**, but its coupling reaction leading to oligomers would not take place. **5** and **7** would be formed by another route such as protonation to **1b** and **1c**, followed by the ring-opening. Here, the reaction products from **1b** and **1c** are different. This might be due to the different contributions of electron-transfer reactions and protonation, arising from the difference in electron-donating abilities between **1b** and **1c**. The electron-transfer reaction would take place preferentially for the stronger electron donor **1b**, and the radical-cation intermediate would be formed, leading to **6** and oligomers. On the other hand, for the weaker electron donor **1c**, both electron transfer and protonation would take place simultaneously, and both **7** and **8** would be formed. This mechanism is also supported by the fact that the same reaction of **1a**, being a stronger electron donor than **1c**, gave a mixture of **9** via protonation and **10** via electron transfer, and the **9**/**10** ratio was 47/53 by weight, where the **10** content is higher.



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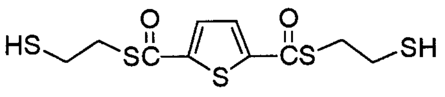

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A Possible Polymerization Mechanism. All three compounds **1a**−**c** polymerized only in the presence of oxygen to give the corresponding polymers composed of the three different structural units, the α or α′ units bearing two thioester groups obtained by ring-opening, the *β* or *β*′ units bearing one thioester group from ring-opening and one cyclic dithioacetal ring obtained without ring-opening, and the *γ* or *γ*′ units bearing two cyclic dithioacetal rings obtained with no ring-opening. Moreover, the reactions of **1a**−**c** with excess water in the presence of oxygen provided the ring-opening compounds, **6**−**10**, and also oligomers. On the basis of these results, it is presumed that the polymerizations of **1a**−**c** proceed by the mechanism shown in Scheme 4.

On heating, the one-electron-transfer reaction from the strong donors **1a**−**c** to the weak acceptor oxygen would take place to form radical-cation intermediates A (int-A), which would react with oxygen present in the system at their radical sites to afford radical-cation intermediates B (int-B) through ring-opening of the dithioacetal rings. Then, the resulting thiyl radical of int-B would add to the exocyclic carbons of monomers, **1a**−**c**, to form the dimer radical-cation intermediates C (int-C). Here, if int-C repeated a series of reactions, addition of oxygen, formation of the thiyl radical by ring-opening, and addition to monomers, the *β* or *β*′ units might be formed in the polymers. If the dithioacetal radicals of int-C reacted with other radicals such as the thiyl radicals or the dithioacetal radicals before the addition of oxygen, the *γ* or *γ*′ units would be incorporated into the polymers. On the other hand, if int-B reacted with a very small amount of water in the system or with a superoxide anion,[9] derived from an electron transfer from the monomers to oxygen, intermediates (diradical and/or radical-anion) bearing two thioester groups would be formed through ring-opening, and by their reactions with other radical-cation intermediates, the α and α′ units would be formed in the polymers. Also, thiol groups at the polymer terminal groups would be formed via proton abstraction by the thiolate anions or hydrogen abstraction by the thiyl radicals.

In summary, novel electron-donating quinonoids, **1b** and **1c**, were synthesized successfully. They exhibited improved solubility in comparison with **1a** because of the existence of the methyl groups on the 1,3-dithioacetal rings and of the six-membered rings at the exocyclic positions. The homopolymerizations of **1b** and **1c** took place only in the presence of oxygen to give the corresponding polymers composed of the three different structural units, 2,5-bis(thioester)thiophene units (α or α′ units), 2-dithioacetal-5-(thioester)thiophene units (β or β' units), and 2,5-bi(dithioacetal)thiophene units (γ or γ' units), as for **1a**. Moreover, an increase in the polymerization temperature and in the polarity of the solvent induced a decrease in the number of γ or γ' units and an increase in the number of α or α′ units because of fast decomposition of the formed polymers. The formation of different structural units in the polymers obtained in the polymerizations of **1a**−**c** in oxygen was explained well by a polymerization mechanism via a radical-cation intermediate, derived from one-electron-transfer reactions from **1a**−**c** to oxygen.

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