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Synthesis of 2,5-Bis(1,3-dithiolan-2-ylidene)-2,5-dihydrothiophene and Its Novel Polymerization in the Presence of Oxygen

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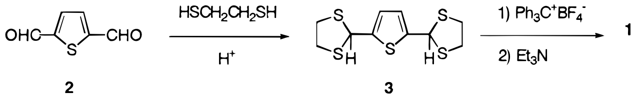
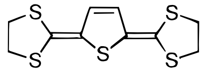
Introduction. Unsubstituted quinonoid compounds such as *p*-quinodimethane, *p*-quinone methide, *p*-quinone methide imine, and 2,5-dimethylene-2,5-dihydrothiophene and -dihydrofuran are so reactive that they polymerize immediately to form polymeric materials at room temperature, and hence it is very hard to handle them in a pure state.[1−4] However, substituted quinonoid compounds, where the electron-accepting or the electron-donating substituents are introduced on their exocyclic methylenes, are isolable as crystals at room temperature and easy to handle. Crystals allowed us to easily study the chemistry of quinonoid compounds in the polymerization. To date, our studies have been mainly focused to the polymerizations of electron-accepting substituted quinonoid compounds such as *p*-quinodimethanes,[5−13] *p*-quinone methides,[14−16] and *p*-quinone methide imines.[17,18] On the polymerizations of these isolable electron-accepting substituted quinonoid compounds, we have found interesting polymerization behaviors such as equilibrium polymerizations,[12,16,18] alternating copolymerizations,[5−8,13,14,18] and changes in the polymerization mode[8,10,12,16] from random copolymerization to alternating copolymerization depending upon polymerizability.[19] In contrast to many studies of the electron-accepting substituted quinonoid compounds with regard to their polymerization behavior, very little is known about the polymerization behavior of the electron-donating substituted quinonoid compounds except for 7,7,8,8-tetrakis(ethylthio)quinodimethane[20] and 2,5-bis[di(ethylthio)methylene]-2,5-dihydrothiophene,[13] which are neither homopolymerizable with any initiator nor copolymerizable with styrene. From the standpoint of exploring the chemistry of quinonoid compounds in the polymerization, many novel electron-donating substituted quinonoid compounds should be prepared and investigated for their polymerization behavior.

Cyclic ketene acetals[21−23] such as 2-methylene-1,3-dioxolanes, 2-methylene-1,3-dioxanes, and 2-methylene-1,3-dioxepanes and their sulfur analogues[24,25] such as 2-methylene-1,3-oxathiolane and 2-methylene-1,3-dithiolane are reported to polymerize in the presence of radical and cationic initiators to give polymers bearing ring-opening and/or cyclic units, the contents of which significantly depend on the ring sizes, initiators, and substituents.[26,27] This suggests that the introduction of the electron-donating strained ring onto the exocyclic methylenes of quinonoid structure would provide the polymerizability, driven by release of the strain energy and the aromatization, to electron-donating substituted quinonoid compounds. 2,5-Bis(1,3-dithiolan-2-ylidene)-2,5-dihydrothiophene (**1**) is expected to be one of the most promising isolable and polymerizable electron-donating substituted quinonoid compounds.

Scheme 1



In this communication, the synthesis of **1**, its polymerization, especially in the presence of oxygen, and the characterization of polymers obtained are described.



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Results and Discussion. 2,5-Bis(1,3-dithiolan-2-ylidene)-2,5-dihydrothiophene (**1**) was successfully prepared according to Scheme 1.

2,5-Thiophenedicarbardehyde (**2**)[28] reacted with 1,2-ethanedithiol in the presence of boron trifluoride etherate to yield 2,5-bis(1,3-dithiolan-2-yl)thiophene (**3**) as white needles in a 85% yield. The dithioacetal **3** was converted to tetrafluoroborate salt by the reaction with trityl tetrafluoroborate in dichloromethane, followed by deprotonation with triethylamine to afford **1** as yellow needles in a 59% yield. The chemical structure of **1** was confirmed by IR, ^{1}H and ^{13}C NMR, UV−vis spectroscopy, and elemental analysis.

The polymerization of **1** was carried out in chloroform at 0, 40, and 60 °C in the presence or absence of oxygen, and the results are summarized in Table 1. All polymerizations proceeded in homogeneous state except for the concentration of **1** as high as 6.9 mol/L (run no. 7), where the polymerization proceeded in the heterogeneous state. All products obtained are pale yellow powders with number-average molecular weights of about 2000, which were soluble in chloroform, dichloromethane, and acetone but insoluble in hexane and isopropyl ether. For the polymerization with radical initiator AIBN, polymer was obtained in the presence of oxygen, but not in the absence of oxygen (run nos. 1 and 2), indicating that oxygen greatly participates in the polymerization of **1**. This was also confirmed from the results of the polymerization of **1** without AIBN at 60 °C in the absence of oxygen and in the presence of oxygen, where no polymerization occurred and unreacted **1** was recovered quantitatively (run no. 3) for the polymerization in the absence of oxygen, and for that in the presence of oxygen polymer was obtained in a 64% yield (run no. 4). The effect of the polymerization temperature on the polymerization of **1** in the presence of oxygen was also examined (run nos. 4−6). At 0 °C, no polymerization of **1** took place and unreacted **1** was recovered quantitatively, but above 40 °C, polymerization occurred, and also the polymer yield increases with increase in the polymerization temperature. When one drop of water was added to the polymerization system in the presence of oxygen at 60 °C, **4** and **5** were obtained in a 38% yield as pale yellow solids and in a 34% yield as pale yellow viscous oils, respectively,

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Table 1. Homopolymerizations[a] of 1 in Chloroform at Various Conditions and Mole Fractions of α, β, and γ Structural Units in the Polymer

run no.	[**1**] × 10^2, mol/L	[AIBN] × 10^3, mol/L	temp, °C	oxygen	yield, %	M_n	structural unit α	β	γ
1	3.5	3.4	60	absence	0				
2	3.5	3.4	60	presence	45	2100	0.33	0.53	0.14
3	3.5		60	absence	0				
4	3.5		60	presence	64	2600	0.34	0.46	0.20
5	3.5		40	presence	21	2200	0.25	0.57	0.18
6	3.5		0	presence	0				
7	6.9		60	presence	71	2600	0.33	0.55	0.12

[a] **1**: 100 mg. Reaction time: 24 h.

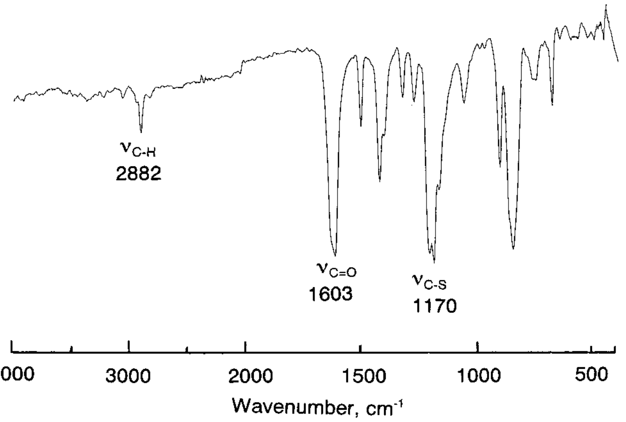
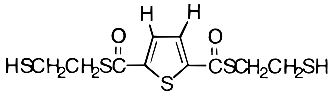


Figure 1. IR spectrum of the polymer obtained from run no. 2 (KBr).

indicating that a large amount of water inhibits the polymerization of **1**, suggesting the existence of ionic species as an intermediate, although its structure is not clear at present. Studies on the polymerization mechanism are now in progress.



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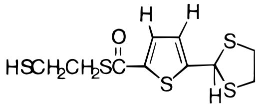

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The structure of polymers obtained was identified by comparing their ^1H and ^{13}C NMR and IR spectra with those of **3**, **4**, and **5**. In the IR spectrum of the polymer obtained in run no. 2 (Figure 1), the absorption peak due to the cyano group, generally appearing at 2200 cm^{-1},[29] is not observed, and new peaks are observed at 1603 and 1170 cm^{-1}, which are assigned to the C=O and C−S stretching vibrations of the thioester group, respectively, being in good agreement with the corresponding ones of **4** (1614 and 1171 cm^{-1}) and **5** (1597 and 1185 cm^{-1}). Moreover, in its ^{13}C NMR spectrum, the peak due to the C=S group of dithioester group as ring opening unit of dithioacetal ring, generally appearing at 220−240 ppm,[30] is not observed, and instead the peak due to the C=O group of the thioester group is observed at 183.4 ppm, which is in good agreement with the corresponding ones of **4** (183.4 ppm) and **5** (182.8 ppm), supporting strongly the existence of the thioester group as ring opening unit in the polymer. The polymers obtained in run nos. 4, 5, and 7 also showed IR and ^{13}C NMR spectra similar to those for run no. 2.

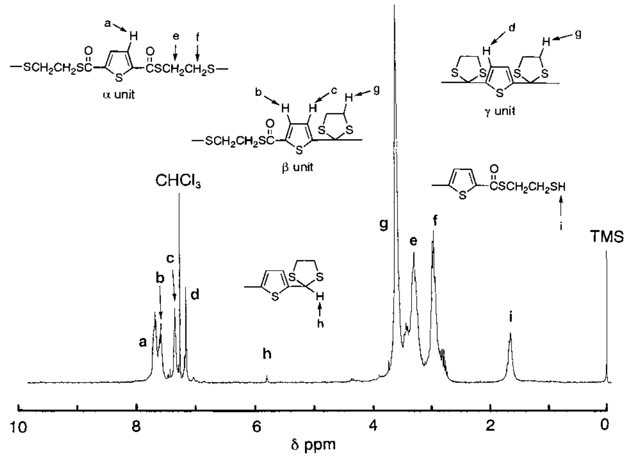
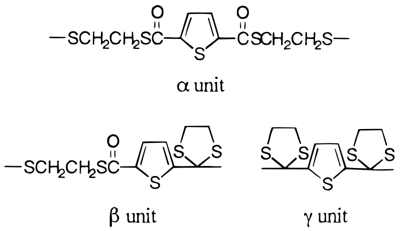


Figure 2. ^1H NMR spectrum of the polymer obtained from run no. 4 in chloroform-*d*.

^1H NMR spectrum of polymer obtained in run no.4 is shown in Figure 2, where each peak is assigned to each proton of the three different structural units, α, β, and γ, and the terminal units illustrated in the figure on the basis of the ^1H NMR spectra of **3**, **4**, and **5**: peaks at 7.70, 3.29−3.24, and 3.00−2.93 ppm are assigned to each proton of the α structural unit, peaks at 7.60, 7.35, 3.59, 3.29−3.24, and 3.00−2.93 ppm are for the β structural unit, and peaks at 7.17 and 3.59 ppm are for the γ structural unit, a peak at 5.79 ppm is for the methine proton on the terminal end bearing a dithioacetal ring, and a peak at 1.71 ppm is for the thiol proton on the terminal end bearing *S*-2-mercaptoethyl carbothioate, respectively.



The ratios of each structural unit in the polymers obtained are calculated from the peak area ratios of the protons on the each thiophene unit and summarized in Table 1. The ratios of the structural units calculated from the protons on the thiophene unit are also in good agreement with those calculated from peak area ratios of the ethylene protons at 3.59, 3.29−3.24, and 3.00−2.93 ppm. The sum of the α and β unit contents is much larger than the γ unit one at both temperatures of 60 and 40 °C, indicating that the polymerization of **1** in the presence of oxygen provides polymers containing a large amount of the ring-opening unit. From the calculation on the basis of both the ratios of the structural units and the M_n of the polymers, the polymers obtained are considered to be composed of three α units, four β units, and two γ units for run no. 4, and of two α units, four β units, and one γ unit for run no. 2, respectively.

In summary, **1** was synthesized successfully as an isolable and polymerizable electron-donating quinonoid compound for the first time. An interesting polymerization behavior was found that polymerization of **1** takes place only in the presence of oxygen and proceeds with ring opening to give a polymer bearing three different kinds of structural units. Further studies on the preparation of **1** derivatives and on their polymerization mechanism are currently underway.

Experimental Section. 2,5-Bis(1,3-dithiolan-2-yl)-thiophene (3). 2,5-Thiophenedicarbaldehyde (**2**)[28] (6.70

g, 47.8 mmol), 1,2-ethanedithiol (11.30 g, 120.0 mmol), and *p*-toluenesulfonic acid hydrate (1.21 g) were dissolved in 60 mL of benzene and refluxed for 3 h. The reaction mixture was washed three times with 20 mL of saturated sodium bicarbonate and then dried over anhydrous magnesium sulfate. The filtrate was placed under reduced pressure to remove solvent to give a brown viscous oil, which was dissolved in a small amount of benzene. The resulting solution was passed through a silica gel column using benzene as eluent. The pale yellow elution band was collected and then placed under reduced pressure to remove benzene to afford a pale yellow solid, which was recrystallized from hexane to give 11.90 g (85.1% yield) of **3** as white needles: mp 79.0−80.0 °C. IR (KBr): $\nu_{C-H} = 2876$, $\nu_{C=C} = 1594$, $\nu_{C-S} = 809$ cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 6.83 (s, 2H), 5.82 (s, 2H), 3.55−3.44 (m, 8H). ^{13}C NMR (CDCl$_3$): δ 147.1 (thiophene ring), 125.1 (thiophene ring), 50.8 (−CH<), 40.2 (−CH$_2$−). Anal. Calcd for $C_{10}H_{12}S_5$: C, 41.06; H, 4.13; S, 54.81. Found: C, 40.97; H, 4.26; S, 54.77.

2,5-Bis(1,3-dithiolan-2-ylidene)-2,5-dihydrothiophene (1). **3** (5.30 g, 18.11 mmol) and trityl tetrafluoroborate (7.11 g, 21.51 mmol) were dissolved in 50 mL of dichloromethane and stirred for 5 h at room temperature. The reaction mixture was placed under reduced pressure to remove solvent to give a black viscous oil, to which 50 mL of diethyl ether was added and washed to remove triphenylmethane and unreacted **3**. The resulting brown powder was dissolved in 50 mL of dichloromethane and cooled at 0 °C. To the resulting solution was added dropwise 10 mL of dichloromethane containing triethylamine (2.75 g, 27.18 mmol), and then it was stirred for 3 h. The reaction mixture was placed under reduced pressure to remove solvent to give a brown solid, which was dissolved in a small amount of dichloromethane. The resulting solution was passed through a silica gel column using dichloromethane as an eluent and the red elution band was collected and then was concentrated until 100 mL, to which a large amount of hexane was added to deposit 3.10 g (58.9% yield) of **1** as yellow needles: mp 186.0−188.0 °C. IR (KBr): $\nu_{C-H} = 2890$, $\nu_{C=C} = 1520$, $\nu_{C-S} = 825$ cm^{-1}. UV−vis (CHCl$_3$): 261 ($\epsilon = 9.92 \times 10^3$), 432 ($\epsilon = 2.67 \times 10^4$) nm. ^{1}H NMR (CDCl$_3$): δ 6.49 (s, 2H), 3.49 (m, 8H). ^{13}C NMR (CDCl$_3$): δ 129.16 (dihydrothiophene), 128.19 (dihydrothiophene), 120.57 (=C<), 39.36 (−CH$_2$−), 40.2 (−CH$_2$−). Anal. Calcd for $C_{10}\ H_{10}S_5$: C, 41.34; H, 3.47; S, 55.19. Found: C, 41.16; H, 3.48; S, 55.18.

Polymerization. Given amounts of **1** (100 mg), 10 mL of chloroform as solvent, and 5.6 mg of AIBN as a radical initiator if necessary were placed in a glass ampule, which was bubbled with oxygen gas for 15 s or was degassed by the freeze−thaw method (repeatedly three times) and then sealed. The ampule was placed in a bath thermostated at a given temperature for 24 h and then opened. The reaction mixture was poured into an excess of hexane to precipitate the product, which was purified in three or more cycles of a redissolution−reprecipitation method. Chloroform and hexane were used as solvent and precipitant, respectively. The product obtained was dried under reduced pressure at room temperature until a constant weight was reached.

For the polymerization of **1** in the presence of water, the following polymerization procedure was applied: **1** (50 mg, 0.17 mmol), 3.0 mL of chloroform as solvent, and 1 drop of water were placed in a glass ampule, which was bubbled with oxygen gas for 15 s and then sealed. The ampule was placed in a bath thermostated at 60 °C for 48 h and then opened. The reaction mixture was placed under reduced pressure to remove solvent to give an orange viscous oil, which was dissolved in a small amount of dichloromethane. The resulting solution was passed through a silica gel column using dichloromethane as an eluent, and the second yellow elution band was collected and then was placed under reduced pressure to remove dichloromethane to give a 36 mg (72% yield) of pale yellow solids, which were composed of two products, **4** and **5**, separated by thin-layer chromatography, and then characterized. The spectral data and elemental analysis are given below.

4: pale yellow solids; yield 38%; mp 122−123.5 °C. IR (KBr): $\nu_{C-H} = 4040$, 2886, $\nu_{SH} = 2532$, $\nu_{C=O} = 1614$, $\nu_{C(=O)S} = 1171$, $\nu_{C-S} = 841$ cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 7.73 (s, 2H), 3.33 (t, J = 7.25 Hz, 4H), 2.82 (m, 4H), 1.69 (t, J = 8.58 Hz, 2H). ^{13}C NMR (CDCl$_3$): δ 183.4 (C=O), 146.5 (thiophene), 130.6 (thiophene), 33.4 (−CH$_2$−), 24.5 (−CH$_2$−). Anal. Calcd for $C_{10}H_{12}O_2S_5$: C, 37.00; H, 3.73; O, 9.86; S, 49.41. Found: C, 37.03; H, 3.80; O, 9.79; S, 49.38.

5: pale yellow viscous oil; yield 34%; IR (NaCl): $\nu_{C-H} = 4038$, 2884, $\nu_{SH} = 2526$, $\nu_{C=O} = 1597$, $\nu_{C(=O)S} = 1185$, $\nu_{C-S} = 815$ cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 7.60 (d, J = 3.96 Hz, 1H), 7.04 (d, J = 3.96 Hz, 1H), 5.80 (s, 1H), 3.50−3.30 (m, 4H), 3.26 (t, J = 7.25 Hz, 2H), 2.80−2.70 (m, 2H), 1.69 (t, J = 8.42 Hz, 1H). ^{13}C NMR (CDCl$_3$): δ 182.8 (C=O), 156.9 (thiophene), 140.4 (thiophene), 131.2 (thiophene), 125.9 (thiophene), 50.1 (−CH$_2$−), 39.8 (−CH$_2$−), 32.9 (−CH$_2$−), 24.7 (−CH$_2$−). Anal. Calcd for $C_{10}H_{12}OS_5$: C, 38.92; H, 3.92; O, 5.19; S, 51.97. Found: C, 39.01; H, 3.87; O, 5.13; S, 51.99.

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