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Mechanism of Polymerization Reaction of 2,5-Bis(tetrahydrothiopheniomethyl)thiophene Dichloride

Bong Rae Cho,* Tae Hoon Kim, Yong Kwan Kim, and Nam Soo Kim

Department of Chemistry, Korea University, 1-Anamdong, Seoul 136-701, Korea

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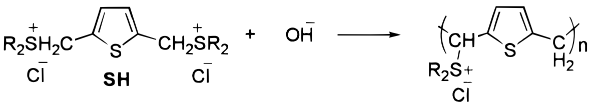
ABSTRACT: The polymerization kinetics of 2,5-bis(tetrahydrothiopheniomethyl)thiophene dichloride were studied. The reaction proceeds via a 2,5-dihydrothiophene intermediate **M**. Results of kinetic and product studies revealed that the 1,6-elimination proceeded by an $(E1cb)_{irr}$ mechanism. The rate of the disappearance of **M** was not influenced by the addition of OH^-, carbanions, and tetrahydrothiophene but was accelerated by $S_2O_8^{2-}$ and inhibited by TEMPO. In addition, the reaction mixture exhibited an electron spin resonance signal with a *g* value of 2.003 G and induced the polymerization of acrylamide. These results indicated a free radical polymerization mechanism.

Conjugated polymers have been the subjects of intensive research because of their potential applications in electrochemical, electronic, and optical materials.[1] The most intensively investigated conjugated polymers are poly(*p*-phenylene vinylene) (PPV) and its derivatives.[2,3] PPV is obtained by thermal elimination of poly(α-tetrahydrothiophenio-*p*-xylene) chloride which is readily synthesized by the reaction between α,α′-bis(tetrahydrothiophenio)-*p*-xylene dichloride (**SH′**) and OH^-.[2a] The results of the mechanism studies have revealed that the reaction proceeds via the *p*-xylylene intermediate, which undergoes a free-radical polymerization reaction.[4,5]

Recently, thiophene analogues of PPV have attracted much attention because of their lower band gaps.[6,7] Among the various methods used to synthesize poly(2,5-thienylene vinylene) (PTV) and its derivatives, the soluble precursor routes using the bis(sulfoniomethylene) and bis(sulfoxomethylene) derivatives as the monomers appear most promising.[7] However, virtually nothing is known about the mechanism of these reactions.

In this work, we studied the mechanism of the polymerization reaction of 2,5-bis(tetrahydrothiopheniomethyl)thiophene dichloride (**SH**) with OH^- in H_2O at 25.0 °C (eq 1). The nature of the intermediate was identified by UV−vis and NMR spectroscopy. Rates of elimination and polymerization processes were determined independently by monitoring the change in the intermediate concentration with reaction time. The results reveal that the reaction proceeds via the 2,5-dihydrothiophene intermediate by an elimination-free-radical polymerization mechanism.



(1)

Experimental Section

Materials. 2,5-Bis(tetrahydrothiopheniomethyl)thiophene dichloride was synthesized by the reaction of 2,5-bis(chloromethyl)thiophene with tetrahydrothiophene as described in the literature.[8] NaOH solution was prepared by dissolving reagent grade NaOH in distilled water or by adding clean pieces of Na to deionized water. NaOD solution was prepared by adding clean pieces of Na to D_2O.

NMR Experiments. To determine whether the methylene C−H protons of **SH** undergo hydrogen−deuterium exchange, 22 μL of 0.23 M OD^- ($[OD^-] = 0.01$ M) was added to an NMR tube containing 0.1 M **SH** in 0.5 mL of D_2O at −5 °C. The spectrum was obtained as a function of time. No change in the spectrum was noted after 60 min.

The NMR spectrum of the intermediate was obtained by adding 57 μL of 0.9 M OD^- ($[OD^-] = 0.1$ M) to an NMR tube containing 0.1 M **SH** in 0.5 mL of D_2O at −5 °C. The spectrum was recorded immediately after mixing. Because the peaks began to broaden in a few minutes, we could not perform more detailed experiments to assign each peak unambiguously.

UV−vis Spectrum of the Intermediate. The UV−vis spectra for the reaction of **SH** with OH^- in H_2O were obtained by adding 2.0×10^{-5} M of **SH** to a cuvette containing 3.0 mL of 1.00×10^{-4} M OH^- in H_2O at 25.0 °C. The spectrum was scanned periodically.

Rates of Elimination Reactions. Cuvettes containing 3.0 mL of 1.00×10^{-3} M NaOH(aq) were covered with rubber septa and purged for at least 20 min with nitrogen while being temperature-equilibrated prior to kinetic runs. The ionic strength was maintained at 0.20 M with KCl. Reactions were initiated by injecting 3.0 μL of 2.0×10^{-2} M aqueous solution of **SH** into the cuvette ($[\mathbf{SH}] = 2.0 \times 10^{-5}$ M). Rates of elimination reactions from **SH** were determined by monitoring the increase of the absorbance for the intermediate **M** with time at 337 nm. Because the rates were much faster than those for the subsequent polymerization reaction, no problem was encountered in the rate studies. When the base concentration was higher than 1.00×10^{-3} M, the rates were too fast to be measured by this method, so the rate studies utilized a stopped-flow spectrophotometer. In all cases, plots of $-\ln(A_\infty - A_t)/(A_\infty - A_0)$ versus time were linear over two half-lives of the reaction. The slope was the pseudo-first-order rate constant.

Rates of Polymerization Reactions. The 2,5-dihydrothiophene intermediate **M** (2.0×10^{-5} M) was produced in a cuvette by reacting 2.0×10^{-5} M **SH** with 1.00×10^{-2} M NaOH(aq) as described above. Rates of the polymerization reactions were determined by monitoring the decrease of the absorbance at 337 nm. Because the rates were too slow to follow to completion, a Guggenheim method was employed.[9]

Effects of Tetrahydrothiophene, OH^-, Carbanions, HCl, TEMPO, and $S_2O_8^{2-}$ on the Polymerization Reaction. The effect of these additives on the polymerization reaction was determined by adding 5.0×10^{-3} M tetrahydrothiophene (THT), 1.0 M OH^-, 1 equiv of HCl(aq), 3.3×10^{-5} M of TEMPO, and 0.0165−0.0617 M of $S_2O_8^{2-}$ to a solution containing 2.0×10^{-5} M of **M** and 1.0×10^{-2} M of OH^- and measuring the rate of disappearance of **M** by UV−vis

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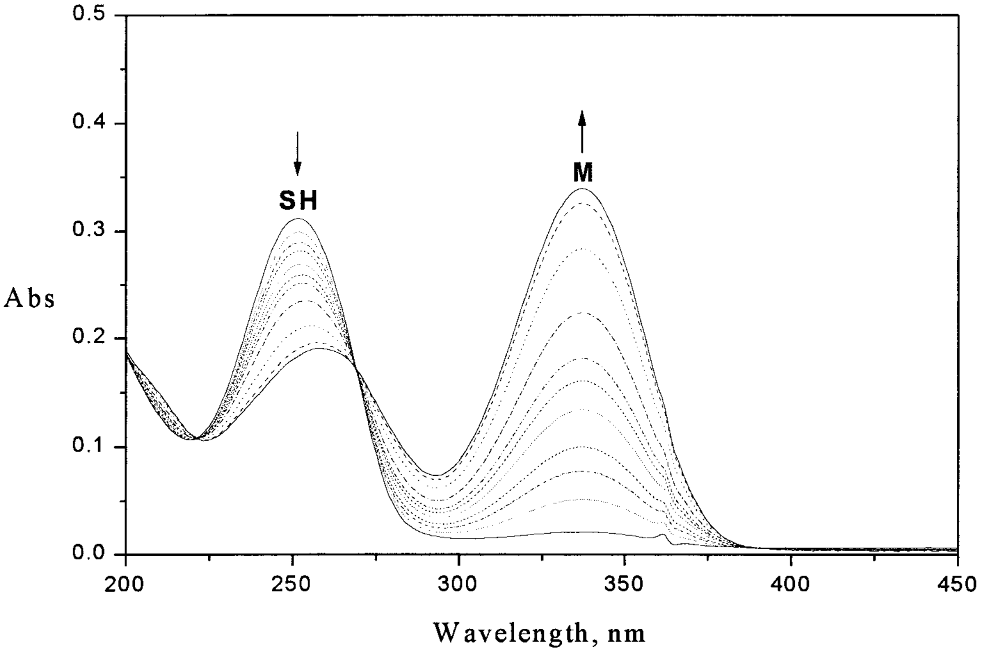


Figure 1. Change of the UV−vis spectrum with time for the reaction of **SH** promoted by OH^- in H_2O at 25.0 °C: [substrate] = 2.00×10^{-5} M, $[OH^-] = 1.00 \times 10^{-4}$ M, $\mu = 0.20$ M (KCl).

spectroscopy.[5b] The effect of carbanion was determined by the same method except that 0.10 M CH_3NO_2 and $CH_3CH_2NO_2$ were added to the solution containing 2.0×10^{-5} M **M** and 1.0 M OH^-. Except when TEMPO and $S_2O_8^{2-}$ were added, no change in the rate was observed.

Product Studies. A solution containing **SH** (0.079 g, 0.22 mmol) in 5.0 mL of H_2O was mixed with 2.0 L of 0.01 M NaOH and allowed to react for 30 min at 25.0 °C under nitrogen. The solution was neutralized with HCl(aq) and the solvent was evaporated in vacuo. The product was dialyzed for a week by using a dialysis sack whose molecular weight cutoff was 12 000. A film cast from the product mixture was first warmed to 60 °C under reduced pressure, subjected to heat treatment at 150 °C, and analyzed by elemental analysis as reported in the literature.[7] Anal. Calcd for $(C_6H_4S)_n$: C, 66.63; H, 3.73; S, 29.64. Found: C, 67.05; H, 3.94; S, 29.01.

An identical experiment was performed except that the two solutions were mixed in the dark after purging with argon for 20 min. The product was treated by the same procedure. Anal. Found: C, 66.10; H, 4.02; S, 29.88.

The possibility of copolymerization reaction of **SH** with acrylamide was examined by reacting a solution containing **SH** (0.20 g, 0.56 mmol), acrylamide (2.0 g, 28 mmol) in 4.0 mL of H_2O, and 0.7 mL of 1.0 M NaOH for 2 days at 0 °C. The product was dialyzed as described above. The precursor film cast from the aqueous solution was dried in vacuo and analyzed by elemental analysis. Anal. Found: C, 58.22; H, 5.50; N, 1.54; S, 22.82.

Similar experiments were performed with mixtures of acrylamide/OH^-, acrylamide/terahydrothiophene/OH^-, and **SH**/acrylamide/terahydrothiophene.

ESR Spectrum of the Reaction Mixture. To an ESR tube containing 0.5 mL of 1.0 M NaOH was added 0.1 g of **SH**. The tube was thoroughly purged with argon and sealed at room temperature. The X-band ESR spectrum was obtained at 9.22 GHz with 100 kHz modulation.

Cyclic Voltammetry. Cyclic voltametric experiments were performed by the literature procedure using platinum wire as both the working and the auxiliary electrodes, a Ag/AgCl electrode as a reference electrode, and 0.4 M $LiClO_4$ as the supporting electrolyte.[5b,10] Cyclic voltammograms for **SH**, tetrahydrothiophene, and OH^- were obtained with 2.0×10^{-3} M solution at sweep rates of 100 mV s^{-1} from −1.0 to +1.0 V versus Ag/AgCl. To obtain the cyclic voltammogram for the 2,5-dihydrothiophene intermediate **M**, 2.0×10^{-3} M of **SH** was allowed to react with 1.0×10^{-2} M NaOH in the electrochemical cell. The solution was sweeped when the maximum concentration of **M** was accumulated.

Calculations. Structures of the singlet and triplet states for the (*E*)- and (*Z*)-isomers of the 2,5-dihydrothiophene intermediate **M** were calculated on a Silicon Graphics workstation using the Gaussian 94, revision A.1, quantum mechanical package developed by Pole and co-workers.[11] All structures were fully optimized using 6-31G basis set.

Results

SH was synthesized by the reaction of 2,5-bis(chloromethyl)thiophene with tetrahydrothiophene by the literature method.[8] The product of reaction between **SH** and OH^- in H_2O was obtained by employing 1×10^{-4} M **SH** and 1×10^{-2} M OH^- under nitrogen. The film cast from the high-molecular-weight fraction collected by dialysis had a golden lustrous color and analyzed as $(C_{6.2}H_{4.4}S)_x$ after heat treatment. Similarly, the product obtained in the dark under argon atmosphere analyzed as $(C_{5.9}H_{4.3}S)_x$. Although there is small discrepancy between the theoretical and experimental values, the results are consistent with the formation of the PTV precursor polymer under the given reaction conditions.

The UV−vis spectra for the reaction of **SH** with OH^- in H_2O at 25.0 °C are depicted in Figure 1. The absorption at 337 nm increased gradually as the reaction proceeded. A clean isosbestic point was observed at 270 nm. Figure 2 shows that the absorbance decreases slowly after reaching a maximum point. In addition, the rate of the former was 200−10 000-fold faster than the latter (Tables 1 and 2). Therefore, the molar extinction coefficient for the intermediate ($\epsilon = 1.68 \times 10^4$ L mol^{-1} cm^{-1}) could be calculated from the maximum absorbance. Furthermore, the rates of elimination and polymerization reactions could be measured independently (vide infra).

When 0.1 equiv of OD^- was added to an NMR tube containing **SH** in D_2O, the methylene C−H proton resonance at δ 4.62 remained nearly the same for 60 min, indicating that the protons did not undergo H−D exchange (Figure S1). The similar peak areas for the thienyl and methylidene protons of **M** provide additional

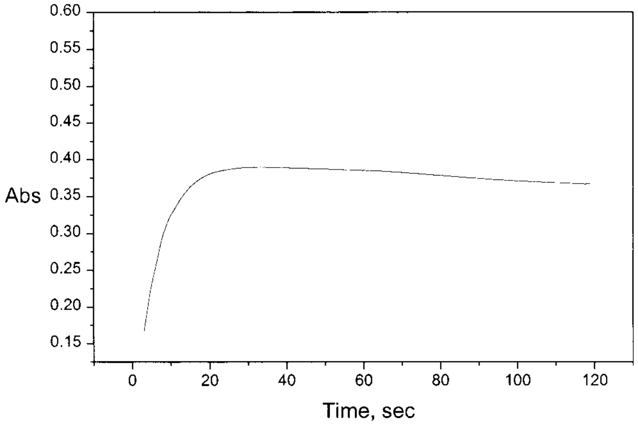


Figure 2. Change of the UV absorption at 337 nm with time for the reaction of **SH** promoted by OH^- in H_2O at 25.0 °C: [substrate] = 2.00×10^{-5} M, $[OH^-] = 1.00 \times 10^{-3}$ M, and m = 0.20 M (KCl).

support for this conclusion (Figure 3). If there were significant hydrogen−deuterium exchange, the peak areas for the latter should have been much smaller.

The NMR spectrum of the reaction mixture was obtained immediately after mixing 1 equiv of OD^- with 0.1 M **SH** in D_2O at −5 °C. The spectrum indicated the presence of unreacted **SH**, 2,5-dihydrothiophene intermediates, oligomers, and the expelled tetrahydrothiophene (Figure S2). The NMR spectrum in the region δ 7.5−5.5 is reproduced in Figure 3. It shows four doublets at δ 7.33−6.95 (J = 5.7 Hz) and five singlets at δ 6.37−5.67, which can be assigned to the thienyl and methylidene protons of the (*E*)- and (*Z*)-**M**, respectively (vide infra). The one pair of smaller doublets with J = 3.4 Hz at δ 7.30 and 7.13 appears to be due to the thienyl protons of the oligomers.

Rates of elimination from **SH** were determined by monitoring the increase in the absorbance at 337 nm with a UV−vis or a stopped-flow spectrophotometer (Figure 1). Figure 4 shows the plot of $\ln(A_\infty - A_t)$ versus time for the reaction between 2.0×10^{-5} M **SH** and 1.00×10^{-3} M OH^-. For all reactions, excellent pseudo-first-order plots were obtained over three half-lives. The rate constants for the elimination reactions are summarized in Table 1. The rate data show first-order dependence on $[OH^-]$ and $[OD^-]$, i.e., $k_{obs} = k^{OH^-}[OH^-]$ and $k_{obs} = k^{OD^-}[OD^-]$ (Figure 5). The second-order rate constants obtained from the slopes of these plots are $k^{OH^-} = 66.3 \pm 0.7$ and $k^{OD^-} = 143 \pm 1$ $M^{-1}s^{-1}$, respectively. The Brönsted β value for the elimination reaction was calculated by using the relationship $k^{OD^-}/k^{OH^-} = 2.0^{\beta}$.[12] The value is 1.11 ± 0.01.

The rates of polymerization reaction were measured by monitoring the decrease in absorption at 337 nm with a UV−vis spectrophotometer (Figure 2). Because the rate was too slow to measure to completion, a Guggenheim method was employed.[9] The observed rate constant for the polymerization reaction is 2.18×10^{-4} s^{-1} (Table 2). The rate did not change when 5.0×10^{-3} M of tetrahydrothiophene, 1.0 M of OH^- and 0.10 M of nitromethane and nitroethane, and 1 equiv of HCl(aq) were added to the solution containing **M** and OH^-. However, the k_{obs} decreased from 2.18×10^{-4} to 1.85×10^{-4} s^{-1} by the addition of 3.3×10^{-5} M of TEMPO, and increased when a free-radical initiator, $S_2O_8^{2-}$, was added (Table 2). Moreover, the plot of k_{obs} versus $[S_2O_8^{2-}]^{1/2}$ was linear with excellent correlation (Figure 6).

Figure 7 shows the ESR spectrum of the product mixture obtained at 9.22 GHz with 100 kHz modulation. The mixture exhibited an ESR signal with g value of 2.003 G, which persisted for 2 h.

To determine whether a free-radical intermediate may exist under the given reaction conditions, a reaction mixture containing acrylamide, **SH**, and OH^- was allowed to react in aqueous solution for 2 days at 0 °C. Elemental analysis of the high-molecular-weight fraction obtained by dialysis revealed that the C/H/N/S ratio is 58.22/5.50/1.54/22.82 by weight. This indicates that

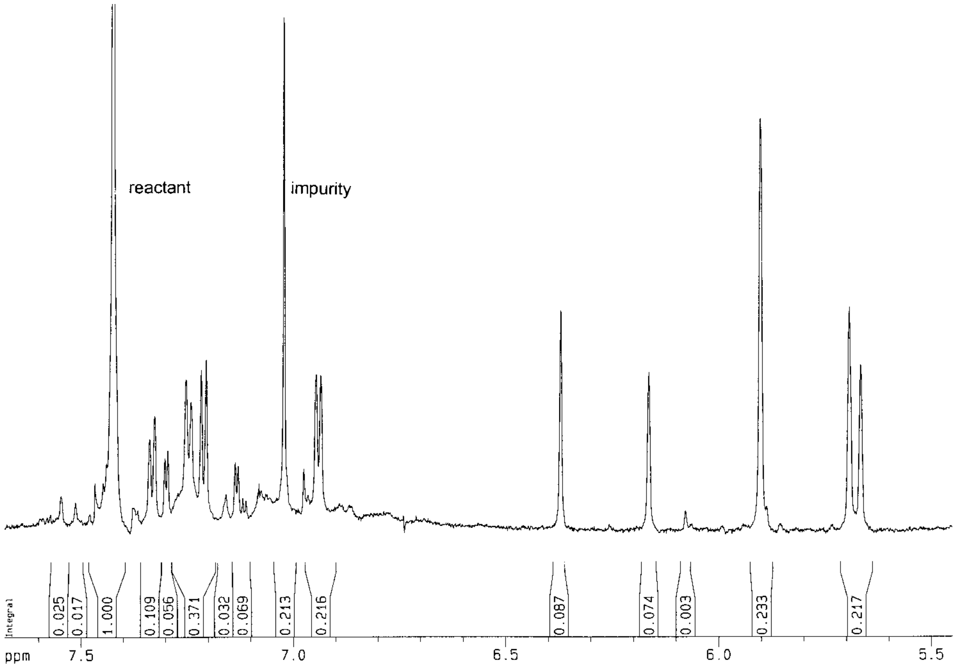


Figure 3. NMR spectrum of the reaction mixture for the reaction of **SH** with OD^- in D_2O in the range δ 7.5−5.5. The four doublets at δ 7.33−6.95 (J = 5.7 Hz) and five singlets at δ 6.37−5.67 can be assigned to the thienyl and methylidene protons of the (*E*)- and (*Z*)-**M**, respectively (see text). The one pair of smaller doublets with J = 3.4 Hz at δ 7.30 and 7.13 may be due to the oligomers.

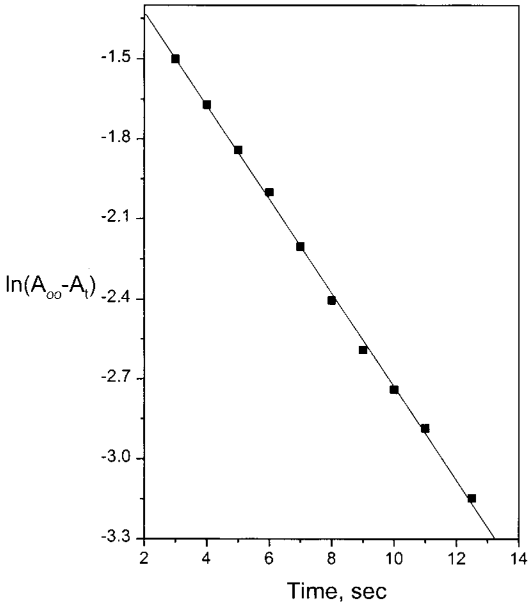


Figure 4. Plot of $\ln(A_\infty - A_t)$ vs time for the reaction of **SH** promoted by OH^- in H_2O at 25.0 °C: [substrate] = 2.00×10^{-5} M, $[OH^-] = 1.00 \times 10^{-3}$ M, and $\mu = 0.20$ M (KCl).

Table 1. Observed Rate Constants for Eliminations from 2,5-Bis(tetrahydrothiopheniomethyl)thiophene Dichloride Promoted by OH^- in H_2O and OD^- in D_2O at 25.0 °C[a]

10^3[base], M	$k_{obs}^{OH^-}$, s^{-1} [b]	$k_{obs}^{OD^-}$, s^{-1} [b]
1.00	0.0474 ± 0.0004	0.119 ± 0.002
5.00	0.293 ± 0.004	0.636 ± 0.003
10.0	0.604 ± 0.018	1.40 ± 0.08
40.0	2.62 ± 0.08	5.68 ± 0.10

[a] Ionic strength = 0.2 M (KCl). [b] Average and standard deviation for more than three kinetic runs.

approximately 13% of acrylamide is incorporated into the polymer. However, no polymer was produced when the same experiment was performed with mixtures of acrylamide/OH^-, acrylamide/terahydrothiophene/OH^-, and **SH**/acrylamide/terahydrothiophene.

Cyclic voltammogram for the 2,5-dihydrothiophene intermediate **M** is shown in Figure 8. It was reversible with $E_{pc} = -0.514$ V and $E_{pa} = -0.306$ V. From this result $E_{1/2} = -0.410$ V versus Ag/AgCl was obtained. However, **SH**, tetrahydrothiophene, and OH^- did not exhibit any redox peak within the potential range.

Structures of the singlet and triplet states for the (*E*)- and (*Z*)-isomers of 2,5-dihydrothiophene intermediate **M** were calculated by an ab initio method.[11] The Hartree−Fock energies, bond lengths, and total atomic charges for the two structures are summarized in Tables S1 and S2 in the Supporting Information.

Discussion

Reaction of **SH** with OH^- in H_2O produced the PTV precursor polymers under conditions comparable to those for the kinetic studies. Figure 1 shows that the reaction of **SH** with OH^- in H_2O produces an intermediate that has a strong absorption at 337 nm. Moreover, the rate of the increase was much faster than the decrease, indicating that the formation of the intermediate proceeds at a much faster rate than the subsequent polymerization reaction (Figure 2). Therefore, each step could be studied independently.

Structures of the Intermediates. The structures of the intermediates were determined by using UV−vis and NMR spectroscopy. The λ_{max} of the intermediate is redshifted by 85 nm from that of the reactant, indicating that the intermediate should have a highly conjugated structure (Figure 1). Moreover, the NMR spectrum in Figure 3 can reasonably be explained by assuming that both (*E*)- and (*Z*)-isomers of **M** are produced under the given reaction conditions (Scheme 1). For example, the four doublets at δ 7.33−6.95 with *J* = 5.7 Hz can be attributed to the thienyl protons (H_b, H_c, H_b', and H_c') of the (*E*) and (*Z*)-**M**. The two singlets at δ 6.37 and 6.16 appear to be due to the tetrahydrothiopheniomethylidene groups (H_a and H_a'). Similarly, the three singlets at δ 5.90, 5.69, and 5.67 can be assigned to the methylidene protons (H_d, H_e, H_d', and H_e') by assuming that two of them are overlapped at δ 5.90. Unfortunately, however, more rigorous assignment of each peak was not possible because of the instability of the intermediates. Finally, the similar peak areas for both isomers reveal that they are produced in similar amounts. This result is consistent with the similar Hartree−Fock energies calculated for the two isomers (Tables S1 & S2).

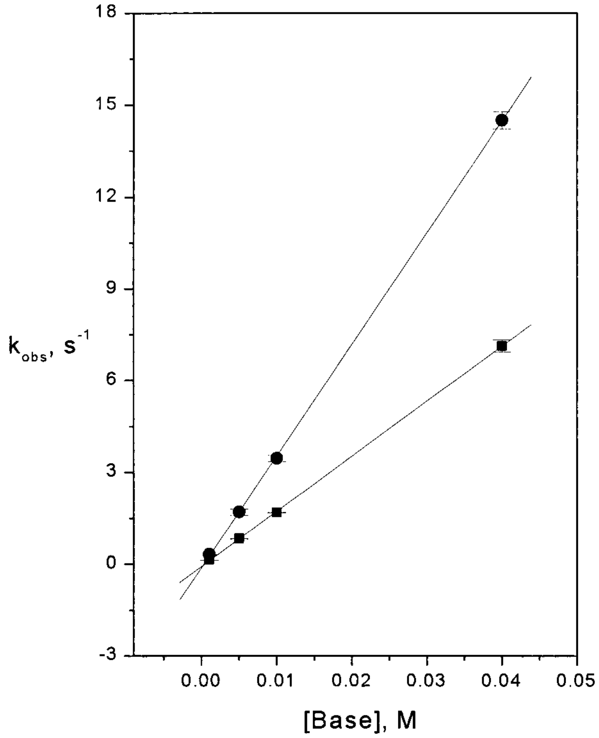


Figure 5. Plots of k_{obs} vs base concentration for elimination reactions of **SH** promoted by OH^- in H_2O (■) and OD^- in D_2O (●) at 25.0 °C: $\mu = 0.20$ M (KCl).

Table 2. Observed Rate Constants for the Disappearance of 2,5-Dihydrothiophene Intermediate upon Addition of $S_2O_8^{2-}$ at 25.0 °C

	$10^2 \times [S_2O_8^{2-}]$, M				
	0.00	1.65	3.00	4.70	6.17
10^3k_{obs}, s^{-1} [a]	0.218 ± 0.10[b]	1.54 ± 0.10	1.98 ± 0.04	2.44 ± 0.09	2.77 ± 0.11

[a] Average and standard deviation for more than three kinetic runs. [b] $10^3k_{obs} = 0.185 \pm 0.10$ s^{-1} when 3.3×10^{-5} M TEMPO was added.

Mechanism of Elimination Reaction from SH Forming the 2,5-Dihydrothiophene Intermediate. Results of kinetic and product studies reveal that the OH^--promoted elimination from **SH** proceeds by the

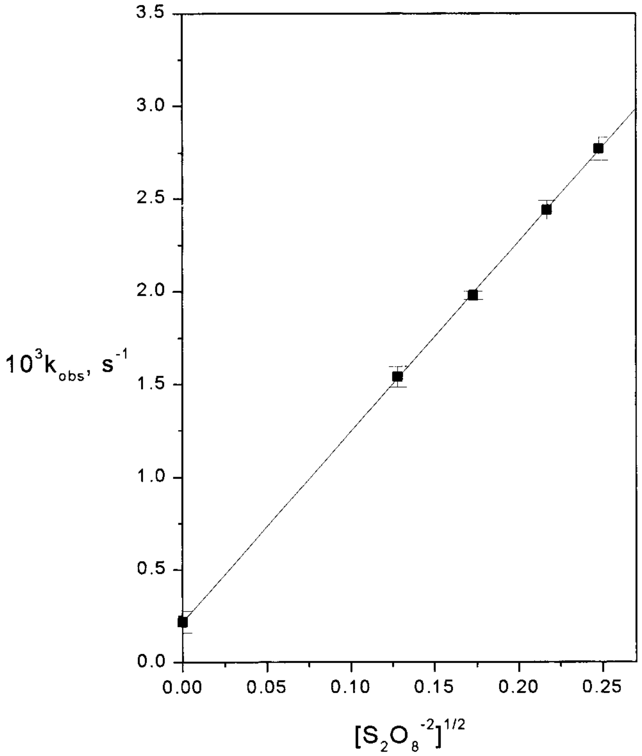


Figure 6. Plot of k_{obs} vs $[S_2O_8^{-2}]^{1/2}$ for the reaction of the 2,5-dihydrothiophene intermediate **M** with $S_2O_8^{-2}$ at 25.0 °C.

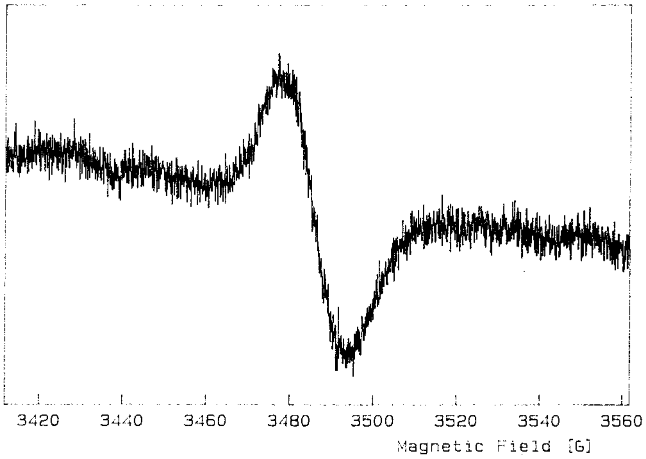


Figure 7. ESR spectrum of the reaction mixture for the polymerization reaction of **SH** with OH^- in H_2O at room temperature. The spectrum was taken at 9.22 GHz with 100 kHz modulation.

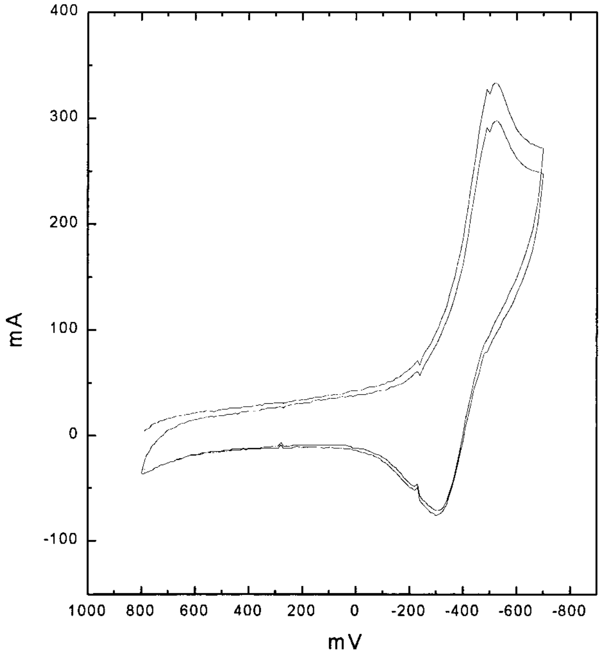
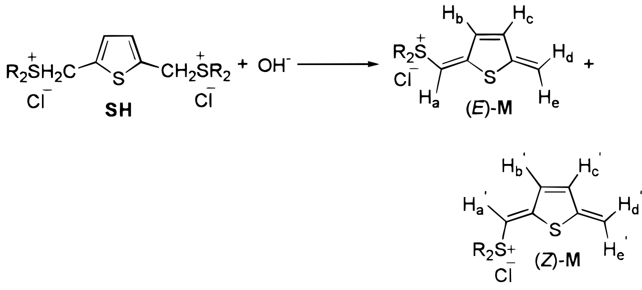
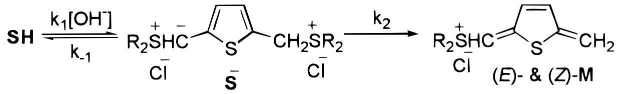


Figure 8. Cyclic voltammogram for the **M** in H_2O. Sweep rate = 100 mV s^{-1}.

Scheme 1



Scheme 2



$(E1cb)_{irr}$ mechanism to afford both of the (*Z*)- and (*E*)-isomers of **M**. Observation of the second-order kinetics and general base-catalysis rule out all but E2, $(E1cb)_{irr}$, $(E1cb)_R$, and $(E1cb)_{ip}$ mechanisms.[13] The $(E1cb)_R$ mechanism, in which $k_{-1} \gg k_2$, is negated by the absence of the H−D exchange of the methylene protons of **SH**.[13] A variation of the $(E1cb)_R$ mechanism is the $(E1cb)_{ip}$ mechanism, which requires the formation of an intimate ion-pair between $\mathbf{S}^-$ and the conjugate acid of the promoting base, i.e., H_2O, in the preequilibrium step.[13] However, this mechanism can also be ruled out because it is highly unlikely that such an intermediate could be produced under the given reaction conditions. The distinction between the E2 and $(E1cb)_{irr}$ mechanisms has been made by using the Brönsted β value. The Brönsted β value for the elimination reaction is 1.11 ± 0.01, indicating that the C_β−H bond must be completely broken in the transition state. This result negates the possibility of the E2 mechanism, for which $0 < \beta < 1.0$ is expected.[12,13] Therefore, the most reasonable mechanism for this elimination reaction appears to be $(E1cb)_{irr}$, in which $k_{-1} \ll k_2$. Moreover, both (*E*)- and (*Z*)-**M** should be produced by the same mechanism because the reaction proceeds via a common intermediate $\mathbf{S}^-$ and the first step is rate limiting. Finally, the negligible effect of the tetrahydrothiophene concentration on the rate of disappearance of **M** indicates the irreversibility of the k_2 step (Scheme 2).

The rate equation for the formation of **M** can be expressed as $k_{obs} = k_1k_2[\mathbf{SH}][OH^-]/(k_{-1} + k_2)$. Because the reaction is assumed to proceed by the $(E1cb)_{irr}$ mechanism, i.e., $k_{-1} \ll k_2$, the rate equation can be simplified as $k_{obs} = k_1[\mathbf{SH}][OH^-]$. The value of k_1 can be taken from the slope of the plot in Figure 5, i.e., $k_1 = 66.3 \pm 0.7$ $M^{-1}s^{-1}$. When $[\mathbf{SH}] = 2.0 \times 10^{-5}$ M and $[OH^-] = 1.0 \times 10^{-3}$ M, the rate of production of **M** is 1.3×10^{-6} M s^{-1}. For comparison, the rate of elimination from **SH′** is 5.7×10^{-9} M s^{-1} when $[\mathbf{SH'}] = 2.0 \times 10^{-5}$ M and $[OH^-] = 1.0 \times 10^{-3}$ M.[5b] The much faster rate of the former may be attributed to the smaller aromatic resonance energy of thiophene than that of benzene.[14]

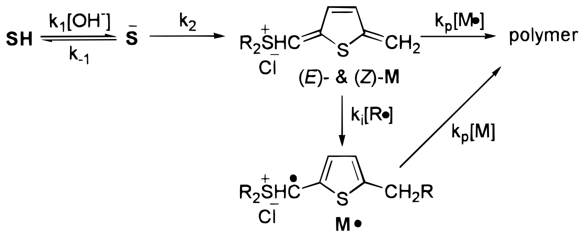
Because the aromatic resonance energy is lost as the intermediates are produced in both reactions, the former should be less endothermic than the latter, which would in turn decrease the free energy of activation to enhance the rate.

Polymerization Reaction Mechanism. There are two possibilities by which the intermediates **M** may undergo a polymerization reaction. If the reaction proceeds by the anionic mechanism, a nucleophile should be added to **M** to afford a carbanion, which may in turn propagate the polymerization. This requires a high reactivity of **M** toward a nucleophile. To assess this possibility, 0.10 M of nitroethane and nitromethane were added to a reaction mixture containing 2.0×10^{-5} M **M** and 1.0 M OH^-, and a change in the rate of disappearance of **M** was observed. Because the pK_a values of these carbon acids are 8.5 and 10.2, respectively, they should be completely converted to the corresponding carbanions under the given reaction conditions.[15] Hence, if these carbanions are added to **M**, the rate is expected to increase. However, no change in the rate was observed. Similarly, the rate was not influenced by the addition of 1.0 M OH^-. The results are in contrast to the facile reaction between α-tetrahydrothiophenio-*p*-xylylene chloride and these nucleophiles.[5b] The lower reactivity of **M** toward the nucleophiles apparently results from the smaller resonance energy that can be gained from aromatization of **M** than from the *p*-xylylene intermediate in the addition reaction (vide supra).[5b,14] Finally, the rate remained nearly the same when the reaction mixture was neutralized by adding 1 equiv of HCl. Because the acid would undoubtedly have quenched all of the anionic nucleophiles present under given the reaction conditions, the rate should have decreased if the addition of these nucleophiles to **M** or anionic polymerization were the major reaction pathway. Therefore, the possibility of the anionic mechanism is negated by these results.

In contrast, convincing evidence for the free radical mechanism has been observed. First, when 3.3×10^{-5} M TEMPO was added to the neutralized solution containing **M**, the k_{obs} decreased from 2.18×10^{-4} to 1.85×10^{-4} s^{-1}. Second, the rate increased significantly when a small amount of free radical initiator, $S_2O_8^{2-}$, was added to **M** (Table 2). Moreover, the plot of k_{obs} versus $[S_2O_8^{2-}]^{1/2}$ is linear with excellent correlation (Figure 6). This result indicates that the rate equation can be expressed as $k_{obs} = a + k_p(k_i/k_t)^{1/2}[S_2O_8^{2-}]^{1/2}$, as required for the free-radical polymerization.[16] Third, the reaction mixture exhibited an ESR signal with a *g* value of 2.003 G, which persisted for 2 h (Figure 7). Fourth, when acrylamide (which readily polymerizes by a free-radical mechanism) **SH**, and OH^- were allowed to react in aqueous solution for 2 days at 0 °C, a copolymer was produced. Elemental analysis of the high-molecular-weight fraction obtained by dialysis revealed that the C/H/N/S ratio is 58.22/5.50/1.54/22.82 by weight. This indicates that approximately 13% of acrylamide is incorporated into the copolymer. Because the acrylamide did not polymerize in the absence of **SH**, this result can only be explained if the former was copolymerized with **M** by the growing free-radical chain. All of these results are in excellent agreement with the free-radical polymerization mechanism.

The k_p value was estimated from the slope of Figure 6 by using $k_i = 4.62 \times 10^{-8}$ s^{-1} for the decomposition of $S_2O_8^{2-}$ and $k_t = 1 \times 10^6$ M^{-1} s^{-1} for the polymerization of the vinyl monomers.[16,17] The calculated k_p value is 4.78×10^4 M^{-1} s^{-1}, which is between the $k_p = 1 \times 10^3$ and 1.05×10^7 M^{-1} s^{-1} values determined for the polymerization of vinyl acetate and α-tetrahydrothiophenio-*p*-xylylene chloride, respectively.[5b,16] The result can readily be understood if the relative reactivities of these monomers are considered (vide supra). The free-radical concentration was calculated from the intercept of Figure 6 by assuming that $k_{obs} = k_p[M\cdot]$ when $[S_2O_8^{2-}] = 0$. The value of $[M\cdot]$ is 4.6×10^{-9} M, which is larger by 1 order of magnitude than the $[M\cdot] = 4.8 \times 10^{-10}$ M value estimated under the condition for the polymerization of **SH′**.[5b]

Scheme 3



The rate constants can explain why the intermediates **M** are accumulated under kinetic conditions, whereas the polymerization reaction proceeds readily under synthetic conditions. When $[\mathbf{M}] = 2.0 \times 10^{-5}$ M and $[\mathbf{M\cdot}] = 4.6 \times 10^{-9}$ M, the rate of disappearance of **M** by the $k_p[\mathbf{M}][\mathbf{M\cdot}]$ pathway is 4.4×10^{-10} M s^{-1}, which is slower by approximately 3.0×10^3-fold than the 1.3×10^{-6} M s^{-1} value for the formation of the intermediates under the kinetic conditions (vide supra). This would predict that the former cannot compete with the latter and **M** should be accumulated until all of the reactant is consumed. On the other hand, if the reaction is carried out with 0.20 M **SH** and OH^- for the practical synthesis, the maximum rates of the formation of **M** and its consumption would be $k_1[\mathbf{SH}][OH^-] = 2.7$ and $k_p[\mathbf{M}][\mathbf{M\cdot}] = 0.44$ M s^{-1}, respectively. Hence, the intermediate could be accumulated, but only for a short period of time, because the polymerization reaction would be completed within a second.

All of these results are consistent with the elimination-free-radical polymerization mechanism as shown in Scheme 3. Both isomers of **M** are assumed to react by the same mechanism because they would produce the same intermediates in the subsequent steps and their reactivities toward the free-radical addition reaction should be very similar.

Free-Radical Initiator. There are several possibilities by which a free-radical initiator may be produced. One is the photoexcitation of the intermediate **M** or other species, which may produce a free-radical species. A free radical may also be produced by the hydrogen abstraction by the molecular oxygen. These possibilities are negated by the facile polymerization reaction observed in the dark under argon atmosphere (vide supra). Alternatively, the electron-transfer reaction between **M** and an electron donor may produce the charged radical species, which may initiate the reaction. Because the reduction potential of **M** is −0.21 V versus SCE, any electron donor with $E_{ox} \leq 0.45$ V should in principle be able to produce the charged radical species whose concentration is higher than 0.01% of **SH**, which is sufficient to initiate the polymerization reaction (Figure 8).[4] However, no species present under the given reaction conditions exhibited oxidation potential within the potential range. The fourth possibility is the dimer biradical formed by the spontaneous dimerization of **M** as postulated by Wessling in the polymerization reaction of **SH′**.[3] An ab initio calculation with 93-G basis set for the (*E*)- and (*Z*)-**M** reveals that the singlet states are more stable than the triplet states (Tables S1 and S2). Hence, it is not evident how the dimer biradical could be produced from these singlet molecules. On the other hand, it is well-known that *p*-xylylene readily reacts with mono radicals and is particularly prone to homo- and copolymerization even at −78 °C.[18,19] It is so reactive in the free-radical reactions that it is called a pseudodiradical.[18a] If the high reactivity of *p*-xylylene is due to the large resonance stabilization energy gained upon aromatization, the 2,5-dihydrothiophene intermediate should also be quite reactive. Therefore, it seems difficult to rule out the possibility that the dimer biradical may be the initiator in the polymerization reaction.

Conclusions

Results of kinetic and product studies reveal that polymerization reaction of **SH** with OH^- proceed by the elimination−free-radical polymerization mechanism as shown in Scheme 3. The validity of each elementary step was confirmed by independent experiments. The calculated rate constants provide quantitative interpretations for the qualitative observations made in these reactions.

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Supporting Information Available: NMR spectrum of the reaction mixture taken 60 min after mixing 0.01 M OD^- and 0.1 M **SH** in D_2O, NMR spectrum of the reaction mixture taken immediately after mixing 0.1 M OD^- and 0.1 M **SH** in 0.5 mL of D_2O at −5 °C, Hartree−Fock energies, bond lengths, total atomic charge, and spin density for the singlet and triplet states of (*E*)- and (*Z*)- isomers of 2-tetrahydrothiopheniomethylidene-5-methylidene-2,5-dihydrothiophene calculated by the *Gaussian 94*, revision A.1 with 6-31G basis set (4 pages). See any current masthead page for ordering information and Web access instruction.

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