Mechanism of Polymerization Reaction of 2,5-Bis(tetrahydrothiopheniomethyl)furan Dichloride. Effect of Aromatic Resonance Energy on the Polymerization of Bis(sulfonium) Salts

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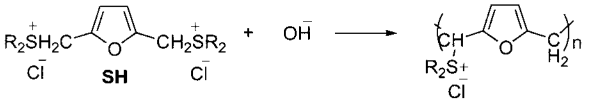
ABSTRACT: The mechanism of polymerization reaction of 2,5-bis(tetrahydrothiopheniomethyl)furan dichloride was studied kinetically. The reaction proceeds by the $(E1cb)_{irr}$ mechanism to afford a 2,5-dihydrofuran intermediate **M**, which undergoes a free radical polymerization reaction. Comparison of the kinetic results reveals that the rate of elimination reaction increases, whereas that for the subsequent polymerization reaction decreases as the aromatic moiety of the bis(sulfonium) salts is changed from phenyl to thiophene to furan. The results have been attributed to the decreased resonance energy of the aromatic rings.

Recently, we reported that polymerization reactions of α,α′-bis(tetrahydrothiophenio)-*p*-xylene dichloride (**SH″**) and 2,5-bis(tetrahydrothiopheniomethyl)thiophene dichloride (**SH′**) with OH^- in H_2O proceed via a *p*-xylylene type of intermediate **M″** and **M′**, respectively, by the common elimination free radical polymerization mechanism (Scheme 1).[1,2] As the substrate was changed from **SH″** to **SH′**, the mechanism of the elimination pathway changed from $(E1cb)_R$ to $(E1cb)_{irr}$, the rate of the elimination reaction increased, and that of polymerization process decreased. The addition of OH^- to **M″**, the k_3 pathway, competes with the polymerization reaction under kinetic conditions where 10^{-5} M **SH″** is employed but becomes negligible under the synthetic conditions. In sharp contrast, such a pathway does not exist in the polymerization reaction of **M′**. The differences have been attributed to the smaller aromatic resonance energy of thiophene than benzene.

To further expand our understanding of the polymerization reaction mechanism of the bis(sulfonium) salts, we studied the reaction of 2,5-bis(tetrahydrothiopheniomethyl)furan dichloride (**SH**) with OH^- in H_2O (eq 1).



(1)

This reaction is of considerable interest not only because of the mechanistic aspects but also because it produces the precursor polymer of poly(2,5-furanovinylene) (PFV). Although this polymer has not been used as extensively as poly(phenylenevinylene) (PPV) or poly(2,5-thienylenevinylene) (PTV), it has potential applications in electrochemical, electronic, and optical materials.[3−6]

In this work, we have identified the reactive intermediate and obtained quantitative kinetic data for both elimination and polymerization pathways. A reasonable mechanism consistent with these results is proposed. Finally, the effect of the aromatic resonance energy on the polymerization reaction of the closely related bissufonium salts **SH″**, **SH′**, and **SH** is discussed.

Experimental Section

Materials. 2,5-Bis(tetrahydrothiopheniomethyl)furan dichloride was synthesized by the reaction of 2,5-bis(chloromethyl)furan with tetrahydrothiophene as described in the literature.[6] Solutions of NaOH in H_2O and NaOD in D_2O were prepared as reported before.[1,2] In all cases, the ionic strength was maintained at 0.20 M with KCl.

NMR Experiments. The H−D exchange experiment for the methylene C−H protons of **SH** was performed as reported previously.[1,2] No change in the spectrum was noted after 60 min.

The NMR spectrum of the intermediate was obtained by adding 9.1 μL of 1.3 M OD^- ($[OD^-] = 0.012$ M) to a NMR tube containing 0.012 M of **SH** in 1.0 mL of D_2O at 25 °C.

UV−vis Spectrum of the Intermediate. The UV−vis spectra for the reaction of **SH** with OH^- in H_2O were obtained, as reported previously.[1,2]

Rates of Elimination Reactions. The rates of elimination reactions of **SH** with OH^- in H_2O were determined by monitoring the increase of the absorbance for **M** with time at 308 nm with a stopped-flow spectrophotometer, as reported previously.[2] Since the rates were much faster than those for the subsequent polymerization reaction, no problem was encountered in the rate studies. In all cases, plots of $-\ln(A_\infty - A_t)/(A_\infty - A_o)$ vs time were linear over two half-lives of the reaction. The slope was the pseudo-first-order rate constant.

Effects of $S_2O_8^{2-}$, OH^-, and TEMPO on the Rate of Polymerization Reaction. 2,5-Dihydrofuran intermediate (**M**) (4.87×10^{-5} M) was produced in a cuvette (path length = 10 mm) by reacting 4.87×10^{-5} M of **SH** with 1.74×10^{-3} M of NaOH(aq). A solution of $S_2O_8^{2-}$ (1.0 M, 80−300 μL) was added to this solution, and the decrease of the absorbance for **M** was monitored at 308 nm.[1,2] To determine the effects of OH^- and TEMPO, a higher concentration of 2,5-dihydrofuran intermediate (6.64×10^{-4} M) was produced in a cuvette (path length = 1 mm), and the rate of disappearance of **M** was measured before and after the addition of the additives as described above.

Product Studies. The product of reaction between **SH** (0.075 g, 0.22 mmol) in 5.0 mL of H_2O and 2.0 L of 0.01 M NaOH was obtained as described previously. After dialysis against water, a cast film of the polyelectrolyte was subjected to the heat treatment and analyzed by elemental analysis as reported in the literature.[2,6] Anal. Calcd for $(C_6H_4O)_n$: C, 78.25; H, 4.38. Found: C, 78.03; H, 4.62.

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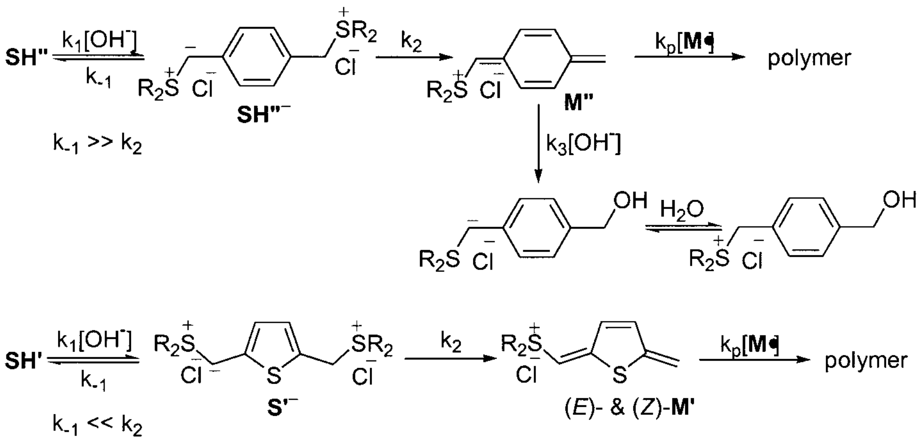
Scheme 1



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. Calcd for $(C_6H_4O)_n$: C, 78.25; H, 4.38. Found: C, 77.92; H, 4.58.

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. However, no signal was detected.

Cyclic Voltammetry. Cyclic voltametric experiments for **SH** and **M** were performed as reported previously.[2,8] However, no oxidation or reduction peak was noted from these samples within the potential range.

Calculation. Structures of the singlet and triplet states for the (*E*)- and (*Z*)-isomers of **M** were calculated on a Silicon Graphics workstation using the Gaussian 94, Revision A.1 quantum mechanical package developed by Pole and coworkers.[9] All structures were fully optimized using the 6-31G basis set.

Results

SH was synthesized by the reaction of 2,5-bis(chloromethyl)furan with tetrahydrothiophene by the literature method.[6] The product of reaction between **SH** and OH^- in H_2O was obtained by using 1×10^{-4} M **SH** and 1×10^{-4} M OH^- as reported previously.[2] The film casted from the high molecular weight fraction collected by dialysis had a golden lustrous color and showed satisfactory C and H analysis. A similar result was observed from the product obtained in the dark under argon atmosphere. This result indicates that the PFV precursor polymer is produced 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 308 nm increased gradually as the reaction proceeded. A clean isosbestic point was observed at 267 nm. Figure 2 shows that the absorbance decreases slowly after reaching at the maximum point. Because the rate of the former was much faster than the latter, the rates of both steps could be measured independently (vide infra).

When 0.1 equiv of OD^- was added to a 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.

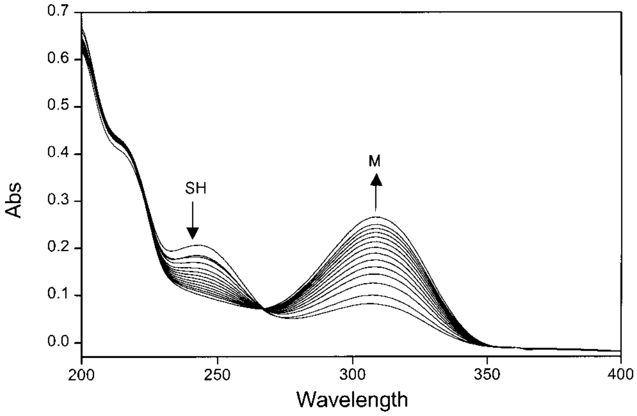


Figure 1. Change of the UV−vis spectrum with time for the reaction of 2,5-bis(tetrahydrothiopheniomethyl)furan dichloride (**SH**) promoted by OH^- in H_2O at 25.0 °C; [**SH**] = 4.87×10^{-5} M, $[OH^-] = 1.74 \times 10^{-3}$ M, $\mu = 0.20$ M (KCl).

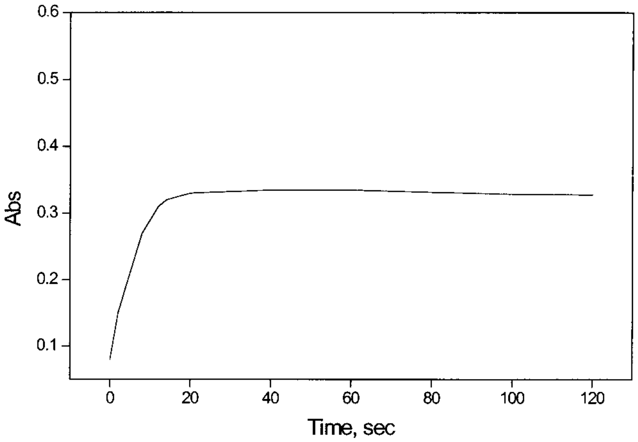


Figure 2. Change of the UV absorption at 308 nm with time for the reaction of 2,5-bis(tetrahydrothiopheniomethyl)furan dichloride (**SH**) promoted by OH^- in H_2O at 25.0 °C; [**SH**] = 4.87×10^{-5} M, $[OH^-] = 1.74 \times 10^{-3}$ M, $\mu = 0.20$ M (KCl).

The NMR spectrum of the reaction mixture was obtained by mixing 1 equiv of OD^- with 0.012 M of **SH** in D_2O at 25 °C (Figure S1). The spectrum indicated the presence of unreacted **SH**, **M**, and the expelled tetrahydrothiophene. The NMR spectrum in the region δ 7.5−4.9 is reproduced in Figure 3. It shows three doublets at δ 7.2−6.7 (J = 5.4 Hz), two singlets at δ 5.8−5.5, and poorly resolved four doublets at 5.2−4.9 (J = 3.0 Hz), which can be assigned to the furyl protons, the vinyl protons adjacent to the sulfonium group of **M**, and methylidene protons of **M**, respectively. The singlet

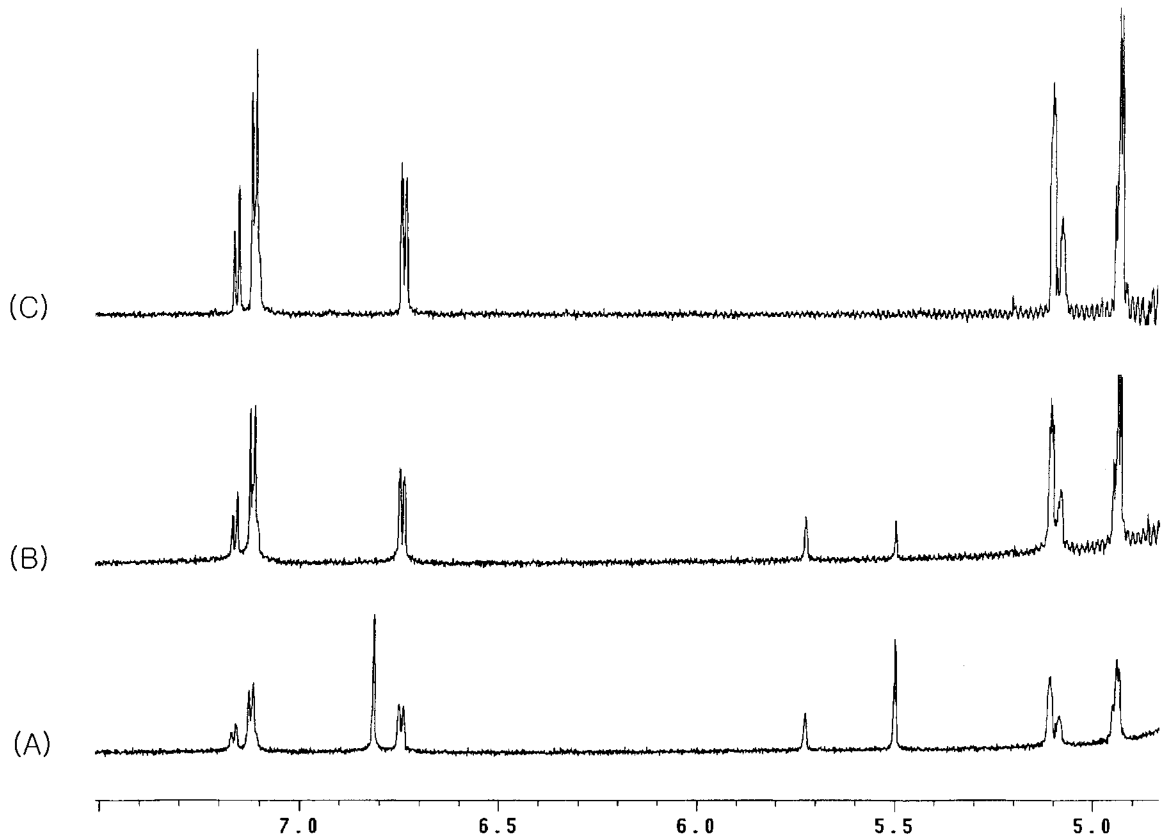


Figure 3. NMR spectrum of the reaction mixture for the reaction of 2,5-bis(tetrahydrothiopheniomethyl)furan dichloride 0.012 M of **SH** with OD^- in D_2O in the range δ 7.5–4.9. (A) $[OD^-] = 0.012$ M; (B) $[OD^-] = 0.060$ M; (C) $[OD^-] = 0.084$ M. The three doublets at δ 7.20–6.70 ($J = 5.4$ Hz), two singlets at δ 5.72 and 5.48, and four poorly resolved doublets at δ 5.20–4.90 can be attributed to the furyl, vinyl, and methylidene protons of (*E*)- and (*Z*)-**M**, respectively (see text).

Table 1. Observed Rate Constants for Eliminations from 2,5-Bis(tetrahydrothiopheniomethyl)furan 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	0.133 ± 0.001	0.316 ± 0.001
5.00	0.826 ± 0.010	1.70 ± 0.08
10.0	1.69 ± 0.01	3.45 ± 0.07
40.0	2.62 ± 0.08	14.5 ± 0.2

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

at δ 6.82 in Figure 3A is due to the methylene protons of unreacted **SH**. In addition, the peak areas for the furyl and methylidene protons of **M** are similar, whereas those for the vinyl protons adjacent to the sulfonium group (two singlets at δ 5.8–5.5) are smaller than the others and decrease as the base concentration increases.

Rates of elimination from **SH** were determined by monitoring the increase in the absorbance at 308 nm with a stopped-flow spectrophotometer. For all reactions, excellent pseudo-first-order plots were obtained over three half-lives (Figure S2). 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 4). The second-order rate constants obtained from the slopes of these plots are $k^{OH^-} = 180 \pm 1$ and $k^{OD^-} = 365 \pm 2$ M^{-1} s^{-1}, respectively. The Brönsted β value for the elimination reaction was calculated by using the relationship $k^{OD^-}/k^{OH^-} = 2.0^{\beta}$.[10] The value of β is 1.01 ± 0.01.

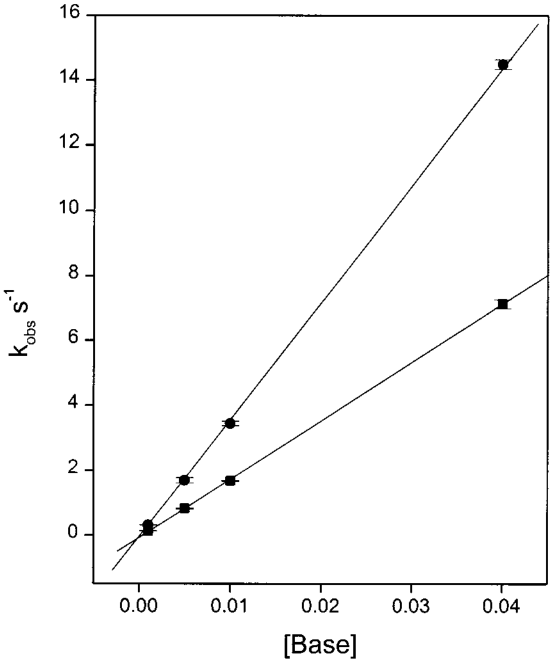


Figure 4. Plots of k_{obs} vs base concentration for elimination reactions of 2,5-bis(tetrahydrothiopheniomethyl)furan dichloride (**SH**) promoted by OH^- in H_2O (■) and OD^- in D_2O (●) at 25.0 °C; $\mu = 0.20$ M (KCl).

The rates of polymerization reaction were measured by monitoring the decrease in the absorption of **M** at 308 nm with a UV–vis spectrophotometer. The rate increased significantly and could be determined accurately when a free radical initiator, $S_2O_8^{2-}$, was added (Figure S3). The k_{obs} values measured in the presence of $S_2O_8^{2-}$ are summarized in Table 2. The plot of k_{obs} vs

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

$10^2[S_2O_8^{2-}]$, M	0.00	2.99	4.69	16.0	26.0	34.5	37.6
$10^4 k_{obs}$, s^{-1} [b]	0.0102 ± 0.0012[c,d]	2.23 ± 0.04	2.55 ± 0.05	4.73 ± 0.03	5.58 ± 0.08	6.64 ± 0.12	7.25 ± 0.10

[a] [SH] = 4.87×10^{-5} M except otherwise noted. [b] Average and standard deviation for more than three kinetic runs. [c] [SH] = 6.64×10^{-4} M. [d] $k_{obs} = 5.99 \times 10^{-7}$ s^{-1} when 4.8×10^{-5} M TEMPO was added.

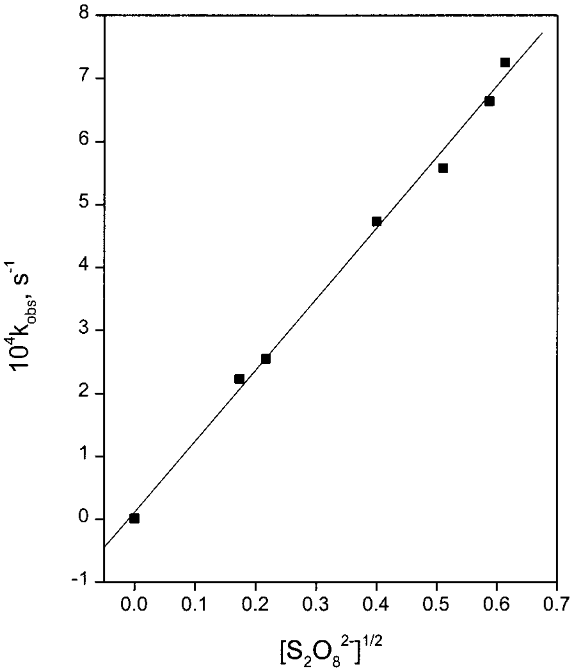


Figure 5. Plot of k_{obs} vs $[S_2O_8^{2-}]^{1/2}$ for the reaction of the 2,5-dihydrofuran intermediate **M** with $S_2O_8^{2-}$ at 25.0 °C.

$[S_2O_8^{2-}]^{1/2}$ is linear with excellent correlation (Figure 5). However, the rate was too slow to measure accurately under this condition either before or after the addition of TEMPO and OH^-. To determine the effects of these additives on the polymerization rates, the kinetic experiments were conducted by employing a higher concentration of **M** (6.64×10^{-4} M). The k_{obs} decreased from 1.02×10^{-6} to 5.99×10^{-7} s^{-1} when 4.8×10^{-5} M TEMPO was added. On the other hand, no appreciable change in the rate was observed by the addition of up to 0.12 M OH^-.

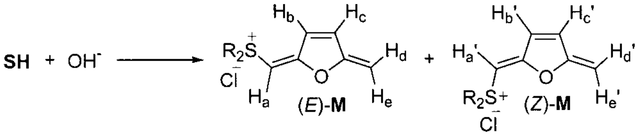
In contrast to the reaction between **SH′** and OH^-, the reaction mixture of **SH** and OH^- did not exhibit the ESR spectrum under the same conditions. Similarly, no redox peak could be detected in the cyclic voltammograms for **SH**, tetrahydrothiophene, OH^-, and **M**.

Structures of the singlet and triplet states for the (*E*)- and (*Z*)-isomers of **M** were calculated by an ab initio method with the 6-31G basis set.[9] For both isomers, the singlet state is the ground state. In addition, the Hartree–Fock energy for the (*Z*)-isomer is lower than the (*E*)-isomer by 2.417 kcal/mol.

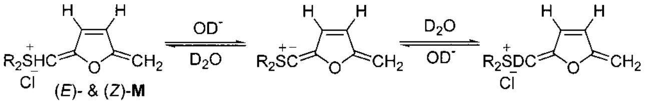
Discussion

It was previously reported that the polymerization reactions of **SH″** and **SH′** with OH^- in H_2O proceed via intermediates **M″** and **M′**, respectively, by the common elimination free radical polymerization mechanism (Scheme 1).[1,2] Results of the kinetic and product studies reveal that the reactions of **SH** with OH^- in H_2O proceed by a similar mechanism. Figure 1 shows that the reaction of **SH** with OH^- in H_2O produces an intermediate, which has a strong absorption at 308 nm. Because the rate of the former was much faster than the subsequent polymerization reaction (Figure 2), each step could be studied independently.

Scheme 2



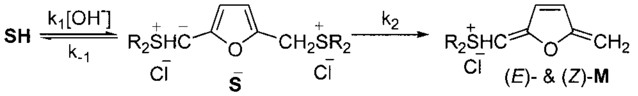
Scheme 3



Structures of the Intermediates. The UV–vis spectra in Figure 1 show that λ_{max} of the intermediate is red-shifted by 66 nm from that of the reactant. This result indicates that the intermediate has more extended π orbital conjugation than **SH**. Moreover, the NMR spectrum in Figure 3 can reasonably be explained by assuming that (*E*)- and (*Z*)-isomers of **M** are produced under the reaction conditions. For example, the three doublets at δ 7.20–6.70 with $J = 5.4$ Hz can be assigned to the furyl protons of (*E*)- and (*Z*)-**M** (H_b, H_c, H_b', and H_c'), if one assumes that two of them are overlapped at δ 7.12. The two singlets at δ 5.72 and 5.48 appear to be due to the vinyl protons adjacent to the sulfonium group (H_a and H_a'). Similarly, the poorly resolved four doublets at δ 5.20–4.90 can be attributed to the methylidene protons of (*E*)- and (*Z*)-**M** (H_d, H_e, H_d', and H_e'). In addition, the peak areas corresponding to one of the isomers are approximately 2-fold larger than those for the other. Along with the lower Hartree–Fock energy calculated for the (*Z*)-isomer than the (*E*)-isomer (vide supra), this result can most reasonably be interpreted with the formation of the sterically less hindered (*Z*)-isomer as the major intermediate. Finally, the smaller peak areas for H_a and H_a' than those for furyl and methylidene protons appear to be due to the partial H–D exchange in the intermediate (Scheme 3). Because the acidities of H_a and H_a' should be higher than those of H_d, H_e, H_d', and H_e' due to the presence of the strongly electron-withdrawing sulfonium group, they could undergo H–D exchange preferentially. The decreased peak area for the former at higher base concentration provides additional evidence for this interpretation.

Mechanism of Elimination Reaction from SH Forming the 2,5-Dihydrofuran Intermediate. The mechanism of the elimination reaction was assessed by the kinetic and product studies. The reaction produced elimination product **M** quantitatively and exhibited second-order kinetics, first-order to the substrate and first-order to the base. This result rules out all but E2, $(E1cb)_{irr}$, $(E1cb)_R$, and $(E1cb)_{ip}$ mechanisms.[11] The $(E1cb)_R$ mechanism, in which $k_{-1} \gg k_2$, is negated by the absence of H–D exchange.[11] The $(E1cb)_{ip}$ mechanism requires the formation of an intimate ion pair between S^- and the conjugate acid of the promoting base, i.e., H_2O, along

Scheme 4



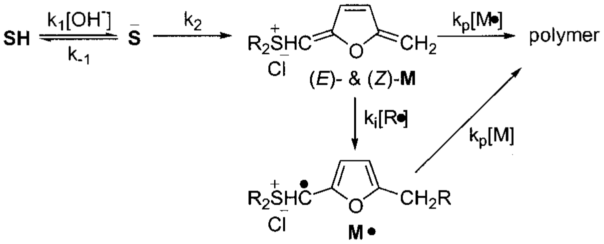
the reaction pathway. However, this mechanism is highly unlikely because such an intermediate cannot exist in a dipolar protic solvent. The distinction between the E2 and $(\mathrm{E1cb})_{\mathrm{irr}}$ mechanism has been made by the Brönsted β value. The value of β for the OH^--promoted elimination from **SH** is 1.01 ± 0.01, indicating that the $\mathrm{C}_\beta{-}\mathrm{H}$ bond is completely broken in the transition state. This result negates the possibility of the E2 mechanism, for which $0 < \beta < 1.0$ is expected.[10,11] Hence, the most reasonable mechanism for this elimination reaction appears to be $(\mathrm{E1cb})_{\mathrm{irr}}$. Moreover, both (*E*)- and (*Z*)-**M** should be produced by the same mechanism because the reaction proceeds via the same intermediate $\mathbf{S}^-$ and the first step is rate-limiting (Scheme 4).

It is interesting to note that the mechanism of elimination reaction changes from $(\mathrm{E1cb})_{\mathrm{R}}$ to $(\mathrm{E1cb})_{\mathrm{irr}}$ as the substrates is changed from **SH″** to **SH′** and **SH**. The result may be attributed to the smaller aromatic resonance energy of the five-membered heterocyclic aromatic compounds than benzene.[12] Because the aromatic resonance energy is lost in the k_2 step, the reaction would become gradually less endothermic with the change of the substrate, to increase the rate in the order $k_2^{\mathrm{SH}''} < k_2^{\mathrm{SH}'} < k_2^{\mathrm{SH}}$. On the other hand, k_{-1} should be less sensitive than k_2 to the aromatic resonance energy of the substrates. Therefore, the rate-limiting step for the elimination process could change from k_2 to k_1, to result in the change of the elimination reaction mechanism from $(\mathrm{E1cb})_{\mathrm{R}}$ for **SH″**, i.e., $k_{-1}^{\mathrm{SH}''} \gg k_2^{\mathrm{SH}''}$, to $(\mathrm{E1cb})_{\mathrm{irr}}$ for **SH′** and **SH**, i.e., $k_{-1}^{\mathrm{SH}'} \ll k_2^{\mathrm{SH}'}$ and $k_{-1}^{\mathrm{SH}} \ll k_2^{\mathrm{SH}}$, respectively.

The rate equation for the formation of **M** can be expressed as $k_{\mathrm{obs}} = k_1k_2[\mathbf{SH}][\mathrm{OH}^-]/(k_{-1} + k_2)$. Because the reaction is assumed to proceed via the $(\mathrm{E1cb})_{\mathrm{irr}}$ mechanism, i.e., $k_{-1} \ll k_2$, the equation can be simplified as $k_{\mathrm{obs}} = k_1[\mathbf{SH}][\mathrm{OH}^-]$. The value of k_1 can be taken from the slope of the plot in Figure 4, i.e., $k_1 = 180 \pm 1\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$. When $[\mathbf{SH}] = 5.0 \times 10^{-5}$ M and $[\mathrm{OH}^-] = 2.0 \times 10^{-3}$ M, the rate of production of **M** is $1.8 \times 10^{-5}\ \mathrm{M\ s}^{-1}$. For comparison, the rates of elimination from **SH″** and **SH′** are 2.9×10^{-8} and $6.5 \times 10^{-6}\ \mathrm{M\ s}^{-1}$, respectively, under the same conditions.[1,2] The rate increases gradually in the order **SH″** < **SH′** < **SH**. This result can also be attributed to the decreased aromatic resonance energy of the substrate.[12] The reaction becomes less endothermic with decreasing loss of aromatic resonance energy by the formation of the intermediate in the elimination pathway. This leads to decrease in free energy of activation and enhances the rate.

Polymerization Reaction Mechanism. The polymerization reactions of **M″** and **M′** are known to proceed by a common free radical mechanism.[1,2] The results of kinetic experiments reveal that the polymerization reaction of **M** also proceeds by the same mechanism. As previously observed for **M′**, **M** did not react with OH^-. In addition, $\mathbf{S}^-$ is not likely to initiate the polymerization reaction because it would not exist in appreciable amount under the reaction condition as indicated by the absence of H−D exchange in **SH** (vide supra). Hence, the possibility of the anionic mechanism can be ruled out. On the other hand, when a small amount of free radical initiator, $\mathrm{S_2O_8}^{2-}$, was added to **M**, the rate increased significantly (Table 2). Moreover, the plot of k_{obs} vs $[\mathrm{S_2O_8}^{2-}]^{1/2}$ is linear with excellent correlation (Figure 4). This result indicates that the rate equation can be expressed as $k_{\mathrm{obs}} = a + k_{\mathrm{p}}(k_{\mathrm{i}}/k_{\mathrm{t}})^{1/2}[\mathrm{S_2O_8}^{2-}]^{1/2}$, as required for the free radical polymerization.[13] Furthermore, the rate was retarded when 2.1×10^{-3} M TEMPO was added.

Scheme 5



The k_{p} value was estimated from the slope of Figure 5 by using $k_{\mathrm{i}} = 4.62 \times 10^{-8}\ \mathrm{s}^{-1}$ for the decomposition of $\mathrm{S_2O_8}^{2-}$ and $k_{\mathrm{t}} = 1 \times 10^{6}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$ for the polymerization of the vinyl monomers.[12,13] The calculated k_{p} value is $5.26 \times 10^{3}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$. For comparison, the k_{p} values for the polymerization of **M″** and **M′** are 1.05×10^{7} and $4.78 \times 10^{4}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$, respectively.[1,2] The k_{p} value decreases systematically as the aromatic resonance energy of the substrate is decreased. The result is not unexpected because the aromatic resonance energy is gained upon polymerization (vide supra).

The free radical concentration was calculated from the intercept of Figure 5 by assuming that $k_{\mathrm{obs}} = k_{\mathrm{p}}[\mathbf{M}^\bullet]$ when $[\mathrm{S_2O_8}^{2-}] = 0$. The value of $[\mathbf{M}^\bullet]$ is 2.1×10^{-9} M, which is between $[\mathbf{M}'^\bullet] = 1.1 \times 10^{-8}$ M and $[\mathbf{M}''^\bullet] = 1.2 \times 10^{-9}$ M estimated under the same conditions.[16]

The validity of the calculated rate constants and the free radical concentration is confirmed by comparing the microscopic rates with the experimental facts. Figure 2 shows that the intermediate **M** is produced rapidly and accumulated under the kinetic conditions, and the subsequent polymerization reaction is very slow. In contrast, under synthetic conditions where higher concentrations of the reactants are employed, the polymerization reaction proceeds immediately after mixing the reactants. When $[\mathbf{M}] = 5.0 \times 10^{-5}$ M and $[\mathbf{M}^\bullet] = 2.1 \times 10^{-9}$ M, the rate of disappearance of **M** by the k_{p} pathway is $k_{\mathrm{p}}[\mathbf{M}][\mathbf{M}^\bullet] = 5.5 \times 10^{-10}\ \mathrm{M\ s}^{-1}$. The rate is slower by approximately 3.3×10^{4} fold than $1.8 \times 10^{-5}\ \mathrm{M\ s}^{-1}$ for the formation of **M** under the same conditions (vide supra). This predicts 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 each of **SH** and OH^- for the practical synthesis, the maximum rates of the formation of **M** and its consumption would be $k_1[\mathbf{SH}][\mathrm{OH}^-] = 7.2$ and $k_{\mathrm{p}}[\mathbf{M}][\mathbf{M}^\bullet] = 0.0088\ \mathrm{M\ s}^{-1}$, respectively. Hence, the intermediate could be accumulated, but only for a short period of time, because the polymerization reaction would be completed within 23 s. All of these results are consistent with the elimination free radical polymerization mechanism shown in Scheme 5. 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. Although we failed to detect the ESR signal from the reaction mixture, one should not rely too heavily on the negative result in proposing the reaction mechanism.

An important question is regarding the nature of the free radical initiator. Polymerization reactions of **M″**, **M′**, and **M** can be classified as spontaneous or self-initiated polymerization because they proceed by the free radical mechanism even though no free radical initiator is added. There is much precedent on the self-initiated polymerization especially for styrene and acrylic monomers.[17−19] Various types of mono- or diradicals have been proposed as the initiators. For the polymerization reactions of **M″** and **M′**, others and we have concluded that the Wessling type of dimer diradicals may be the initiator.[1,2,20,21] The conclusion was based on both the experimental evidence that ruled out the possibilities of (i) the photoexcitation, (ii) hydrogen abstraction by the molecular oxygen, and (iii) oxidation−reduction reaction as the origin of the free radical initiator formation and the literature results that indicated the high reactivity of the *p*-xylylene in spontaneous free radical reaction.[22,23]

Similar conclusion can be made for the polymerization of **M**. The reaction proceeded readily both in the presence and absence of air or light to rule out the possibility (i) and (ii). No redox peak was observed in the cyclic voltammograms of the reaction mixture to negate the possibility (iii). Finally, the kinetic behavior of **M″**, **M′**, and **M** are very similar. Therefore, the most likely initiator for the polymerization of **M** appears to be the dimer diradicals of **M**.

Conclusions

The polymerization reaction of **SH** with OH^- proceeds by the elimination free radical polymerization mechanism via the intermediates (*E*)- and (*Z*)-**M**, as shown in Scheme 5. The mechanism of elimination pathways changes from $(E1cb)_R$ to $(E1cb)_{irr}$ as the substrates is changed from **SH″** to **SH′** and **SH**. The rate of elimination increases, whereas that for the subsequent polymerization reaction decreases as the aryl moiety of the substrate is changed from phenyl to thiophene to furan. The results are interpreted with the decreased aromatic resonance energy of the latter.

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Supporting Information Available: NMR spectrum of the reaction mixture taken after mixing 0.012 M OD^- and 0.012 M **SH** in 1 mL of D_2O at 25 °C, plot of $\ln(A_\infty - A_t)$ vs time for the reaction of 2,5-bis(tetrahydrothiopheniomethyl)-furan dichloride (**SH)** with OH^- in H_2O at 25.0 °C, and plot of $\ln(A_t - A_\infty)$ vs time for the reaction of 2,5-dihydrofuran intermediate (**M)** with $S_2O_8^{2-}$ in H_2O at 25.0 °C. This material is available free of charge via the Internet at http://pubs.acs.org.

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