Macromolecules **1998,** *31,* 2098−2106

Kinetics of Polymerization Reaction of α,α′-Bis(tetrahydrothiophenio)-*p*-xylene Dichloride

Bong Rae Cho,* Yong Kwan Kim, and Man So Han[†]

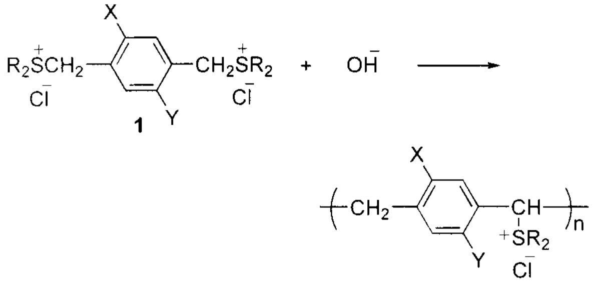
Department of Chemistry, Korea University, 1-Anamdong, Seoul 136-701, Korea

Received November 12, 1997; Revised Manuscript Received January 29, 1998

ABSTRACT: Polymerization reactions of α,α′-bis(tetrahydrothiophenio)-*p*-xylene dichlorides with OH^- in H_2O have been studied kinetically. The reactions proceeded via the α-tetrahydrothiophenio-*p*-xylylene intermediates. Results of the H−D exchange experiments and kinetic studies reveal that the 1,6-elimination forming the intermediates proceeds reversibly via the ylide intermediate. The observed rate of disappearance of the intermediate was increased by the addition of OH^-, tetrahydrothiophene, and $S_2O_8^{2-}$ as well as by the photoirradiation with a tungsten lamp in the presence of Rose Bengal and was inhibited by TEMPO. However, the rate was found to be independent of ylide concentration. From these results, an elimination−free radical polymerization mechanism is proposed. The microscopic rate constants for each step of this mechanism were calculated from the change in the intermediate concentration with time. All of the rate data showed excellent correlations with the substituent constants in the Hammett plot.

Poly(*p*-phenylenevinylene) (PPV) and its derivatives have been the subject of intensive research because of their useful applications as conducting materials, polymer-based light-emitting diodes, lasing materials, and nanocomposites.[1] PPV is obtained by thermal elimination of poly(α-tetrahydrothiophenio-*p*-xylylene) chloride, which is readily synthesized by reacting α,α′-bis(tetrahydrothiophenio)-*p*-xylene dichloride with OH^-.[1a] Several mechanisms have been proposed for the polymerization reaction. Wessling postulated that the reaction proceeds via a *p*-xylylene intermediate by a free radical mechanism initiated by a biradical intermediate.[2] On the other hand, Lahti had originally proposed an anionic mechanism based on the failure of detection of the free radical intermediate[3] but later reported strong evidence for the free radical mechanism.[4] More recently, we reported that the change in the concentration of the *p*-xylylene intermediate with reaction time could be explained with the elimination−addition mechanism utilizing computer modeling.[5] However, the detailed mechanism of this reaction has not been clearly elucidated.

In this work, we have conducted a kinetic investigation on the reactions of substituted α,α′-bis(tetrahydrothiophenio)-*p*-xylene dichlorides **1a**−**e** with OH^- in aqueous solution (eq 1). The validity of the previously proposed mechanisms have been examined by independent experiments. Microscopic rate constants of each step were calculated. A detailed mechanism consistent with all of the existing evidences is proposed.



(1)

a: X = H, Y = H, **b**: X = H, Y = CH_3O, **c**: X = CH_3O, Y = CH_3S
d: X = H, Y = Br, **e**: X = CH_3O, Y = Br

Results and Discussion

The reaction has been proposed to proceed via the *p*-xylylene intermediate M, which undergoes polymerization either by an anionic or by a free radical mechanism (Scheme 1).[2−5] It is well established that M is produced via the ylide intermediate. However, it is not known which of the two mechanisms is the major pathway of the polymerization step and what is the initiator. We have initiated qualitative studies aimed at probing the mechanisms of the elementary steps in Scheme 1. The microscopic rate constants have also been calculated to provide quantitative interpretations for the qualitative observations. Finally, the nature of the free radical initiator is briefly discussed.

Formation of the *p*-Xylylene Intermediate. The first step of the polymerization reaction is the formation of the *p*-xylylene intermediate M. This reaction was assumed to proceed via the ylide intermediate, which expels tetrahydrothiophene to afford the polymerizing monomer M.[2−5] The mechanism of this step was assessed by the H−D exchange experiment. When 0.01 M of OD^-−D_2O was added to the NMR tubes containing 0.1 M **1a**−**e** in D_2O, the benzylic proton resonances at δ 4.05−4.75 disappeared completely before an appreciable amount of the polymer was produced. This result indicates that the deprotonation step is reversible and is much faster than the formation of the intermediate.

The formation of the *p*-xylylene intermediate from the ylide has been proposed by Lahti to proceed reversibly.[4] The validity of this proposal was examined by adding an excess amount of tetrahydrothiophene (THT) to M after neutralizing the solution and measuring the rate of disappearance of M (Table 1). The rate showed a first-order dependence on [THT] (Figure 1) i.e., $k_{obs} = a + k_{-2}[THT]$, indicating that THT is added to M to produce $\mathbf{1}^-$, as shown in Scheme 2, where $\mathbf{1}^-$, M, M^-,

---

[†] Current address: Department of Chemistry, Dae Jin University, San 11-1, Pochun, Kyungki 487-711, Korea.

S0024-9297(97)01664-1 CCC: $15.00

Scheme 1

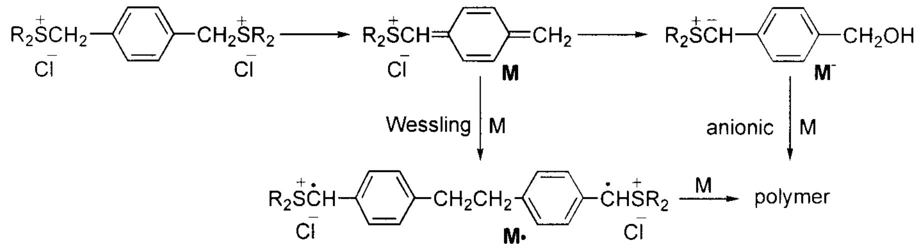


Table 1. Observed Rate Constants for the Disappearance of the *p*-Xylylene Intermediates upon Addition of Tetrahydrothiophene at 25.0 °C

10^4[THT], M	$10^2 k_{obs}$, s^{-1} [a]				
	1a	**1b**	**1c**	**1d**	**1e**
1.91	0.992	1.57	3.77	8.53	14.1
3.81	1.88	2.67	6.87	15.1	26.6
5.71	2.65	3.98	9.06	21.8	36.6
7.62	3.47	5.08	11.8	27.5	48.9

[a] Estimated uncertainty, ±5%.

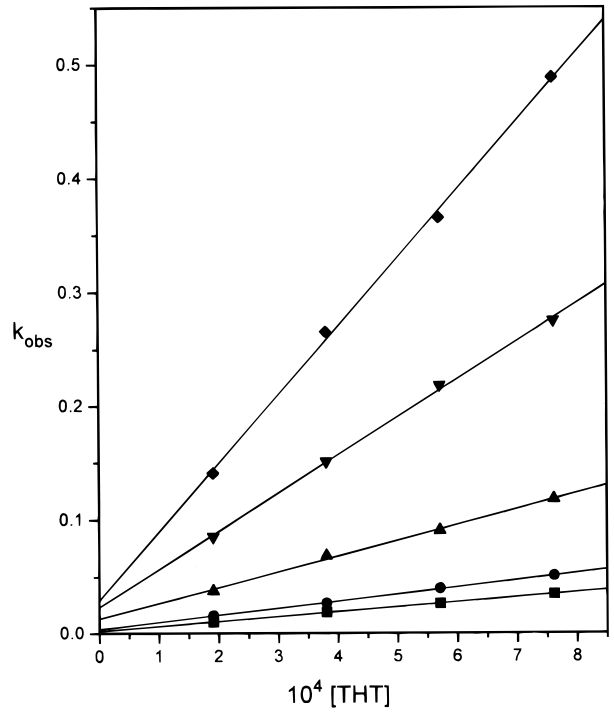
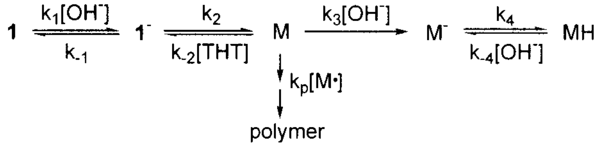


Figure 1. Plots of k_{obs} vs [THT] for the reactions of the *p*-xylylene intermediates with tetrahydrothiophene (THT) at 25.0 °C: **1a** (■); **1b** (●), **1c** (▲); **1d** (▼); **1c** (◆).

Scheme 2



MH, and M• are the conjugate bases of **1a**–**c**, the *p*-xylylene intermediate, adduct anions produced by the reactions between M and OH⁻, conjugate acids of M⁻, and a free radical initiator, respectively.

Addition of OH⁻ to M. The possibility that the OH⁻ ion may add to M to afford M⁻ was assessed by both kinetic and product studies. When an excess amount of OH⁻ was added to M, the concentration of M showed first-order decay with a rate equation $k_{obs} = a + k_3[OH^-]$ (Table 2 and Figure 2). This result can only be explained if the OH⁻ ion is added to M. The conclusion was confirmed by isolating the [*p*-(hydroxymethyl)-benzyl]tetrahydrothiophenium chloride (MH) from the reaction mixture. On the other hand, when 2×10^{-5} M of MH was added to 0.010 M OH⁻(aq), no trace of *p*-xylylene was detected by UV–vis spectroscopy, indicating that the addition is irreversible. In addition, the facile H–D exchange observed for MH is consistent with the reversible protonation of M⁻ (Scheme 2).[6]

Table 2. Observed Rate Constants for the Disappearance of the *p*-Xylylene Intermediates upon Addition of OH⁻ at 25.0 °C

10^2[OH⁻], M	$10^3 k_{obs}$, s^{-1} [a]				
	1a	**1b**	**1c**	**1d**	**1e**
0.00[b]	2.01	3.92	13.2	23.1	29.8
1.00	2.83	4.93	14.7	31.8	39.4
4.00	5.21	7.42	18.3	54.6	65.9
8.00	8.29	11.3	24.1	90.2	101
12.0	11.7	15.3	30.1	125	142
16.0	15.1	20.0	35.2	159	181
20.0	18.1	23.2	41.7	194	217

[a] Estimated uncertainty, ±5%. [b] Reaction mixture was neutralized by adding 1 equiv of HCl when maximum concentration of M was accumulated.

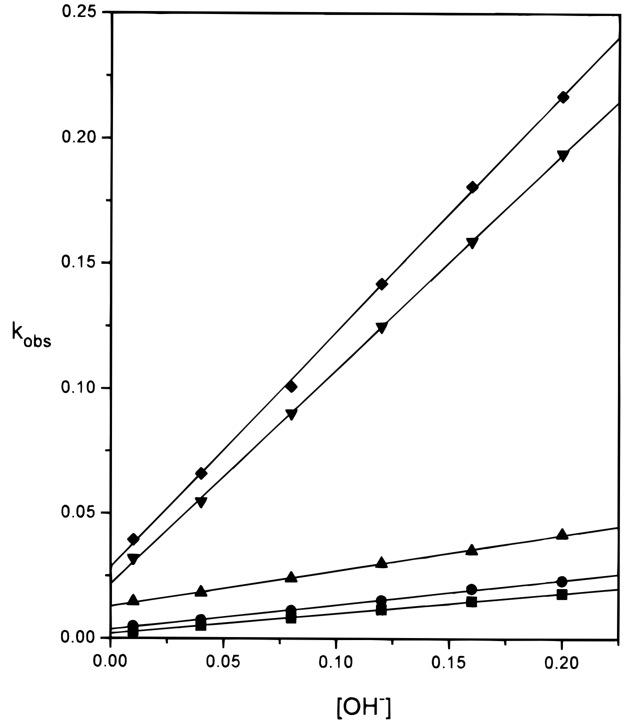


Figure 2. Plots of k_{obs} vs [OH⁻] for the reactions of the *p*-xylylene intermediates with OH⁻ at 25.0 °C: **1a** (■); **1b** (●); **1c** (▲); **1d** (▼); **1c** (◆).

Polymerization Reaction. Both anionic and free radical polymerization mechanisms have been proposed

Table 3. Observed Rate Constants for the Disappearance of the *p*-Xylylene Intermediates upon Addition of Carbanions at 25.0 °C

$10^4[R_3C^-]$,[b] M	10^3k_{obs}, s^{-1} [a]			
	$CH_3CH_2NO_2$[c]	$(CH_3CO)_2CH_2$[c]	CH_3NO_2[c]	p-$O_2NC_6H_4CH_2CN$[c,d]
2.00	5.01	8.94	13.3	74.0
4.00	6.95	14.1	22.2	143
6.00	8.42	20.1	32.1	213
8.00	10.1	25.1	42.0	282

[a] Estimated uncertainty, ±5%. [b] Carbanion concentration except otherwise noted. [c] R_3CH. [d] $10^4[R_3C^-]$ = 2.39, 4.77, 7.14, and 9.50 M in the descending order.

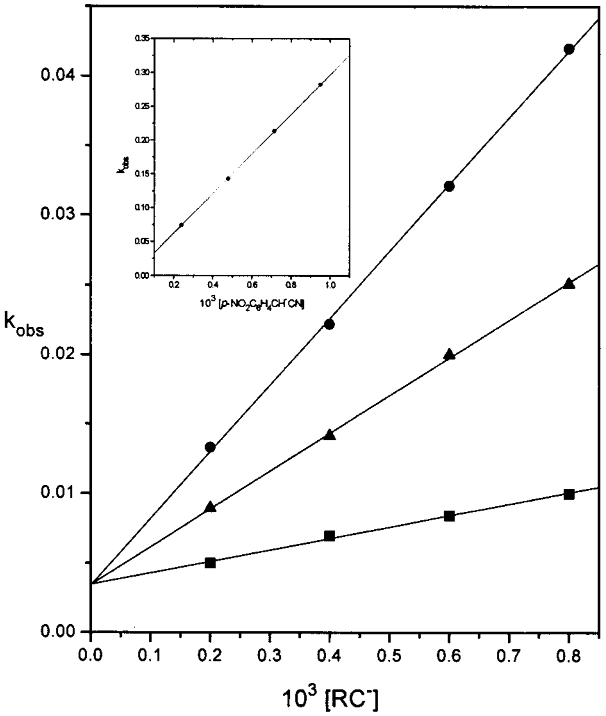


Figure 3. Plots of k_{obs} vs [carbanion] for the reactions of the p-xylylene intermediate M with carbanions at 25.0 °C. R_3CH = nitroethane (■), acetylacetone (▲), nitromethane (●). Inset: The same plot for the reaction of M with the conjugate base of p-nitrobenzyl cyanide.

for the polymerization of the p-xylylene intermediate.[2-5] The key step in the anionic mechanism is the addition of a nucleophile to M to afford M^-, which may initiate the polymerization (Scheme 1). Since the deprotonation of **1** proceeds reversibly and OH^- is added to M, a significant amount of $\mathbf{1}^-$ and M^- should exist under the reaction conditions. Furthermore, if OH^- is added to M, other carbanions should also add to M. This possibility was examined by adding a series of carbon acids with $pK_a < 14$ to the reaction mixture and measuring the rates (Table 3). In all cases, the rate showed first-order dependence on the carbanion concentration, i.e., $k_{obs} = b + k_A[\text{carbanion}]$ (Figure 3). The k_A values obtained from the slopes of the these plots are 8.23, 27.0, 48.0, and 293 for the conjugate bases of nitroethane, acetylacetone, nitromethane, and p-nitrobenzyl cyanide. Moreover, rate data correlated satisfactorily with the pK_a values of the carbon acids in the Brönsted plot (Figure 4). The rate constants for the addition of $\mathbf{1}^-$ and M^- to M were estimated from the Brönsted plot and their pK_a values.[6] The values are 264 and 387 M^{-1} s^{-1} for $\mathbf{1}^-$ and M^-, respectively. Hence, if the polymerization reaction proceeds by an anionic mechanism, the addition of these carbanions to M should proceed at these rates. In contrast, when an excess amount of α,α′-bis(tetrahydrothiophenio)-*m*-xylene dichloride and MH were added to the reaction mixture, no change in the rate was observed.[7] The negligible rate of addition may be attributed to the steric hindrance caused by the bulky tetrahydrothiophenio substituent. Alternatively, the reactivity of the carbanion may be significantly reduced because it is most likely heavily solvated due to the presence of the nearby onium salt. Whatever might be the interpretation, the anionic polymerization is inconsistent with this result.

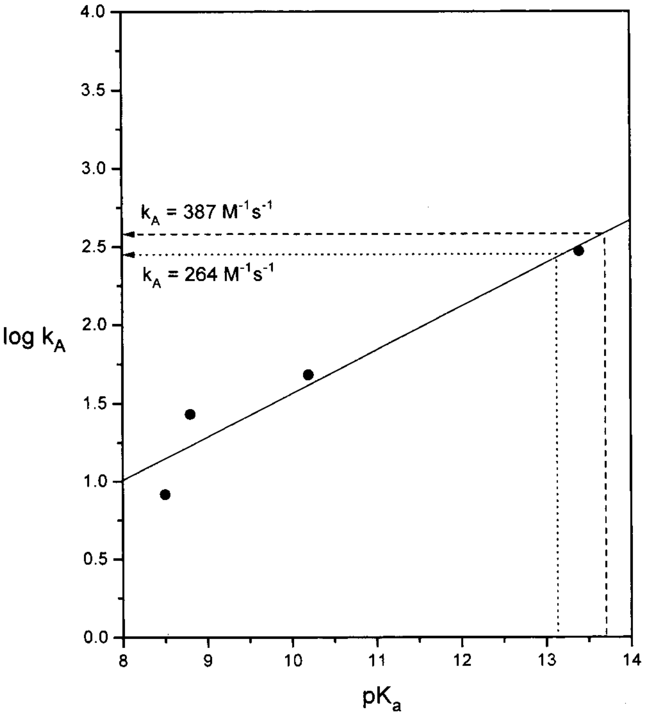


Figure 4. Brönsted plot for the reactions of the p-xylylene intermediate with carbanions at 25.0 °C. The rate constants for the addition of $\mathbf{1}^-$ and M^- to M estimated from this plot and their pK_a values are 264 and 387 M^{-1} s^{-1}, respectively (see text).

Support for this conclusion is provided by the quenching experiment. When the reaction mixture was neutralized by adding 1 equiv of HCl, the rate of disappearance of the p-xylylene intermediate decreased only slightly (Table 2). Since there should be little, if any, OH^- or carbanions in the neutral solution, the rate should be negligible, if addition of OH^- to M or anionic polymerization were the major reaction pathway. This result strongly indicates that there must be a reactive species other than the anions that react with M under the reaction condition.

Convincing evidences for the free radical mechanism have been provided by Lahti in the molecular weight studies.[4] His work has clearly shown that the efficient radical scavenging agents such as TEMPO and hydrogen atom donor 2,4,6-tri-*tert*-butylaniline reduce the degree of polymerization and in some cases completely suppress formation of high molecular weight polymer. We have observed similar results in our kinetic and product studies. First, when 1.0×10^{-5} M of TEMPO was added to the neutralized solution, the k_{obs} decreased from 2.01×10^{-3} to 1.12×10^{-3} s^{-1}. Second, the rate increased significantly when a small amount of free radical initiator, $S_2O_8^{2-}$, was added (Table 4). Moreover,

Table 4. Observed Rate Constants for the Disappearance of the *p*-Xylylene Intermediates upon Addition of $S_2O_8{}^{2-}$ at 25.0 °C

$10^3[S_2O_8{}^{2-}]$, M	10^2k_{obs}, s^{-1} [a]				
	1a	**1b**	**1c**	**1e**	**1e**
0.500	0.121	0.544	1.47	2.05	2.57
1.00	0.161	0.756	2.03	2.88	3.28
1.50	0.194	0.928	2.45	3.41	4.08
2.00	0.221	1.06	2.82	4.00	4.77
2.50	0.246	1.18	3.14	4.34	5.19

[a] Estimated uncertainty, ±5%.

Table 5. Microscopic Rate Constants for Each Step of the OH^--Induced Polymerization of α,α′-Bis(tetrahydrothiophenio)-*p*-xylene Dichlorides 1a−e

compd	$10^{-3}k_1$ [a]	$10^{-3}k_{-1}$ [a]	pK_a [b]	k_2 [c]	k_{-2} [a,d]	k_3 [a,e]	$10^{-8}k_p$ [a,f,g]
1a	2.67	1.34	13.7	0.142	38.0	0.0781	0.105
1b	4.50	0.714	13.2	0.126	78.0	0.0921	0.255
1c	8.57	0.270	12.5	0.109	162	0.131	0.530
1d	11.6	0.184	12.1	0.094	321	0.684	1.27
1e	12.4	0.600	11.7	0.082	792	0.776	1.32

[a] M^{-1} s^{-1}. [b] $pK_a = 14 - \log(k_1/k_{-1})$. [c] s^{-1}. [d] Estimated k_{-2} values are 43.1, 62.3, 138, 334, and 600 M^{-1} s^{-1} for **1a**, **1b**, **1c**, **1d**, and **1e**, respectively. [e] Estimated k_3 values are 0.0820, 0.101, 0.145, 0.869, and 0.956 M^{-1} s^{-1} for **1a**, **1b**, **1c**, **1d**, and **1e**, respectively. [f] Estimated $10^{-8}k_p$ values are 0.0662, 0.338, 0.887, 1.22, and 1.44 M^{-1} s^{-1} for **1a**, **1b**, **1c**, **1d**, and **1e**, respectively. [g] Estimated $10^{10}[M\cdot]$ values are 2.39, 0.976, 1.33, 1.63, and 1.65 M for **1a**, **1g**, **1c**, **1d**, and **1e**, respectively.

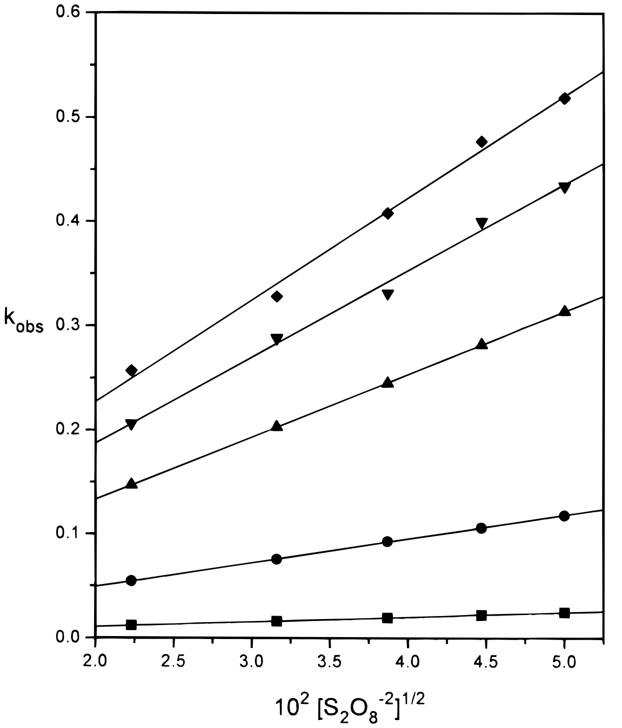


Figure 5. Plots of k_{obs} vs $[S_2O_8{}^{2-}]$ for the reactions of the *p*-xylylene intermediates with $S_2O_8{}^{2-}$ at 25.0 °C: **1a** (■); **1b** (●); **1c** (▲); **1d** (▼); **1c** (◆).

the plots of k_{obs} vs $[S_2O_8{}^{2-}]^{1/2}$ are straight lines with excellent correlations (Figure 5). 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.[8] Third, when a mixture of **1a**, acrylamide, and OH^- in H_2O was allowed to react for 2 days at room temperature, a copolymer was produced. Elemental analysis of the high molecular weight fraction obtained by dialysis revealed that it contained C, H, S, and N in 58.4, 6.70, 8.52, and 1.11%, respectively. This result indicates that approximately 23% of the acrylamide is incorporated in the copolymer. In contrast, no polymer was produced when the same reaction was conducted without **1a** or OH^- under the same conditions. The result can only be explained if the acrylamide was copolymerized with M by the free radical mechanism under the reaction conditions. All of these results are consistent with the elimination−free radical polymerization shown in Scheme 2.

Estimation of the k_{-2}, k_3, and k_p Values and Free Radical Concentration. The calculation of the microscopic rate constants for Scheme 2 requires the initial values of each rate constant and the free radical concentration (*vide infra*). The k_{-2} and k_3 values were estimated from the slopes of the plots in Figures 1 and 2. The k_p values were obtained from the slopes of the plots in Figure 5 by assuming $k_i = 4.62 \times 10^{-8}$ s^{-1} for the decomposition of $S_2O_8{}^{2-}$ and $k_t = 1 \times 10^7$ M^{-1} s^{-1} for the polymerization of the vinyl monomers.[8,9] The free radical concentration was calculated from the k_{obs} for the disappearance of M under the absence of base ($[OH^-] = 0.00$ M in Table 2) by assuming the k_{-2} and k_p steps are the major reaction pathways, i.e., $k_{obs} = k_{-2}[THT] + k_p[M\cdot]$. Since the reactions were quenched after approximately half of the reactant was consumed, [THT] was assumed to be 1.0×10^{-5} M. This value and the k_{-2} and k_p values evaluated as above were used in the calculation.[11] The estimated values of k_{-2}, k_3, and k_p and the free radical concentration are summarized in the footnote of Table 5.

The estimated rate constants are in reasonable agreement with the calculated values (*vide infra*). On the other hand, the free radical concentrations are $(1-2) \times 10^{-3}$% of the polymerizing monomer M, which is smaller by 1 order of magnitude than the 0.01% postulated by Lahti to explain the high molecular weight of the polymers.[4] Considering the qualitative nature of both estimations, the disparity in the two values is not too unreasonable.[12] Moreover, since the same values of $k_p[M\cdot]$ are obtained from the calculation regardless of $[M\cdot]$, the relative rates involving $M\cdot$ and thus the conclusions in the following discussion are not influenced by the magnitude of $[M\cdot]$.[13]

Microscopic Rate Constants. The microscopic rate constants for Scheme 2 were calculated from the change in the absorbance with time, as described in the Experimental Section. For all reactions, the absorbance first increased to a maximum value and then decreased with time, indicating that the intermediate accumulated before undergoing polymerization. Figure 6 shows the correlation of the experimental data with the theoretically fitted curve for the reaction of **1a** with OH^-. In all cases, the correlations were excellent with R^2 values larger than 0.99. The calculated rate constants are in reasonable agreement with the estimated values (Table 5).

The microscopic rate constants provide additional support for the mechanism shown in Scheme 2. The calculated k_{-1} value is approximately 10^4-fold larger than k_2. The result is consistent with the $(E1cb)_{rev}$ mechanism in which the departure of the leaving group is rate-limiting.[14]

The pK_a values of **1a**−**e** calculated from the k_1/k_{-1} rate ratios are in the range 11.7−13.7. The similarity between the calculated pK_a value of 13.7 for **1a** and the measured value of 13.1 for the α,α′-bis(tetrahydrothiophenio)-*m*-xylene chloride provides additional evidence for

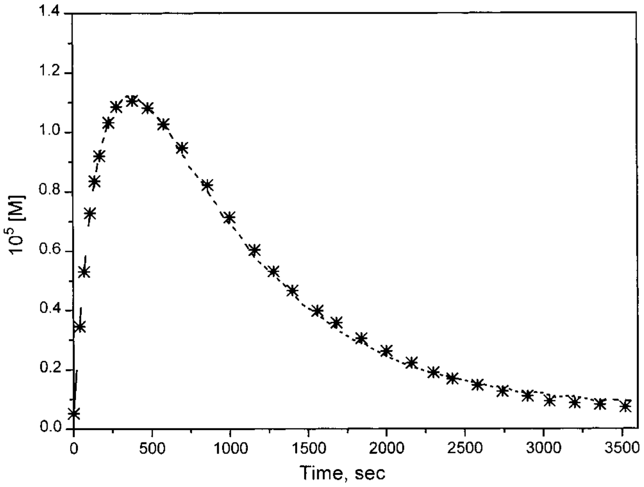


Figure 6. Change of the concentration of the *p*-xylylene intermediate M with time for reaction of α,α′-bis(tetrahydrothiophenio)-*p*-xylene dichloride **1a** with OH^- at 25.0 °C. The experimental data (*) show an excellent correlation with theoretical curve (---).

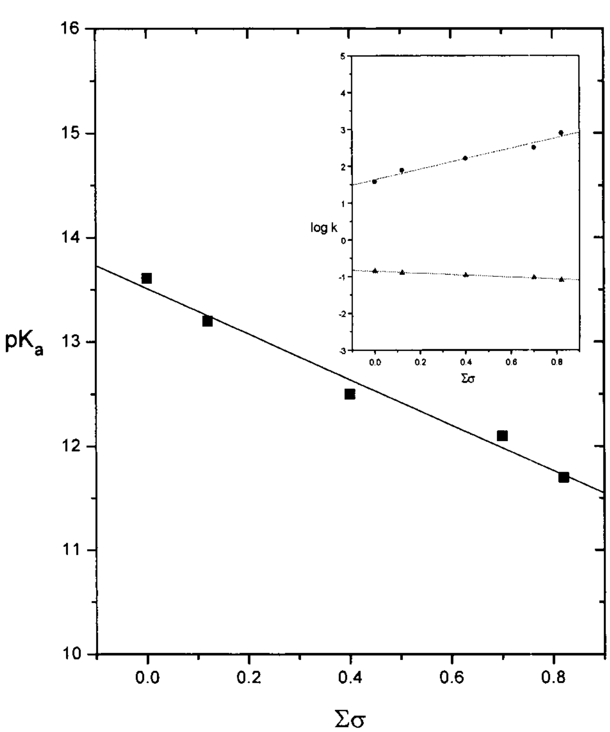


Figure 7. Hammett plot for the pK_a values for the polymerization of α,α′-bis(tetrahydrothiophenio)-*p*-xylene dichlorides with OH^- at 25.0 °C. Inset: The same plot for the k_2 (●, top) and k_{-2} values (▲, bottom).

Table 6. Hammett ρ Values for the pK_a Values and the Microscopic Rate Constants for the Polymerization Reaction

	pK_a	k_2	k_{-2}	k_3	k_p
ρ	-2.1 ± 0.2	-0.27 ± 0.02	1.4 ± 0.2	1.3 ± 0.2	1.3 ± 0.2

the reliability of this calculation.[6] Moreover, the influence of aryl substituents upon the pK_a values correlated satisfactorily with the Hammett equation using $\Sigma\sigma = \sigma_o + \sigma_m$ (Figure 7). Values of σ_o were either taken from the literature or estimated by the literature method.[15-17] The Hammett ρ value is -2.1 (Table 6). The negative ρ value is not unexpected, as the acidity of the benzylic C−H bonds should increase with the electron-withdrawing ability of the aryl substituents. In addition, the value is less negative than $\rho = -4.0$ observed for the pK_a values of the substituted benzyltetrahydrothiophenium halides.[6] The result may be attributed to the presence of an additional sulfonium group in **1**. It has been previously shown that the pK_a values of α,α′-bis(tetrahydrothiophenio)-*m*-xylene dichloride and MH exhibit a negative deviation from the Hammett plot for the benzyltetrahydrothiophenium halides probably because the conjugate bases of the former are better stabilized by hydrogen bonding due to the presence of the extra hydrophilic groups.[6] This would predict that the conjugate bases of **1** should also be more stable and thus be less susceptible to the electron-withdrawing ability of the aryl substituent than those of the latter. The significant acidity of the benzylic C−H bonds and excellent correlation of the pK_a values in the Hammett plot are entirely consistent with the reversible deprotonation for all substrates (Scheme 2).

The reversibility of the k_2 path has been assessed by comparing the relative rates of reactions involving M. Under kinetic conditions for the reaction of **1a** where $[THT] = 10^{-5}$ M, $[OH^-] = 0.01$ M, and $[M\bullet] = 2 \times 10^{-10}$ M, the rates of the three pathways by which M is consumed can be calculated (Scheme 2). Inserting $k_{-2} = 38.0$, $k_3 = 7.81 \times 10^{-2}$, and $k_p = 1.05 \times 10^7$ M^{-1} s^{-1} (Table 5), then $k_{-2}[THT] = 0.1(k_3[OH^-] + k_p[M\bullet])$, indicating that the k_{-2} step is insignificant under this condition. On the other hand, when 0.2 M **1a** and OH^- are employed for the practical synthesis, the maximum values of $k_{-2}[THT]$, $k_3[OH^-]$, and $k_p[M\bullet]$ terms are 7.6, 1.6×10^{-2}, and 5.0 s^{-1}, respectively.[18] However, since M does not accumulate under synthetic conditions, the actual value of $[M\bullet]$ and thus $k_p[M\bullet]$ should be much less than the maximum values, i.e., $k_{-2}[THT] \gg k_3[OH^-] + k_p[M\bullet]$. This would predict that the k_2 step is reversible under synthetic conditions. Therefore, the high molecular weight polymers obtained in the two-phase solvent system, in which the THT is removed as it is produced, may in part be attributed to the increased concentration of M available for the polymerization reaction.[4,19-21]

The k_2 and k_{-2} values for **1a**−**e** show excellent correlations with the Hammett equation (Figure 7). The ρ values are -0.27 and $+1.4$ for the k_2 and k_{-2} pathways, respectively (Table 6). The negative ρ value for the k_2 step is not unexpected since the formation of the neutral M from the anionic intermediate $\mathbf{1}^-$ should be retarded by the electron-withdrawing substituent. In addition, the positive ρ value for the addition of THT to M is also reasonable considering the opposite charge requirement. All of these results are consistent with the equilibrium formation of M from $\mathbf{1}^-$ (Scheme 2).

The appreciable values of k_3 indicate that the OH^- is added to M at an appreciable rate. The positive ρ value for the k_3 step is consistent with the formation of M^- from neutral M for all substrates (Figure 8 and Table 6). Since the addition is irreversible, it could reduce the polymer yield. However, the k_3 values are much smaller than k_{-2} and k_p and only compete with the latter two when [THT] and $[M\bullet]$ are very small (*vide infra*).

The calculated k_p values are in the range $(0.105-1.32) \times 10^8$ M^{-1} s^{-1}, which are much larger than the $k_p = 10^2-10^3$ M^{-1} s^{-1} determined for typical vinyl polymers (Table 5).[8] The result can readily be understood if the high reactivity of the *p*-xylylene intermediate is considered.[22,23] Moreover, the rate constants can also explain why M is accumulated under kinetic conditions whereas

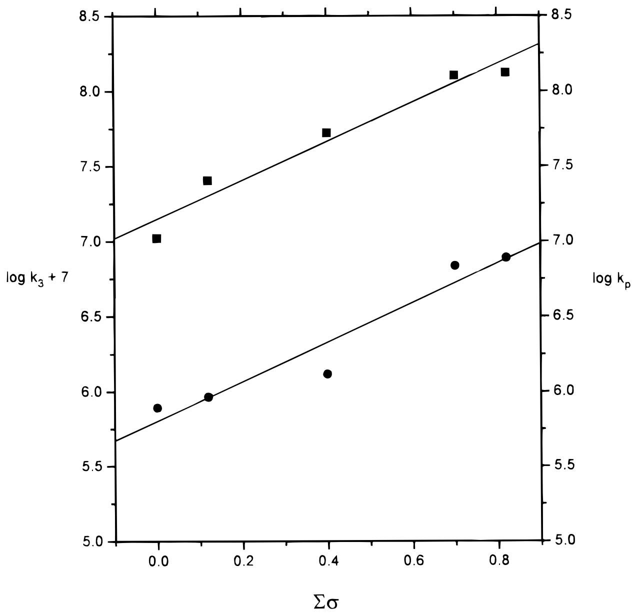
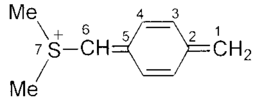


Figure 8. Hammett plot for the k_3 (●) and k_p values (▲) for the polymerization of α,α′-bis(tetrahydrothiophenio)-*p*-xylene dichlorides with OH^- at 25.0 °C.

polymerization reactions become predominant under synthetic conditions.[4,19,20] The rate of production of M under kinetic conditions, where 2×10^{-5} M of **1a** and 0.01 M of OH^- are employed, is approximately $k_1k_2[OH^-][\mathbf{1a}]/k_{-1} = 6 \times 10^{-8}$ M s^{-1}. When $[M] = 1 \times 10^{-5}$ M, $[THT] = 1 \times 10^{-5}$ M, and $[M\cdot] = 2 \times 10^{-10}$ M, the rates of $k_{-2}[M][THT]$, $k_3[M][OH^-]$, and $k_p[M][M\cdot]$ pathways would become 4×10^{-9}, 8×10^{-9}, and 2×10^{-8} M s^{-1}, respectively. This would predict that a significant amount of M should be accumulated until half of the reactant is consumed. However, if the polymerization reaction is carried out with 0.2 M each of **1a** and OH^- for the practical synthesis, the maximum rates of the formation of M is 1×10^{-2} and the three pathways of its consumption are roughly 1×10^{-2}, 3×10^{-4}, and 5×10^{-2} M s^{-1}, respectively, if $[M] = [THT] = 1.6 \times 10^{-2}$ M, and $[M\cdot] = 3.2 \times 10^{-7}$ M.[18] Under this condition, the radical polymerization reaction should be the major pathway of its consumption and proceed at a much faster rate than its formation. On the other hand, if $[M\cdot] \ll 3.2 \times 10^{-7}$ M (*vide supra*), the k_{-2} step could become more important but the polymerization reaction will proceed to completion anyway because the equilibrium will be shifted toward M as it is consumed in the k_p path.

The k_p value increased as the electron-withdrawing ability of the substituent increased (Figure 8). The Hammett ρ value for the k_p step is 1.3 (Table 6). The small positive ρ value is consistent with a polar transition state for the polymerization process, in which the partial negative charge is developed at the benzylic carbon.[24] However, it should be noted that the rate data indicate how fast the product is produced but do not dictate the molecular weight of the polymers. The formation of a high molecular weight polymer is determined by the degree of polymerization, $P = KL_{kin} = Kk_p[M]\tau = k_p[M]/k_t[M\cdot]$, where K, L_{kin}, τ, and k_t are a constant, kinetic chain length, lifetime of the radical, and the rate constant for the termination step, respectively.[8] Our data reveal that k_p increases gradually but $[M]/[M\cdot]$ remains nearly the same as the electron-withdrawing ability of the substituent increases.[25] Hence, the difficult synthesis of high molecular weight PPV with an electron-withdrawing substituent seems to indicate that the k_t increases more steeply than k_p and $[M]/[M\cdot]$ as the substituent is made more electron withdrawing. On the other hand, an impressive increase in the molecular weight of dichloro-substituted PPV observed from highly purified monomer precursor suggests that the lifetime of the radical could be influenced by the impurities.[1a] However, we could not estimate the k_t values under our experimental conditions. Therefore, it seems difficult to correlate the k_p values with the molecular weight of the PPV polymers at this stage.

Table 7. Hartree−Fock Energies, Bond Lengths, and Total Atomic Charges for the Singlet and Triplet States of α-(Dimethylsulfonic)-*p*-xylylene Calculated by an *Ab Initio* Method with 6-311G Basis Set



	singlet	triplet
ΔE, kcal/mol[a]	0	16.6
$D(1, 2)$[b]	1.335	1.457
$D(2, 3)$[b]	1.460	1.398
$D(3, 4)$[b]	1.335	1.382
$D(4, 5)$[b]	1.462	1.398
$D(5, 6)$[b]	1.346	1.453
$D(6, 7)$[b]	1.825	1.839
ρ_1[c]	−0.302	−0.308
ρ_2[c]	−0.017	+0.060
ρ_5[c]	+0.319	+0.084
ρ_6[c]	−0.668	−0.422
ρ_7[c]	+0.504	+0.513

[a] Calculated from Hartree−Fock energies for the singlet and triplet states of the α-(dimethylsulfonio)-*p*-xylylene intermediate. [b] Bond distance, Å. [c] Atomic charge.

Free Radical Initiator. There are several possibilities by which a free radical initiator may be produced. One is the photoexcitation of the intermediate M by the room light. However, when the reaction mixture was irradiated with a 120 W tungsten lamp, no change in the rate was observed. An *ab initio* calculation with the 93-G basis set for the α-(dimethylsulfonio)-*p*-xylylene reveals that the triplet state is higher in energy than the singlet ground state by 16.6 kcal/mol (Table 7). Hence, a triplet biradical could be produced if the solution is irradiated in the presence of a triplet sensitizer. Accordingly, when the solution was irradiated with a 120 W tungsten lamp in the presence of Rose Bengal, the k_{obs} increased from 2.01×10^{-3} to 5.42×10^{-3} s^{-1}, which seems consistent with the prediction.[26] Alternatively, a free radical may also be produced by the hydrogen abstraction by molecular oxygen. These two possbilities are negated by the facile polymerization reaction observed in the dark under an argon atmosphere.

Thirdly, the electron transfer reaction between M and an electron donor may produce the charged radical species, which may initiate the reaction. Since the reduction potential of M is −0.20 V vs Ag/AgCl, any electron donor with $E_{ox} \leq 0.39$ V should in principle be able to produce the charged radical species whose concentration is higher than 0.001% of [M], which is sufficient to initiate the polymerization reaction. However, no species present under the reaction conditions exhibited an oxidation potential within that range. Moreover, the significant reaction rate observed in the neutral solution provides additional evidence against this possibility, since there should be little carbanion or OH^- in the solution, which are potential electron donors.

The fourth possibility is the dimer biradical formed by the spontaneous dimerization of M, as postulated by Wessling.[2] As stated above, the singlet state is the ground state for the α-(dimethylsulfonio)-*p*-xylylene (*vide supra*). Similarly, *p*-xylylene is diamagnetic at low temperature.[22] Thus it is not readily apparent how this singlet molecule could react to afford the dimer biradical. Moreover, the [2.2]paracyclophane derivative, which could be produced by coupling of the dimer biradical, has not been detected even from the photosensized reaction of the very dilute solution.[28,29] However, it is discomfiting to rely too heavily upon negative evidence in postulating a reaction mechanism. The failure to detect the paracyclophane derivative could be due to the strain energy and/or the steric effect of the tetrahydrothiophenio substituents in the dimer biradical, which may hinder the coupling (*vide supra*). Furthermore, *p*-xylylene in the gas phase undergoes polymerization at the moment of condensation even at −190 °C.[23] In dilute solution, it readily reacts with mono radicals, halogen molecules, O_2, NO, and SO_2.[22] It is so reactive that it is called a pseudodiradical.[22c] Therefore, although direct evidence for the dimer biradical has never been observed, it seems difficult to rule out the possibility that it may be the initiator in the polymerization reaction.

Conclusions. Results of H−D exchange, kinetic, and product studies reveal that polymerization reactions of **1a**−**e** with OH^- proceed by the elimination−free radical polymerization mechanism shown in Scheme 2. The validity of each elementary step was confirmed by independent experiments. The microscopic rate constants for each step were calculated with the change of the *p*-xylylene concentration with time by using a computer program. The calculated rate constants provide quantitative interpretations for the qualitative observations made in these reactions. Finally, all of the rate data showed excellent correlations with the Hammett equation. Therefore, although the exact nature of the free radical initiator is not clear, it seems reasonable to conclude that the reactions of **1a**−**e** with OH^- proceed by the elimination−free radical polymerization mechanism shown in Scheme 2.

Experimental Section

Materials. α,α′-Bis(tetrahydrothiophenio)-*p*-xylene dichlorides **1a**−**e**, α,α′-bis(tetrahydrothiophenio)-*m*-xylene dichloride, and *p*-(hydroxymethyl)benzyltetrahydrothiophenium bromide were synthesized as described in the literature.[6,19−21]

NaOH solution was prepared by dissolving reagent grade NaOH in distilled water or by adding clean pieces of Na to deionized water. The NaOD solution was prepared by adding clean pieces of Na to D_2O. In all cases the ionic strength was maintained to be 1.0 with NaCl.

H−D Exchange. To an NMR tube containing 0.1 M **1a**−**e** in D_2O was added 40 μL of 1.25 M NaOD in D_2O with a microsyringe. The solution was quickly shaken, filtered to remove the white solid, and then analyzed by NMR.

Effects of Tetrahydrothiophene, OH^-, Carbanions, $S_2O_8^{2-}$, TEMPO, and Light. The effect of THT on the reaction was assessed by adding THT to the solution containing M and measuring the rate of its disappearance by UV−vis spectroscopy. Cuvettes containing 3.0 mL of 0.01 M NaOH(aq) were covered with rubber septa and purged for at least 20 min with argon while being temperature equilibrated prior to kinetic runs. Reactions were initiated by injecting 5−10 μL of a ca. 10^{-2} M aqueous solution of the substrate into the cuvette. The solution was neutralized by adding 1 equiv of HCl(aq) when the maximum concentration of M was accumulated, and then $(1.91-7.62) \times 10^{-4}$ M THT was added with a microsyringe. The cuvette was quickly shaken and returned to the cuvette compartment. The decrease of absorption at 318 nm with time was monitored. Plots of $-\ln(A_\infty - A_t)/(A_\infty - A_0)$ vs time were linear over two half-lives of the reaction. The slope was the pseudo-first-order rate constant.

The effects of free radical initiator and inhibitor TEMPO on the reaction were determined similarly by adding $(0.500-2.50) \times 10^{-3}$ M $S_2O_8^{2-}$ and 1.0×10^{-5} M TEMPO, respectively, to the neutral solution containing M. The influence of OH^- and carbanion on the reaction was determined by the same procedure except that 0.0100−0.200 M OH^- and $(2.00-9.50) \times 10^{-4}$ M $C_2H_5NO_2$, acetylacetone, CH_3NO_2, and *p*-nitrobenzyl cyanide, respectively, were added when the formation of M did not compete appreciably with its disappearance.

To determine whether the polymerization reaction is influenced by the light, the cuvette containing M was irradiated with a 120 W tungsten lamp in both the presence and absence of Rose Bengal as a triplet sensitizer and the reaction rates were measured.

The reversibility of the addition of OH^- to M was assessed by adding 2×10^{-5} M **1a**−**e** to 0.010 M OH^-(aq) and measuring the change in absorbance at 318−332 nm.

Microscopic Rate Constants. The polymerization reactions were followed by monitoring the change in the absorbance at 318, 306, 330, 328, and 332 nm for **1a**, **1b**, **1c**, **1d**, and **1e**, respectively, with a UV−vis spectrophotometer as described above. In all cases, the absorbance first increased to a maximum value and then decreased with time, indicating that the intermediate accumulated before undergoing the polymerization reaction (Figure 6).

The microscopic rate constants were calculated from the change in the absorbance with time using a computer program.[31] The polymerization reactions were assumed to proceed by the mechanism shown in Scheme 2. Calculation of the rate data requires the initial values for each rate constants and the concentrations of OH^- and M•. The estimated values of k_{-2}, k_3, k_p, and [M•] in Table 1, $[OH^-] = 1.00 \times 10^{-2}$ M, and the literature values of k_1, k_{-1}, and k_2 were used as the initial values.[5,6] The values of [M•] and $[OH^-]$ were assumed to remain constant throughout the reaction. The reaction constants were allowed to vary between 0.1 and 10-fold the initial values. Since the concentration of M is not influenced by the k_4 and k_{-4} steps, they are not included in the calculation (Scheme 3). The reactivity of M• and ∼M• in the polymerization processes were assumed to be the same to simpify the kinetics; $\sim M\bullet = \sim(M)_n M\bullet$ (a growing polymer chain).[8] Calculations were repeated until the best fit between the spectral data and the kinetic scheme was obtained.

Scheme 3

$$\mathbf{1} + OH^- \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} \mathbf{1}^-$$

$$\mathbf{1}^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} M + THT$$

$$M + OH^- \xrightarrow{k_3} M^-$$

$$M + M\bullet \xrightarrow{k_p} P$$

Isolation of [*p*-(Hydroxymethyl)benzyl]tetrahydrothiophenium Chloride (MH). To a 1 L beaker containing 500 mL of 1.0 M NaOH and 200 mL of hexane was added **1a** (0.20 g, 0.57 mmol) in 10 mL of H_2O at the rate of 40 μL/min for 4 h with vigorously stirring. The aqueous layer was neutralized with HCl and evaporated under reduced pressure. The product mixture was taken into 200 mL of methanol, stirred vigorously for 1 h, filtered to remove the solid residue, and then evaporated to obtain a small amount of the white solid. The same procedure was repeated by adding 5 mL of methanol until all of the insoluble salts were removed. To this mixture was added 1 mL of water, and the mixture was stirred and filtered to remove less soluble polymers and oligomers. An excess amount of acetone was poured into this solution to precipitate out the product. The product was filtered, dried over P_2O_5, and identified by NMR. The NMR spectrum (500 MHz) of the isolated product showed two doublets at δ 7.62 and 7.68, two singlest at δ 4.78 and 4.68, and two multiplets at δ 3.62 and 2.42, which were identical to those of the authentic adduct. The reversibility of the addition of OH^- to the *p*-xylylene intermediate was checked by adding 5 μL of a ca. 10^{-2} M aqueous solution of [*p*-(hydroxymethyl)benzyl]-tetrahydrothiophenium bromide to a cuvette containing 3.0 mL of 0.010 M NaOH(aq) and measuring the UV spectral change at 318 nm. However, no trace of *p*-xylylene was detected by UV−vis spectroscopy.

Product Studies. A solution containing **1a** (0.20 g, 0.57 mmol) in 4.0 mL of H_2O was mixed with 0.7 mL of 1.0 M NaOH and allowed to react at room temperature. A similar experiment was performed by purging the two solutions with argon for 20 min and mixing in the dark. For both reactions, the polymer was produced immediately after mixing.

To detect the paracyclophane derivative from the reaction, 40 mL of 0.18 M NaOH solution was added slowly for 1 h to a solution containing **1a** (0.20 g, 0.57 mmol) and Rose Bengal (0.20 g, 0.20 mmol) as a triplet sensitizer in 200 mL of H_2O while irradiating with a 120 W tungsten lamp. The solvent was removed by evaporation with a rotary evaporator. The product mixture was treated with methanol, water, and acetone as described above to remove inorganic salts and less soluble polymers. The low molecular weight products contained the reactant and oligomers. No trace of the paracyclophane derivative could be detected by NMR.

The possibility of a copolymerization reaction of **1a** with acrylamide was examined by reacting a solution containing **1a** (0.20 g, 0.57 mmol), acrylamide (2.0 g, 28 mmol) in 4.0 mL of H_2O, and 0.7 mL of 1.0 M NaOH for 48 h at room temperature. The product was dialyzed for 30 days using a dialysis sack whose molecular weight cutoff was 12 000. The precursor film cast from the aqueous solution was analyzed by elemental analysis. However, no polymer was obtained when the same experiment was performed with mixtures of acrylamide/OH^-, acrylamide/tetrahydrothiophene/OH^-, and **1a**/acrylamide/tetrahydrothiophene.

Cyclic Voltammetry. Cyclic voltammetric experiments were performed by the literature procedure using platinum wire both as the working electrode and as the auxiliary electrode, a Ag/AgCl electrode as a reference electrode, and 0.4 M $LiClO_4$ as the supporting electrolyte.[32] Cyclic voltammograms for **1a** and tetrahydrothiophene were obtained with 1×10^{-3} M solution at sweep rates of 100 mV/s from −1.0 to +1.0 V vs Ag/AgCl. Cyclic voltammograms for [*p*-(hydroxymethyl)benzyl]tetrahydothiophenium chloride and α,α′-bis(tetrahydrothiophenio)-*m*-xylene dichloride were obtained both in the presence and absence of 0.1 M NaOH. To obtain the cyclic voltammogram for the *p*-xylylene intermediate M, 2×10^{-5} M **1a** was allowed to react with 0.01 M NaOH in the electrochemical cell. The solution was sweeped when the maximum concentration of M was accumulated.

Calculation. Structures of the singlet and triplet states for α-(dimethylsulfonio)-*p*-xylylene were calculated on a Silicon Graphics workstation using the Gaussian 94, Revision A.1 quantum mechanical package developed by Pole and coworkers.[33] All structures were fully optimized using the 6-311G basis set.

Acknowledgment. This research was supported in part by OCRC-KOSEF and the Basic Science Research Institute Program, Ministry of Education, 1996 (Project No. BSRI-96-3406).

References and Notes

(1) (a) McCoy, R. K.; Karasz, F. E.; Sarker, A.; Lahti, P. M. *Chem. Mater.* **1991**, *3*, 941−947 and references cited therein. (b) Burn, P. L.; Holms, A. B.; Kraft, A.; Bradley, D. D. C.; Brown, A. R.; Friend, R. H.; Gymer, R. W. *Nature* **1992**, *356*, 47−49. (c) Hide, F.; Schwartz, B. J.; Diaz-Garcia, M. A.; Heeger, A. *Chem. Phys. Lett.* **1996**, *256*, 424-427. (d) Smith, R. C.; Fisher, W. M.; Gin, D. L. *J. Am. Chem. Soc.* **1997**, *119*, 4092−4093.

(2) (a) Wessling, R. A.; Zimmerman, R. G. U.S. patents 3 401 152, **1968**. (b) Wessling, R. A. *J. Polym. Sci., Polym. Symp.* **1985**, *72*, 55−66.

(3) Lahti, P. M.; Modarelli, D. A.; Denton, F. R., III; Lenz, R. W.; Karasz, F. E. *J. Am. Chem. Soc.* **1988**, *110*, 7258−7259.

(4) (a) Denton, F. R., III; Lahti, P. M.; Karasz, F. E. *J. Polym. Sci. A* **1992**, *30*, 2223−2231. (b) Denton, F. R., III; Sarker, A.; Lahti, P. M.; Garay, R. O.; Karasz, F. E. *J. Polym. Sci. A* **1992**, *30*, 2233−2240.

(5) Cho, B. R.; Han, M. S.; Suh, Y. S.; Oh, K. J.; Jeon, S. J. *J. Chem. Soc., Chem. Commun.* **1993**, 564−566.

(6) Cho, B. R.; Kim, Y. K.; Han, M. S. *Bull. Korean Chem. Soc.* **1995**, *16*, 1218−1222.

(7) α,α′-Bis(tetrahydrothiophenio)-*m*-xylene dichloride was used to place of **1a** because it cannot undergo 1,6-elimination and has a similar structure. Since the pK_a values of this compound and MH are 13.1 and 13.7, respectively,[6] significant amounts of $\mathbf{1}^-$ and M^- should be produced if an excess amount of these are added to 0.01 M NaOH(aq). We did not use (*p*-methylbenzyl)tetrahydrothiophenium bromide and benzyltetrahydrothiophenium bromide employed by Lahti[4] because of their low acidities. For example, the former did not undergo H−D exchange under the reaction conditions and the latter exhibited the pK_a value of 15.3.[6]

(8) Vollmert, B. *Polymer Chemistry*; Springer-Verlag: New York, 1973; p 73−90.

(9) Estimated from the k_d values for $S_2O_8{}^{2-}$ determined at higher temperatures.[10]

(10) House, D. A. *Chem. Rev.* **1962**, *62*, 185−203.

(11) The values in Table 5 and those estimated from the intercepts in Figures 1 and 2 were in excellent agreement.

(12) A reviewer raised an interesting question, which of the two estimates is more realistic? Since the formula weight of M is 226.5, approximately 2500 to 5000 monomers must add to one radical in order to produce a polymer with a MW of 5×10^5 to 1×10^6. This would predict of [M•]/[M] = $(2-4) \times 10^{-4}$, if $k_p/k_t = 1$ and the degree of polymerization is equal to the kinetic chain length. However, since $k_p/k_t \ll 1$, [M•]/[M] should be much less than these values. On the other hand, under synthetic conditions where a significant amount of low molecular weight polymers is produced, the ratio could be larger. Therefore, we feel that both estimates are reasonable.

(13) Since the computer program calculates optimum rates that can explain the change in the intermediate concentration with time, and the k_2 and k_p[M•] are the major pathways of the formation and consumption of M, respectively, the same values of k_p[M•] are obtained regardless of whether k_p[M•] is calculated directly from Scheme 3 or k_p is calculated by inserting estimated values of [M•] and then multiplied by [M•].

(14) Gandler, J. R. In *The Chemistry of Double Bonded Functional Groups*; Patai, S., Ed.; Chichester: New York, 1989; Vol. 2, Part 1, pp 734−797.

(15) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*; Harper and Row: New York, 1987; p 144.

(16) Hine, J. *Structural Effects on Equilibria in Organic Chemistry*; John Wiley & Sons Inc.: Chichester; U.K., 1975; pp 80−98.

(17) Charton, M. *Prog. Phys. Org. Chem.* **1971**, *8*, 235−317.

(18) The maximum concentration of M under synthetic conditions is calculated using the relationship $k_1k_2/k_{-1}k_{-2}$ = [M][THT]/[**1**][OH^-] by assuming that M is in equilibrium with **1** and OH^- and does not participate in other reactions. The value is 1.59×10^{-2} M when [**1**] = [OH^-] = 0.2 M. If the [M•]/[M] ratio is the same as estimated under kinetic conditions. i.e., [M•]/[M] = 2×10^{-5} (see text), the maximum concentration of the radical should be 3.2×10^{-7} M. However, since M does not accumulate under synthetic conditions, the actual concentrations of M and free radical are expected to be smaller than these values.

(19) Lenz, R. W.; Han, C. C.; Stenger-Smith, J.; Karaz, F. E. *J. Polym. Sci., Part A: Polym. Chem.* **1988**, *26*, 3241−3249.

(20) Liang, W. B.; Lenz, R. W.; Karaz, F. E. *J. Polym. Sci., Part A: Polym. Chem.* **1990**, *28*, 2867−2875.

(21) Mireille, B. L.; Jean, M.; Noel, C.; Abdelkader, B.; Eliane, d. T.; Eugene, N. *Tetrahedron* **1990**, *46*, 7793−7802.

(22) (a) Errede, L. A.; Landrum, B. F. *J. Am. Chem. Soc.* **1957**, *79*, 4952−4955. (b) Errede, L. A.; Hoyt, J. M. *J. Am. Chem. Soc.* **1960**, *82*, 436−439. (c) Errede, L. A.; Pearson, W. A. *J. Am. Chem. Soc.* **1961**, *83*, 954−959.

(23) Auspos, L. A.; Hall, A. R.; Hubbard, J. K.; Schaefgen, J. R.; Speck, S. B. *J. Polym. Sci.* **1955**, *15*, 9−17.

(24) Giese, B. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 753−764.

(25) The [M]/[M•] ratios for **1a**−**e** calculated with [M] in ref 18 and estimated [M•] values in Table 5 are similar and do not show a systematic change with the aryl substituent.

(26) The triplet energy of Rose Bengal is 39.2−42.0 kcal/mol,[27] which is higher than that of α-(dimethylsulfonio)-*p*-xylylene. Therefore, it could excite M to the triplet state.

(27) Gilbert, A.; Baggott, J. *Essentials of Molecular Photochemistry*; CRC Press: Boca Raton, FL, 1991; p 503.

(28) Cram, D. J.; Cram, J. M. *Acc. Chem. Res.* **1971**, *4*, 204−213.

(29) Lahti also attempted to find the evidence for the paracyclophane derivative. However. no trace of such compound was detected by GC−MS.[30]

(30) Lahti, P. Private communication.

(31) Zimmerle, C. T. A data analysis and graphical plotting program, "*FITSIM*" *Version 1.5*, 1987.

(32) Cho, B. R.; Suh, Y. S.; Lee, S. J.; Cho, E. J. *J. Org. Chem.* **1994**, 59, 3681−3682.

(33) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Peterson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Lahman, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foreman, J. B.; Ciolowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogie, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, M.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, Revision A.1; Gaussian, Inc.: Pittsburgh, PA, 1995.

MA9716645