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

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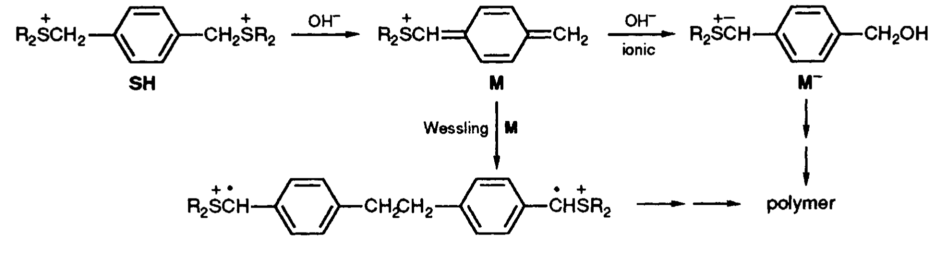
The polymerization in the title proceeds *via* an $(\mathrm{E1cb})_R$ elimination to form a quinodimethane intermediate followed by an anionic polymerization.

Polymerization of α,α′-bis(tetrahydrothiophenio)-*p*-xylene dichloride (**SH**) derivatives is of considerable interest because they are precursor polymers of poly(*p*-phenylenevinylene) (PPV), which has useful conducting and nonlinear optical properties.[1] The reaction is known to proceed *via* the quinodimethane intermediate (**M**) which is probably formed by 1,6-elimination. Both radical and anionic mechanisms have been proposed for the polymerization step (Scheme 1).[2–4] However, the detailed mechanism of the elimination and polymerization processes is not clearly understood.

In the present work, we have conducted a kinetic investigation of the reactions of **SH** with OH^-, OD^-, and HPO_4^{2-}/PO_4^{3-} buffer in aqueous solution. The reaction was followed by monitoring the change of the absorbance at 320 nm, which was previously assigned to **M** by Lahti *et al.*,[3] with a UV–VIS spectrophotometer. In all cases, the absorbance first increased to a maximum value and then decreased with time, indicating that the intermediate accumulated before undergoing polymerization. Neither Wessling's mechanism nor the ionic mechanism could explain the spectral change on the basis of computer modelling.[6]

NMR spectroscopy showed that the benzylic C–H bonds are completely converted to C–D bonds in the presence of OD^- in D_2O before an appreciable amount of polymer is formed. This result is consistent with the work of Lahti *et al.*[3] and indicates that the deprotonation step must be reversible and proceed at a much faster rate than the formation of the intermediate. Therefore, an appreciable amount of $\mathbf{S}^-$ must be present while **M** is being produced. Furthermore, since **M** must be highly reactive, OH^- should readily add to **M**. If OH^- reacts with **M**, then both $\mathbf{M}^-$ and $\mathbf{S}^-$ should also react with **M**. Accordingly, the ionic mechanism in Scheme 1 has been modified to include the reversibility of the deprotonation step and initiation of the polymerization processes by $\mathbf{M}^-$ and $\mathbf{S}^-$ (Scheme 2). The reactivities of $\mathbf{S}^-$, $\mathbf{M}^-$, and $\sim\mathbf{M}^-$ in the polymerization processes were assumed to be the same to simplify the kinetics; $\sim\mathbf{M}^- = \sim(\mathbf{M})_n\text{–}\mathbf{M}^-$ (a growing polymer chain).

Calculation of the rate constants requires a value for the concentration **M**, and this can be obtained from the absorptivity ε_{max} of **M**. The ε_{max} of **M** is not known, although the corresponding values for more stable derivatives are in the range $1.65–6.36 \times 10^4$ dm^3 mol^{-1} cm^{-1}.[5] The ε_{max} value calculated from the maximum absorbance in the kinetic runs was approximately 2×10^4 dm^3 mol^{-1} cm^{-1}, and some $\mathbf{S}^-$ is assumed to react with **M**; its disappearance in subsequent steps would compete with its formation, so the real ε_{max} must be greater than 2×10^4 dm^3 mol^{-1} cm^{-1}. Therefore, the rate constants were calculated by changing the ε_{max} value from 2 ×

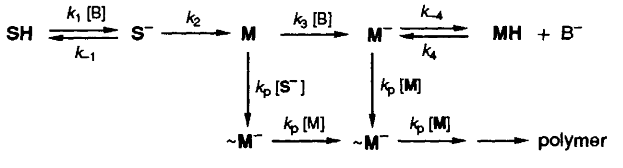


Scheme 1

Table 1 Rate constants for reactions of **SH** with OH^-, OD^- and HPO_4^{2-}/PO_4^{3-} buffer in H_2O at 25.0 °C

Base	$10^2[B]$	$10^{-3}k_1{}^a$	$10^{-3}k_{-1}{}^b$	$k_2{}^b$	$k_3{}^a$	$10^{-3}k_4{}^a$	$10^{-3}k_{-4}{}^b$	$10^{-3}k_p{}^a$
OH^-	1.00	1.05	3.28	1.14	0.202	1.00	4.40	0.858
	0.75	1.24	3.21	1.20	0.221	1.13	4.21	0.918
	0.50	1.24	3.31	1.11	0.243	1.17	3.73	0.872
	average	1.18	3.27	1.15	0.222	1.10	4.11	0.883
OD^-	1.00	0.881	0.729	1.33	0.357	0.814	2.00	2.060
PO_4^{3-}/HPO_4^{2-c}	1.00	0.080	10.2	1.06	0.0716	0.073	14.5	0.900

[a] Units $dm^3\ mol^{-1}\ s^{-1}$. [b] Units s^{-1}. [c] $PO_4^{3-}/HPO_4^{2-} = 1.00$.



Scheme 2

$10^4\ dm^3\ mol^{-1}\ cm^{-1}$ in increments of 10^3 until the best fit between the spectral data and the kinetic scheme was obtained.[6]† Fig. 1 shows the correlation of the experimental data with the theoretically fitted curve for reactions of **SH** and OH^- utilizing $\varepsilon_{max} = 2.9 \times 10^4\ dm^3\ mol^{-1}\ cm^{-1}$. In all cases, the correlation was excellent with χ^2 values of less than 5×10^{-7}. The calculated rate constants for these reactions are summarized in Table 1. The rate constants in each elementary step are nearly the same at three different base concentrations, demonstrating the reliability of this calculation.

The rate data reveal that 1,6-elimination forming the intermediate **M** proceeds *via* a second-order reaction and k_1, $k_{-1} \gg k_2$. Thus an $(E1cb)_R$ mechanism is operative.[7] The change in rate constants with the variation of the base–solvent system is consistent with this mechanism. The $k_1(OD^-)/k_1(OH^-)$ value of 0.75 can be attributed to the difference in basicity and the primary isotope effect. Since OD^- is a stronger base than OH^-, the former should deprotonate the benzylic hydrogens faster than the latter. On the other hand, a simple calculation of the H–D exchange rate using the k_1 and k_{-1} values as well as the results of NMR experiments indicate that all the C–H bonds at the benzylic positions must be completely converted to C–D in the presence of OD^- in D_2O before the kinetic experiment is initiated. Therefore, the OD^- promoted dedeuteriation should exhibit a primary isotope effect. Combination of these two factors would predict that $k_1(OD^-)/k_1(OH^-)$ should be less than unity, as observed. The much slower rate of deprotonation by HPO_4^{2-}/PO_4^{3-} buffer, *i.e.*, $k_1(OH^-)/k_1(\text{buffer}) = 15$, apparently results from its much lower basicity. Similarly, $k_{-1}(\text{buffer})/k_{-1}(H_2O)/k_{-1}(D_2O) = 12/4.5/1$ reflects the relative acidity of the bonds to the hydrogen (or D) in the respective solvents (or buffer). In contrast, the k_2 value decreases only slightly with the same variation of the base–solvent system because it refers to a unimolecular process and the solvation of S^- would become less favourable as the solvent is changed in the same order.

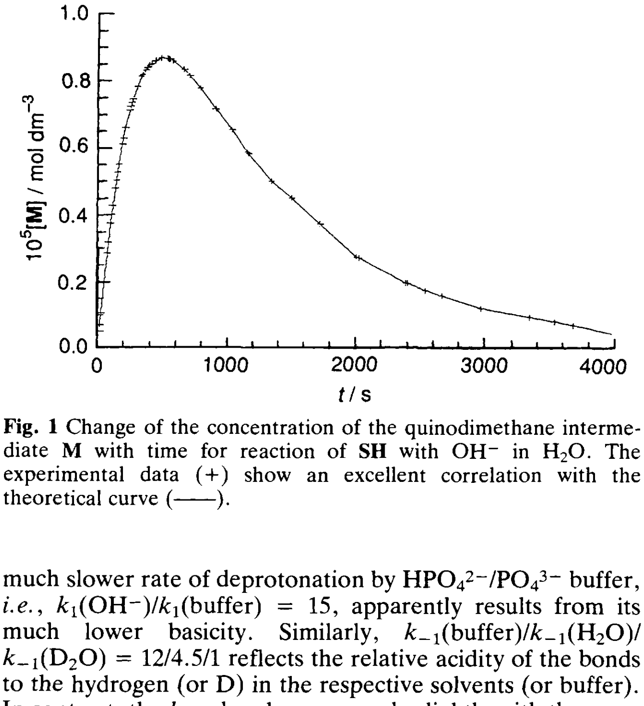


Fig. 1 Change of the concentration of the quinodimethane intermediate **M** with time for reaction of **SH** with OH^- in H_2O. The experimental data (+) show an excellent correlation with the theoretical curve (——).

The polymerization proceeds *via* an anionic mechanism, the initiators being the carbanions generated by deprotonation of the reactant (S^-) and by the addition of OH^- to the intermediate (M^-) (Scheme 2). The rate of addition increases, $k_3(\text{buffer})/k_3(OH^-)/k_3(OD^-) = 1/3/5$, as the basicity of the promoting base increases. M^- must be in equilibrium with **MH** as S^- is with **SH** under the reaction condition. Since M^- is a stronger base than S^- and **MH** a weaker acid than **SH**, k_{-4} must be larger than k_{-1} and k_4 be smaller than k_1, respectively. This expectation is borne out by the experimental results (Table 1). Finally, the k_p values for OH^- and buffer catalysed reactions are similar but approximately one half of that for the OD^- promoted reaction. This result appears to be consistent with the relative solvation ability of the solvents

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† Owing to limitations of the computer program, which can calculate up to five rate constants with a maximum of 50 data points, the initial rate constants were calculated by assuming $k_1 = k_4$ and $k_{-1} = k_{-4}$. The initial values of k_2 and k_3 were then fixed and the remaining five rate constants were calculated. The calculation of five rate constants by fixing different sets of two rate constants was repeated until all the rate coefficients converged.

(*vide supra*). However, it should be noted that the k_p values are not as reliable as the other rate constants because neither the χ^2 values nor other rate constants are significantly altered by a change in k_p values of up to several fold. $k_p[M^-]$ and $k_p[S^-]$ are so small compared with other variables that variation of the k_p value does not seem to influence the overall correlation between the experimental and the calculated data.

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