PPS Preparation. A Kinetic Study and the Effect of Water on the Polymerization

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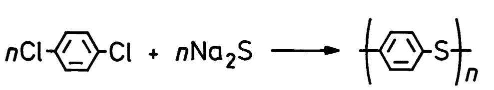
A kinetic study on poly (*p*-phenylene sulfide) formation from *p*-dichlorobenzene (**1**) and sodium sulfide reveals that the initiation rection is first order with respect to **1** and sodium sulfide, respectively. Reaction on the surface of solid sodium sulfide has proved to be negligible when the reaction is carried out in the presence of the solid. The time course of the concentration of **1** and its dimer can be explained with a simplified eight step kinetic model for the initial stage, in which each of the step is firest order with respect to the reactant in concern. Kinetic parameters for each of the steps were estimatied. Increase in [Na_2S]/[**1**] ratio causes the increase both in polymer yield and in the degree of polymerization. Presence of a small amount of water enhances cosiderably the rate of polymerization and increases the polymer yield, but the highest degree of polymerization was observed in the presence of water approximately equimolar to **1**.

Poly(*p*-phenylene sulfide) (PPS) has recently attracted attention as a potential engineering plastic. Its industrial preparation is first reported by Edmonds and Hill[1)] (the Phillips' Method), which consists of the reaction of *p*-dichlorobenzene (**1**) with sodium sulfide (Eq. 1). Its mechanism, however, is still ambiguous. Koch and Heitz examined the mechanism of the reaction by comparing the yields of oligomers formed from various model compounds, and suggested the participation of arylthio radical, which substitutes the halogen atom attached to the aromatic ring.[2)] Annenkova et al. suggests the participation of polysulfide anion radicals,[3a)] which lead to the formation of anion radical of **1** and the thiolate (see Scheme 1).[3b)] Rajan et al. studied the time course of consumption of the reactants, with sodium sulfide dispersed in *N*-methyl-2-pyrrolidone at 195 °C, and reported that the reaction is overall second order.[4)] However detailed study on the kinetics of the initial stage of the reaction, as well as the effect of water contained in crystalline sodium sulfide on the reaction, has hitherto not been elucidated.



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(1)

We examined the time course of the concentration of the dimer (**2**) and trimer (**3**), in addition to the monomer (**1**) and suggest a plausible reaction path and kinetic parameters. We also report the effect of water on yield of the polymer and degree of polymerization.

Experimental

Materials. *p*-Dichlorobenzene (**1**) and *N*-methyl-2-pyrrolidone (NMP, guaranteed grade) were purchased from Tokyo Kasei Kogyo and were used as served. Sodium sulfide (guaranteed grade) was purchased from Wako Pure Chemical Industries and was dehydrated by heating at 120—150 °C over phosphorus pentaoxide for 2—3 h in vacuo. Complete dehydration was ascertained both by gravimetry and iodometry. An authentic sample for bis(*p*-chlorophenyl) disulfide (**4**) was purchased from Tokyo Kasei Kogyo.

Kinetics. Reactions were carried out under argon atmosphere. Anhydrous sodium sulfide was dissolved in NMP (100 ml) at 180—195 °C and the reaction was started by addition of *p*-dichlorobenzene. At appropriate intervals 0.10 ml of the reaction mixture was pipetted out, diluted to 1.0 ml with acetonitrile, and 0.010 ml of the solution was subject to quantitative analysis. The remainder of the samples at early stages were collected and were subject to separation by high performance liquid chromatography. At the end of the reaction the mixture was poured into water. The precipitates were collected by filtration, washed with acetone, and air-dried at room temperature. Average degree of polymerization for the precipitates was determined from its melting point, using the calibration curve based on the procedure and data by Montaudo et al.,[5)] and Koch and Heitz.[2)]

Quantitative Analysis. The analytical sample was separated with Shimadzu LC-6A high-performance liquid chromatograph system attached with SPD-6A UV Spectrophotometer and CR-3A Chromatogram processor. The sample was separated by elution through Shimpack CLC-ODS (Shimadzu) with acetonitrile–water (90:10) and its components were quantified with the absorption at 254 nm.

Table 1. Analytical Data for the Dimer (**2**) and Trimer (**3**)

Product		C	H	S	Cl
$ClC_6H_4SC_6H_4Cl$	Found (%)	56.70	3.90	12.49	26.89
2	Calcd (%)	56.48	3.17	12.57	27.79
$Cl(C_6H_4S)_2C_6H_4Cl$	Found (%)	59.44	3.72	17.86	19.10
3	Calcd (%)	59.50	3.34	17.65	19.51

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Separation of Products. Separation of the reaction mixture was carried out with high performance liquid chromatography using preparative column. The acetonitrile solution of the mixture was separated by elution through ULTRON S-C18 (Shinwa Kakou) with acetonitrile–water (90 : 10) or through JAIGEL ODS-90 (Japan Analytical Industry) with acetonitrile. Each fraction afforded a single peak in analytical HPLC (vide supra).

The dimer (**2**) and trimer (**3**) were identified with elementary analysis (Table 1). The deviation between found and calculated data for **2** was not sufficiently small, but the found data were accurate enough to distinguish from other oligomers. The disulfide (**4**) was identified by comparison of the retention time of the product with that of the authetic sample of (**4**) in analytical HPLC.

Estimation of Rate Constants. Rate constants were estimated with the SALS System for nonlinear least-squares treatment.[6] Calculation was carried out at The Computer Center of The University of Tokyo.

Results and Discussion

Kinetics. Figure 1 shows a typical time-course of the reaction at 195 °C. In addition to the dimer (**2**) and trimer (**3**), the disulfide (**4**) was formed in considerable amount in the early stage. This suggests the formation of *p*-chlorobenzenethiolate (**5**), which is oxidized under the reaction conditions by trace of oxygen or sulfur, or oxidized after sampling.

Kinetic studies were carried out by changing the initial concentration of **1**, with initial concentration of sodium sulfide fixed, and vice versa. Figures 2a and 2b plot the initial rate for the consumption of **1** against initial concentration of each of the reactants. The slopes of the logarithmic plots are 1.16 and 0.93, respectively. This suggests that the initial step of the reaction is first order with respect to both *p*-dichlorobenzene (**1**) and sodium sulfide. On this basis, the rate for consumption of *p*-dichlorobenzene is

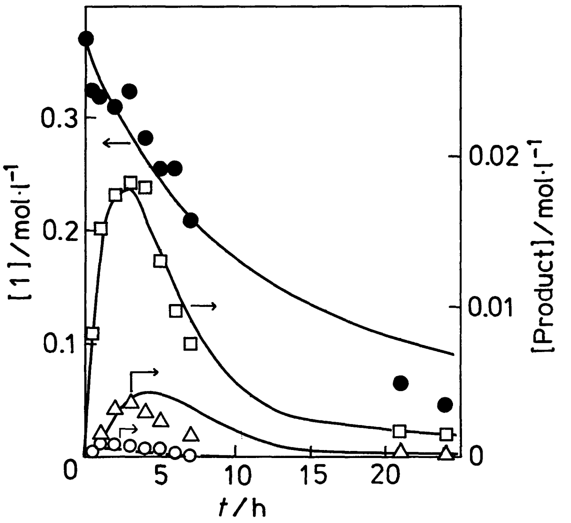


Fig. 1. A typical time course of concentration change at 195 °C in *N*-methylpyrrolidone. $[\mathbf{1}]_0=0.38$ mol dm^{-3}, $[\mathrm{Na_2S}]_0=0.38$ mol dm^{-3}. ●: *p*-dichlorobenzene (**1**), □: bis(*p*-chlorophenyl) sulfide (**2**), △: *p*-(*p*-chlorophenylthio)phenyl *p*-chlorophenyl sulfide (**3**), ○: bis(*p*-chlorophenyl) disulfide (**4**). Solid lines represent the curves calculated for **1**, **2**, and **3** based on Scheme 1 and the rate constants shown in Table 2. Broken line represents that for thiolate **5**.

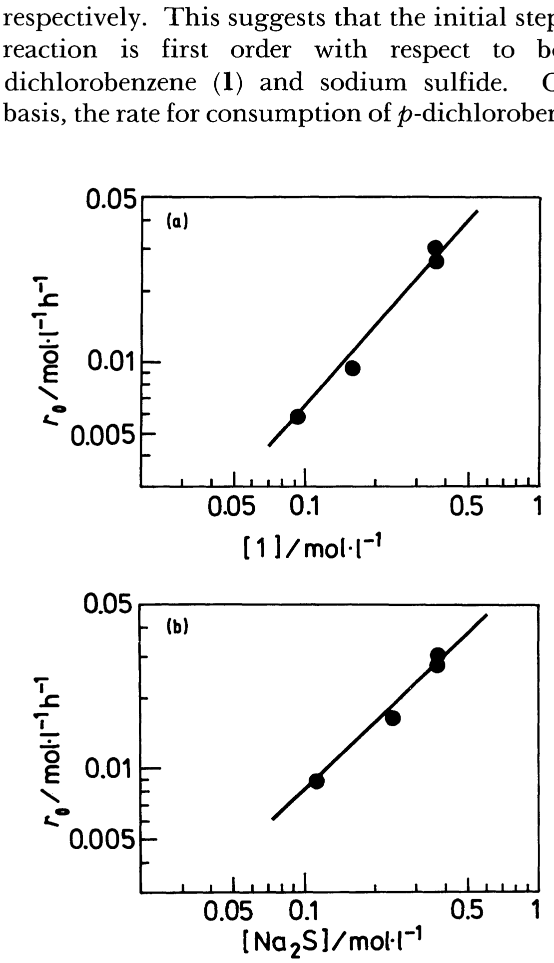


Fig. 2. Dependence of initial rate for *p*-dichlorobenzene (**1**) consumption on initial concentration of a reactant at 195 °C in *N*-methylpyrrolidone. (a) $[\mathrm{Na_2S}]_0=0.38$ mol dm^{-3}. (b) $[\mathbf{1}]_0=0.38$ mol dm^{-3}.

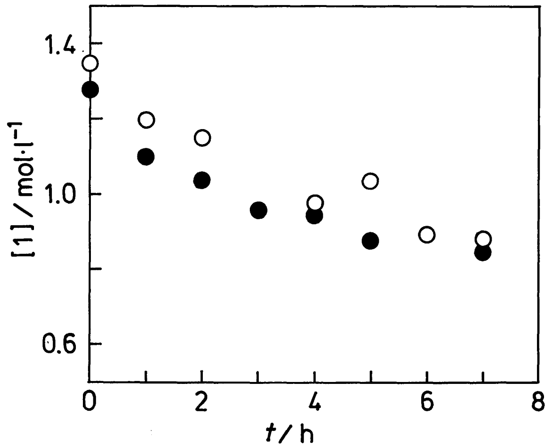


Fig. 3. Time course of concentration change in the presence (○, 0.11 mol dispersed in 100 ml) and absence (●) of solid sodium sulfide (anhydrous) at 180 °C in *N*-methylpyrrolidone. $[\mathbf{1}]_0=1.3$ mol dm^{-3}, $[\mathrm{Na_2S}]_0=1.3$ mol dm^{-3}.

expressed as

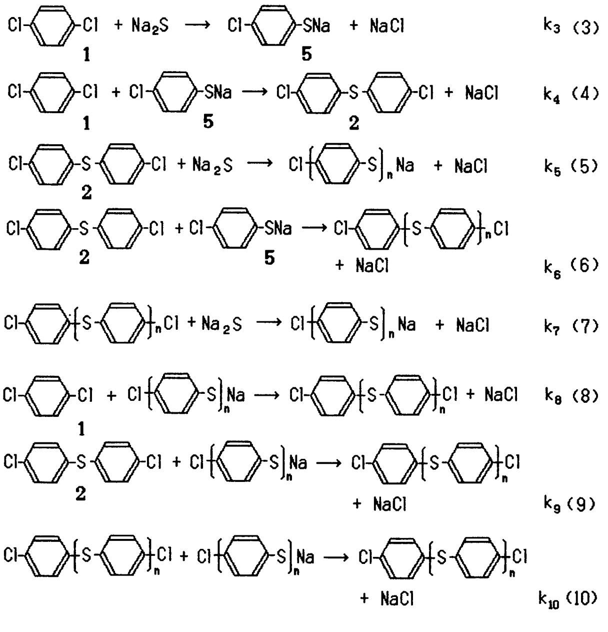
$$r_c = k_c[\mathbf{1}][\mathrm{Na_2S}]$$
$$k_c = (3.0 \pm 0.4) \times 10^{-3}\,\mathrm{dm^3\,mol^{-1}\,min^{-1}}. \qquad (2)$$

Reaction in the Presence of Solid Sodium Sulfide. Usually, PPS polymerization is carried out in the presence of solid sodium sulfide. Thus, reaction may occur on the surface of the solid, in addition to homogeneous reaction. To investigate whether this actually holds, time course of the reaction was examined at 180 °C in the presence and absence (with liquid phase just saturated with sodium sulfide) of the solid (Fig. 3). The profiles in Fig. 3 shows that no appreciable difference exists in the time course of the reaction regardless of the presence of the solid.

In addition, the reaction was examined at various amount of solid sodium sulfide. Also in this case, no appreciable difference was observed among profiles of the time course of the reaction.

These results clearly indicate that the reaction on the solid surface, if any, is slow compared with the homogeneous reaction.

Mechanism for the Early Stage of the Polymerization. The Mechanism for the present polymerization has been proposed by Koch and Heitz[2] and by Rajan et al.[4] The proposed reaction paths are similar to each other (Scheme 1).[7] Neither of the studies have examined the time course of the intermediates, namely, dimer (**2**) and trimer (**3**). Since the time course of consumption of **1** presented in Fig. 1 is in agreement with Scheme 1, we further tried to estimate the rate constants for the initial steps of the polymerization (Eqs. 3—10), based on the following criteria:



Scheme 1. A plausible reaction path for the initial stages of the polymerization.

i) Each path is first order with respect to each of the reactants.

ii) The rate constants for the formation of thiolate of $n>2$ (k_7) do not depend on n.

iii) The rate constants for the coupling of the thiolates ($n>1$) with *p*-dichlorobenzene (**1**) (k_8) do not depend on n.

iv) The rate constants for the coupling of the thiolates ($n>1$) with the dimer (**2**) (k_9) do not depend on n.

v) The rate constants for the coupling of the thiolates ($n>1$) with the polymers ($n>2$) (k_{10}) do not depend on n.

This simplified model enables the estimation of the rate constants k_3—k_{10} by means of least square fitting for the time course of the concentration of the dimer **2**. The estimated rate constants are summarized in Table 2. Based on the estimated rate constants, time course of the concentration of the monomer (**1**), thiolate (**5**), dimer (**2**), and trimer (**3**) is calculated for various initial concentrations of the reactants. The calculated values are in good agreement with the observed ones, in particular in the initial stage ($t<7$ h); a typical time course is shown in Fig. 1. In the later stage, however, there exists ample discrepancy between the calculated and observed results, in particular for **1**. It would suggest that the criteria ii)—v) is oversimplified for the kinetics involving polymers.[8]

The Effect of Water on Polymerization. Commercial sodium sulfide is nonahydrate. Neither Rajan et

Table 2. Rate Constants Estimated for Paths 3—10 (in $\mathrm{dm^3\,mol^{-1}\,min^{-1}}$)

k_3	0.0023±0.0006	k_7	0.024±0.017
k_4	1.3 ±0.8	k_8	0.019±0.008
k_5	0.006 ±0.004	k_9	12 ±9
k_6	6 ±4	k_{10}	0.6 ±0.4

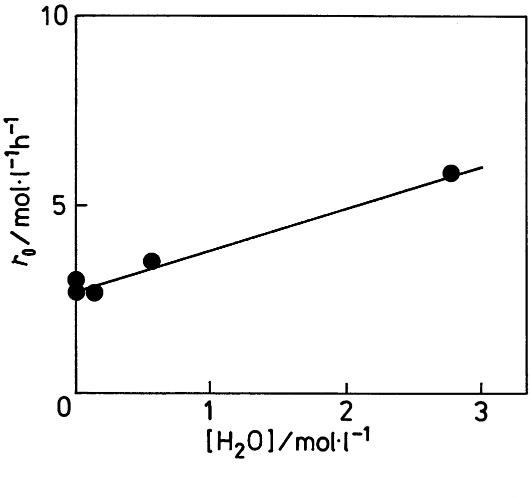


Fig. 4. Effect of water on initial rate for *p*-dichlorobenzene (**1**) consumption at 195 °C in *N*-methylpyrrolidone. $[\mathbf{1}]_0=0.38\,\mathrm{mol\,dm^{-3}}$, $[\mathrm{Na_2S}]_0=0.38\,\mathrm{mol\,dm^{-3}}$.

Table 3. Polymer Yield and the Degree of Polymerization (n).[a] Values in Parentheses are those Calculated Based on the Kinetic Parameters in Table 2 for Polymers of $n \geqq 3$

[**1**]	[Na_2S]	[H_2O]	Yield/%[b]	n
mol dm^{-3}	mol dm^{-3}	mol dm^{-3}	Obsd (Calcd)	Obsd (Calcd)
0.095	0.38	0	—[c] (86)	— (24)
0.15	0.38	0	55 (85)	>25[d] (15)
0.38	0.38	0	45 (73)	15 (9.6)
1.25	0.38	0	25 (30)	7 (6.1)
0.38	0.23	0	28 (51)	11 (7.5)
0.38	0.11	0	20 (20)	6 (6.2)
0.38	0.38	0.011	61	16
0.38	0.38	0.055	65	21
0.38	0.38	0.28	83	14

a) Reaction was carried out at 195 °C for 24 h in *N*-methyl-2-pyrrolidone. b) Yields based on consumed **1**. c) No polymer was isolated. d) Melting Point >300 °C.

al. nor Koch and Heitz noted on the effect of water on the polymerization reaction, nor did they mention the dehydration of sodium sulfide.[2,4] Recently, it has been suggested that the presence of water considerably affects the conversion and degree of polymerization in the present reaction.[9] Thus, we examined the kinetics in the presence of various amount of water.

Figure 4 shows the dependence of initial rate on the amount of water added at 195 °C. It is evident that the presence of water 'enhances' the initial rate. Linear relationship seems to hold between the amount of water added and the rate enhancement; the degree of increase in rate is proportional to the amount of water added. Thus, the initial rate can be expressed as

$$r_c = (k_c + k_w[H_2O])[\mathbf{1}][Na_2S], \qquad (11)$$

$$k_c = (3.2 \pm 0.2) \times 10^{-3}\ \mathrm{dm^3\ mol^{-1}\ min^{-1}}$$

$$k_w = (1.3 \pm 0.1) \times 10^{-3}\ \mathrm{dm^6\ mol^{-2}\ min^{-1}}.$$

Effect on Degree of Polymerization. At the end of the reaction, the polymeric (acetone-insoluble) material was collected and its average degree of polymerization (n) was determined. Yields and n are shown in Table 3 for various initial concentrations of the reactants. It is clearly found that increase in [Na_2S]/[**1**] ratio tends to increase both in the polymer yield and in the degree of polymerization, except for the case of [**1**]<0.1 mol dm^{-3} in which we failed to isolate the polymers.[10]

Using the kinetic parameters shown in Table 2, we further calculated the yields and degree of polymerization for polymers of $n \geqq 3$ (Table 3). The dependence of the calculated values on the initial concentrations was qualitatively in good agreement with that of the observed one. The smaller observed yields and larger observed degree of polymerization compared with the calculated ones may suggest that the method for collecting polymers (see experimental) causes the loss of part of the polymers of smaller n values.

It was found that the presence of water causes the increase in polymer yield (Table 3). For the increase in the degree of polymerization, addition of water approximately equimolar to **1** would be appropriate (Table 3).

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7) Koch and Heitz have suggested the mechanism involving addition of sulfhydryl radical (HS·) at the initiation reaction, based on the product analysis in the model reaction using *p*-chlorobenzenethiol.[2] Rajan et al. has suggested the analogous mechanism except that nucleophilic substitution of sulfide ion (S^{2-}) is involved in the

initiation reaction, on the basis of time course of the consumption of *p*-dichlorobenzene and the increase in the degree of polymerization.[4]

8) Although the proposed reaction path includes no radical species, this does not necessarily exclude the participation of radical species.[7] Annenkova et al. reported the formation of polysulfide anion radicals in heated solution of sodium sulfide in *N*-methylpyrrolidone [V. Z. Annenkova, L. M. Antonik, A. K. Khaliullin, N. A. Gorban, T. I. Vakul'skaya, and M. G. Voronkov, *Zh. Obshch. Khim.*, **53**, 2409 (1983); see also Ref. 3a]. These radical species may participate in the present reaction, in which case kinetic profiles would be similar to those shown in Fig. 1.

9) Y. Iizuka, T. Iwasaki, T. Katto, and Y. Shiiki, Japan Kokai Tokkyo Koho, 7332 (1986).

10) This is probably because the amount of polymers formed is so small that they were washed out by acetone.