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Cyclopolymerization Initiated by Peroxydisulfate Ion and Metal Ion Catalysis*

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ABSTRACT

The kinetics of cyclopolymerization of N,N'-methylenebisacrylamide (MBA) was carried out using peroxydisulfate ion as initiator. The rate of polymerization, R_p, was found to be proportional to [M] and $[S_2O_8^{2-}]^{1/2}$ for the uncatalyzed system. A cyclopolymerization mechanism was found to fit the experimental results. The $k_{21}/k_t^{1/2}$ value for MBA polymerization was evaluated. Evidence in favor of the cyclopolymerization mechanism is provided. The addition of Ag^+ ion enhances R_p.

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INTRODUCTION

Ordinarily peroxydisulfate can be employed along with reducing agents as a redox system for initiating polymerization [1-3]. Use of this compound as a sole initiator is, however, rare. We have recently published our findings on such an application in the polymerization of acrylamide, methacrylamide, acrylic acid, methacrylic acid, and acrylonitrile, all monovinyl monomers [4-8]. Now we have taken up similar work with a divinyl monomer and peroxydisulfate as sole initiator. N,N'-Methylenebisacrylamide is a symmetrical nonconjugated diolefin that may be expected to lead to cross-linking. However, when this monomer was polymerized by redox systems, unexpectedly smooth kinetics were obtained. Therefore, a cyclopolymerization step was invoked [9-11] for propagation on the lines of the Butler and Ingley [12] mechanism for analogous cases. It would now be interesting to see how this monomer behaves with peroxydisulfate as a single initiator for polymerization. Ag^+ ion catalysis is also covered in this study.

EXPERIMENTAL

N,N'-Methylenebisacrylamide (Koch-Light) was recrystallized from acetone at 40°C [9]. Potassium peroxydisulfate, $K_2S_2O_8$, (E. Merck) was recrystallized twice from doubly distilled water. Water, twice distilled over alkaline permanganate, was used to prepare all solutions. Nitrogen purified by passing through Fieser's solution was used to deaerate the reaction mixture. Temperature was controlled to ±0.01°C in a thermostat.

The reaction mixture (20 mL) containing monomer and a neutral salt K_2SO_4 (to adjust the ionic strength, μ) was deaerated for 30 min in a thermostat, and the reaction was started by the addition of $K_2S_2O_8$ solution. The rate of polymerization was followed by estimating the monomer concentrations by bromometry [13] at two different time intervals and after the attainment of the steady state. Homogeneous polymerization was obtained only at low monomer concentrations and at polymerization conversions below 70%. Hence kinetic studies were restricted to conditions leading to homogeneous polymerization. Because of the low solubility of monomer in water ($< 3.2\%$), polymerization could be studied only in low monomer concentration ranges. This made the separation of polymers from the reaction mixture difficult, and no characterization was possible under the experimental conditions chosen here for kinetic studies.

Polymerization experiments involving Ag^+ ions in the reaction mixture were carried out in the dark.

RESULTS AND DISCUSSIONS

Uncatalyzed Polymerization

The rate of polymerization R_p was found to depend on [M] (Fig. 1) and $[S_2O_8^{2-}]^{1/2}$ (Fig. 2) under steady-state conditions. The activation energy for the polymerization reaction was calculated to be ~25.2 kcal/mol from the Arrhenius plot of log k_p vs 1/T (Fig 3). R_p was found to decrease slightly with increasing ionic strength (Table 1).

Results on the kinetics of nonconjugated diolefin polymerization seem to indicate that, while initiation and termination processes are similar to those for monovinyl polymerization, a novel chain mechanism is involved in propagation [14]. We propose here a kinetic scheme incorporating cyclopolymerization as the new propagation step to derive the rate expression.

I. Initiation

$$S_2O_8^{2-} \xrightarrow{k_0} 2SO_4^{\bullet -} \tag{1}$$

$$SO_4^{\bullet -} + H_2O \xrightarrow{k_1} HSO_4^- + {}^{\bullet}OH \tag{2}$$

$$SO_4^{\bullet -} + M \xrightarrow{k_2} M_1^{\bullet} \tag{3}$$

$${}^{\bullet}OH + M \xrightarrow{k_3} M_1^{\bullet} \tag{4}$$

II. Propagation

a) $M_1^{\bullet} \xrightarrow{k_c} M_2^{\bullet}$ cyclization

b) $M_1^{\bullet} + M_1 \xrightarrow{k_{11}} M_1^{\bullet}$ linear propagation

c) $M_2^{\bullet} + M_1 \xrightarrow{k_{21}} M_1^{\bullet}$ propagation

d) $M_1^{\bullet} + M_3 \xrightarrow{k_{13}} M_3^{\bullet}$ crosslinking

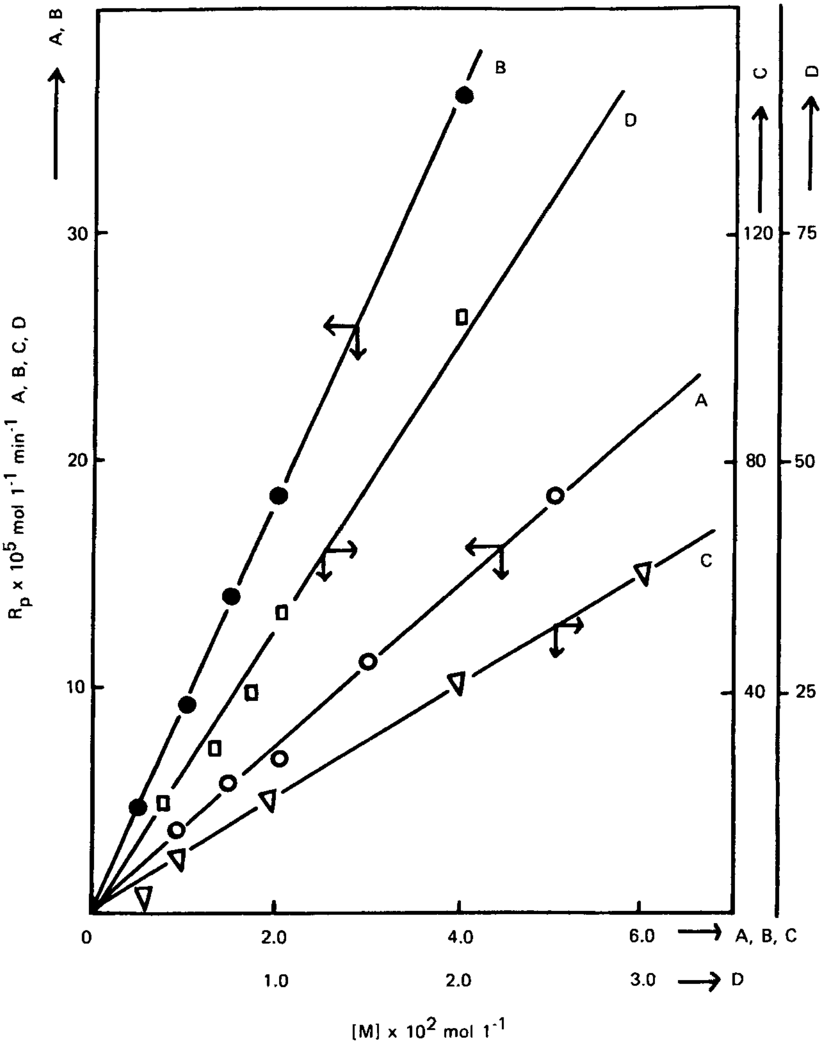


FIG. 1. Dependence of R_p on [M]. R_p vs [M] in uncatalyzed and Ag^+-catalyzed polymerization, t = 35°C, μ = 0.5 mol/L (A, [$S_2O_8^{2-}$] = 0.005 mol/L; B, [$S_2O_8^{2-}$] = 0.008 mol/L; C, [$S_2O_8^{2-}$] = 0.01 mol/L; D, [$S_2O_8^{2-}$] = 0.01 mol/L, [Ag^+] = 1.0 × 10^{-4} mol/L).

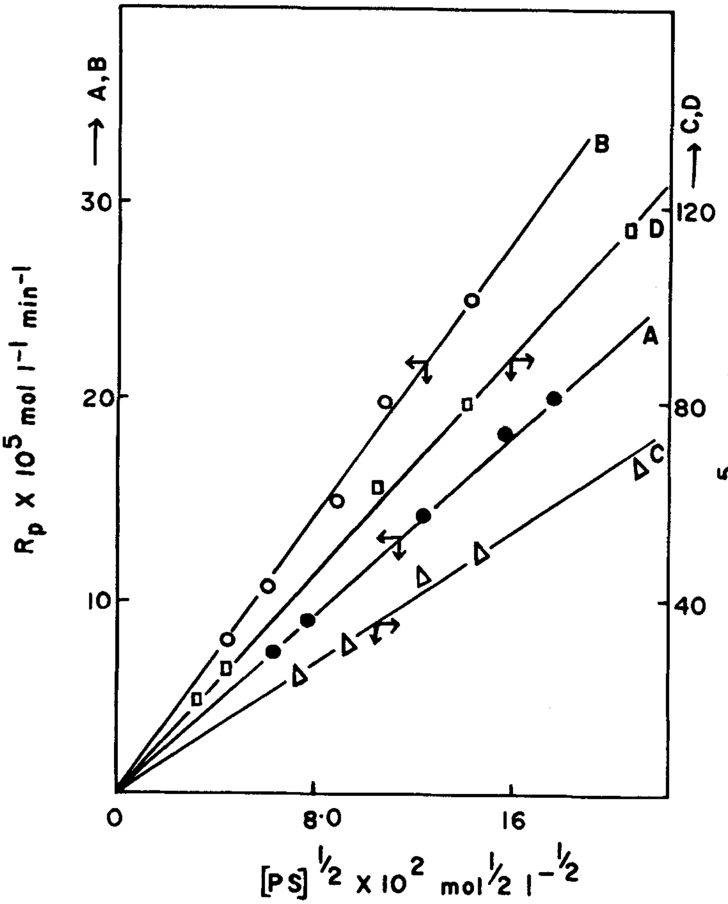


FIG. 2. Dependence of R_p on $[S_2O_8^{2-}]^{1/2}$. R_p vs $[S_2O_8^{2-}]^{1/2}$ in uncatalyzed and Ag^+-catalyzed polymerization, t = 35 °C, μ = 0.5 mol/L (A, [M] = 0.016 mol/L; B, [M] = 0.02 mol/L; C, [M] = 0.035 mol/L; D, [M] = 0.02 mol/L, $[Ag^+] = 1.0 \times 10^{-4}$ mol/L).

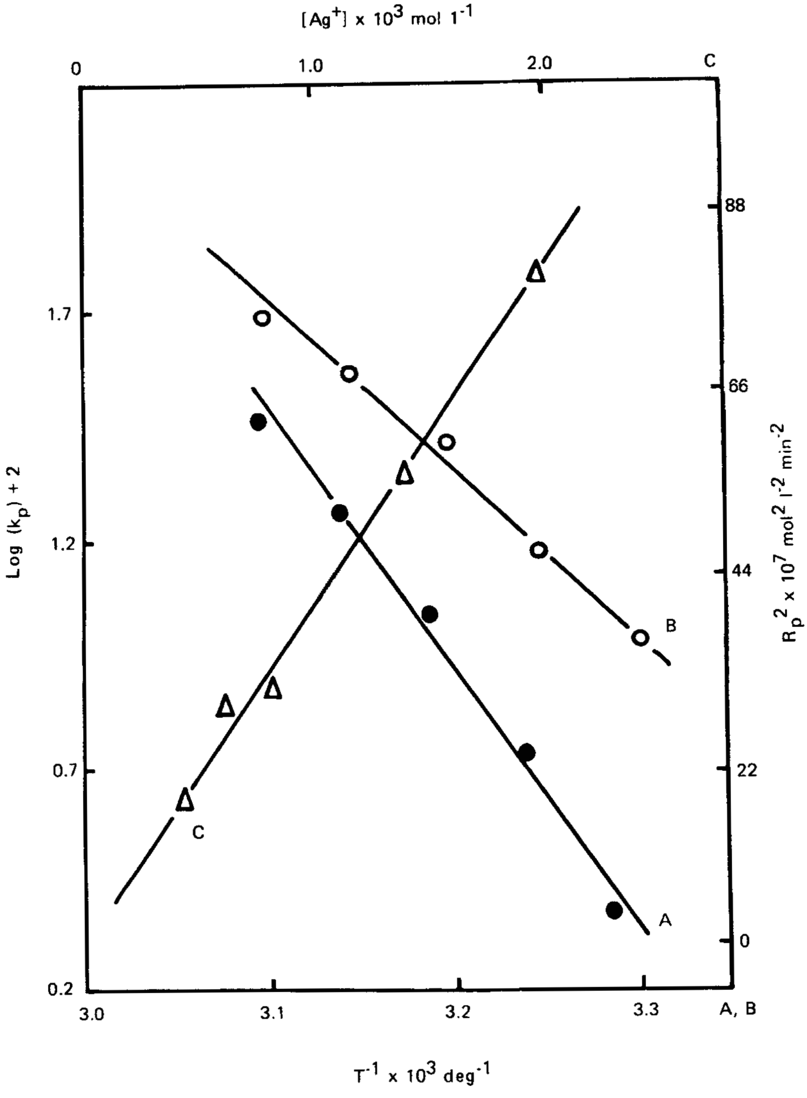


FIG. 3. Plot of log k vs T^{-1} for the polymerization of N,N'-methylenebisacrylamide in the uncatalyzed and Ag^+-catalyzed system. [M] = 0.02 mol/L, $[S_2O_8^{2-}]$ = 0.01 mol/L, μ = 0.5 mol/L (A, $[Ag^+]$ = 0; B, $[Ag^+] = 1.0 \times 10^{-4}$ mol/L). Dependence of R_p^2 on $[Ag^+]$. C, [M] = 0.02 mol/L, $[S_2O_8^{2-}]$ = 0.01 mol/L, μ = 0.5 mol/L, t = 35°C.

TABLE 1. Effect of Ionic Strength on the Rate of Polymerization: [M] = 0.02 mol/L, $[S_2O_8^{2-}]$ = 0.01 mol/L, 35°C

$Ag^+ \times 10^4$ mol/L	Ionic strength μ, mol/L	$R_p \times 10^4$ $mol \cdot L^{-1} \cdot min^{-1}$
-	0.03	2.41
-	0.07	2.30
-	0.13	2.22
-	0.25	2.06
-	0.50	2.00
-	1.00	1.86
1.0	0.03	17.9
1.0	0.11	14.4
1.0	0.19	10.9
1.0	0.40	9.40
1.0	0.50	7.02
1.0	1.00	3.90

e) $M_2^{\bullet} + M_3 \xrightarrow{k_{23}} M_3^{\bullet}$ crosslinking

f) $M_3^{\bullet} + M_1 \xrightarrow{k_{31}} M_1^{\bullet}$ pendant radical propagation

g) $M_3^{\bullet} + M_3 \xrightarrow{k_{33}} M_3^{\bullet}$ crosslinking

III. Termination

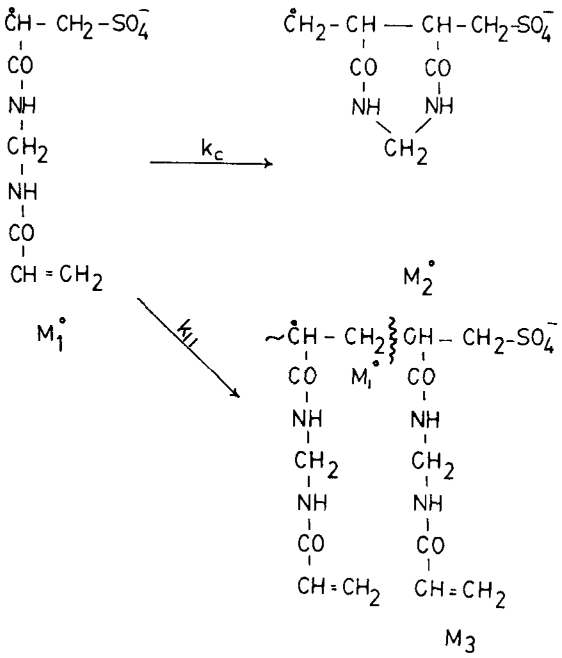
$$M_2^{\bullet} + M_2^{\bullet} \xrightarrow{k_t} \text{polymer}$$

Here M_1 could represent either of the double bonds of the previously unreacted symmetrical monomer. $M_1^{\bullet}$ is the radical produced when M_1 is attacked by a radical. $M_2^{\bullet}$ is the radical when $M_1^{\bullet}$ cyclizes. M_3 may be taken as a pendant double bond present in $M_1^{\bullet}$ and capable of acting as a new site for further radical attack. $M_3^\bullet$ may be the radical when M_3 is attacked by a radical. The reactions under such categories as "pendant double bond propagation" and "crosslinking" take place when the pendant double bond M_3 reacts with the radical.

The initiating radicals $SO_4^{\bullet -}$ and $^\bullet OH$ are produced by the slow homolysis of $S_2O_8^{2-}$. M_1 is converted to $M_1^\bullet$ by the attack of these radicals (Step 3 and Step 4).

There are two competing pathways for propagation: (i) intramolecular cyclization of $M_1^\bullet$ between the radical part and the double bond present in the same repeating unit as in II(a), and (ii) normal intermolecular propagation as in II(b) forming a radical containing the unreacted pendant double bonds M_3 (Scheme 1).

The relative probability of these two modes depends on monomer structure and on the stability of the ring formed during cyclization. The monomer is a symmetrical nonconjugated diolefin capable of forming a seven-membered ring during cyclization [9]. If the ring formed during cyclization is five- or six-membered, highly cyclized polymers



SCHEME 1.

are formed. This is due to the reduced strain during cyclization [15]. Monomers that can form rings of seven or more members on cyclization would contain fewer cyclized units. However, Ziegler and Holl [16] revealed that substitution of carbonyl or oxygen for methylene groups in the ring reduces the strain by decreasing the number of interfering hydrogens. In the present case the presence of two carbonyl groups accounts for the stability of the ring by lowering the ring strain. The probability of cyclization is, therefore, enhanced.

The monovinyl-type linear propagation, II(b), would be a sterically hindered path because of the long pendant group which provides a shielding effect to the approach of another monomer unit to $M_1^\bullet$. Further, the monomer concentration in our studies was very low and, therefore, $M_1^\bullet$ will have relatively little opportunity to encounter another monomer molecule compared to intramolecular cyclization. From the above considerations, Step II(a) is preferred over Step II(b). All reactions involving M_3 and $M_3^\bullet$ arise only if Reaction II(b) takes place. In view of the low probability of II(b), such reactions can be ruled out for practical purposes.

Now the polymer chain grows by Step II(c), where $M_2^\bullet$, the cyclized radical, reacts with another monomer molecule. This can take place at a faster rate because there is no steric hindrance to the approach of another monomer molecule because it does not contain the pendant group. The resulting $M_1^\bullet$ cyclizes, and the sequence repeats itself.

For a symmetrical nonconjugated diolefin, when cyclization is the preferred path, termination is predominantly by mutual interaction between growing radicals [15]. Taking the mutual termination and the above-discussed initiation and propagation, a rate expression can be derived for steady-state conditions on the assumption of an initiator efficiency of unity:

$$R_p = \frac{d[M_1]}{dt} = \sqrt{2}\,\frac{k_{21}}{k_t^{1/2}}\,k_0^{1/2}\,[M][S_2O_8^{2-}]^{1/2}$$

This expression is in agreement with our experimentally observed dependence on R_p on [M] (Fig. 1) and $[S_2O_8^{2-}]^{1/2}$ (Fig. 2). Taking the rate of initiation as the rate of aqueous decomposition of $S_2O_8^{2-}$ under the same experimental conditions, $k_{21}/k_t^{1/2}$ was calculated at different temperatures (Table 2). Butler et al. [17] polymerized divinyl monomers, and compared $k_{21}/k_t^{1/2}$ with reported values for the monovinyl counterparts. The $k_{21}/k_t^{1/2}$ value was almost always larger than $k_p/k_t^{1/2}$ for the monovinyl analogs. Butler et al. [17] took these

TABLE 2. Ratio of Propagation and Termination Rate Constants in the Uncatalyzed Polymerization of N,N'-Methylenebisacrylamide at Various Temperatures

Temperature, °C	$k_{21}/k_t^{1/2}$, $mol^{-1/2} \cdot L^{1/2} \cdot s^{-1/2}$
35	3.54
40	4.51
45	6.27
50	7.04

results as supporting evidence for cyclopolymerization of the divinyl monomer.

In this work, $k_{21}/k_t^{1/2}$ of N,N'-methylenebisacrylamide (MBA) is compared with acrylamide (AA) and also methacrylamide (MAA). For comparison $k_p/k_t^{1/2}$ for AA [18] and MAA [19], 0.42 $mol^{-1/2} \cdot L^{1/2} \cdot s^{-1/2}$ and 5.60 $mol^{-1/2} \cdot L^{1/2} \cdot s^{-1/2}$, respectively, at 50°C were used. The lower $k_p/k_t^{1/2}$ value for MAA than for AA can be attributed to the steric hindrance given by the α-methyl group for MAA propagation. MBA has a bulky substituent as in MAA and is expected to have a lower value for $k_p/k_t^{1/2}$ than for AA if a monovinyl-type propagation prevails. What is significant here is that the observed higher value of $k_{21}/k_t^{1/2}$ (7.04 $mol^{-1/2} \cdot L^{1/2} \cdot s^{-1/2}$, 50°C) adds evidence for cyclopolymerization as a propagation mode for MBA. The comparison of the overall rate of polymerization of MBA with AA and MAA under identical conditions also supports this because the order of reactivity is MBA > AA > MAA (Table 3).

The initiation and termination steps thus appear to be the same as found with systems based on $S_2O_8^{2-}$ and monovinyl monomers [4-8]. However, propagation involves cyclopolymerization, as found with the divinyl monomer and redox systems [9-11].

Ag^+-Catalyzed Polymerization

The activation energy for the polymerization was reduced from 25.2 kcal/mol (uncatalyzed) to ~11.2 kcal/mol (catalyzed). This reveals that Ag^+ catalyzes the polymerization. In the presence of Ag^+, R_p depended on $[S_2O_8^{2-}]^{1/2}$, [M], and $[Ag^+]^{1/2}$. Plots of R_p versus

TABLE 3. Comparison of Overall Rate of Polymerization: $[S_2O_8^{2-}] = 0.02$ mol/L, $\mu = 0.5$ mol/L, 40°C

Monomer M	[M], mol/L	$R_p \times 10^4$ $mol \cdot L^{-1} \cdot min^{-1}$
Acrylamide (AA)	0.04	10.8
Methacrylamide (MAA)	0.04	0.97
N,N'-Methylenebisacrylamide (MBA)	0.04	17.7

[M] (Fig. 1) and $[S_2O_8^{2-}]^{1/2}$, (Fig. 2) were linear and passed through the origin. The plot of R_p^2 versus Ag^+ (Fig. 3) was also linear without intercept on the Y-axis, indicating that the contribution of uncatalyzed polymerization is very small. R_p decreases with increasing ionic strength (Table 1). The following additional steps along with the initiation reactions given for uncatalyzed polymerization are added to explain the kinetics in the presence of Ag^+ ions.

$$Ag^+(aq) + S_2O_8^{2-} \overset{K}{\rightleftharpoons} AgS_2O_8^-(aq) \qquad (5)$$

$$AgS_2O_8^-(aq) \xrightarrow{k_4} Ag^+ + SO_4^{\cdot -} + HSO_4^- + {}^{\cdot}OH \qquad (6)$$

With cyclopolymerization as the propagation step and with mutual termination, a kinetic expression is derived for steady-state conditions:

$$R_p = \sqrt{2}\, k_{21} \left(\frac{k_4 K}{k_t} \right)^{1/2} [Ag^+]^{1/2} [S_2O_8^{2-}]^{1/2} [M] \qquad (7)$$

Rate expression (7) agrees well with our experimental results. Complexation between $Ag^+(aq)$ and $S_2O_8^{2-}$ was suggested in our earlier studies [5-7]. The observed slight negative salt effect (Table 1) may be due to the involvement of Equilibrium (5). By substituting the $k_{21}/k_t^{1/2}$ value from the uncatalyzed system (Table 1), the k_4K value is found to be 0.010 $mol^{-1} \cdot L \cdot s^{-1}$ at 25°C. It is remarkable that this is in close agreement with the value reported (0.012 $mol^{-1} \cdot L \cdot s^{-1}$, 25°C) in the Ag^+-catalyzed decomposition study of just $S_2O_8^{2-}$ in aqueous solution [20].

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