CHAPTER III

REACTION SCHEMES AND RATE EXPRESSIONS

The experimental results presented in the previous chapter may be subjected to a detailed kinetic analysis. Rate expressions are derived on the basis of the following schemes involving all possible reactions that are likely to occur in the system. The manner of arriving at each rate expression and choosing the appropriate set of reactions is presented here. Detailed discussion of the results is presented in the next chapter.

3.1. GENERAL MECHANISM FOR THE MONOVINYL POLYMERIZATION IN THE PRESENCE OF PEROXODISULPHATE AND ULTRASOUND

I. Production of radicals followed by initiation

i) Production primary radicals

a) Formation of sulphate ion radical by the self decomposition of peroxodisulphate

\[ k_0 \]

\[
\text{PDS} \quad \xrightarrow{k_0} \quad 2 \text{SO}_4^- 
\]

b) Formation of hydroxyl radical by the reaction between sulphate ion radical and water.

\[ k_1 \]

\[
\text{SO}_4^- + \text{H}_2\text{O} \quad \xrightarrow{k_1} \quad \text{HSO}_4^- + \cdot\text{OH} 
\]
c) The hydroxy radicals may form water and oxygen by mutual interaction

\[ \text{\'OH + \text{\'OH} \xrightarrow{k_2} \text{H}_2\text{O} + \text{O}} \]

ii) Initiation may take place by the following reactions

a) Initiation by sulphate ion radical

\[ \text{SO}_4^{2-} + \text{M} \xrightarrow{k_3} \text{M}_1^{\cdot} \]

b) Initiation by hydroxyl radical

\[ \text{\'OH} + \text{M} \xrightarrow{k_4} \text{R}_1^{\cdot} \]

c) Initiation

\[ \text{PDS} + \text{M} \xrightarrow{k_5} \text{R}_1^{\cdot} + \text{SO}_4^{2-} \]

Here \( \text{M}_1 \) denotes the primary radical containing one monomer unit, \( \text{M} \) irrespective of the end group present. Steps (a) and (c) wherein sulphate ion radical adds on to the double bond are more probable with monomers having electron withdrawing groups like -COOH, -CONH₂, -CN, -COOR etc. Steps (b) and (d) are known to take place with facility in monomers containing electron releasing groups like -C₆H₅, -NR₁R₂.
II. Propagation

\[
\begin{align*}
M_1^- + M & \xrightarrow{k_p} M_2^- \\
\quad & \quad \\
M_{n-1}^- + M & \xrightarrow{k_p} M_n^-
\end{align*}
\]

(M_n^- is the polymer radical containing ‘n’ monomer units)

III. Termination

The final step is the termination of radical chain which may take place by any of the following reactions.

a) Mutual termination of chain radicals by combination or disproportionation

\[
M_n^- + M_m^- \xrightarrow{k_{11}} \text{Polymer}
\]

b) Linear termination by primary radicals

\[
\begin{align*}
M_n^- + 'OH & \xrightarrow{k_{12}} \text{Polymer} \\
M_n^- + SO_4^- & \xrightarrow{k_{13}} \text{Polymer}
\end{align*}
\]
The reaction scheme outlined above has been used for the derivation of rate expressions for the rate of monomer disappearance assuming the stationary state concentrations of free radical and non-dependence of rare constants \((k_p\) and \(k_t\)) on chain length. Chain transfer to the initiator, monomer, polymer and solvent has not been considered in deriving the rate expressions.

**Case I:**

Considering initiation by PDS, \(\text{SO}_4^{2-}\) and \(\cdot\text{OH}\) with mutual termination.
Assuming steady state conditions for all radicals.

\[
\frac{d [M_n^*]}{dt} = k_5 [\text{PDS}] [M] + k_3 [\text{SO}_4^{2-}] [M] + \\
\quad k_4 [\cdot\text{OH}] [M] - k_{t1} [M_n^*]^2 = 0 \quad (1)
\]

\[
\frac{d [\text{SO}_4^{2-}]}{dt} = 2 k_0 [\text{PDS}] + k_5 [\text{PDS}] [M] - \\
\quad k_1 [\text{SO}_4^{2-}] - k_2 [\text{SO}_4^{2-}] [M] = 0 \quad (2)
\]

\[
\frac{d [\cdot\text{OH}]}{dt} = k_1 [\text{SO}_4^{2-}] - k_2 [\cdot\text{OH}]^2 - k_4 [\cdot\text{OH}] [M] = 0 \quad (3)
\]

Adding equations (1), (2) and (3),

\[
2 k_0 [\text{PDS}] + 2 k_5 [\text{PDS}] [M] - k_{t1} [M_n^*]^2 - k_2 [\cdot\text{OH}]^3 = 0 \quad (4)
\]
a) Under the condition \( k_4 \cdot \text{OH} \cdot \text{M} \gg k_2 \cdot \text{OH}^2 \), Equation (4) becomes

\[
2 k_0 \cdot \text{PDS} + 2 k_5 \cdot \text{PDS} \cdot \text{M} - k_{t1} \cdot [\text{M}_n^\cdot]^2 = 0
\]  

\[
[M_n^-] = \left( \frac{2 k_0 \cdot \text{PDS} + 2 k_5 \cdot \text{PDS} \cdot \text{M}}{k_{t1}} \right)^{1/2}
\]

\[
R_p = k_p \cdot [M_n^\cdot] \cdot [\text{M}]
\]

\[
= \frac{k_p \cdot [\text{M}]}{k_{t1}^{1/2}} \left( 2 k_0 \cdot \text{PDS} + 2 k_5 \cdot \text{PDS} \cdot \text{M} \right)
\]

\[
R_p^2 = \frac{2 k_p^2 k_0}{k_{t1}} \cdot [\text{PDS} \cdot \text{M}]^2 + \frac{2 k_p^2 k_3}{k_{t1}} \cdot [\text{PDS} \cdot \text{M}]^3
\]

b) Under the condition \( k_2 \cdot \text{OH}^2 \gg k_4 \cdot \text{OH} \cdot \text{M} \)

From Equation (3),

\[
[\cdot \text{OH}]^2 = \frac{k_1 \cdot [\text{SO}_4^{2-}]}{k_2}
\]
From Equation (2),

\[
[SO_4^{\text{\textminus}}] = \frac{2k_0 [\text{PDS}] + k_5 [\text{PDS}] [\text{M}]}{k_1 + k_3 [\text{M}]} \quad (10)
\]

Substituting \([SO_4^{\text{\textminus}}]\) from Equation (10) into Equation (9)

\[
[\cdot \text{OH}]^2 = \frac{2k_0 k_1 [\text{PDS}] + k_1 k_5 [\text{PDS}] [\text{M}]}{k_1 k_2 + k_2 k_3 [\text{M}]} \quad (11)
\]

Substituting Equation (11) into Equation (4) and multiplying by the denominator of Equation (11),

\[
2k_0 k_2 k_3 [\text{PDS}] [\text{M}] + k_1 k_2 k_5 [\text{PDS}] [\text{M}] + 2k_2 k_3 [\text{PDS}] [\text{M}]^2 +
\]

\[
k_1 k_2 k_{11} [M_n^\cdot]^2 - k_2 k_3 k_{11} [M_n^\cdot]^2 [\text{M}] = 0 \quad (12)
\]

\[
[M_n^\cdot] = \left(\frac{(2k_0k_2k_3 + k_1k_2k_5)[\text{PDS}][\text{M}] + 2k_2k_3k_{11}[\text{PDS}][\text{M}])^2}{k_1k_2k_{11} + k_2 k_3 k_{11} [\text{M}]}\right)^{1/2} \quad (13)
\]

\[R_p = k_p [\text{M}] [M_n^\cdot]\]
\[
R_p^2 = \left( \frac{(2k_0k_3 + k_1k_5) k_p^2 [PDS][M]^3 + 2k_3k_5 k_p^2 [PDS][M]^4}{k_1k_{t1} + k_3 k_{t1} [M]} \right)^{1/2} (15)
\]

\textit{Case II}

Considering initiation by PDS, SO$_4^{2-}$ and \('\text{OH}' with linear termination by sulphate ion radical

\[
\frac{d [M_n^*]}{dt} = k_5 [PDS][M] + k_3 [SO_4^{2-}][M] + k_4 [\cdot \text{OH}][M] - k_{t3} [M_n^*][SO_4^{2-}] = 0 \quad (16)
\]

\[
\frac{d [\cdot \text{OH}]}{dt} = k_1[SO_4^{2-}] - k_2[\cdot \text{OH}]^2 - k_4 [\cdot \text{OH}][M] = 0 \quad (17)
\]
\[ R_p = k_p [M] [M_n^-] \]

\[ R_p = \frac{k_p k_1}{k_2} [M] + \frac{(k_0 k_3 + k_1 k_5) k_p}{k_0 k_3} [M]^2 + \frac{k_3 k_5 k_p}{k_0 k_3} [M]^3 \quad (23) \]

**Case III:**

Considering initiation by PDS, \( \text{SO}_4^{2-} \) and \( \cdot \text{OH} \) with linear termination by hydroxyl radical

\[
\frac{d [M_n^-]}{dt} = k_3 [\text{PDS}] [M] + k_5 [\text{SO}_4^{2-}] [M] + k_4 [\cdot \text{OH}] [M] - k_2 [M_n^-] [\cdot \text{OH}] = 0 \quad (24)
\]

\[
\frac{d [\text{SO}_4^{2-}]}{dt} = 2 k_0 [\text{PDS}] + k_5 [\text{PDS}] [M] - k_1 [\text{SO}_4^{2-}] - k_3 [\text{SO}_4^{2-}] [M] = 0 \quad (25)
\]

\[
\frac{d [\cdot \text{OH}]}{dt} = k_1 [\text{SO}_4^{2-}] - k_2 [\cdot \text{OH}]^2 - k_4 [\cdot \text{OH}] [M] - k_{t_2} [R_n^+] [\cdot \text{OH}] = 0 \quad (26)
\]

Adding Equations (24), (25) and (26),

\[
2 k_0 [\text{PDS}] + 2 k_5 [\text{PDS}] [M] - 2 k_{t_2} [M_n^+] [\cdot \text{OH}] - k_2 [\cdot \text{OH}]^2 = 0 \quad (27)
\]
when $k_2 [M_n^+] [\cdot \text{OH}] \gg k_2 [\cdot \text{OH}]$.

From Equation (26)

$$k_1 [\text{SO}_4^-] \quad [\cdot \text{OH}] = \frac{k_1 + k_4 [M_n^+]}{k_1 + k_4 [M_n^+]}$$

From Equation (25),

$$2k_0 [\text{PDS}] + k_5 [\text{PDS}] [\text{M}] \quad [\text{SO}_4^-] = \frac{k_1 + k_3 [\text{M}]}{k_1 + k_3 [\text{M}]}$$

Substituting $[\text{SO}_4^-]$ from Equation (29) in Equation (28),

$$2k_0k_1 [\text{PDS}] + k_5k_1 [\text{PDS}] [\text{M}] \quad [\cdot \text{OH}] = \frac{k_1k_4 [\text{M}] + k_1k_2 [M_n^+] + k_3k_4 [\text{M}]^2 + k_3k_2 [M_n^+] [\text{M}]}{k_1k_4 [\text{M}] + k_1k_2 [M_n^+] + k_3k_4 [\text{M}]^2 + k_3k_2 [M_n^+] [\text{M}]}$$

Substituting Equation (30) into Equation (27) and multiplying by the denominator of Equation (30),
\[ 2k_0k_1k_4 [\text{PDS}] [\text{M}] + 2k_0k_3k_4 [\text{PDS}] [\text{M}]^2 + 2k_0k_3k_{12} [M_n^*] [\text{M}][\text{PDS}] + 
\]

\[ 2k_1k_5k_4 [\text{PDS}] [\text{M}]^2 + 2k_0k_1k_{12} [M_n^*] [\text{PDS}] = 0 \quad (31) \]

\[
[M_n^*] = \frac{k_0k_1k_4[M] + (k_0k_3k_4 + k_1k_5k_4)[M]^2 + k_3k_3k_4[M]^3}{k_0k_1k_{12} - (k_3k_3k_{12} [M]^2 + k_0k_3k_{12} [M])} \quad (32)
\]

\[ R_p = k_p [M][M_n^*] \]

\[
k_0k_1k_4[M] + (k_0k_3k_4 + k_1k_5k_4)[M]^2 + k_3k_3k_4[M]^3
\]

\[ = k_p [M] \frac{k_0k_1k_{12} - (k_3k_3k_{12} [M]^2 + k_0k_3k_{12} [M])}{k_0k_1k_4[M] + (k_0k_3k_4 + k_1k_5k_4)[M]^2 + k_3k_3k_4[M]^3} \quad (33) \]

Rate of peroxodisulphate (PDS) disappearance for both cases

\[ - \frac{d [\text{PDS}]}{dt} = k_0 [\text{PDS}] + k_5 [M] [\text{PDS}] \quad (34) \]
3.2 GENERAL MECHANISM FOR THE MONOVINYL POLYMERIZATION IN THE PRESENCE OF PEROXOMONOSULPHATE AND ULTRASOUND

I. Production of radicals

\[ k_6 \]

a) \[ \text{PMS} \] \[ \rightarrow \] \[ \text{SO}_4^{--} + \cdot \text{OH} \]

\[ k_1 \]

b) \[ \text{SO}_4^{--} + \text{H}_2\text{O} \] \[ \rightarrow \] \[ \cdot \text{OH} + \text{HSO}_4^- \]

II. Initiation

\[ k_3 \]

a) \[ M + \text{SO}_4^{--} \] \[ \rightarrow \] \[ M_1' \] where \[ M_1' = \text{SO}_4^-\text{-CH}_2\cdot\text{CH-CONH}_2 \]

\[ k_4 \]

b) \[ M + \cdot \text{OH} \] \[ \rightarrow \] \[ M_1'' \] where \[ M_1'' = \text{HO-CH}_2\cdot\text{CH-CONH}_2 \]

\[ k_7 \]

c) \[ M + \text{PMS} \] \[ \rightarrow \] \[ M_1'' + \text{SO}_4^{--} \]

III Propagation

\[ k_p \]

\[ M_1'' + M \] \[ \rightarrow \] \[ M_2 \]
IV. Termination

a) Mutual termination

\[ 2 \, M_n^* \, (M_n') \rightarrow \text{Polymer} \]

Assuming steady state conditions for all the radicals present in the system, the rate expressions are derived for various possible polymerization paths.
**Case I:**

Considering initiation by all the reactions in step II and termination by step IV (a).

\[-d\left[SO_4^{2-}\right]/dt = k_6[PMS] - k_3[M][PMS] - k_1[SO_4^{2-}] + k_7[M][PMS] = 0 \tag{35}\]

\[-d[\cdot OH]/dt = k_{66}[PMS] + k_1[SO_4^{2-}] - k_4[M][\cdot OH] = 0 \tag{36}\]

\[-d[M_n^*]/dt = k_3[M][SO_4^{2-}] + k_3[M][\cdot OH] + k_7[M][PMS] - k_{11}[M_n^*]^2 = 0 \tag{37}\]

Adding Equation (35), (36) and (37)

\[2k_6[PMS] + 2k_7[M][PMS] = k_{11}[M_n^*] \tag{38}\]

\[\frac{2k_6[PMS]}{k_{11}} + \frac{2k_7[M][PMS]}{k_{11}} = [M_n^*]^2 \tag{39}\]

For monovinyl polymerization

\[R_p = k_p[M_n^*][M] \tag{40}\]
130

\[ R_p^2 = k_p^2 [M_n^*]^2 [M]^2 \] (40A)

Substituting for \([M_n]^2\) from Equation (39) into Equation (40A),

\[
R_p^2 = \frac{2 k_p^2 k_6 [M]^2 [PMS]}{k_{11}} + \frac{2 k_p^2 k_7 [M]^3 [PMS]}{k_{11}} \] (41)

Rate of disappearance of PMS

\[
- \frac{d [PMS]}{dt} = k_6 [PMS] + k_7 [M] [PMS] \] (42)

3.3 GENERAL MECHANISM FOR THE DIVINYL POLYMERIZATION IN THE PRESENCE OF PEROXODISULPHATE AND ULTRASOUND

I. Primary reactions

The formation of sulphate ion radical by the decomposition of peroxodisulphate

\[ k_0 \]

a) \[ \text{PDS} \rightarrow 2 \text{SO}_4^{2-} \]
b) $SO_4^{-} + H_2O \rightarrow HSO_4^{-} + \cdot OH$

II. Initiation

a) Initiation by sulphate ion radical

\[ k_8 \]
\[ M + SO_4^{2-} \rightarrow M_{1}^{'}, \]

where $M_{1}^{'} = \cdot SO_4-\cdot CH_2-\cdot CH-CH_2-NH-CH_2-CH=CH_2$

b) Initiation by hydroxyl radical

\[ k_9 \]
\[ M + \cdot OH \rightarrow M_{1}^{''}, \]

where $M_{1}^{''} = HO- CH_2-\cdot CH-CH_2-NH-CH_2-CH=CH_2$

c) Initiation by the interaction of monomer with peroxodisulphate

\[ k_{10} \]
\[ M + PDS \rightarrow M_{1}^{'} + SO_4^{-} \]
III. Propagation

In cyclopolymerization, propagation describes how the radical end of $M_1^\prime$ is converted into $M_2^\prime$ by cyclization reaction and subsequently to $M_1^\prime$ through intermolecular reaction.

\[ \text{Intramolecular cyclization} \]

\[ k_e \]

$M_1^\prime \xrightarrow{k_e} M_2^\prime$ (Intramolecular cyclization)

\[ \text{Intermolecular propagation} \]

\[ k_{21} \]

$M_2^\prime + M \xrightarrow{k_{21}} M_1^\prime$ (Intermolecular propagation)

In cyclopolymerization, the rate of change of $M_1^\prime$ with time is given by

\[
\frac{d[M_1^\prime]}{dt} = k_{21} [M_2^\prime] [M] - k_e [M_1^\prime] \quad (43)
\]

Under stationary conditions, the rate of change of $[M_1^\prime]$ with time is very much smaller than either of the rate of formation or disappearance of $[M_1^\prime]$, then

\[
k_{21} [M_2^\prime] [M] - k_e [M_1^\prime] = 0 \quad (44)
\]

Hence

\[
k_{21} [M_2^\prime] [M] = k_e [M_1^\prime] = 0 \quad (45)
\]
Under conditions where the kinetic chain length is sufficiently large, only negligible amount of double bonds will be consumed by reactions other than propagation, the rate of monomer disappearance can be written as

\[ -\frac{d[M]}{dt} = R_p = \frac{1}{2} k_c [M_{1'}] + \frac{1}{2} k_{21} [M_{2'}][M] \quad (46)\]

where \( R_p \) is the rate of polymerization. The factor half comes since in each step of double bond consumption corresponds to half the monomer concentration.\(^{215}\)

Substituting from Equation (45)

\[ -\frac{d[M]}{dt} = R_p = k_{21} [M_{2'}][M] = k_c [M_{1'}] \quad (47)\]

Hence \( R_p^2 = k_{21}^2 [M_{2'}]^2 [M]^2 \quad (48)\)

IV. Termination

a) Mutual termination

\[ k_{14} \]

i) \( M_{2'} + M_{2'} \rightarrow \text{Polymer} \)
Assuming stationary state concentrations for primary and growing chain radicals, the following rate expressions are derived for various polymerization pathways.

**Case I:**

Considering initiation by all reactions in step II and termination by step IV (a) \( \cdot \)
(steps IB (b) and (c) are neglected in the scheme)
i) Termination is between $M_2^\cdot$ Radicals

\[
\frac{d \left[ SO_4^{2-} \right]}{dt} = 2 k_0 \left[ PDS \right] + k_{10} \left[ M \right] \left[ PDS \right] - k_8 \left[ M \right] \left[ SO_4^{2-} \right] - k_1 \left[ SO_4^{2-} \right] = 0 \quad (49)
\]

\[
\frac{d \left[ \cdot OH \right]}{dt} = k_1 \left[ SO_4^{2-} \right] - k_9 \left[ M \right] \left[ \cdot OH \right] = 0 \quad (50)
\]

Equating rate of formation and disappearance of chain radicals

\[
K_8 \left[ M \right] \left[ SO_4^{2-} \right] + k_9 \left[ M \right] \left[ \cdot OH \right] + k_{10} \left[ M \right] \left[ PDS \right] - k_{t4} \left[ M_2^\cdot \right] = 0 \quad (51)
\]

Adding Equations (49), (50) and (51),

\[
2 k_0 \left[ PDS \right] + 2 k_{10} \left[ M \right] \left[ PDS \right] = k_{t4} \left[ M_2^\cdot \right]^2 \quad (52)
\]

Rearranging for $\left[ M_2^\cdot \right]^2$

\[
\left[ M_2^\cdot \right]^2 = \frac{2 k_0}{k_{t4}} \left[ PDS \right] + \frac{2 k_{40}}{k_{t4}} \left[ M \right] \left[ PDS \right] \quad (53)
\]

Knowing $R_p^2 = k_{21}^2 \left[ M \right]^2 \left[ M_2^\cdot \right]^2 \quad (48)$
ii) Termination is between $M_1^*$ radicals

Equating rate of initiation and terminations

$$K_8[M][SO_4^{2-}] + k_9[M][\cdot OH] + k_{10}[M][PDS] - k_{t_5} [M_1^*]^2 = 0 \quad (55)$$

Adding Equations (55), (49) and (50)

$$2 k_0 [PDS] + 2 k_{10} [M][PDS] = k_{t_5} [M_1^*]^2 \quad (56)$$

Rearranging for $[M_1^*]^2$ and from Equation (47)

$$R_p^2 = \frac{2 k_c^2 k_0}{k_{t_5}} [PDS] + \frac{2 k_c^2 k_{10}}{k_{t_5}} [M][PDS] \quad (57)$$

iii) Termination is between $M_1^*$ and $M_2^*$

$$k_8[M][SO_4^{2-}] + k_5 [M][\cdot OH] + k_4 [M][PDS] - k_{t_6} [M_1^*][M_2^*] = 0 \quad (58)$$

Adding Equations (58), (49) and (50),

$$2 k_0 [PDS] + 2 k_{10} [M][PDS] = k_{t_6} [M_1^*][M_2^*] \quad (59)$$
Substituting for $[M^+]$ from Equation (45)

$$2 k_0[PDS] + 2 k_{10}[M][PDS] = k_{16} k_{21} [M^+] [M] / k_c$$  \( (60) \)

Rearranging for $[M_2^+]^2$ and from Equation (48)

$$R_p^2 = k_{21}^2 [M_2^+]^2 [M]^2$$  \( (48) \)

$$R_p^2 = \frac{2k_c k_{21} k_0}{k_{16}} [M][PDS] + \frac{2k_c k_{21} k_{10}}{k_{16}} [M]^2 [PDS]$$  \( (61) \)

**Case II:**

Considering initiation by all reactions in step II and termination by step IV (b) (steps IV (a) and (c) are neglected in the scheme)

i) Termination is between $M^-$ and $SO_4^{2-}$

$$\frac{d[SO_4^{2-}]}{dt} = 2 k_0[PDS] + k_{10}[M] [PDS] - k_8[M][SO_4^{2-}] - k_7[M^+] [SO_4^{2-}] = 0$$  \( (62) \)

$$k_8[M][SO_4^{2-}] + k_0[M][OH] + k_{10}[M][PDS] - k_7[M^+][SO_4^{2-}] = 0$$  \( (63) \)
Adding Equations (62), (63) and (50),

\[ k_0[PDS] + k_{410}[M][PDS] = k_{t7} [M_1'] [SO_4^{2-}] \]  \hspace{1cm} (64)

From Equation (62),

\[ 2 k_0[PDS] + k_{10}[M][PDS] \]
\[ [SO_4^{2-}] = \frac{-k_1 + k_8[M] + k_{t7}[M'_t]}{k_0 k_{17}} \]  \hspace{1cm} (65)

Substituting for \([SO_4^{2-}]\) in Equation (64) and rearranging

\[ k_0k_1 + k_0k_8 [M] + k_1k_{10}[M] + k_8k_{10}[M]^2 - k_0k_{17}[M_1'] = 0 \]  \hspace{1cm} (66)

\[ [M_1'] = \frac{k_0k_1 + (k_0k_8 + k_1k_{10})[M] + k_8k_{10}[M]^2}{k_0k_{17}} \]  \hspace{1cm} (67)

\[ R_p = k_c [M_1'] \]  \hspace{1cm} (47)

\[ k_0k_1 + k_0(k_0k_8 + k_1k_{10})[M] + k_8k_{10}[M]^2 \]
\[ [M_1'] = \frac{-k_0k_{17}}{k_0k_{17}} \]  \hspace{1cm} (68)
ii) Termination is between $M_2^+$ and $SO_4^{2-}$

$$\frac{d [SO_4^{2-}]}{dt} = 2 k_0[PDS] + k_{10}[M][PDS] - k_8[M][SO_4^{2-}] - k_i[M][PDS] - k_{18}[M_2^+][SO_4^{2-}] = 0 \tag{69}$$

$$k_8[M][SO_4^{2-}] - k_9[M][OH] + k_{10}[M][PDS] - k_{18}[M_2^+][SO_4^{2-}] = 0 \tag{70}$$

Adding Equations (69), (70) and (50)

$$k_0[PDS] + k_{10}[M][PDS] = k_{18}[M_2^+][SO_4^{2-}] \tag{71}$$

From Equation (69)

$$2 k_0[PDS] + k_{10}[M][PDS]$$

$$[SO_4^{2-}] = \frac{k_1 + k_8[M] + k_{18}[M_2^+]}{k_1 + k_8[M] + k_{18}[M_2^+]} \tag{72}$$

Substituting for $[SO_4^{2-}]$ into Equation (71) and rearranging

$$k_0 k_1 + k_0 k_8[M] + k_1 k_{10}[M]^2 + k_8 k_{10}[M]^2 - k_0 k_{18} [M_2^+] = 0 \tag{73}$$

$$[M_2^+] = \frac{k_0 k_1 + (k_0 k_8 + k_1 k_{10}) [M] + k_8 k_{10} [M]^2}{k_0 k_{18}} \tag{74}$$

$$R_p = k_{21} [M_2^+][M] \tag{47}$$
Case III:

Considering initiation by all reactions in step II and termination by step IV (c) (steps IV (a) and (b) are neglected in the scheme)

1) Termination is between \( M_1^- \) and \( \cdot \text{OH} \)

\[
\begin{align*}
\frac{d}{dt} [ \cdot \text{OH}] &= k_1 [\text{SO}_4^{2-}] - k_9[M][\cdot \text{OH}] - k_\theta [M_1^-][\cdot \text{OH}] = 0 \quad (76) \\
\frac{d}{dt} [\text{SO}_4^{2-}] &= 2k_0[\text{PDS}] + k_{10}[M][\text{PDS}] - k_8[M][\text{SO}_4^{2-}] - k_1[\text{SO}_4^{2-}] = 0 \quad (49)
\end{align*}
\]
Adding Equations. (76), (77) and (49),

\[ k_0[PDS] + k_{10}[M][PDS] = k_{19} [M_1' \cdot OH] \]  

(78)

\[ k_1 \left[ SO_4^{2-} \right] \]

\[ [\cdot OH] = \frac{k_1}{k_9[M] + k_{99}[M_1']} \]  

(79)

From Equation (49)

\[ \left[ SO_4^{2-} \right] = \frac{2 k_0[PDS] + k_{10}[M][PDS]}{k_1 + k_8[M]} \]  

(80)

Substituting for \[ [SO_4^{2-}] \] from Equation (80) in Equation (79)

\[ [\cdot OH] = \frac{2 k_0 k_1 [PDS] + k_1 k_4 [M][PDS]}{k_1 k_9[M] + k_9 k_{10}[M]^2 + k_9 k_{19}[M][M_1'] + k_1 k_{99}[M_1']} \]  

(81)

Substituting equation (81) in Equation (78) and rearranging, we get

\[ k_0 k_1 k_9[PDS][M] + k_0 k_8 k_{10}[M]^2[PDS] + k_0 k_8 k_{10}[M_1'][M][PDS] + k_1 k_9 [M]^2[PDS] + k_8 k_9 k_{10}[M]^3[PDS] + k_8 k_9 k_{10}[M_1'][M]^2[PDS] + k_0 k_{99}[M_1'][PDS] = 0 \]  

(82)
\[
[M_1'] = \frac{k_0 k_1 k_9 [M] + (k_0 k_8 k_9 + k_1 k_9 k_{10}) [M]^2 + k_8 k_9 k_{10} [M]^3}{k_0 k_1 k_9 - (k_0 k_8 k_9 [M] + k_8 k_{10} k_9 [M]^2)} \quad (83)
\]

\[
R_p = k_c [M_1'] \quad (47)
\]

\[
R_p = \frac{k_c}{k_{i5}} \cdot \frac{k_0 k_1 k_9 [M] + (k_0 k_8 k_9 + k_1 k_9 k_{10}) [M]^2 + k_8 k_9 k_{10} [M]^3}{k_0 k_1 - (k_0 k_8 [M] + k_8 k_{10} [M]^2)} \quad (84)
\]

ii) Termination is between \( M_2' \) and \( \cdot OH \)

\[
d[\cdot OH] = \frac{k_1 [SO_4^{2-}] - k_9 [M][\cdot OH] - k_{19} [M_2'][\cdot OH]}{dt} = 0 \quad (85)
\]

\[
k_8 [M][SO_4^{2-}] + k_9 [M][\cdot OH] + k_{10} [M][PDS] - k_{90} [M_2'][\cdot OH] = 0 \quad (86)
\]

\[
d[SO_4^{2-}] = \frac{2 k_0 [PDS] + k_{10} [M][PDS] - k_8 [M][SO_4^{2-}] - k_1 [SO_4^{2-}]}{dt} = 0 \quad (49)
\]

Adding Equations (85), (86) and (49)

\[
k_0 [PDS] + k_{10} [M][PDS] = k_{10} [M_2'][\cdot OH] \quad (87)
\]
From Equation (85)

\[
[\cdot \text{OH}] = \frac{k_1 [\text{SO}_4^{2-}]}{k_9[M] - k_{10} [\cdot \text{OH}]} 
\]

(88)

From Equation (49)

\[
[\text{SO}_4^{2-}] = \frac{k_0[\text{PDS}] + k_{10}[M][\text{PDS}]}{k_1 + k_8 [M]} 
\]

(89)

Substituting for \([\text{SO}_4^{2-}]\) in Equation (88)

\[
[\cdot \text{OH}] = \frac{k_0 k_1[\text{PDS}] + k_1 k_{10} [M][\text{PDS}]}{k_1 k_9[M] + k_8 k_9[M]^2 + k_1 k_{110}[M^2] + k_8 k_{110} [M][M^2]} 
\]

(90)

Substituting for \([\cdot \text{OH}]\) in Equation (87) and rearranging, we get

\[
[M_2^+] = \frac{k_0 k_1 k_9[M] + (k_0 k_8 k_9 + k_1 k_{10}) [M]^2 + k_8 k_9 k_{10} [M]^3}{k_0 k_1 k_{110} - (k_0 k_8 k_{110}[M] + k_8 k_{10} k_{110}[M]^2} 
\]

(91)

\[
R_p = k_{21} [M_2^+][M] 
\]

(47)
3.4 GENERAL MECHANISM FOR THE DIVINYL POLYMERIZATION IN THE PRESENCE OF PEROXOMONOSULPHATE AND ULTRASOUND

I) Primary reactions

\[ \frac{k_{21}[M]}{k_{410}} \cdot \frac{k_{0}k_{1}[M]}{k_{0}k_{1} - k_{0}k_{8}[M] + k_{8}k_{10}[M]^{2}} \]  

(92)

a) PMS

\[ \text{SO}_{4}^{-} + \cdot \text{OH} \]

b) \text{SO}_{4}^{-} + \text{H}_{2}\text{O}

\[ \cdot \text{OH} + \text{HSO}_{4}^{-} \]

II) Initiation

a) Initiation by sulphate ion radical

\[ \frac{k_{8}}{M + \text{SO}_{4}^{-} \rightarrow M_{1}'} \]

where \( M_{1}' = \text{SO}_{4}^{-}\text{-CH}_{2}\cdot\text{CH-CH}_{2}\cdot\text{NH-CH}_{2}\cdot\text{CH=CH}_{2} \)

a) Initiation by hydroxyl radical

\[ \frac{k_{9}}{M + \cdot \text{OH} \rightarrow M_{1}''} \]

where \( M_{1}'' = \text{HO-CH}_{2}\cdot\text{CH-CH}_{2}\cdot\text{NH-CH}_{2}\cdot\text{CH=CH}_{2} \)
c) Initiation by the interaction of monomer with peroxomonosulphate

\[ k_{10} \]

\[
M + \text{PMS} \rightarrow M_1^\cdot + \cdot\text{OH} \quad \text{or} \quad (M_1^\cdot + \text{SO}_4^{2-})
\]

III) Propagation

In cyclopolymerization, propagation describes how the radical end of \( M_1^\cdot \) is converted into \( M_2^\cdot \) by cyclization reaction and subsequently to \( M_1^\cdot \) through intermolecular reaction. It is independent of initiation.

\[
k_e
\]

\[
M_1^\cdot \rightarrow M_2^\cdot \quad \text{(intramolecular cyclization)}
\]

\[
k_{21}
\]

\[
M_2^\cdot + M \rightarrow M_1^\cdot \quad \text{(intermolecular cyclization)}
\]

In cyclopolymerization, the rate of change of \( M_1^\cdot \) with time is given by

\[
\frac{d[M_1^\cdot]}{dt} = k_{21}[M_2^\cdot][M] + k_e[M_1^\cdot] \quad \text{(93)}
\]

Under stationary state conditions, the rate of change of \( M_1^\cdot \) with time is very smaller than either of the rate of formation of disappearance of \( M_1^\cdot \), then
Hence, \( k_{21} [M_2^*] [M] = k_c [M_1^*] \) \hspace{1cm} (94)

\( K_{21} [M_2^*] [M] - k_c [M_1^*] = 0 \) \hspace{1cm} (95)

Under conditions where kinetic chain length is sufficiently large, only negligible amount of double bonds will be consumed by reactions other than propagation, the rate of monomer disappearance can be written as

\[
\frac{d [M]}{dt} = R_p = \frac{1}{2} k_c [M_1^*] + \frac{1}{2} k_{21} [M_2^*] [M]
\] \hspace{1cm} (96)

where \( R_p \) is the rate of polymerization. The factor half comes since in each step of double bond consumption corresponds to half the monomer concentration. \(^3\)

\[
\frac{-d [M]}{dt} = R_p = k_{21} [M_2^*] [M] = k_c^* [M_1^*]
\] \hspace{1cm} (97)

Hence, \( R_p^2 = k_{21}^2 [M_2^*]^2 [M]^2 \) \hspace{1cm} (98)

IV) Mutual termination

\[
[M_2^*] + [M_2^*] \xrightarrow{k_i} \text{Polymer}
\]
Under steady state conditions the following rate expressions are derived for various possible polymerization paths.

Considering initiation by all reactions in step II and termination by step IV.

\[
\frac{d[SO_4^{2-}]}{dt} = k_6[PMS] - k_8[M][SO_4^{2-}] - k_1[SO_4^{2-}] + k_{10}[M][PMS] = 0 \quad (99)
\]

\[
\frac{d[\cdot OH]}{dt} = k_6[PMS] + k_1[SO_4^{2-}] - k_9[M][\cdot OH] = 0 \quad (100)
\]

\[
\frac{d[M_2^*]}{dt} = k_8[M][SO_4^{2-}] + k_9[M][\cdot OH] + k_{10}[M][PMS] - k_{14}[M_2^*] = 0 \quad (101)
\]

Adding Equations (99), (100) and (101)

\[
2k_0[PMS] + 2k_{10}[M][PMS] = k_{14}[M_2^*]^2 \quad (102)
\]

\[
[M_2^*]^2 = \left( \frac{2k_6[PMS]}{k_{14}} \right) + \left( \frac{2k_{10}[M][PMS]}{k_{14}} \right) \quad (103)
\]
Knowing \( R_p^2 = k_{21}^2 [M_2^*]^2 [M]^2 \) \( (98) \)

\[
R_p^2 = \frac{2 k_{21}^2 k_0}{K_{14}} + \frac{2 k_{21}^2 k_{10}}{k_{64}} [M]^2 [\text{PMS}] + [M]^3 [\text{PMS}] \quad (104)
\]

Rate of PMS disappearance

\[
- \frac{d [\text{PMS}]}{dt} = k_{6}[\text{PMS}] = k_{10} [M] [\text{PMS}] \quad (105)
\]