CHAPTER IV

RESULTS AND DISCUSSION

The discussion of results relating to the systems studied here are arranged in the following sequence.

4.1.1. PMS-\(H_2A\) redox initiated graft copolymerization of AN onto PET.

4.1.2. PMS-\(H_2A\) redox initiated graft copolymerization of AN onto nylon 6.

4.1.3. PMS-\(H_2A\) redox initiated graft copolymerization of AN onto nylon 66.

4.2.1. PMS-\(H_2A\) redox initiated graft copolymerization of MMA onto nylon 6.

4.2.2. PMS-\(H_2A\) redox initiated graft copolymerization of MMA onto nylon 66.

4.3.1. PDS-\(H_2A\) redox initiated graft copolymerization of MMA onto PET.

4.3.2. PDP-\(H_2A\) redox initiated graft copolymerization of MMA onto PET.

4.3.3. PDP-\(H_2A\) redox initiated graft copolymerization of AN onto PET.
Ascorbic acid ($H_2A$) has been effectively coupled with various oxidising agents to form redox systems capable of initiating vinyl polymerization [59-65]. The use of peroxydisulphate (PDS) as one component in redox pair has been extensively studied [66,67]. Recently, peroxomonosulphate (PMS) finds application for the initiation of vinyl polymerization [68,69]. Graft copolymerization studies involving peroxyosalt as one component of the initiating systems were known earlier [103,106]. Several metal ions like Ce(IV) [97], Mn(IV) [93], Mn(III) redox systems like Ce(IV)-thiourea [91] and peroxydiphosphate (PDP) as lone initiator have been employed earlier for grafting studies. However, the use of peroxomonosulphate (PMS) in the initiation of graft copolymerization is limited to a few studies [112,142].

The present study on Peroxosalt-Ascorbic acid redox initiated polymerization and graft copolymerization is an extension in this direction. The discussion here begins with the first system.

4.1.1.4 Results on PMS-$H_2A$ Redox Initiated Graft Copolymerization of AN onto PET

Effect of time on graft parameters:
Rate of grafting \( (R_g) \), rate of homopolymerization \( (R_h) \), kinetic chain length of the grafted polymer \( (n_g) \), and kinetic chain length of the homopolymer \( (n_h) \) were determined at various time intervals while keeping other experimental conditions as given in Table 1.

Both \( R_g \) and \( R_h \) show initial increase with time and thereafter they fall (Table 1). To follow the kinetics of graft copolymerization in a smooth fashion under steady-state conditions, a reaction time more than four hours was selected for the present study.

The plots \( R_g \) Vs time (Fig. 1A), \( R_h \) Vs time (Fig. 1B), were drawn.

\( n_g \) and \( n_h \) also increase with time initially and then they fall (Table 1). The plots \( n_g \) Vs time (Fig. 1C) and \( n_h \) Vs Time (Fig. 1D) were also drawn.

**Effect of [AN] on Graft Parameters**

Experimental results obtained by changing [AN] in the range from \( 5.724 \times 10^{-2} \text{ mol l}^{-1} \) to \( 71.55 \times 10^{-2} \text{ mol l}^{-1} \) while keeping

\[
\begin{align*}
[PMS] &= 6.00 \times 10^{-3} \text{ mol l}^{-1} & T &= 45^\circ C \\
[H_2A] &= 6.00 \times 10^{-3} \text{ mol l}^{-1} & \text{Wt. of PET} &= 0.20 \text{ g}
\end{align*}
\]
are given in Table 2. A close look at Table 2 clearly indicates that \( R_g \) increases steadily with \([AN]\). In order to obtain the order with respect to AN in the graft copolymerization, a plot of \( \log R_g \) Vs \( \log [AN] \) (Fig. 2A) was drawn. This was found to be a straight line with a slope of unity. This points out the first order dependence of \( R_g \) on \([AN]\). The direct plot \( R_g \) Vs \([AN]\) (Fig. 3A) was therefore drawn and found to be a straight line passing through the origin and thus confirming the order of \( R_g \) with respect to AN. \( R_h \) was also found to increase with \([AN]\) (Table 2). The plot \( \log R_h \) Vs \( \log [AN] \) (Fig. 2B) was also found to be a straight line with a slope of 1.5 suggesting a three halfth order dependence of \( R_h \) on \([AN]\). The direct plot \( R_h \) Vs \([AN]^{1.5}\) (Fig. 3B) was drawn and found to pass through the origin and confirm the 1.5 order dependence of \( R_h \) on \([AN]\).

In an attempt to have a further confirmation, the effect of \([AN]\) on \( R_g \) and \( R_h \) was also studied with a different set of experimental condition such as:

\[
[PMS] = 6.00 \times 10^{-3} \text{ mol l}^{-1} \quad T = 45^\circ\text{C}
\]
\[
[H_2A] = 3.00 \times 10^{-3} \text{ mol l}^{-1} \quad \text{Wt. of PET} = 0.20 \text{ g}
\]

\([AN]\) was varied in the range from \( 2.29 \times 10^{-1} \text{ mol l}^{-1} \) to \( 6.583 \times 10^{-1} \text{ mol l}^{-1} \) and \( R_g \) and \( R_h \) values obtained under such conditions are presented in Table 3.
R was found to increase with [AN]. The plot log $R_g$ vs log [AN] (Fig. 2C) was a straight line with a slope of unity, pointing out a first order dependence of $R_g$ on [AN]. Direct plot $R_g$ vs [AN] (Fig. 3C) was therefore drawn and also found to be a straight line passing through the origin, confirming the order of $R_g$ on AN.

$R_h$ was also found to increase with increase in [AN]. The plot log $R_h$ vs log [AN] (Fig. 2D) was a straight line with a slope of 1.5 pointing out a three half order dependence of $R_h$ on [AN]. The direct plot $R_h$ vs [AN]$^{1.5}$ (Fig. 3D) confirms the 1.5 order dependence of $R_h$ on [AN].

The effect of change in [AN] on graft parameters like % grafting and % efficiency were given in Table 4. It was observed that the % grafting increases steadily with increase in [AN] but the % efficiency show an increasing trend initially and then decreases (Table 4).

The kinetic chain lengths of the grafted backbone ($n_g$) and the homopolymer ($n_h$) were determined separately by viscometric method for the polymer/copolymer formed while changing [AN] are presented in Table 5. Both $n_g$ and $n_h$ were found to increase with [AN] (Table 5). Plots of log $n_g$ vs log [AN] (Fig. 4A) and log $n_h$ vs log [AN] (Fig. 4B) were drawn and found to be straight lines with slopes unity and 0.5 respectively. It was therefore inferred
as first order dependence of \( n_g \) on \([AN]\) and half order on \( n_h \). To ascertain this, direct plots \( n_g \) Vs \([AN]\) (Fig. 4C), and \( n_h \) Vs \([AN]\)^{1/2} (Fig. 4D) were drawn. The linear nature of these plots support these findings.

**Effect of \([AN]\) on Rate of Disappearance of PMS (-R\textsubscript{PMS})**

Rate of disappearance of PMS (-R\textsubscript{PMS}) was followed volumetrically under all the conditions at which graft copolymerizations were carried out. It was found that -R\textsubscript{PMS} values remain almost constant for the conditions mentioned in Tables 2 and 3 (-R\textsubscript{PMS} = 2.54 x 10^{-6} mol l^{-1} sec^{-1}).

The values of \( R_g \) and \( R_h \) obtained by changing \([PMS]\) in the range \((10.0 \times 10^{-4} - 80.0 \times 10^{-4})\) mol l^{-1} while keeping

\[
[AN] = 28.62 \times 10^{-2} \text{ mol l}^{-1} \quad T = 45^\circ\text{C} \\
[H_2A] = 6.00 \times 10^{-3} \text{ mol l}^{-1} \quad \text{Wt. of PET} = 0.20 \text{ g}
\]

are given in Table 6. A glance at Table 6 reveals that both \( R_g \) and \( R_h \) increase with a change in \([PMS]\). The plot log \( R_g \) Vs log \([PMS]\) (Fig. 5A) was found to be straight line with a slope of 0.5 indicating square root order with respect to PMS on \( R_g \). Direct plot \( R_g \) Vs \([PMS]\)^{1/2} (Fig. 6A) was drawn and found to be a straight line passing through the origin with negligible intercept, confirming the 0.5 order of \( R_g \) on PMS.
R. was also found to increase with increase in [PMS]. The plot log $R$ Vs log [PMS] (Fig. 5B) was a straight line with a slope of 0.5, indicating half order dependence of $R$ on PMS. The direct plot $R$ Vs $[\text{PMS}]^{1/2}$ (Fig. 6B) was also drawn and found to support the order 0.5 with respect to $R$ on PMS.

In a separate set of experimental conditions, different from the previous one, the effect of [PMS] on $R_g$ and $R_h$ was studied (Table 7).

$[\text{AN}] = 22.9 \times 10^{-2}$ mol l$^{-1}$ \hspace{1cm} $T = 45^\circ$C

$[\text{H}_2\text{A}] = 3.00 \times 10^{-3}$ mol l$^{-1}$ \hspace{1cm} Wt. of PET = 0.20 g

Under the above conditions, [PMS] was varied in the range $(10.0 \times 10^{-4}$ to $66.0 \times 10^{-8})$ mol l$^{-1}$ and $R_g$ and $R_h$ values obtained were presented in Table 7.

$R_g$ was found to increase with increase in [PMS]. Plot of log $R_g$ Vs log [PMS] (Fig. 5C) was a straight line with a slope of 0.5 indicating half order dependence of $R_g$ on PMS. Direct plot $R_g$ Vs $[\text{PMS}]^{1/2}$ (Fig. 6C) was also drawn and found to be a straight line passing through the origin, thus confirming the 0.5 order of $R_g$ on PMS.

$R_h$ was also found to increase with [PMS]. A plot of $R_h$ Vs log [PMS] (Fig. 5D) gave a slope of 0.5, showing
showing half order of $R_h$ on PMS. This was confirmed by drawing a plot $R_h$ Vs $(PMS)^{1/2}$ (Fig. 6D), indicating half order of $R_h$ on PMS.

Table 8 gives the % grafting and % efficiency obtained during graft copolymerizations for the change in [PMS]. It was observed that both % grafting and % efficiency steadily increase with increase in [PMS] (Table 8).

$n_g$ and $n_h$ were determined separately for the polymer/copolymer formed while varying the [PMS] and the values were presented in Table 9. It was observed that both $n_g$ and $n_h$ decrease with [PMS]. A plot of log $n_g$ Vs log [PMS] (Fig. 8A) was found to be a straight line with a slope of negative 0.5 indicating inverse square root order of $n_g$ on PMS. Direct plot $n_g$ Vs [PMS]$^{-1/2}$ (Fig. 8C) was also drawn and found to be a straight line passing through the origin with negligible intercept, confirming the order $-0.5$ of $n_g$ on PMS.

Plot of log $n_h$ Vs log [PMS] (Fig. 8B) was drawn and found to give a slope of negative 0.5, inverse square root order of $n_h$ on PMS. Direct plot $n_h$ Vs [PMS]$^{-1/2}$ (Fig. 8D) confirms the order negative 0.5 of $n_h$ with respect to PMS.
Effect of [PMS] on Rate of Disappearance of PMS (-R_PMS)

Rate of disappearance of PMS (-R_PMS) was followed volumetrically under all the experimental conditions mentioned in Tables 6 and 7 at which graft copolymerization were carried out and found that -R_PMS values increase with PMS. A plot of log (-R_PMS) Vs log [PMS] (Fig. 7A) was a straight line with a slope of unity suggesting first order dependence of -R_PMS on PMS. The direct plot -R_PMS Vs [PMS] (Fig. 7B) was also drawn and found to confirm the first order with respect to PMS.

Under a set of different experimental conditions given in Table 7, plot of log (-R_PMS) Vs log [PMS] (Fig. 7C) was drawn and found to be a straight line with a slope of unity indicating a first order on PMS. The direct plot -R_PMS Vs [PMS] (Fig. 7D) was also drawn and found to pass through the origin with almost negligible intercept confirming the first order with respect to PMS.

Effect of [H_2A] on Craft Parameters

R_g and R_h values obtained by varying the [H_2A] in the range (10.0 x 10^{-2} - 80.0 x 10^{-2}) mol l^{-1} while keeping

\[ [AN] = 28.62 \times 10^{-2} \text{ mol l}^{-1} \quad T = 45^\circ C \]
\[ [PMS] = 6.00 \times 10^{-3} \text{ mol l}^{-1} \quad \text{Wt. of PET} = 0.20 \text{ g} \]

are given in Table 10.
Both \( R_g \) and \( R_h \) increase steadily with increase in \([H_2A]\) (Table 10).

\( R_g \) was found to increase with \([H_2A]\). Plot of \( \log R_g \) Vs \( \log [H_2A] \) (Fig. 9A) was a straight line with a slope of 0.5 suggesting a half order dependence of \( R_g \) on \( H_2A \). Direct plot \( R_g \) Vs \( [H_2A]^{1/2} \) (Fig. 10A) was also drawn and found to be a straight line passing through the origin with almost negligible intercept with a slope of 0.5 indicating half order on \( H_2A \).

\( R_h \) was also found to increase with \([H_2A]\). A plot of \( \log R_h \) Vs \( \log [H_2A] \) (Fig. 9B) was found to be a straight line with a slope of 0.5 pointing out a half order of \( R_h \) on \( H_2A \). The direct plot \( R_h \) Vs \( [H_2A]^{1/2} \) (Fig. 10B) was also drawn and found to confirm the order 0.5 of \( R_h \) on \( H_2A \).

The above order dependences was further confirmed by performing the experiments with a set of different experimental conditions such as

\[
[AN] = 22.9 \times 10^{-2} \text{ mol l}^{-1} \quad T = 45^\circ\text{C}
\]
\[
[PMS] = 8.00 \times 10^{-3} \text{ mol l}^{-1} \quad \text{Wt. of PET} = 0.20 \text{ g}
\]

\( R_g \) and \( R_h \) were determined by changing \([H_2A]\) in the range \((10.0 \times 10^{-6} - 66.0 \times 10^{-4}) \text{ mol l}^{-1}\) and presented in Table 11. Both \( R_g \) and \( R_h \) values were found to increase with \([H_2A]\).
A plot of log $R_g$ Vs log $[H_2A]$ (Fig. 9C) was drawn giving a slope of 0.5, suggesting half order of $R_g$ on $H_2A$. Direct plot $R_g$ Vs $[H_2A]^{1/2}$ (Fig. 10C) was also drawn in order to confirm the 0.5 order dependence of $R_g$ on $H_2A$.

Plot of log $R_h$ Vs log $[H_2A]$ (Fig. 9D) was a straight line with a slope of 0.5 indicating half order of $R_h$ on $H_2A$. Direct plot $R_h$ Vs $[H_2A]^{1/2}$ (Fig. 10D) also gave a slope of 0.5 suggesting half order with respect to $H_2A$.

The values of graft parameters like % grafting and % efficiency while changing $H_2A$ are given in Table 12. It was observed that both % grafting and % efficiency were found to have increasing trend with $[H_2A]$ (Table 12).

$n_g$ and $n_h$ values were determined separately by viscometric method for the polymer/copolymer formed while changing $[H_2A]$ in the range $(10.0 \times 10^{-6} - 60.0 \times 10^{-6})$ mol l$^{-1}$ (Table 13). It was observed that both $n_g$ and $n_h$ decrease with increase in $[H_2A]$.

A plot of log $n_g$ Vs log $[H_2A]$ (Fig. 11A) was found to be a straight line with a slope of $-0.5$ indicating inverse square root order of $n_g$ on $H_2A$. Direct plot $n_g$ Vs $[H_2A]^{-1/2}$ (Fig. 11C) was also drawn to support $-0.5$ order dependence with respect to $H_2A$. 

Plot of log $n_h$ Vs log $[H_2A]$ (Fig. 11B) was drawn and gave a slope of minus 0.5 suggesting inverse square root dependence of $n_h$ on $H_2A$. The direct plot $n_h$ Vs $[H_2A]^{-1/2}$ (Fig. 11D) was a straight line passing through the origin with a slope of -0.5 pointing out inverse square root order with respect to $H_2A$.

Effect of [PMS] on -$R_{PMS}$

$-R_{PMS}$ was found to be almost constant ($2.54 \times 10^{-6}$ mol l$^{-1}$ sec$^{-1}$) while changing $[H_2A]$ for the conditions mentioned in Table 10. The change in $[H_2A]$ in a different experimental condition as given in Table 11 also shows the same behaviour. The constant value, however, comes as $3.45 \times 10^{-6}$ mol l$^{-1}$ sec$^{-1}$.

Effect of [PET] on Graft Parameters

The amount of backbone material was varied from 0.05 g to 0.30 g under the experimental conditions as:

$[AN] = 22.9 \times 10^{-2}$ mol l$^{-1}$  \hspace{1cm} $[H_2A] = 4.00 \times 10^{-3}$ mol l$^{-1}$

$[PMS] = 6.00 \times 10^{-3}$ mol l$^{-1}$  \hspace{1cm} $T = 45^\circ C$

and the rate parameters were found out (Table 14). It was observed that both $R_g$ and $R_h$ values increase steadily with increase in the backbone material. A plot of log $R_g$ Vs log [Wt. of PET] (Fig. 12A) gave a slope of 0.5 suggesting half
order dependence of $R_g$ on PET. Direct plot $R_g$ Vs [Wt. of PET]$^{1/2}$ (Fig. 13A) was also drawn and found to be a straight line with a slope of 0.5 indicating half order on PET.

Log $R_h$ Vs log [Wt. of PET] (Fig. 12B) was a straight line with a slope of 0.5 indicating half order dependence on PET. The direct plot $R_h$ Vs [Wt. of PET]$^{1/2}$ (Fig. 13B) was also a straight line passing through the origin with negligible intercept and with a slope of 0.5 suggesting half order on PET.

$R_g$ and $R_h$ values were determined under different experimental conditions as

$$[AN] = 28.62 \times 10^{-2} \text{ mol l}^{-1}$$
$$[H_2A] = 6.00 \times 10^{-3} \text{ mol l}^{-1}$$
$$[PMS] = 6.00 \times 10^{-3} \text{ mol l}^{-1}$$
$$T = 45^\circ C$$

are given in Table 15 with a change in the backbone amount from 0.05 g to 0.35 g.

It was observed that both $R_g$ and $R_h$ increase steadily with the increase in backbone amount.

Log $R_g$ Vs log [Wt. of PET] (Fig. 12C) plot was drawn and found to be a straight line with a slope of 0.5 suggesting half order on PET. The direct plot $R_g$ Vs [Wt. of PET]$^{1/2}$ (Fig. 13C) was also a straight line with a slope of 0.5 indicating half order dependence of $R_g$ on PET.
Plot of $\log R_h^1/Vs \log [\text{Wt. of PET}]$ (Fig. 12D) was a straight line giving a slope of 0.5 indicating half order on PET. Direct plot $R_h^1 Vs [\text{Wt. of PET}]^{1/2}$ (Fig. 13D) was also drawn and found to be a straight line passing through the origin with a slope of 0.5 pointing out a half order on PET.

The % grafting and % efficiency values obtained with a change in backbone amount under two different experimental conditions are given in Table 16. It was observed that % grafting increases initially and thus decrease (Table 16). On the other hand, % efficiency showed an increasing trend with the backbone material.

$n_g$ and $n_h$ values were determined separately by viscometric method under the experimental conditions:

\[
[\text{AN}] = 28.62 \times 10^{-2} \text{ mol l}^{-1} \quad [\text{H}_2\text{A}] = 6.00 \times 10^{-3} \text{ mol l}^{-1} \\
[\text{PMS}] = 6.00 \times 10^{-3} \text{ mol l}^{-1} \quad T = 45^\circ\text{C}
\]

are presented in Table 17 with a change in the backbone material from 0.05 g to 0.35 g. It was observed that both $n_g$ and $n_h$ decrease with PET.

A plot of $\log n_g/Vs \log [\text{Wt. of PET}]$ (Fig. 14A) was drawn and found to give a slope of negative 0.5 indicating inverse square root order dependence of $n_g$ on PET. The direct plot $n_g Vs [\text{Wt. of PET}]^{-1/2}$ (Fig. 14C)
was a straight line passing through the origin with negligible intercept and a slope of negative 0.5 pointing out inverse square root order dependence of \(n_g\) on PET.

Plot of \(\log n_h\) Vs \(\log [\text{Wt. of PET}]\) (Fig. 14B) was found to be a straight line with a slope of -0.5 suggesting minus half order of \(n_h\) on the backbone material. The direct plot \(n_h\) Vs \([\text{Wt. of PET}]^{-1/2}\) (Fig. 14D) also confirms the order dependence of \(n_h\) on PET.

Effect of the Amount of PET on Rate of Disappearance of PMS \((-R_{PMS})\)

\(-R_{PMS}\) was found to be almost constant \((2.54 \times 10^{-6}\) mol l\(^{-1}\) sec\(^{-1}\)) while varying the backbone amount for the conditions mentioned in Tables 14 and 15.

Effect of Temperature on Graft Parameters

\(R_g\) and \(R_h\) values obtained by changing the temperature from 35\(^\circ\)C to 50\(^\circ\)C under the experimental conditions such as:

\[
\begin{align*}
[\text{AN}] &= 28.62 \times 10^{-2} \text{ mol l}^{-1} \\
[H_2A] &= 4.00 \times 10^{-3} \text{ mol l}^{-1} \\
[\text{PMS}] &= 4.00 \times 10^{-3} \text{ mol l}^{-1} \\
\text{Wt. of PET} &= 0.20 \text{ g}
\end{align*}
\]

are presented in Table 18. It was observed that both \(R_g\) and \(R_h\) increase initially up to 45\(^\circ\)C and then they fall (Table 18). Arrhenius plot of \(\log R_g\) Vs 1 (Fig. 15A) was
drawn and energy of activation $E_a$ was determined and found to be 3.67 Kcal/mol. Log $R_h$ Vs 1 ($\text{Fig. 15B}$) plot was also drawn and the energy of activation ($E_a$) for homopolymer was calculated by 2.86 Kcal/mol.

The other graft parameters such as % grafting and % efficiency under the conditions mentioned in Table 19 with increase in temperature are given in Table 19. It was observed that both the values initially increase upto 45°C and then they decrease.

$n_g$ and $n_h$ values were determined separately under the experimental conditions as:

$[\text{AN}] = 28.62 \times 10^{-2}$ mol l$^{-1}$  \quad $[\text{H}_2\text{A}] = 4.00 \times 10^{-3}$ mol l$^{-1}$  \\
$[\text{PMS}] = 4.00 \times 10^{-3}$ mol l$^{-1}$  \quad \text{Wt. of PET} = 0.20 g

are listed in Table 19. It was found that $n_g$ values increase with temperature. Arrhenius plot of log $n_g$ Vs 1 ($\text{Fig. 15C}$) was drawn and the energy of activation $E_a$ was calculated to be 15.9 Kcal/mol. $n_h$ values also found to increase steadily with increase in temperature. Arrhenius plot of log $n_h$ Vs 1 ($\text{Fig. 15D}$) was drawn and the energy of activation $E_a$ was calculated to be 16.3 Kcal/mol.

**Effect of Temperature on $-R_PMS$**
-R_pms was found to be nearly constant \(2.54 \times 10^{-6}\) mol \(^{-1}\) sec\(^{-1}\) while varying the temperature for the conditions given in Table 18.

4.1.1.2 Discussion on Results

The above experimental results obtained during graft copolymerization studies can be adequately explained only by knowing the probable reaction sequences for the system.

The oxygen-oxygen single bond in peroxides is weak with the bond dissociation energy ranging from 210 KJ mol\(^{-1}\) for HOOH to 100 KJ mol\(^{-1}\) for compounds barely stable at room temperature. Presumably as a consequence of the weakness of this bond, the first step in photolysis of symmetrical peroxides (eg: HOOH, \(S_2O_8^{2-}\), ROOR) is the homolytic scission.

\[
\text{XOOX} + hv \rightarrow 2 \times \cdot \\
\text{XOOX}^\prime + hv \rightarrow \text{X}^\prime + \text{X}^\prime \cdot \\
\text{HOOSO}_3^- \rightarrow \cdot \text{OH} + \text{SO}_4^{2-}
\]

It is assumed that the same type of scission pertains to unsymmetrical peroxides also.
It was known that in all oxidation studies involving H₂A the reaction proceeded through a free radical pathway with the formation of ascorbate anion free radical (A⁻) [56-64]. The intermediary of A⁻ was also confirmed by ESR measurements [65].

Polymerization of AN by PDP-H₂A system, polymerization of acrylamide, methacrylamide and MMA by PDS-H₂A system were reported to be initiated by A⁻, produced during the interaction between oxidant and reductant [54,55].

A similar type of initiation can therefore be thought of for the present graft copolymerization using PMS-H₂A system (PMS) HSO₅⁻ + H₂A → SO₄⁻ + OH⁻ + 2H⁺ + A⁻.

A likely additional possibility is the step

SO₄⁻ + H₂O → HSO₄⁻ + OH⁻ [189]

The OH can further interact with H₂A to generate A⁻ as

H₂A + OH⁻ → A⁻ + H₂O + H⁺ [190]

Based on the above consideration, in the present system initiation by A⁻ is taken as predominant, though OH and SO₄⁻ are produced during the interaction between PMS and H₂A.
In the polymerization of AN by PDS-H$_2$A system, Ariff and coworkers [67] proposed a complex formation between PDS and H$_2$A.

$$\text{PDS} + \text{H}_2\text{A} \underset{\text{complex}}{\xrightarrow{\text{S}_2\text{O}_8^{2-}}} \text{H}_2\text{A}$$

A transfer of A$^\cdot$ to monomer during interaction between PDS-H$_2$A complex and monomer was reported to be the initiation step in such a study.

A similar complexation can be considered for the present case with PMS as oxidant.

$$\text{H}_2\text{A} + \text{(PMS)} \underset{\text{complex}}{\xrightarrow{\text{HSO}_5^-}} \text{HSO}_5^- - \text{H}_2\text{A}$$

The present work relates to the graft copolymerization of AN onto PET. Hence the role of the backbone [PET] must also be taken into consideration in the initiation step. The fact that observed $R_g$ showed square root order dependence on the backbone gives an indication of such a probable involvement.

Three probable grafting initiation routes can then be envisaged.

In the first one of grafting initiation, the A$^\cdot$ produced by the decomposition of H$_2$A-PMS complex can interact with the backbone and generate a radical site in the backbone.
where PET' is produced by the abstraction of a proton from the -CH₂ group in the main chain of the backbone by A⁺

\[
\text{PET}' = \text{PET} + H^+ \rightarrow \text{PET} + \text{other products}
\]

Similar proton abstraction reaction was reported to cause initiation of graft copolymerization onto nylon 6/nylon 66 from the group NH [91]

\[
\text{NH} + \text{R} \rightarrow \text{N} + \text{RH}
\]

Similar initiation was proposed in earlier graft copolymerization studies by Pradhan and coworkers [91] in the graft copolymerization of MMA onto nylon 6 with tetravalent cerium-thiourea complex.

The second possible initiation path may be of the following type.

\[
\text{PET} + \text{H}_2\text{A} - \text{PMS} \rightarrow \text{PET} + \text{other products}
\]

The third initiation possibility may involve the following sequence:

\[
\text{H}_2\text{A} - \text{PMS} + \text{PET} \rightarrow \text{H}_2\text{A} - \text{PMS} - \text{PET}
\]
Complexation involving backbone prior to initiation was considered by Nayak and coworkers [97] in the graft copolymerization of MMA onto nylon 6 by hexavalent chromium ion, Gupta and coworkers [190] in the grafting of N,N'-methylenediacrylamide onto silk using vanadyl acetate complex, Pradhan and coworkers [191], in the graft copolymerization of MMA onto nylon 6 using Fe²⁺-thiourea redox system, and by Sahoo and coworkers [192] in the grafting of acrylamide onto cotton using potassium permonosulphate-Co(II) redox system.

Propagation of graft copolymerization can then take place by the successive addition of monomer units to $\text{PETM}^*$:

$$
\text{PETM}^* + \text{M} \rightarrow \text{PETM}^*_1
$$

$$
\text{PETM}^*_{n-1} + \text{M} \rightarrow \text{PETM}^*_n
$$

The growing grafted chain may be terminated by any one of the following termination reactions.

$$
\text{PETM}^*_n + \text{A}^* \rightarrow \text{graft copolymer}
$$

$$
\text{PETM}^*_n + \text{PETM}^*_n \rightarrow \text{graft copolymer}
$$
Various Possible Reaction Schemes

Taking into account of the above said initiation, propagation and termination reactions, one can arrive at various possible reaction schemes. Out of the various possible schemes, the most probable scheme can be selected as the one which agrees with all experimental observations.

The following schemes can thus be thought of for the critical analysis to fix up the most probable one.

Schemes I, II and III consider initiation by the first initiation route with production of $A^*$ and its consequent initiation steps and three different termination possibilities.

Scheme I

Initiation:

\[
\begin{align*}
H_2A + PMS & \xrightarrow{K_1} H_2A - PMS \\
\text{Complex 1, } C_1 \\
C_1 & \xrightarrow{K_1} A^* + H_2O + H^+ + SO_4^- 
\end{align*}
\]
Propagation:

\[ \text{SO}_4^2- + H_2O \xrightarrow{k_2} \cdot \text{OH} + \text{HSO}_4^- \]

\[ \cdot \text{OH} + H^+ \xrightarrow{k_3} \text{A}^+ + H_2O + H^+ \]

\[ \text{A}^+ + \text{PET} \xrightarrow{k_4} \text{PET}^+ + \text{HA}^- \]

\[ \text{PET}^+ + M \xrightarrow{k_5} \text{PETM}^+ \]

Termination:

\[ \text{PETM}^+ + \text{PETM}^+ \xrightarrow{k_6} \text{Graft copolymer} \]

Scheme II

Initiation:

As in Scheme I.

Propagation:

As in Scheme I.

Termination:

\[ \text{PETM}^+_n + \text{PETM}^+_n \xrightarrow{k_{T1}} \text{Graft copolymer} \]
Scheme III

Initiation:

As in Scheme I.

Propagation:

As in Scheme I.

Termination:

\[ \text{PETM}^* + C_1 \xrightarrow{k_{12}} \text{Graft copolymer} + \text{SO}_4^2 - + \text{H}_2\text{O} + \text{H}^+ \]

The formed \( \text{SO}_4^2 - \) during termination by transfer can reinitiate grafting reaction.

Reinitiation:

\[ \text{SO}_4^2 - + \text{H}_2\text{O} \xrightarrow{k_2} \cdot \text{OH} + \text{HSO}_4^- \]
\[ \cdot \text{OH} + \text{H}_2\text{A} \xrightarrow{k_3} \text{A}^+ + \text{H}_2\text{O} + \text{H}^+ \]
\[ \text{A}^+ + \text{PET} \xrightarrow{k_4} \text{PET}^* + \text{AA}^- \]
\[ \text{PET}^* + \text{M} \xrightarrow{k_5} \text{PETM}^* \]

In schemes IV, V and VI, direct interaction between \( \text{H}_2\text{A}-\text{PMS} \) complex and backbone is assumed. Hence with the relevant termination reactions, schemes IV, V and VI are constituted.
Initiation:

\[
\begin{align*}
H_2A + \text{PMS} & \overset{k_1}{\underset{K_5}{\rightleftharpoons}} \text{Complex}_1 \text{C}_1 \\
\text{PET} + \text{C}_1 & \overset{k_6}{\rightarrow} \text{PET}^* + \text{SO}_4^- + \text{HA}^- + \text{H}_2\text{O} + \text{H}^+
\end{align*}
\]
\[
\begin{align*}
\text{SO}_4^+ + \text{H}_2\text{O} & \overset{k_2}{\rightarrow} \text{OH}^- + \text{HSO}_4^- \\
\text{OH} + \text{H}_2\text{A} & \overset{k_3}{\rightarrow} \text{H}_2\text{O} + \text{A}^+ + \text{H}^+ \\
\text{PET}^* + \text{M} & \overset{k_5}{\rightarrow} \text{PETM}^*
\end{align*}
\]
\[
\begin{align*}
\text{A}^+ + \text{C}_1 & \overset{k_7}{\rightarrow} \text{SO}_4^- + 2\text{HA}^- + \text{H}_2\text{O} + \text{H}^+
\end{align*}
\]

Propagation:

As in Scheme I.

Termination:

As in Scheme I.

Scheme V:

Initiation:

As in Scheme IV.

Propagation:

As in Scheme I.

Termination:

As in Scheme II.
Scheme IV

Initiation:

As in Scheme IV.

Propagation:

As in Scheme I.

Termination:

As in Scheme III.

Reinitiation:

\[
SO_4^{2-} + H_2O \xrightarrow{k_2} OH + HSO_4^-
\]

\[
\cdot OH + H_2A \xrightarrow{k_3} A^+ + H_2O + H^+
\]

\[
A^+ + PET \xrightarrow{k_4} PET^* + HA^-
\]

\[
PET^* + M \xrightarrow{k_5} PETM^*
\]

In the Schemes VII, VIII, IX and X, two complexes, one between \(H_2A\) and PMS and another between \(H_2A\)-PMS and backbone [PET] are considered. Hence, the Schemes VII, VIII, IX and X are formulated using initiation through reactions involving these two complexes and termination by different possibilities.
Scheme VII

Initiation:

\[ \text{PMS} + H_2A \xrightarrow{K_1} \text{Complex}_1 \ C_1 \]

\[ C_1 + \text{PET} \xrightarrow{K_2} \text{PMS} - H_2A - \text{PET} \]

\[ \text{Complex}_2 \ C_2 \]

\[ C_2 \xrightarrow{k_8} \text{PET}^+ + H_2O + H^+ + SO_4^{2-} \]

\[ SO_4^{2-} + H_2O \xrightarrow{k_2} OH^- + HSO_4^- \]

\[ OH^- + H_2A \xrightarrow{k_3} A^+ + H_2O + H^+ \]

\[ \text{PET}^+ + M \xrightarrow{k_5} \text{PETM}^+ \]

\[ C_1 + A^+ \xrightarrow{k_7} SO_4^{2-} + 2HA^- + H_2O + H^+ \]

Propagation:

As in Scheme I.

Termination:

As in Scheme I.

Scheme VIII

Initiation:

As in Scheme VII.

Propagation:

As in Scheme I.
Termination:

As in Scheme II.

Scheme IX

Initiation:

As in Scheme VII.

Propagation:

As in Scheme I.

Termination:

As in Scheme III.

Reinitiation:

\[ \text{SO}_4^\cdot + \text{H}_2\text{O} \xrightarrow{k_2} \text{OH} + \text{HSO}_4^- \]
\[ \text{OH} + \text{H}_2\text{A} \xrightarrow{k_3} \text{A}^\cdot + \text{H}_2\text{O} + \text{H}^+ \]
\[ \text{A}^\cdot + \text{PET} \xrightarrow{k_4} \text{PET}^\cdot + \text{HA}^- \]
\[ \text{PET}^\cdot + \text{M} \xrightarrow{k_5} \text{PETM}^\cdot \]

Scheme X

Initiation:

As in Scheme VII.
Propagation:

As in Scheme 1.

Termination:

\[ \text{PETM}^n + C_2 \xrightarrow{k_{13}} \text{graft copolymer} + \]
\[ \text{PET'} + \text{SO}_4^2 + \text{HA}^{-} + \text{H}_2\text{O} + \text{H}^+ \]

Reinitiation:

\[ \text{SO}_4^2 + \text{H}_2\text{O} \xrightarrow{k_2} \text{OH} + \text{HSO}_4^- \]
\[ \text{OH} + \text{HA} \xrightarrow{k_3} \text{H}_2\text{O} + \text{A}^- + \text{H}^+ \]
\[ \text{A}^- + \text{PET} \xrightarrow{k_4} \text{PET}' + \text{HA}^- \]
\[ \text{PET}' + M \xrightarrow{k_5} \text{PETM}' \]

4.1.1.4. Selection of Most Probable Scheme

From the above proposed ten schemes consisting of different initiation and termination, one can derive expression for the rate of graft polymerization under stationary state conditions.

The scheme which can suitably explain all the experimental observations relating to grafting and homopolymerization in a concurrent manner would be selected as the most probable one. Hence, all the schemes will be analysed
for explaining the results obtained through $R_g$, $R_h$, $n_g$ and $n_h$.

The observed results in the graft copolymerization studies clearly indicated that $R_g$ showed square root order dependences on [PMS], [H$_2$A], PET and first order dependence on [AN]. This obviously suggested a mutual type termination operating in the graft copolymerization [190,193-196]. Hence, scheme I with a linear type termination between the growing grafted macroradical and A$^-$ may not be suitable to explain the experimental observations.

Scheme III with termination by a complex may not also be suitable to explain the experimental observation because if a derivation for rate expression to $R_g$ is attempted, it would not give half order dependences on PET, [PMS], [H$_2$A] in a combined way. Hence, the rate expressions for $R_g$ for Scheme II is derived to compare with the experimental results.

Applying steadystate approximations to all radicals,

$$\frac{d[SO^+_4]}{dt} = k_1 K_1 [PMS] [H_2A] - k_2 [SO^+_4] = 0 \quad E_1$$

$$\frac{d[A^-]}{dt} = k_1 K_1 [PMS] [H_2A] + k_3 [OH] [H_2A] - k_4 [PET] [A^-] \quad E_2$$
\[
\text{d}[\text{OH}] = k_2 [\text{SO}_4^2] - k_3 [\text{OH}][\text{H}_2\text{A}] = 0 \quad E_3
\]

\[
\text{d}[\text{PET}^*] = k_4 [\text{PET}][\text{A}^+] - k_5 [\text{PET}^*][\text{M}] = 0 \quad E_4
\]

\[
\text{d}[\text{PET} M^*] = k_5 [\text{PET}^*][\text{M}] - k_{t1} [\text{PET} M^*]^2 = 0 \quad E_5
\]

Adding \( E_1, E_2, E_3, E_4 \) and \( E_5 \)

\[
2 k_1 k_4 [\text{PMS}][\text{H}_2\text{A}] = k_{t1} [\text{PET} M^*]^2 \quad E_6
\]

\[
[\text{PET} M^*]_{\text{n}}^{1/2} = \left( \frac{2 k_1 k_4}{k_{t1}} \right)^{1/2} [\text{PMS}]^{1/2} [\text{H}_2\text{A}]^{1/2} \quad E_7
\]

Knowing \( R_g = k_9 [\text{PET} M^*][\text{M}] \quad E_8 \)

\[
R_g = k_9 \left( \frac{2 k_1 k_4}{k_{t1}} \right)^{1/2} [\text{M}] [\text{PMS}]^{1/2} [\text{H}_2\text{A}]^{1/2} \quad E_9
\]

In the above expression for \( R_g \), though square root order dependences on [PMS] and [H\text{\text}_2\text{\text}A], and first were found power dependence on [M] the experimentally observed square root order dependence on PET (Fig. 13A) the backbone could not be seen. Hence, Scheme III may not be considered suitable to explain the experimental observations here.
Further, for the same Scheme III, an expression for $n_g$ can also be derived.

$$\boxed{\Sigma g = n_g = \frac{\text{rate of grafting}}{\text{rate of initiation}} = \frac{k_g [\text{PET M*}][M]}{k_5 [\text{PET*}][M]} \quad E_{10}$$

$$= \frac{k_g [\text{PET M*}][M]}{k_{t1} [\text{PET M*}]^2} \quad E_{11}$$

Substituting for $[\text{PET M*}]$ from $E_7$,

$$n_g = \frac{k_g [M]}{k_{t1}^{1/2} (2k_1 K_1)^{1/2} [\text{PMS}]^{1/2} [\text{H}_2A]^{1/2}} \quad E_{12}$$

$E_{12}$ accounts for the experimentally observed inverse square root dependences on $[\text{PMS}]$ (Fig. 8C), $[\text{H}_2A]$ (Fig. 11C) and first order dependence on $[\text{AN}]$ (Fig. 4C). However, it fails to account for the observed inverse square root order dependence on $\text{PET}$ (Fig. 14C). Hence, scheme III may not be suitable to explain the observations.

With the proposed possible primary reactions and grafting initiation as in Scheme II, it would be possible to think about the initiation of homopolymerization in a concurrent way as follows:
Initiation:

\[ \begin{align*}
H_2A + PMS & \overset{K_1}{\longrightarrow} H_2A - PMS \\
\text{Complex 1, C}_1 & \\
C_1 & \overset{k_1}{\longrightarrow} A^+ + H_2O + H^+ + SO_4^- \\
SO_4^- + H_2O & \overset{k_2}{\longrightarrow} OH^- + HSO_4^- \\
OH^- + H_2A & \overset{k_3}{\longrightarrow} A^+ + H_2O + H^+ \\
C_1 + M & \overset{k_9}{\longrightarrow} M_1^+ + H_2O + H^+ + SO_4^- \\
M + A^+ & \overset{k_{10}}{\longrightarrow} M_1^-
\end{align*} \]

Propagation of the homopolymerization can then occur by

\[ M_1^+ + M \longrightarrow M_2^+ \]
\[ M_{n-1}^+ + M \longrightarrow M_n^+ \]

The observed results on homopolymerization such as three half order dependence on [AN] (Fig. 3B), and half order dependences on [PMS] (Fig. 6B), \([H_2A]\) (Fig. 10B), and [PET] (Fig. 13B) favours mutual type termination.

Hence, termination for the homopolymerization may be

\[ M_n^+ + M_n^- \overset{k_4}{\longrightarrow} \text{homopolymer} \]
If a derivation for \( R_h \) for the above possible reaction in the homopolymerization is attempted, one can see such an expression would consist of square root order dependences on PMS and \( H_2A \) only but not on \([PET]\). Hence, the initiation reactions in Scheme II cannot explain all the experimental observations related to homopolymerization.

The experimentally observed inverse square root order dependences of \([PET]\) (Fig. 14D) on \( n_h \) could not also be accounted for through Scheme II.

Schemes IV, V and VI consider initiation by the direct interaction through the Complex \( C_1 \) and the backbone. Hereagain, in Schemes IV and VI, a linear type termination was proposed. For both the Schemes, if an expression for rate expressions for \( R_g \) was derived, those would not contain any square root dependence terms on \([PMS]\), \([H_2A]\) and \([PET]\). On the other hand, it is worthwhile to derive expression for \( R_g \) for Scheme V as it considers mutual termination.

Applying steadystate approximations to all radicals,

\[
\frac{d[SO^\cdot]}{dt} = k_6 K_1 [PMS] [H_2A] [PET] - k_2 [SO^\cdot] + k_7 K_1 [PMS] [H_2A] [A^\cdot] = 0 \quad \text{(E13)}
\]

\[
\frac{d[OH]}{dt} = k_2 [SO^\cdot] - k_3 [OH] [H_2A] = 0 \quad \text{(E3)}
\]
\[
\frac{d[A^-]}{dt} = k_3 \text{[OH]} [H_2A] - k_7 K_p [PMS] [H_2A] [A^+] = 0 \quad E_{14}
\]

\[
\frac{d(PET^+)}{dt} = k_6 K_p [PMS] [H_2A] [PET^] - k_5 [PET^+] [M] = 0 \quad E_{15}
\]

\[
\frac{d(PET M^*)}{dt} = k_5 [PET^+] [M] - k_{t1} [PET M_n^*] = 0 \quad E_5
\]

Adding, \(E_{13}, E_3, E_{14}, E_{15}, E_5\), and rearranging,

\[
\left( \frac{2 k_6 K_p}{k_{t1}} \right)^{1/2} [PMS]^{1/2} [H_2A]^{1/2} [PET]^{1/2} = [PET M_n^*] \quad E_{16}
\]

Knowing \(R_g = k_g [PET M_n^*] [M]\)

\[
R_g = k_g \left( \frac{2 k_6 K_p}{k_{t1}} \right)^{1/2} [M]^{1/2} [PMS]^{1/2} [H_2A]^{1/2} [PET]^{1/2} \quad E_{17}
\]

In the above expression for \(R_g\), square root order dependences on [PMS] (Fig. 6A), [H_2A] (Fig. 10A), [PET] (Fig. 13A) and first order dependence on [M] (Fig. 3A), could be accounted.

For the same Scheme V, an expression for \(n_g\) can be derived by knowing,
Using Eq. 18,

\[ n_g = \frac{k_{t1} [PET M'] [M]}{k_2 [PET'] [M]^2} \quad \text{Eq. 18} \]

Substituting for \([PET M']\) from Eq. 16,

\[ n_g = \frac{k_{t2} [M]}{k_7 K_1 [PMS] [H_2A] [PET]} \quad \text{Eq. 19} \]

Substituting for \([PET M']\) from Eq. 16,

\[ n_g = \frac{k_{t2} / k_7 K_1 [PET]^{1/2} [PMS]^{1/2} [H_2A]^{1/2}}{(2k_6 K_1)^{1/2} [H_2A]^{1/2} [PMS]^{1/2} [PET]^{1/2}} \quad \text{Eq. 20} \]

\[ n_g = \frac{k_{t2} [M]}{k^{1/2} t_1 (k_7 K_1)^{1/2} [PMS]^{1/2} [H_2A]^{1/2} [PET]^{1/2}} \quad \text{Eq. 21} \]

Scheme V gives a first power dependence on monomer and inverse square root order dependences on PET, [H_2A] and [PMS], through equation Eq. 21 and the first power dependence on AN and agrees with the experimental observations. Hence, Scheme V may be suitable to explain the observed results with respect to \(n_g\) also.
The primary reactions in Scheme V would lead to homopolymerization by

Initiation

\[ H_2A + PMS \xrightleftharpoons{K_1} H_2A - PMS \]

Complex \( C_1 \)

\[ \text{PET} + C_1 \xrightarrow{k_6} \text{PET}^- + SO_4^{2-} + HA^- + H_2O + H^+ \]

\[ SO_4^{2-} + H_2O \xrightarrow{k_2} OH^- + HSO_4^- \]

\[ OH^- + H_2A \xrightarrow{k_3} H_2O + A^+ + H^+ \]

\[ A^+ + C_1 \xrightarrow{k_4} SO_4^{2-} + 2HA^- + H_2O + H^+ \]

\[ C_1 + M \xrightarrow{k_g} M_1^+ + SO_4^{2-} + HA^- + H_2O + H^+ \]

\[ M + A^+ \xrightarrow{k_{10}} M_1^+ \]

Propagation

\[ M_1^+ + M \rightarrow M_2^+ \]

\[ M_{n-1}^+ + M \rightarrow M_n^+ \]

Termination

\[ M_n^+ + M_{n-1}^+ \xrightarrow{k_{18}} \text{homopolymer} \]
Applying stationary state approximation to the various radical species involved in the system,

\[
\frac{d[SO_{4}^{2-}]}{dt} = k_{6} K_{1} [H_{2}A] [PMS] [PET] - k_{2} [SO_{4}^{2-}] + k_{7} K_{1} [A^{+}] [PMS][H_{2}A] + k_{9} K_{1} [M][PMS][H_{2}A] = 0
\]  \( \ldots E_{22} \)

\[
\frac{d[A^{+}]}{dt} = k_{3} [OH] [H_{2}A] - k_{7} K_{1} [A^{+}][PMS][H_{2}A] - k_{10} [M][A^{+}] = 0
\]  \( \ldots E_{23} \)

\[
\frac{d[OH]}{dt} = k_{2} [SO_{4}^{2-}] - k_{3} [OH] [H_{2}A] = 0 \quad \ldots E_{24}
\]

\[
\frac{d[M^{*}]}{dt} = k_{9} K_{1} [M] [PMS] [H_{2}A] + k_{10} [M] [A^{+}] - k_{14} [M^{*}]^{2} = 0
\]  \( \ldots E_{25} \)

Adding \( E_{22}, \ E_{23}, \ E_{24} \) and \( E_{25} \),

\[
[M_{n}^{*}] = \left( 2 k_{9} K_{1} [PMS][H_{2}A][M] + k_{6} K_{1} [H_{2}A][PMS][PET] \right)^{1/2}
\]

\[
= \left( K_{1} [H_{2}A] [PMS] \right)^{1/2} \left( 2 k_{9} [M] + k_{6} [PET] \right)^{1/2} \frac{1}{k_{14}^{1/2}}
\]

Knowing \( R_{n} = k_{p} [M^{*}] [M] \)
When \( k_g \gg k_6 \) (PET),

\[
R_h = \frac{k_p \left( 2 K_1 k_g [H_2A] [PMS] \right)^{1/2} [M]^{3/2}}{k_1^{1/2}} \quad E_{27}
\]

When \( k_g (M) \ll k_6 (PET) \),

\[
R_h = \frac{k_p \left( K_1 k_6 [H_2A] [PMS] [PET] \right)^{1/2} [M]}{k_1^{1/2}} \quad E_{28}
\]

In \( E_{27} \), the square root order dependences on \([H_2A]\), \([PMS]\) and three halfth order on \([M]\) are in agreement with experimental observations. However, \( E_{27} \) fails to explain the square root order dependence on PET.

In \( E_{28} \), the square root order dependences on \([H_2A]\), \([PMS]\) and \([PET]\) are in agreement with experimental results. But, it fails to account for the three halfth order dependence on \([M]\).

Therefore, Scheme V may not be suitable to explain all the experimental results related to \( R_g, n_g, R_h \) and \( n_h \) in a combined way.
Schemes VII, IX and X are based on termination by linear type and hence the experimental observations could not be explained through the derived expressions for those schemes.

Scheme VIII considers initiation through two complex formation and termination by mutual type. For Scheme VIII, expression for $R_g$ can therefore be derived as follows:

Applying steadystate approximation to all radicals,

\[
\frac{d[SO^\ddagger]}{dt} = \frac{k_8 K_1 K_2 [PMS] [H_2A] [PET] - k_2 [SO^\ddagger]}{\text{E29}}
\]

\[
\frac{d[OH]}{dt} = k_2 [SO^\ddagger] - k_3 [OH] [H_2A] = 0 \quad \text{E3}
\]

\[
\frac{d[A^\ddagger]}{dt} = k_3 [OH] [H_2A] - k_1 K_1 [PMS] [H_2A] = 0 \quad \text{E30}
\]

\[
\frac{d[PET]}{dt} = k_8 K_1 K_2 [PET] [PMS] [H_2A] - k_5 [PET^\ddagger] [M] = 0 \quad \text{E31}
\]

\[
\frac{d[PET M^\ddagger_n]}{dt} = k_5 [PET^\ddagger] [M] - k_t [PET M^\ddagger_n]^2 = 0 \quad \text{E5}
\]

Adding $\text{E29, E3, E30, E31 and E5}$.
Knowing $R_g = k_g [\text{PET}]^{1/2} [\text{M}]$

$$R_g = k_g \left( \frac{2 k_g K_1 K_2}{k_t} \right)^{1/2} [\text{M}] [\text{PET}]^{1/2} [\text{PMS}]^{1/2} [\text{H}_2\text{A}]^{1/2}$$

In $E_{33}$, all the experimental observations such as first power dependence on $[\text{AN}]$ (Fig. 3A), square root order dependences on $[\text{PMS}]^{1/2}$ (Fig. 6A), $[\text{H}_2\text{A}]$ (Fig. 10A) and $[\text{PET}]^{1/2}$ (Fig. 13A) towards $R_g$ can be seen.

For the same Scheme VIII, using $E_2$, $E_{31}$ and $E_{32}$, $n_g$ would be

$$n_g = \frac{k_g [\text{M}]}{(k_t)^{1/2} (2 k_g K_1 K_2)^{1/2} [\text{PET}]^{1/2} [\text{H}_2\text{A}]^{1/2} [\text{PMS}]^{1/2}}$$

In $E_{34}$, all the experimental observations, such as first power dependence on $[\text{M}]$ (Fig. 4C), inverse square root order dependences on $[\text{PMS}]$ (Fig. 8C), $[\text{H}_2\text{A}]$ (Fig. 11C) and on $[\text{PET}]$ (Fig. 14C) towards $n_g$ could be seen.

Through primary reactions in Scheme VIII, the possible homopolymerization in a simultaneous way can take place by
Rfection was found to have three half order dependences on [M] (Fig. 3B), half order dependences on [PMS] (Fig.6B), [H2A] (Fig. 10B), [PET] (Fig. 13B) and thereby shows the predominant mutual termination during homopolymerization with normal propagation,

\[ M_n^+ + M \xrightarrow{k_{11}} M_n^+ + H_2O + H^+ + SO_4^{2-} \]

\[ SO_4^{2-} + H_2O \xrightarrow{k_2} OH^- + HSO_4^- \]

\[ OH^- + H_2A \xrightarrow{k_3} H_2O + A^- + H^+ \]

\[ C_1 + A^- \xrightarrow{k_7} SO_4^{2-} + 2HA^- + H_2O + H^+ \]

\[ M + A^- \xrightarrow{k_{10}} M_1^+ \]

and mutual termination,

\[ M_n^+ + M_n^+ \xrightarrow{k_{ts}} \text{homopolymer} \]
Applying steady-state approximation to all radicals, a rate expression for $R_h$ can be derived.

$$\frac{d[SO_4^2]}{dt} = k_{11}K_1K_2 \left[\text{PET}\right] \left[H_2A\right] \left[PMS\right] \left[M\right] - k_2 \left[SO_4^2\right]$$

$$+ k_7 K_1 \left[H_2A\right] \left[PMS\right] \left[A^\pi\right] = 0 \quad E_{35}$$

$$\frac{d[A^\pi]}{dt} = k_4 \left[OH\right] \left[H_2A\right] - k_7 K_1 \left[H_2A\right] \left[PMS\right] \left[A^\pi\right]$$

$$- k_{10} \left[A^\pi\right] \left[M\right] = 0 \quad E_{36}$$

$$\frac{d[OH]}{dt} = k_2 \left[SO_4^2\right] - k_3 \left[OH\right] \left[H_2A\right] = 0 \quad E_3$$

$$\frac{d[M]}{dt} = k_{11}K_1K_2 \left[\text{PET}\right] \left[H_2A\right] \left[PMS\right] \left[M\right] + k_{10} \left[A^\pi\right] \left[M\right]$$

$$- k_{14} \left[M^*\right] = 0 \quad E_{37}$$

$$[M^*] = \left(\frac{2k_{11}K_1K_2}{k_{14}}\right)^{1/2} \left[\text{PET}\right]^{1/2} \left[H_2A\right]^{1/2} \left[PMS\right]^{1/2} \left[M\right]^{1/2} \quad E_{38}$$

Knowing,

$$R_h = k_p \left[M^*\right] \left[M\right] \quad E_{39}$$

$$R_h = k_p \left(\frac{2k_{11}K_1K_2}{k_{14}}\right)^{1/2} \left[\text{PET}\right]^{1/2} \left[H_2A\right]^{1/2} \left[PMS\right]^{1/2} \left[M\right]^{3/2} \quad E_{40}$$
Here in E₄₀, all the experimental observations such as three halfth order dependence on [AN] (Fig. 3B), square root order dependence on [PMS] (Fig. 6B), [H₂A] (Fig. 10B), [PET] (Fig. 13B) related to Rₜ can be clearly accounted.

For the above scheme, an expression for nₜ can be arrived at as,

\[
\frac{\text{rate of homopolymerization}}{\text{rate of termination}} = \frac{k_p [M]}{k_q [M^*]}
\]

\[
n_t = \frac{k_p [M]}{(k_{1q})^{1/2} (2k_{11}K_1K_2)^{1/2} [PET]^{1/2} [H₂A]^{1/2} [PMS]^{1/2}}
\]

E₄₁ clearly accounts for all the observed experimental results with respect to nₜ such as half order dependences on [AN] (Fig. 4D), inverse square root order dependences on [PMS] (Fig. 8D), [H₂A] (Fig. 11D), and [PET] (Fig. 14D).

Finally, since Scheme VIII adequately explains every one of the experimental observations related to Rₜ, n₉, Rₘ and nₚ, this may be the most probable scheme. Hence, E₃₃, E₃₄, E₄₆ and E₄₁ are the most suitable expressions for Rₜ, n₉, Rₘ and nₚ respectively.
4.1.2.5 Evaluation of Composite Rate Constants for the System and Test for their Invariance

That the rate expression as given by $E_{33}$ is the right choice is further confirmed by the fact that the composite rate constant

$$k_g \left( \frac{2k_1k_2}{k_{t1}} \right)^{1/2}$$

remains invariant for all the variations of $[AN]$, $[PMS]$, $[H_2A]$ and $[PET]$.

The values so obtained can be seen in Table 20A.

This composite rate constant was evaluated from the slope of the plots $R_g$ vs $[AN]$ (Figs. 3A,C), $R_g$ vs $[PMS]^{1/2}$ (Figs. 6A,C), $R_g$ vs $[H_2A]^{1/2}$ (Figs. 10A,C) and $R_g$ vs (Wt. of PET)$^{1/2}$ (Figs. 13A,C) and using the conditions maintained in Tables 2, 3, 6, 7, 10, 11, 14 and 15. The average value of the composite rate constant in $E_{33}$ viz.,

$$k_g \left( \frac{2k_1k_2}{k_{t1}} \right)^{1/2}$$

was calculated to be $5.77 \times 10^{-4}$ mol$^{-1}$ l$^1$ g$^{-1/2}$ sec$^{-1}$ at 45$^\circ$C.
From the slope of the plots \( n_g \) Vs [AN] (Fig. 4C), \( n_g \) Vs [PMS]^{-1/2} (Fig. 8C), \( n_g \) Vs [H₂A]^{-1/2} (Fig. 11C) and \( n_g \) Vs [Wt. of PET]^{1/2} (Fig. 14C) and using the conditions maintained in Tables 5, 9, 13 and 17, the average value of the composite rate constant \( E_{34} \), viz.,

\[
k_g \frac{1}{(k_t)^{1/2} (k_8 K_1 K_2)^{1/2}}
\]

was calculated to be 23.8 mol⁻¹ l sec⁻¹ at 45°C. The values obtained from different plots are given in Table 20(A). The constancy found in these values for the composite rate constant in all these variations of [AN], [PMS], [H₂A] and PET show that the right choice of the rate expression is \( E_{34} \).

Multiplying the composite rate constants obtained from \( R_g \),

\[
k_g \left( \frac{k_9 K_1 K_2}{k_{t1}} \right)^{1/2}
\]

and

\[
n_g \left( \frac{k_g}{(k_{t1})^{1/2} (k_8 K_1 K_2)^{1/2}} \right)
\]

measurements.
value was obtained as 0.117 mol⁻¹/² g⁻¹/² sec⁻¹/² at 45°C.

Taking the ratio of the composite rate constants from R₉ and n₉ measurements respectively, the value of $k₉K₁K₂$ was calculated as $2.43 \times 10^{-5}$ mol⁻¹ sec⁻¹ at 45°C.

That the rate expression as given by $E₄₀$ for $R₉$ is the correct one has been confirmed further by the fact that the composite rate constant

$$k_p \left( \frac{2k_{11}K₁K₂}{k₉} \right)^{1/2}$$

remains invariant for all the variations of [AN], [PMS], [H₂A] and PET. The values so obtained can be seen in Table 20B.

This composite rate constant was evaluated from the slope of the plots $R₉$ Vs [AN]⁻³/² (Figs. 3B,D), $R₉$ Vs [PMS]⁻¹/² (Figs. 6B,D), $R₉$ Vs [H₂A]⁻¹/² (Figs. 10B,D), $R₉$ Vs [Wt. of PET]⁻¹/² (Figs. 13B,D) and using the conditions maintained in Tables 2, 3, 6, 7, 10, 11, 14 and 15 respectively. The average value of the composite rate constant in $E₄₀$, viz.,
was calculated to be $1.13 \times 10^{-2} \text{ mol}^{-1/2} \text{ g}^{3/2} \text{ sec}^{-1}$ at 45°C.

That the rate expression as given in E_41 for $n_h$ is the right selection is further confirmed here by the fact that the composite rate constant

$$k_p \left( \frac{2 k_{11} K_1 K_2}{k_{1q}} \right)^{1/2}$$

remains invariant for all variations of [AN], [PMS], $[H_2A]$ and PET. The values so obtained can be seen in Table 20(B). This composite rate constant was evaluated from the slopes of the plots $n_g$ Vs $[AN]^{1/2}$ (Fig. 4D), $n_h$ Vs $[PMS]^{-1/2}$ (Fig. 8D), $n_h$ Vs $[H_2A]^{-1/2}$ (Fig. 11D), and $n_h$ Vs [Wt. of PET]^{-1/2} (Fig. 14D) and using the conditions maintained in Tables 5, 9, 13 and 17. The average value of the composite rate constant in E_41, viz.,

$$k_p \left( \frac{2 k_{11} K_1 K_2}{k_{1q}} \right)^{1/2}$$

was calculated to be $211 \text{ mol}^{-1} \text{ g}^{1/2} \text{ at 45°C}.$

Multiplying the composite rate constants obtained from $R_h$,
and \( n_h \),

\[
\frac{k_p}{(k_{t4})^{1/2} (2k_{11}k_1k_2)^{1/2}}
\]

measurements,

\[
\frac{k_p}{k_{1/2}^{1/2}}
\]

value was obtained as 1.53 mol\(^{-5/4}\) g\(^{-1/2}\) sec\(^{-1/2}\).

This value differs from the earlier reported one (0.053 mol\(^{-1/2}\) l\(^{1/2}\) sec\(^{-1/2}\)) because of the difference in the initiation path here.

Taking the ratio of the composite rate constants from \( R_h \) and \( n_h \) measurements, the value of \( k_{11}k_1k_2 \) was calculated as 5.27 x 10\(^{-5}\) mol\(^{-1}\) l\(^1\) sec\(^{-1}\) at 45°C.

Knowing \( k_g := k_1k_2 \) value from \( R_g \) and \( n_g \) measurements as 2.43 x 10\(^{-5}\) mol l sec\(^{-1}\) and \( k_{11}k_1k_2 \) value from \( R_h \) and \( n_h \) measurements as 5.27 x 10\(^{-5}\) mol\(^{-1}\) l\(^1\) sec\(^{-1}\), the ratio of the two values \( (k_g/k_{11}) \) was obtained as 0.461.
The ratio indicates that $k_8 < k_{11}$ suggesting that in graft copolymerization studies with AN onto PET using PMS-H$_2$A redox pair, graft copolymerization should be accompanied with homopolymerization and $R_g$ value must be lower than $R_h$. This fact is actually reflected in the present study.

For the scheme VIII, an expression for $-R_{\text{PMS}}$ can be written as,

$$-R_{\text{PMS}} = \frac{(k_{11} K_1 K_2)[M][\text{PMS}]_T [H_2A][\text{PET}] + k_8 K_1 K_2 [\text{PMS}][H_2A][\text{PET}]}{(1 + K_1 [H_2A]) + K_4 K_2 [H_2A][\text{PET}]}$$

where $([\text{PMS}]_T = \text{initial [PMS] taken})$ when $K_1 K_2 [H_2A][\text{PET}] \gg 1 + K_1 [H_2A]$, the expression becomes,

$$-R_{\text{PMS}} = (k_{11} [M] + k_8) [\text{PMS}]$$

The values obtained for $k_{11} K_1 K_2$ and $k_8 K_1 K_2$ from the slopes of the plots $-R_{\text{PMS}}$ vs $[\text{PMS}]$ (Figs. 7C,D) are $8.77 \times 10^{-4}$ sec$^{-1}$ and $2.50 \times 10^{-4}$ sec$^{-1}$ respectively for two different $[M]$. Using the slopes and knowing $-R_{\text{PMS}}$ was independent of the change in $[H_2A]$ and $[\text{PET}]$, the two equations $(k_{11} [M] + k_8)$ with two different $[M]$ as in Tables 6 and 7 solved to obtain the ratio $(k_8/k_{11})$. The calculated value was found to be 0.286. This again supports that $k_8 < k_{11}$ as it was inferred through grafting measurements.
The increase in % grafting (Table 4) with increase in monomer can be explained by the same reasoning as reported earlier [186,197-201]. Similar effect on % grafting with [M] was found by Shukla and coworkers [109-111], Horoshi [185] and Varma and Ray [93]. Varma and Ravisankar [94] reported that the grafting efficiency was good only at low monomer concentration by another system and that sometimes it decreases with increase in [M].

The increase in % grafting and % efficiency by the parameters such as [M] (Table 4), [PMS] (Table 8), [H₂A] (Table 12) and [PET] (Table 16) could be due to the involvement of all these components in the grafting initiation step.

The decrease in % grafting at higher backbone amount may be due to the decrease in the diffusibility of the monomer towards the active site generated in the larger backbone matrix.

4.1.1. PMS-H₂A Redox Initiated Graft Copolymerization of AN onto Nylon 6

In order to get a better insight into the kinetic study of PMS-H₂A redox initiated graft copolymerization of AN, nylon 6 has been chosen as a backbone material. Hereagain, the kinetic results show similar trends.
4.1.2.1 Results on PMS-H₂A Redox Initiated Graft Copolymerization of AN onto Nylon 6

Effect of Time on Graft Parameters

Both $R_g$ and $R_h$ show initial increase with time and thereafter they fall (Table 21). To follow the kinetics of graft copolymerization in a smooth fashion under stationary state conditions, a reaction time more than four hours was selected for the present study.

The plots $R_g$ Vs time (Fig. 16A), $R_h$ Vs time (Fig. 16B) were drawn.

$n_g$ and $n_h$ increase initially with time and then they fall (Table 21). The plots $n_g$ Vs time (Fig. 16C) and $n_h$ Vs time (Fig. 16D) were also drawn.

Effect of [AN] on Graft Parameters

A close look at Table 22 clearly indicates that $R_g$ increases steadily with [AN]. In order to obtain the order with respect to AN, in the graft copolymerization, a plot of $\log R_g$ Vs $\log [AN]$ (Fig. 17A) was drawn. This was found to be a straight line with a slope of unity suggesting a first order dependence of $R_g$ on [AN]. The direct plot $R_g$ Vs [AN] (Fig. 18A) was therefore drawn and found to be a straight line passing through the origin and thus
confirming the order dependence. \( R_h \) was also found to increase with \([AN]\) (Table 22). The plot \( \log R_h \) Vs \( \log [AN] \) (Fig. 17B) was also found to be a straight line with a slope of 1.5 indicating a three halfth order dependence of \( R_h \) on \([AN]\). The direct plot \( R_h \) Vs \([AN]^{1.5} \) (Fig. 18B) was drawn and thus confirms the 1.5 order dependence of \( R_h \) on \([AN]\).

In an attempt to have further confirmation, the effect of \([AN]\) on \( R_g \) and \( R_h \) was also studied with a different set of experimental conditions (Table 23). The plot of \( \log R_g \) Vs \( \log [AN] \) (Fig. 17C) was a straight line with a slope of unity suggesting a first order dependence of \( R_g \) on \([AN]\). Direct plot \( R_g \) Vs \([AN] \) (Fig. 18C) was therefore drawn and also found to be a straight line passing through the origin, thus confirming the order of \( R_g \) on \([AN]\).

The plot \( \log R_h \) Vs \( \log [AN] \) (Fig. 17D) was a straight line with a slope of 1.5 pointing out a three halft order dependence of \( R_h \) on \([AN]\). The direct plot \( R_h \) Vs \([AN]^{1.5} \) (Fig. 18D) confirms the order dependence.

The effect of change in \([AN]\) on % grafting and % efficiency was given in Table 24. It was observed that the % grafting increases steadily with increase in \([AN]\) but % efficiency shows an increasing trend initially and then decreases (Table 24).
Both $n_g$ and $n_h$ were found to increase with $[AN]$ (Table 25). Plots of log $n_g$ Vs log $[AN]$ (Fig. 19A) and log $n_h$ Vs log $[AN]$ (Fig. 19B) were drawn and found to be straight lines with slopes unity and half respectively. It was therefore inferred as first order dependence of $n_g$ on AN and half order on $n_h$. To ascertain this, direct plots $n_g$ Vs $[AN]$ (Fig. 19C), and $n_h$ Vs $[AN]^{1/2}$ (Fig. 19D) were drawn. The linear nature of these plots support the observations.

**Effect of $[AN]$ on Rate of Disappearance of PMS ($-R_{PMS}$)**

It was found that $-R_{PMS}$ values remain almost constant for the conditions mentioned in Tables 22 and 23.

**Effect of $[PMS]$ on Graft Parameters**

Both $R_g$ and $R_h$ increase with a change in $[PMS]$ (Table ). The plot of log $R_g$ Vs log $[PMS]$ (Fig. 20A) was found to be a straight line with a slope of 0.5 indicating square root order dependence of PMS on $R_g$. Direct plot $R_g$ Vs $[PMS]^{1/2}$ (Fig. 21A) was drawn and found to be straight line passing through the origin thus confirming the half order dependence.

$R_h$ was also found to increase with $[PMS]$. The plot log $R_h$ Vs log $[PMS]$ (Fig. 20B) was a straight line
with a slope of 0.5 indicating half order dependence on PMS. The direct plot \( R^h \) Vs [PMS]^{1/2} (Fig. 21B) was also drawn and found to support the order dependence.

In a different set of experimental conditions (Table 27), \( R^g \) and \( R^h \) were found to increase with [PMS]. Plot of log \( R^g \) Vs log [PMS] (Fig. 20C) was a straight line with a slope of 0.5 indicating half order dependence of \( R^g \) on PMS. Direct plot \( R^g \) Vs [PMS]^{1/2} (Fig. 21C) was drawn to support the order dependence.

A plot of log \( R^h \) Vs log [PMS] (Fig. 20D) gave a slope of 0.5 showing half order of \( R^h \) on PMS. This was confirmed by drawing a plot \( R^h \) Vs [PMS]^{1/2} (Fig. 21D) indicating half order dependence of \( R^h \) on PMS.

Both \% grafting and \% efficiency steadily increase with increase in [PMS] (Table 28).

\( n^g \) and \( n^h \) were determined separately with [PMS] (Table 29) and found that both \( n^g \) and \( n^h \) decrease with [PMS]. Plots of log \( n^g \) Vs log [PMS] (Fig. 23A) and log \( n^h \) Vs log [PMS] (Fig. 23B) were drawn and found to be straight line with a slope of negative 0.5 indicating inverse square root order dependences of \( n^g \) and \( n^h \) on [PMS]. Direct plots of \( n^g \) Vs [PMS]^{1/2} (Fig. 23C) and \( n^h \) Vs [PMS]^{-1/2} (Fig. 23D) was drawn in order to support the order dependences.
Effect of [PMS] on $-R_{PMS}$

$-R_{PMS}$ was followed under the conditions mentioned in Tables 26 and 27 and found that $-R_{PMS}$ values increase with PMS. A plot of log $[-R_{PMS}]$ vs log [PMS] (Fig. 22A) was a straight line with a slope of unity suggesting a first order dependence of $-R_{PMS}$ on PMS. The direct plot $-R_{PMS}$ vs [PMS] (Fig. 22C) was also drawn and found to confirm the first order with respect to PMS.

Under a set of different experimental conditions given in Table 27, plot of log $[-R_{PMS}]$ vs log [PMS] (Fig. 22B) was drawn and found to be a straight line with a slope of unity indicating a first order on PMS. The direct plot $-R_{PMS}$ vs [PMS] (Fig. 22D) was also drawn and found to pass through the origin with almost negligible intercept confirming the first order with respect to PMS.

Effect of [H₂A] on Craft Parameters

Both $R_g$ and $R_h$ increase steadily with increase in [H₂A] (Table 20). Plots of log $R_g$ vs log [H₂A] (Fig. 24A) and log $R_h$ vs log [H₂A] (Fig. 24B) were drawn and found to be straight lines with slope 0.5 suggesting half order dependence of $R_g$ and $R_h$ on H₂A. Direct plots $R_g$ vs $[H₂A]^{1/2}$ (Fig. 25A) and $R_h$ vs $[H₂A]^{1/2}$ (Fig. 25B) were also drawn and found to confirm the order 0.5 of $R_g$ and $R_h$ on H₂A respectively.
The above order dependences were further confirmed by performing experiments with a different set of conditions. $R_g$ and $R_h$ values were found to increase with $[H_2A]$ (Table 31). Log $R_g$ Vs log $[H_2A]$ (Fig. 24C) and log $R_h$ Vs log $[H_2A]$ (Fig. 24D) plots were drawn and found to give a slope of 0.5 indicating half order dependences on $R_g$ and $R_h$ respectively. Direct plots $R_g$ Vs $[H_2A]^{1/2}$ (Fig. 25C) and $R_h$ Vs $[H_2A]^{1/2}$ (Fig. 25D) were also drawn in order to confirm the order dependences.

Both % grafting and % efficiency increase steadily under the conditions mentioned in Table 32 with respect to $[H_2A]$.

$n_g$ and $n_h$ were determined separately with $[H_2A]$ and found to decrease with $[H_2A]$ under the conditions mentioned in Table 33.

Plots of log $n_g$ Vs log $[H_2A]$ (Fig. 26A) and log $n_h$ Vs log $[H_2A]$ (Fig. 26B) were drawn to get an idea about the order with respect to $H_2A$. The slopes of the plots were found to be half indicating half order dependence on $H_2A$. In order to confirm the above order dependences, direct plots $n_g$ Vs $[H_2A]^{-1/2}$ (Fig. 26C) and $n_h$ Vs $[H_2A]^{-1/2}$ (Fig. 26D) were also drawn.
Effect of Nylon 6 Weight on Graft Parameters

For the variation of the backbone material from 2.10 to 3.50 g, both $R_g$ and $R_h$ increase steadily under the conditions given in Table 34. Log $R_g$ Vs log [Wt. of nylon 6] (Fig. 27A) and log $R_h$ Vs log [Wt. of nylon 6] (Fig. 27B) were drawn. The slopes of the plots show half order dependence on the backbone amount in both $R_g$ and $R_h$. Direct plots $R_g$ Vs [Wt. of nylon 6] (Fig. 28A) and $R_h$ Vs [Wt. of nylon 6] (Fig. 28B) were also drawn to further support the order dependences.

In an attempt to have further confirmation on the order dependences, the effect of Wt. of nylon 6 on $R_g$ and $R_h$ was also studied under a set of different experimental conditions as specified in Table 35. Log $R_g$ Vs log [Wt. of nylon 6] (Fig. 27C) and log $R_h$ Vs log [Wt. of nylon 6] (Fig. 27D) plots were drawn and found to give a slope of 0.5 suggesting half order dependences on $R_g$ and $R_h$. Direct plots $R_g$ Vs [Wt. of nylon 6]^{1/2} (Fig. 28C) and $R_h$ Vs [Wt. of nylon 6]^{1/2} (Fig. 28D) were also drawn to further support the order dependences.

The effect of change of % grafting and % efficiency with a change in the backbone amount was presented in Table 36. The % grafting decreases but % efficiency gradually increases with the backbone material.
$n_g$ and $n_h$ values were determined separately and they show decreasing trend with the backbone amount. Log $n_g$ Vs log [Wt. of nylon 6] (Fig. 29A) and log $n_h$ Vs log [Wt. of nylon 6] (Fig. 29B) plots were drawn and found to give a slope of negative 0.5 thus showing inverse square root order dependences on $n_g$ and $n_h$. Direct plots $n_g$ Vs $[\text{Wt. of nylon 6}]^{-1/2}$ (Fig. 29C) and $n_h$ Vs $[\text{Wt. of nylon 6}]^{-1/2}$ (Fig. 29D) were also drawn in order to further support the order dependences.

**Effect of Temperature on Graft Parameters**

$R_g$ and $R_h$ values obtained by varying the temperature from 35°C to 50°C under the experimental conditions are presented in Table 38. It was observed that both $R_g$ and $R_h$ increase initially and then they fall (Table 38). Arrhenius plots of log $R_g$ Vs 1 (Fig. 30A) and log $R_h$ Vs 1 (Fig. 30B) were drawn and the energy of activation $E_a$ were determined as 4.12 Kcal/mol for $R_g$ and 2.66 Kcal/mol for $R_h$.

Both % grafting and % efficiency increase initially and then they fall.

$n_g$ and $n_h$ values were determined separately and found that they increase gradually with temperature.
Arrhenius plots of log \( n_g \) Vs \( 1/T \) (Fig. 30C) and log \( n_h \) Vs \( 1/T \) (Fig. 30D) were also drawn and the energy of activation \( E_a \) values were determined for \( n_g \) and \( n_h \) as 11.8 Kcal/mol and 12.4 Kcal/mol respectively.

4.1.2.2 Discussion on Results

The observation made with this system is almost similar to the one as seen in graft copolymerization of AN onto PET through initiation by PMS-H\(_2\)A redox pair. This points out that probable reaction schemes would be the same as in the previous case.

Hence, a similar sequence of reactions as represented in Scheme VIII for the graft copolymerization of AN initiated by PMS-H\(_2\)A redox pair onto PET with a change in the backbone as nylon 6 would be selected as the most probable one for this system of graft copolymerization of AN initiated by PMS-H\(_2\)A redox pair onto nylon 6.

The grafting of nylon 6 was reported to be initiated by the production of nylon radical by the abstraction of a proton from the NH grouping in the backbone polymer[91].

\[
\text{NH} + \text{R} \rightarrow \text{N} + \text{RH}
\]

where 'R' can be radical or metal ion.
4.1.2.3 Selected Most Probable Scheme (With Change in Backbone as Nylon 6)

**Initiation**

\[ \text{PMS} + \text{H}_2\text{A} \xrightarrow{K_1} \text{PMS} - \text{H}_2\text{A} \]

\[ \text{Complex } C_1 \]

\[ \text{C}_1 + \text{nylon 6} \xrightarrow{K_2} \text{PMS} - \text{H}_2\text{A} - \text{nylon 6} \]

\[ \text{Complex } C_3 \]

\[ \text{C}_3 \xrightarrow{k_{12}} (\text{nylon 6})' + \text{H}_2\text{O} + \text{H}^+ + \text{SO}_4^{2-} \]

\[ (\text{Nylon 6})' + \text{M} \xrightarrow{k_{13}} (\text{nylon 6})^* \]

\[ \text{SO}_4^{2-} + \text{H}_2\text{O} \xrightarrow{k_{2}} \text{OH} + \text{HSO}_4^- \]

\[ \text{OH} + \text{H}_2\text{A} \xrightarrow{k_{3}} \text{H}_2\text{O} + \text{A}^+ + \text{H}^+ \]

\[ \text{C}_3 + \text{A}^+ \xrightarrow{k_{14}} \text{SO}_4^{2-} + 2\text{HA}^- + \text{H}_2\text{O} + \text{H}^+ \]

**Propagation**

\[ (\text{nylon 6})^* + \text{M} \xrightarrow{k} (\text{nylon 6})^*_2 \]

\[ (\text{nylon 6})^*_n + \text{M} \xrightarrow{\text{ } k_{-11}} (\text{nylon 6})^*_n \]

**Termination**

\[ 2 (\text{nylon 6})^*_n \xrightarrow{k_{11}} \text{graft copolymer} \]
Utilising kinetic chain length approximation, the same rate constant for termination as in the case with PET \((k_{tr})\) was considered.

For the simultaneous homopolymerization, the similar mechanism would be as follows.

**Initiation**

\[
PMS + H_A \xrightleftharpoons{K_1} \text{Complex}_1 \overset{K_2}{\rightarrow} C_1 + \text{nylon 6}
\]

\[
C_1 + \text{nylon 6} \xrightleftharpoons{K_3} \text{Complex}_3 \overset{K_4}{\rightarrow} PMS - H_A - \text{nylon 6}
\]

\[
C_3 + M \xrightarrow{k_{15}} M^* + H_2O + H^+ + SO_{4}^2- + \text{nylon 6}
\]

\[
SO_{4}^2- + H_2O \xrightarrow{k_{2}} \cdot OH + HSO_{4}^-
\]

\[
\cdot OH + H_2A \xrightarrow{k_{3}} H_2O + A^+ + H^+
\]

\[
C_1 + A^+ \xrightarrow{k_{4}} SO_{4}^2- + 2HA^- + H_2O + H^+
\]

\[
M + A^+ \xrightarrow{k_{10}} M^*_1
\]

**Propagation**

\[
M^*_1 + M \xrightarrow{k_p} M^*_2
\]

\[
\ldots
\]

\[
M^*_{n-1} + M \xrightarrow{k_p} M^*_n
\]
Termination

\[ M_n^* + M_n^* \xrightarrow{k_{tu}} \text{homopolymer} \]

For this scheme, the expressions for \( R_g \), \( n_g \), \( R_h \) and \( n_h \) can then be written based on the discussions in 4.1.2 related to PET.

\[
R_g = k_g \left( \frac{2 k_{12} K_1 K_3}{k_{t1}} \right)^{1/2} \left[ M \right]^{1/2} \left[ \text{nylon 6} \right]^{1/2} \left[ \text{PMS} \right]^{1/2} \left[ \text{H}_2\text{A} \right]^{1/2} \quad \text{E}_{44}
\]

\[
n_g = \frac{k_g \left[ M \right]}{k_{t1}^{1/2} (2 k_{12} K_1 K_3)^{1/2} (\text{nylon 6})^{1/2} (\text{PMS})^{1/2} (\text{H}_2\text{A})^{1/2}} \quad \text{E}_{45}
\]

\[
R_h = k_p \left( \frac{2 k_{15} K_1 K_3}{k_{t4}} \right)^{1/2} (\text{nylon 6})^{1/2} (\text{H}_2\text{A})^{1/2} (\text{PMS})^{1/2} M^{3/2} \quad \text{E}_{46}
\]

\[
n_h = \frac{k_p \left[ M \right]^{1/2}}{k_{t4}^{1/2} (2 k_{15} K_1 K_3)^{1/2} (\text{nylon 6})^{1/2} (\text{H}_2\text{A})^{1/2} (\text{PMS})^{1/2}} \quad \text{E}_{47}
\]
4.1.2.4 Evaluation of Composite Rate Constant for the System and Test for their Invariance

That the rate expression as given by $E_{44}$ is the right choice is further confirmed by the fact that the composite rate constant

$$k_g \left( \frac{2k_{12}k_1k_3}{k_{11}} \right)^{1/2}$$

remains invariant for all the variations of [AN], [PMS], [H₂A] and [nylon 6]. The values so obtained can be seen in 40A.

This composite rate constant was evaluated from the slopes of the plot $R_g$ Vs [AN] (Figs. 18A,C); $R_g$ Vs [PMS] $k$ (Figs. 21A,C), $R_g$ Vs $[H_2A]^{1/2}$ (Figs. 25A,C) and $R_g$ Vs [nylon 6] (Figs. 28A,C) and using the conditions maintained in Tables 22, 23, 26, 27, 30, 31, 34 and 35. The average value of the composite rate constant in $E_{44}$, viz.,

$$k_g \left( \frac{k_{12}k_1k_3}{k_{11}} \right)^{1/2}$$

was calculated to be $4.61 \times 10^{-4}$ mol$^{-1}$ l g$^{-1/2}$ sec$^{-1}$.

That the rate expression as given by $E_{45}$ for $g$ is the right choice is further confirmed by the fact that the composite rate constant
remains invariant for all the variations of \([\text{AN}], [\text{PMS}], [\text{H}_2\text{A}],\) and \([\text{n}ylon\ 6].\) The values so obtained can be seen in Table 40A. This composite rate constant was evaluated from the slopes of the plots \(n_g \text{ Vs } [\text{AN}]\) (Fig. 19C), \(n_g \text{ Vs } [\text{PMS}]^{-1/2}\) (Fig. 23C), \(n_g \text{ Vs } [\text{H}_2\text{A}]^{-1/2}\) (Fig. 26C) and \(n_g \text{ Vs } [\text{Wt. of PET}]^{-1/2}\) (Fig. 29C) and using the conditions maintained in Tables 25, 29, 33 and 37. The average value of the rate constant in \(E_{45}\) viz.,

\[
\frac{k_g}{(k_{t1})^{1/2} (2k_{12}k_1k_3)^{1/2}}
\]

was calculated to be 25.3 mol\(^{-1}\) l sec\(^{-1}\).

Multiplying the composite rate constants from \(R_g',\)

\[
k_g \left(\frac{2k_{12}k_1k_3}{k_{t1}}\right)^{1/2} \quad \text{and} \quad n_g' \left(\frac{k_g}{(k_{t1})^{1/2} (2k_{12}k_1k_3)^{1/2}}\right)^{1/2}
\]

measurements \((k_g/k_t^{1/2})\) value was obtained as

\(0.108\) mol\(^{-1/2}\) l\(^{1/2}\) g\(^{-1/2}\) sec\(^{-1/2}\).
The constancy in the value of $k_g/k_t^{1/2}$ determined for grafting reaction with PET (0.117 mol$^{-1/2}$ g$^{-1/2}$ sec$^{-1}$) and nylon 6 (0.108 mol$^{-1/2}$ g$^{-1/2}$ sec$^{-1}$) as backbone materials support the assumption made in the mechanism and consequent derivation.

Taking the ratio of the values of composite rate constants from $R_g$ and $n\_g$ measurements, the value $k_{12}k_1k_3$ was obtained as $1.82 \times 10^{-5}$ mol$^{-1}$ l sec$^{-1}$. This is lower than the value obtained for $k_8k_1k_2$ as $2.43 \times 10^{-5}$ mol$^{-1}$ l sec$^{-1}$ at 45°C using PET as backbone and indicates that nylon 6 is less effective for grafting than PET.

From the slope of the plots $R_h$ Vs $[AN]^{1.5}$ (Figs. 18B,D), $R_h$ Vs $[PMS]^{1/2}$ (Figs. 21B,D), $R_h$ Vs $[HA]^1$ (Figs. 25B,D) and $R_h$ Vs $[Nylon 6]^{1/2}$ (Figs. 28B,D) and using the conditions maintained in Tables 22, 23, 26, 27, 30, 31, 34 and 35, the average value of the composite rate constant in $E_4$, $$k_p\left(\frac{2k_{15}k_1k_3}{k_{t4}}\right)^{1/2}$$ was calculated to be $7.47 \times 10^{-3}$ mol$^{-1/2}$ g$^{3/2}$ sec$^{-1}$ at 45°C and the values obtained from different plots are given in Table 40B. The constancy found in the value of the composite rate constant for all the variations of $[AN]$, $[PMS]$, $[HA]$, and $[Nylon 6]$. 

The values are tabulated in Table 40B.
[H₂A] and [Nylon 6] shows that the right choice of the rate expression for \( R_h \) is \( E_{46} \).

That the rate expression as given by \( E_{47} \) for \( n_h \) is the right selection is further confirmed by the fact that the composite rate constant

\[
\frac{k_p}{(k_{44})^{1/2} (2 k_{15} K_1 K_3)^{1/2}}
\]

remain invariant for all the variations of AN, PMS, H₂A and nylon 6. The values obtained can be seen in Table 40B.

This composite rate constant was evaluated from the slopes of the plot \( n_h \) Vs [AN] (Fig. 19D), \( n_h \) Vs [PMS] \(^{-1/2}\) (Fig. 23D), \( n_h \) Vs [H₂A] \(^{-1/2}\) (Fig. 26D) and \( n_h \) Vs [Wt. of nylon 6] \(^{-1/2}\) (Fig. 29D) and using the conditions maintained in Tables 25, 29, 33 and 37. The average value of the composite rate constant in \( E_{47} \), viz.,

\[
\frac{k_p}{(k_{44})^{1/2} (2 k_{15} K_1 K_3)^{1/2}}
\]

was calculated to be 220 mol\(^{-1/2}\) l\(^{1/2}\) sec\(^{-1}\).

Multiplying the composite rate constant values from \( R_h \)
\[ k_p \left( \frac{2 k_{15} K_1 K_3}{k_{t4}} \right) \]

and \( n_h \),

\[
\frac{k_p}{(k_{t4})^{1/2} (2 k_{15} K_1 K_3)^{1/2}}
\]

\((k_p/k_{t}^{1/2})\) value was obtained as 1.28 mol\(^{-3/4}\) g\(^{-1/2}\) sec\(^{-1/2}\).

It is important to recollect the value obtained for \((k_p/k_{t}^{1/2})\) from previous study as 1.53. The closeness of these two values also favour the proposed mechanism.

Taking the ratio of the composite rate constants values obtained from \( R_h \),

\[ k_p \left( \frac{2 k_{15} K_1 K_3}{k_{t4}} \right) \]

and \( n_h \),

\[
\frac{k_p}{(k_{t4})^{1/2} (2 k_{15} K_1 K_3)^{1/2}}
\]

measurements at 45\(^\circ\)C, the value \( k_{15} K_1 K_3 \) was calculated as \( 3.39 \times 10^{-5} \) mol\(^{-3/2}\) g\(^{1/2}\) sec\(^{-1}\).
Knowing \( k_{12} \), \( K_1 \), \( K_3 \) value from \( R_g \) and \( n_g \) measurements as \( 1.82 \times 10^{-5} \) \( \text{mol}^{-1} \text{I sec}^{-1} \) and \( k_{15} \), \( K_1 \), \( K_3 \) value from \( R_h \) and \( n_h \) measurements as \( 3.39 \times 10^{-5} \) \( \text{mol}^{-3/2} \text{I}^{3/2} \text{sec}^{-1} \), the ratio of the two values \( (k_{12}/k_{15}) \) can be obtained as \( 0.537 \) \( \text{mol}^{-1/2} \text{I}^{-1/2} \). The ratio shows that \( k_{12} \ll k_{15} \), suggesting that in graft copolymerization studies with AN on nylon 6 using PMS-H_A redox pair graft copolymerization and homopolymerization should occur simultaneously with \( R_g \ll R_h \).

For the selected reaction scheme, an expression for \( -R_{PMS} \) can be written as,

\[
-R_{PMS} = k_{15} K_3 [M] [PMS]_r [H_2A][\text{nylon 6}] + k_{12} K_1 K_3 [PMS][H_2A][\text{nylon 6}]
\]

\[
1 + K_1 [H_2A] + K_3 [H_2A] [\text{nylon 6}]
\]

\[ \therefore E_{48} \]

\([PMS]_r = \text{initial [PMS]} \text{ taken.}\]

when \( K_1 K_3 [H_2A] \text{ [nylon 6]} \gg 1 + K_1 [H_2A] \), the expression becomes,

\[
-R_{PMS} = (k_{15} [M] + k_{11}) [PMS] \quad \therefore E_{49}
\]

The values obtained for \( k_{15} \), \( K_1 \), \( K_3 \) and \( k_{12} \), \( K_1 \), \( K_3 \) from the slopes of the plots \( -R_{PMS} \) Vs [PMS] (Figs. 22C,D) are \( 6.14 \times 10^{-3} \) \( \text{sec}^{-1} \) and \( 2.30 \times 10^{-8} \) \( \text{sec}^{-1} \) respectively.
using the slopes and knowing $-R_{PMS}$ was invariant to the change in $[H_2A]$ and [nylon 6], the two equations $[k_{15} [M] + k_{12}]$ with two different $[M]$ as given in Tables 26 and 27 are solved to obtain the ratio $(k_{12}/k_{15})$ and the calculated value is found to be 0.374. This again supports that $k_{12} < k_{15}$ as it was inferred through grafting measurements.

The effect of % grafting and % efficiency can have relevant explanation as discussed earlier in 4.1.

4.1.3 PMS-H$_2$A Redox Initiated Graft Copolymerization of AN onto nylon 66

The observation made with this system is almost similar to the one as seen in graft copolymerization of AN onto nylon 6 initiated by PMS-H$_2$A redox pair. The kinetic results show similar trends in this system.

4.1.3.1 Results on PMS-H$_2$A Redox Initiated Graft Copolymerization of AN onto nylon 66

Effect of Time on Graft Parameters

Both $R_g$ and $R_h$ show initial increase with time and thereafter fall (Table 41). In order to follow the kinetics of graft copolymerization, a reaction time more than four
hours was selected for the present study. The plots $R_g$ Vs time (Fig. 31A) and $R_h$ Vs time (Fig. 31B) were drawn.

$n_g$ and $n_h$ measurements show an increasing trend initially and then they fall. The plots $n_g$ Vs time (Fig.31C) and $n_h$ Vs time (Fig. 31D) were also drawn.

**Effect of [AN] Craft Parameters**

$R_g$ and $R_h$ measurements were carried out under the experimental conditions specified in Table 42. It was observed that both $R_g$ and $R_h$ increase gradually with [AN].

Log $R_g$ Vs log [AN] (Fig. 32A) and log $R_h$ Vs log [AN] (Fig. 32B) plots were drawn and found to be straight lines with a slope of unity with respect to $R_g$ and 1.5 with regard to $R_h$. Direct plots $R_g$ Vs [AN] (Fig. 33A) and $R_h$ Vs $[AN]^{1.5}$ (Fig. 33B) were also drawn to further support the order dependences.

With a view to confirming the order dependences, the effect of [AN] on $R_g$ and $R_h$ was also studied with a different set of experimental conditions (Table 43). Log $R_g$ Vs log [AN] (Fig. 32C) and log $R_h$ Vs log [AN] (Fig.32D) plots were drawn and found to be straight lines with a slope of unity with respect to $R_g$ and 1.5 with regard to $R_h$. Direct plots $R_g$ Vs [AN] (Fig. 33C) and $R_h$ Vs $[AN]^{1.5}$ (Fig. 32D) were also drawn to confirm the order dependences.
The effect of change in [AN] on % grafting and % efficiency were given in Table 44. It was observed that both % grafting and % efficiency increase with [AN].

\( n_g \) and \( n_h \) values were determined separately and found to increase with [AN] (Table 45). Log \( n_g \) Vs log [AN] (Fig. 34A) and log \( n_h \) Vs log [AN] (Fig. 34B) plots were drawn and found to be straight lines with slopes unity and 0.5 respectively indicating first order dependence with respect to \( n_g \) on AN and half order on \( n_h \). To ascertain this finding, direct plots \( n_g \) Vs [AN] (Fig. 34C) and \( n_h \) Vs [AN]\(^{1/2}\) (Fig. 34D) were also drawn.

It was found that \( -R_{PMS} \) value remains constant for the conditions specified in Table 43.

**Effect of [PMS] on Graft Parameters**

Both \( R_g \) and \( R_h \) increase with a change in [PMS] (Table 46). The plots of log \( R_g \) Vs log [PMS] (Fig. 35A) and log \( R_h \) Vs log [PMS] (Fig. 35B) were drawn and found to be straight lines with a slope of 0.5 indicating half order dependences of \( R_g \) and \( R_h \) respectively on [PMS]. In order to confirm the above order dependences, direct plots of \( R_g \) Vs [PMS]\(^{1/2}\) (Fig. 36A) and \( R_h \) Vs [PMS] (Fig. 36B) were drawn and found to be straight lines passing through the origin.
In an attempt to ascertain the above order dependence in a different set of experimental conditions, \( R_g \) and \( R_h \) measurements were carried out. Both \( R_g \) and \( R_h \) were found to increase with [PMS] (Table 47). Plots of log \( R_g \) Vs log [PMS] (Fig. 35C) and log \( R_h \) Vs log [PMS] (Fig. 35D) were drawn and found to be straight lines with a slope of 0.5 indicating half order dependences of \( R_g \) and \( R_h \) on PMS. Direct plots \( R_g \) Vs [PMS]^{1/2} (Fig. 36C) and \( R_h \) Vs [PMS]^{1/2} (Fig. 36D) were also drawn to support the order dependences.

Both % grafting and % efficiency gradually increase with increase in [PMS] (Table 48).

\( n_g \) and \( n_h \) measurements were carried out separately with [PMS] (Table 49) and found that both \( n_g \) and \( n_h \) decrease with [PMS]. Plots of log \( n_g \) Vs log [PMS] (Fig.38A) and log \( n_h \) Vs log [PMS] (Fig. 38B) were drawn and found to be straight lines with a slope of negative 0.5 indicating inverse square root order dependences of \( n_g \) and \( n_h \) on [PMS]^{-1/2} (Fig. 38D) were drawn and found to confirm the order dependences.

**Effect of [PMS] on \( -R_{PMS} \)**

\( -R_{PMS} \) was followed under the conditions mentioned in Tables 46 and 47 and found that \( -R_{PMS} \) values increase
with PMS. A plot of log \([-R_{PMS}\)] Vs log \([PMS]\) (Fig. 37A) was a straight line with a slope of unity suggesting a first order dependence of \(-R_{PMS}\) on PMS. The direct plot \(-R_{PMS}\) Vs PMS (Fig. 37C) was also drawn and found to confirm the above order dependence.

Under a set of different experimental conditions given in Table 47, plot of log \([-R_{PMS}\)] Vs log \([PMS]\) (Fig. 37B) was drawn and found to be a straight line with a slope of unity suggesting a first order dependence of \(-R_{PMS}\) on PMS. The direct plot \(-R_{PMS}\) Vs PMS (Fig. 37D) was also drawn to confirm the order dependence.

Effect of \([H_A]\) on Graft Parameters

Both \(R_g\) and \(R_h\) increase steadily with increase in \([H_A]\) (Table 50). Plots of log \(R_g\) Vs log \([H_A]\) (Fig. 39A) and log \(R_h\) Vs log \([H_A]\) (Fig. 39B) were drawn and found to be straight lines with a slope of 0.5 suggesting half order dependences of \(R_g\) and \(R_h\). Direct plots \(R_g\) Vs \([H_A]^{1/2}\) (Fig. 40A) and \(R_h\) Vs \([H_A]^{1/2}\) (Fig. 40B) were also drawn in order to confirm the above order dependences.

\(R_g\) and \(R_h\) values were found to increase with \([H_A]\) under a set of different experimental conditions (Table 51). Plots of log \(R_g\) Vs log \([H_A]\) (Fig. 39C) and log \(R_h\) Vs log \([H_A]\) (Fig. 39D) were drawn and found to give a slope of
0.5 indicating half order dependences on $R_g$ and $R_h$. Direct plots $R_g$ Vs $[H_2A]^{1/2}$ (Fig. 40C) and $R_h$ Vs $[H_2A]^{1/2}$ (Fig. 40D) were also drawn to confirm the above order dependences.

Both % grafting and % efficiency increase with increase in $H_2A$ under the experimental conditions specified in Table 52.

$n_g$ and $n_h$ were determined separately with $[H_2A]$ and found to decrease with $H_2A$ under the conditions mentioned in Table 53. Plots of log $n_g$ Vs log $[H_2A]$ (Fig. 41A) and log $n_h$ Vs log $[H_2A]$ (Fig. 41B) were drawn to get an idea with respect to $[H_2A]$. The slopes of the plots were found to be half indicating half order dependence on $H_2A$. In order to confirm the order dependences, direct plots $n_g$ Vs $[H_2A]^{-1/2}$ (Fig. 41C) and $n_h$ Vs $[H_2A]^{-1/2}$ (Fig. 41D) were also drawn.

**Effect of Nylon 66 Weight on Graft Parameters**

For the variation of the backbone amount from 0.05 to 0.35 g, both $R_g$ and $R_h$ increase steadily under the conditions given in Table 54. Log $R_g$ Vs log [Wt. of nylon 66] (Fig. 42A) and log $R_h$ Vs log [Wt. of nylon 66] (Fig. 42B) plots were drawn and the slopes of plots show half order dependence on the backbone amount in both $R_g$ and $R_h$. 
Direct plots $R_g$ Vs [Wt. of nylon 66] (Fig. 43A) and $R_h$ Vs [Wt. of nylon 66] (Fig. 43B) were also drawn to further support the order dependences.

$R_g$ and $R_h$ were also studied under a set of different experimental conditions as specified in Table 55. Log $R_g$ Vs log [Wt. of nylon 66] (Fig. 42C) and log $R_h$ Vs log [Wt. of nylon 66] (Fig. 42D) plots were drawn and found to give a slope of 0.5 suggesting half order dependences on $R_g$ and $R_h$. Direct plots $R_g$ Vs [Wt. of nylon 66]^{1/2} (Fig. 43C) and $R_h$ Vs [Wt. of nylon]^{1/2} (Fig. 43D) were also drawn to further support the order dependences.

The effect of change of % grafting and % efficiency with a change in the backbone amount was presented in Table 56. The % grafting decreases but % efficiency increases with the backbone amount.

$n_g$ and $n_h$ measurements were carried out separately and they show decreasing trend with the backbone amount (Table 57). Log $n_g$ Vs log [Wt. of nylon 66] (Fig. 44A) and log $n_h$ Vs log [Wt. of nylon 66] (Fig. 44B) plots were drawn and found to give a slope of negative 0.5 thus indicating inverse square root order dependences on $n_g$ and $n_h$. Direct plots $n_g$ Vs [Wt. of nylon 66]^{-1/2} (Fig. 44C) and $n_h$ Vs [Wt. of nylon 66]^{-1/2} (Fig. 44D) were also drawn to further support the order dependences.
Effect of Temperature on Graft Parameters

$R_g$ and $R_h$ values obtained by changing the temperature from 303 K to 323 K under the experimental conditions specified in Table 58. It was observed that both $R_g$ and $R_h$ increase initially and then they fall (Table 58). Arrhenius plots log $R_g$ Vs $1/T$ (Fig. 45A) and log $R_h$ Vs $1/T$ (Fig. 45B) were drawn and the energy of activation $E_a$ values for $R_g$ and $R_h$ were determined as 6.27 and 2.61 Kcal/mole respectively. Both % grafting and % efficiency increase gradually initially and then they fall.

$n_g$ and $n_h$ determinations were carried out separately and found that the values increase with temperature. Arrhenius plots of log $n_g$ Vs $1/T$ (Fig. 45C) and log $n_h$ Vs $1/T$ (Fig. 45D) were also drawn and the $E_a$ values for $n_g$ and $n_h$ were determined and found to be 14.3 and 13.4 Kcal/mol respectively.

4.1.7.2 Discussion on Results

It was observed that the results obtained in this system was similar to the one as seen in graft copolymerization of AN initiated by redox pair PMS-$\text{H}_2\text{A}$ onto nylon 6. This points out that probable reaction schemes would be similar to the one as in the previous case.
Hence, a similar sequence of reactions as represented in Scheme VIII for the graft copolymerization of AN initiated by PMS-H₂A redox pair onto PET with a change in the backbone as nylon 66 would be selected as the most probable for this system.

The grafting of nylon 66 was reported to be initiated by the production of nylon radical by the abstraction of a proton from the \( \sim \)NH grouping in the backbone polymer \[91\].

\[
\text{NH} + R \rightarrow \text{N} + \text{RH}
\]

where 'R' can be a radical or metal ion.

4.1.3 Selected Most Probable Scheme

Initiation

\[
PMS + H_2A \xrightleftharpoons[{K_1}]{} PMS - H_2A
\]

Complex 1, \( C_1 \)

\[
C_1 + \text{nylon 66} \xrightarrow[{K_a}]{} PMS - H_2A - \text{nylon 66}
\]

Complex 4, \( C_4 \)

\[
C_4 \xrightarrow[K_{16}]{} (\text{nylon 66})^- + H_2O + H^+ + SO_4^-\]

\[
\text{nylon 66}^- + M \xrightarrow[K_{17}]{} (\text{nylon 66})^- M
\]
SO₄²⁻ + H₂O $\xrightarrow{k_2} \cdot OH + HSO₄⁻$

\dot{OH} + H₂A $\xrightarrow{k_3} H₂O + A⁻ + H^+$

$C_1 + A^- \xrightarrow{k_{18}} SO₄²⁻ + 2HA^- + H₂O + H^+$

**Propagation**

(nylon 66) $M^* + M \xrightarrow{k_9} (nylon 66)^*M₂$

(nylon 66) $M^n_{n-1} + M \xrightarrow{k_9} (nylon 66) M^n_n$

**Termination**

$2(nylon 66) M^n_n \xrightarrow{k_{15}} (nylon 66) M^n_n$

For the simultaneous homopolymerization, the similar mechanism would be followed.

**Initiation**

PMS + H₂A $\xrightarrow{K_1} Complex_1 C_1$

$C_1 + nylon 66 \xrightarrow{K_9} Complex_4 C_4$

$C_4 + M \xrightarrow{k_{19}} M^* + H₂O + H^+ + SO₄²⁻ (nylon 66)$

SO₄²⁻ + H₂O $\xrightarrow{k_2} \cdot OH + HSO₄⁻$

\dot{OH} + H₂A $\xrightarrow{k_3} H₂O + A⁻ + H^+$
\[ C_1 + A^+ \xrightarrow{k_7} 5O_3^- + 2HA^- + H_2O + H^+ \]
\[ M + A^+ \xrightarrow{k_{10}} M_1^- \]

**Propagation**

\[ M_1^- + M \xrightarrow{k_P} M_2^- \]
\[ M_{n-1}^- + M \xrightarrow{k_P} M_n^- \]

**Termination**

\[ M_n^- + M_n^- \xrightarrow{k_{t6}} \text{homopolymer} \]

For this Scheme, the expressions for \( R_g \), \( n_g \), \( R_h \)
and \( n_h \) can then be written based on the discussions in 4.1.2 related to PET.

\[
R_g = k_g \left( \frac{2k_{16} K_1 K_4}{k_{t5}} \right)^{1/2} [M]^{1/2} [\text{nylon 66}]^{1/2} [\text{PMS}]^{1/2} [H_2A]^{1/2} \]
\[
\cdot E_{50} \]

\[
k_g = \frac{[M]}{(k_{t5})^{1/2} (2k_{16} K_1 K_4)^{1/2} [\text{nylon 66}]^{1/2} [\text{PMS}]^{1/2} [H_2A]^{1/2}} \cdot E_{51} \]

\[
R_h = k_p \left( \frac{2k_{16} K_1 K_4}{k_{t6}} \right)^{1/2} [\text{nylon 66}]^{1/2} [H_2A]^{1/2} [\text{PMS}]^{1/2} [M]^{3/2} \]
\[
\cdot E_{52} \]
4.1.2.3 Evaluation of Composite Rate Constant for the System and Test for their Invariance

That the rate expression as given by $E_{50}$ is the right choice is further confirmed by the fact that the composite rate constant $k_g$

$$n_h = \frac{k_p (M)^{1/2}}{(k_{t6})^{1/2} (2k_{10} K_1 K_4)^{1/2} [\text{nylon 66}]^{1/2} [H_2A]^{1/2} [\text{PMS}]^{1/2}}$$

remains invariant for all the variation of $[\text{AN}]$, $[\text{PMS}]$, $[\text{H}_2\text{A}]$, $[\text{Nylon 66}]$. The values so obtained can be seen in Table 60A. This composite rate constant was evaluated from the slope of the plots $R_g$ Vs $[\text{AN}]$ (Figs. 33A,C); $R_g$ Vs $[\text{PMS}]^{1/2}$ (Figs. 36A,C); $R_g$ Vs $[H_2A]^{1/2}$ (Figs. 40A,C); $R_g$ Vs $[\text{nylon 66}]^{1/2}$ (Figs. 43A,C) and using the conditions maintained in Tables 42, 43, 46, 47, 50, 51, 54 and 55. The average value of the composite rate constant in $E_{50}$, viz.,

$$k_g \left( \frac{2 k_{16} K_1 K_4}{k_{t5}} \right)^{1/2}$$

was calculated to be $4.16 \times 10^{-4}$ mol$^{-1}$ l g$^{-1/2}$ sec$^{-1}$. 
From the slopes of the plots \( n_g \) Vs \([AN]\) (Fig. 34C), \( n_g \) Vs \([PMS]\)^{1/2} (Fig. 38C), \( n_g \) Vs \([H_2A]^{-1/2}\) (Fig. 41C) and \( n_g \) Vs \([\text{Wt. of nylon 66}]^{-1/2}\) (Fig. 44C) and using the conditions maintained in Tables 45, 49, 54 and 57. The average value of the composite rate constant in \( E_{51} \)

\[
\frac{k_g}{(k_{t5})^{1/2} (2 k_{16} K_1 K_4)^{1/2}}
\]

was calculated to be 22.8 g^{-1/2} and the values obtained from different plots are given in Table 60A. The constancy found in the value of the composite rate constant for all the variations of \([AN]\), \([PMS]\), \([H_2A]\) and \([\text{nylon 66}]\) shows that the right selection of the rate expression for \( n_g \) is \( E_{51} \).

Multiplying the composite rate constant values from \( R_g \) and \( n_g \) measurements \((k_g/k_t^{1/2})\) value was obtained as 

\[
9.75 \times 10^{-2} \text{ mol}^{-1/2} \text{l}^{1/2} \text{ g}^{-1/2} \text{ sec}^{-1}.
\]

The constancy in the value of \((k_g/k_t^{1/2})\) determined for grafting reaction with PET \((0.117 \text{ mol}^{-1/2} \text{l}^{1/2} \text{ g}^{-1/2} \text{ sec}^{-1})\), nylon 6 \((0.108 \text{ mol}^{-1/2} \text{l}^{1/2} \text{ g}^{-1/2} \text{ sec}^{-1})\) and nylon 66 \((0.0975 \text{ mol}^{-1/2} \text{l}^{1/2} \text{ g}^{-1/2} \text{ sec}^{-1})\) as backbone materials favours the assumption made in the mechanism and consequent derivation.

Dividing the composite rate constant values from \( R_g \) and \( n_g \) measurements at 45°C, the value \( k_{16} K_1 K_4 \) was obtained as \( 1.86 \times 10^{-5} \text{ mol}^{-1} \text{ l sec}^{-1} \).
That the rate expression for \( R_h \) as given by \( E_{32} \)

\[
k_p \left( \frac{2 k_{19} K_1 K_q}{k_{14}} \right)
\]

is the correct selection of the rate expression is confirmed by the fact that the composite rate constant

\[
k_p \left( \frac{2 k_{19} K_1 K_q}{k_{14}} \right)
\]

remains invariant for all the variations of \( \text{AN}, \text{PMS}, \text{H}_2\text{A} \) and nylon 66. The values can be seen in Table 60B.

This composite rate constant was evaluated from the slopes of the plot \( R_h \) Vs \( [\text{AN}]^{1.5} \) (Figs. 33B,D), \( R_h \) Vs \( [\text{PMS}]^{1/2} \) (Figs. 36B,D), \( R_h \) Vs \( [\text{H}_2\text{A}]^{1/2} \) (Figs. 40B,D) and \( R_h \) Vs \( [\text{Wt. of nylon 66}]^{1/2} \) (Figs. 43B,D) and using the conditions maintained in Tables 42, 43, 46, 47, 50, 51, 54 and 55. The average value of the composite rate constant in \( E_{32} \), viz.,

\[
k_p \left( \frac{2 k_{19} K_1 K_q}{k_{14}} \right)
\]

was calculated to be \( 6.08 \times 10^{-3} \text{ mol}^{-3/2} \text{ g}^{-1/2} \text{ sec}^{-1} \).
That the rate expression as given by Eq. 53 for \( n_h \) is the right choice is further confirmed by the fact that the composite rate constant

\[
\frac{k_p}{(k_{\text{th}})^{1/2} (2 k_{19} K_1 K_4)^{1/2}}
\]

remains invariant for all the variations of AN, PMS, \( H_2A \) and nylon 66. The values can be seen in Table 60B.

This composite rate constant value was evaluated from the slopes of the plot \( n_h \) Vs [AN] (Fig. 34D), \( n_h \) Vs [PMS]^{-1/2} (Fig. 36D), \( n_h \) Vs \( [H_2A]^{-1/2} \) (Fig. 41D), and \( n_h \) Vs [Wt. of nylon 66]^{-1/2} (Fig. 44D) and using the conditions maintained in Tables 45, 49, 54 and 57. The average value of the composite rate constant in Eq. 53 viz.,

\[
\frac{k_p}{(k_{\text{th}})^{1/2} (2 k_{19} K_1 K_4)^{1/2}}
\]

was calculated to be 224 mol^{-1} l sec^{-1}.

Multiplying the composite rate constant value from \( R_h \) and \( n_h \) measurements, \( (k_p/k_{\text{th}})^{1/2} \) value was obtained as 1.17 mol^{3/4} l^{3/4} g^{-1/2} sec^{-1/2}. It is important to recollect the value obtained for \( (k_p/k_{\text{th}})^{1/2} \) from the earlier discussed
system, namely, $1.53 \text{ mol}^{-3/4} \text{ g}^{3/4} \text{ g}^{-1/2} \text{ sec}^{-1/2}$. The
closeness of these two values also favour the proposed
mechanism.

Taking the ratio of the composite rate constant
values obtained $R_h$ and $n_h$ measurements at $45^\circ \text{C}$, the value
$k_{19}k_1k_q$ was calculated as $2.7 \times 10^{-5} \text{ mol}^{-3/2} \text{ g}^{3/2} \text{ sec}^{-1}$.

Knowing $k_{16}$, $K_1$, $K_q$ value from $R_g$ and $n_g$
measurements as $1.86 \times 10^{-5} \text{ mol}^{-1} \text{ l sec}^{-1}$ and $k_{19}$, $K_1$, $K_q$
value from $R_h$ and $n_h$ measurements as $2.7 \times 10^{-5}$
$\text{ mol}^{-3/2} \text{ g}^{3/2} \text{ sec}^{-1}$, the ratio of the two values ($k_{16}/k_{19}$)
can be calculated as $0.689 \text{ mol}^{1/2} \text{ l}^{-1/2}$.

The composite rate constant values for the initiation
reactions with PET ($2.43 \times 10^{-5} \text{ mol}^{-1} \text{ l sec}^{-1}$), nylon 6
($1.82 \times 10^{-5} \text{ mol}^{-1} \text{ l sec}^{-1}$) and nylon 66 ($1.86 \times 10^{-5}$
$\text{ mol}^{-1} \text{ sec}^{-1}$) points out that grafting initiation follows an
order PET nylon 6 nylon 66.

For the selected reaction scheme, an expression
for $-R_{\text{PMS}}$ can be written as

$$-R_{\text{PMS}} = \frac{k_{19}k_1k_q[M][\text{PMS}][\text{H}_2A][\text{nylon 66}]+k_{16}k_1k_q[\text{PMS}][\text{H}_2A][\text{nylon 66}]}{(1 + K_1[\text{H}_2A] + K_q[\text{H}_2A][\text{nylon 66}] }$$

where $[\text{PMS}]_T = \text{initial [PMS] taken.}$
When \( K_1 K_4 [H_2A] \) [nylon 66] \( \geq 1 + K_1 [H_2A] \), the expression becomes 
\[
-R_{\text{PMS}} (k_{19} [M] + k_{16}) [\text{PMS}] = E_{55}
\]

The values obtained for \( k_{19} K_1 K_4 \) and \( k_{16} K_1 K_4 \) from the slopes of the plots (Figs. 37C,D) are 4.03 \( \times 10^{-4} \) sec\(^{-1}\) and 2.35 \( \times 10^{-4} \) sec\(^{-1}\). Using the slopes and knowing \( -R_{\text{PMS}} \) was invariant to the change in \([H_2A]\) and [nylon 66], the two equations \( (k_{19} [M] + k_{16}) \) with two different \([M]\) as given in Tables 46 and 47 are solved to obtain the ratio \( (k_{16}/k_{19}) \) and the calculated value is found to be 0.581. This again adds evidence that \( k_{16} < k_{19} \) as it was inferred through grafting measurements.

The effect of % grafting and % efficiency by the parameters can have relevant explanation as discussed in 4.1.1.

### 4.2.1 PMS-H\(_2\)A Redox Initiated Graft Copolymerization of MMA onto nylon 6

The observation made with this system is almost similar to the one as seen in graft copolymerization of AN onto nylon 6 with PMS-H\(_2\)A redox pair but with a different monomer MMA. Hence, kinetic results show similar trends in this system.
4.1.2.1 Results on PMS-H₂A Redox Initiated Graft Copolymerization of MMA onto nylon 66

Effect of Time on Craft Parameters

Both $R_g$ and $R_h$ values show initial increase with time and thereafter they fall (Table 61). Hence, a reaction time more than four hours was selected for this system to follow the smooth kinetics.

The plots $R_g$ Vs time (Fig. 46A) and $R_h$ Vs time (Fig. 46B) were drawn. The % grafting and % efficiency increase with time initially and then they fall (Table 61).

$n_g$ and $n_h$ values increase initially with time and then they fall (Table 61). The plots $n_g$ Vs time (Fig. 46C) and $n_h$ Vs time (Fig. 46D) were also drawn.

Effect of [MMA] on Craft Parameters

A glance at Table 62 clearly indicates that both $R_g$ and $R_h$ values increase with increase in [MMA]. Plots of log $R_g$ Vs log [MMA] (Fig. 47A) and log $R_h$ Vs log [MMA] (Fig. 47B) were drawn and found to be straight lines with the slope of unity showing first power dependence of $R_g$ and $R_h$ on MMA. Direct plots $R_g$ Vs [MMA] (Fig. 48A) and $R_h$ Vs [MMA] (Fig. 48B) were drawn in order to support the order dependences.
The effect of [MMA] on $R_g$ and $R_h$ was also studied under a set of different experimental conditions (Table 63). Both $R_g$ and $R_h$ increase with MMA. Plots of $\log R_g$ Vs $\log [\text{MMA}]$ (Fig. 47C) and $\log R_h$ Vs $\log [\text{MMA}]$ (Fig. 47D) were drawn and found to give an order of unity indicating first power dependence on $R_g$ and $R_h$. Direct plots $R_g$ Vs [MMA] (Fig. 48C) and $R_h$ Vs [MMA] (Fig. 48D) were also drawn to further support the order dependences.

The effect of change in [MMA] on % grafting and % efficiency under the conditions specified in Table 64 was tabulated and observed that both increase initially and then they fall (Table 64).

$n_g$ and $n_h$ values were determined separately and found that both increase steadily with [MMA] under the conditions specified in Table 65.

Plots of $\log n_g$ Vs $\log [\text{MMA}]$ (Fig. 49A) and $\log n_h$ Vs $\log [\text{MMA}]$ (Fig. 49B) were drawn and found to give a slope of unity indicating first power dependence on $n_g$ and $n_h$. Direct plots $n_g$ Vs [MMA] (Fig. 49C) and $n_h$ Vs [MMA] (Fig. 49D) were also drawn to confirm the order dependences of $n_g$ and $n_h$ on MMA.

It was found that $-R_{pMS}$ values remain almost constant for the conditions mentioned in Table 62.
Effect of [PMS] on Graft Parameters

It was observed that both $R_g$ and $R_h$ increase with increase in [PMS] under the conditions specified in Table 66. Plots of log $R_g$ Vs log [PMS] (Fig. 50A) and log $R_h$ Vs log [PMS] (Fig. 50B) were drawn and found to give a slope of 0.5 indicating half order dependences of $R_g$ and $R_h$ on MMA. Direct plots $R_g$ Vs [PMS]$^{1/2}$ (Fig. 51A) and $R_h$ Vs [PMS]$^{1/2}$ (Fig. 51B) were also drawn to confirm the order dependences.

To ascertain the above order dependences of $R_g$ and $R_h$ on PMS, $R_g$ and $R_h$ values were determined under a set of different experimental conditions as mentioned in Table 6n7. Plots of log $R_g$ Vs log [PMS] (Fig. 50C) and log $R_h$ Vs log [PMS] (Fig. 50D) were drawn and found to give a slope of 0.5 indicating half order dependences of $R_g$ and $R_h$ on PMS. Direct plots $R_g$ Vs [PMS]$^{1/2}$ (Fig. 51C) and $R_h$ Vs [PMS]$^{1/2}$ (Fig. 51D) were also drawn to confirm the order dependences.

The graft parameters such as % grafting and % efficiency increase with [PMS] under the conditions specified in Table 68.

$n_g$ and $n_h$ values were determined separately and found that both the values decrease with [PMS] (Table 69).
Plots of log $n_g$ Vs log $[\text{PMS}]$ (Fig. 53A) and log $n_h$ Vs log $[\text{PMS}]$ (Fig. 53B) were drawn and found to give a slope of negative 0.5 indicating inverse square root order dependences of $n_g$ and $n_h$ on PMS. Direct plots $n_g$ Vs $[\text{PMS}]^{-1/2}$ (Fig. 53C) and $n_h$ Vs $[\text{PMS}]^{-1/2}$ (Fig. 53D) were also drawn to confirm the order dependences of $n_g$ and $n_h$ on PMS.

Effect of $[\text{PMS}]$ on $-R_{\text{PMS}}$

$-R_{\text{PMS}}$ was followed under the conditions given in Tables 66 and 67 and found that $-R_{\text{PMS}}$ values increase with PMS. Plot of log $[\text{PMS}]$ Vs log $(-R_{\text{PMS}})$ (Fig. 52A) was drawn and found to give a slope of unity indicating first power dependence of $-R_{\text{PMS}}$ on PMS. Direct plot $-R_{\text{PMS}}$ Vs $[\text{PMS}]$ (Fig. 52C) was also drawn to further support the order dependences.

Under a set of different experimental conditions, specified in Table 67, similar trends were observed (Fig. 52B,D).

Effect of $[\text{H}_2\text{A}]$ on Craft Parameters

It was observed that both $R_g$ and $R_h$ values increase with $[\text{H}_2\text{A}]$ under the conditions specified in Table 70. Plots of log $R_g$ Vs log $[\text{H}_2\text{A}]$ (Fig. 54A) and log $R_h$
Vs log $[H_2A]$ (Fig. 54B) were drawn and found to give a slope of 0.5 showing half order dependences of $R_g$ and $R_h$ on $H_2A$. This was also confirmed by direct plots $R_g$ Vs $[H_2A]^{1/2}$ (Fig. 55A) and $R_h$ Vs $[H_2A]^{1/2}$ (Fig. 55B).

In order to get a better understanding about the order dependences, $R_g$ and $R_h$ values were determined under a set of different experimental conditions (Table 71). Similar trends were observed with respect to slopes and order dependences of $R_g$ and $R_h$ on $H_2A$ (Figs. 54D, 55C, D).

The other graft parameters like % grafting and % efficiency were determined under the conditions mentioned in Table 72 and observed that both increase steadily with $H_2A$.

$n_g$ and $n_h$ values were determined separately and found that both the values decrease with $H_2A$ (Table 73). Plots of log $n_g$ Vs log $[H_2A]$ (Fig. 56A) and log $n_h$ Vs log $[H_2A]$ (Fig. 56B) were drawn and found to give a slope of negative 0.5 indicating inverse square root order dependences of $n_g$ and $n_h$ on $H_2A$. The direct plots $n_g$ Vs $[H_2A]^{-1/2}$ (Fig. 56C) and $n_h$ Vs $[H_2A]^{-1/2}$ (Fig. 56D) were also drawn to give further support for the order dependences.
It was observed that $-R_{PMS}$ values remain constant 
$(1.69 \times 10^{-6} \text{ mol} \cdot \text{sec}^{-1})$ with H$_2$A, under the conditions mentioned in Table 70.

Effect of Weight of nylon 6 on Graft Parameters

For the variation of the backbone material from 0.10 g to 0.45 g, both $R_g$ and $R_h$ values increase under the conditions given in Table 74. Log $R_g$ Vs log [Wt. of nylon 6] (Fig. 57A) and log $R_h$ Vs log [Wt. of nylon 6] (Fig. 57B) were drawn and found to give a slope of 0.5 indicating half order dependences of $n_g$ and $n_h$ on the Wt. of nylon 6. Direct plots $n_g$ Vs [Wt. of nylon 6]$^{1/2}$ (Fig. 58A) and $n_h$ Vs [Wt. of nylon 6]$^{1/2}$ (Fig. 58B) were drawn to confirm the order dependences.

$R_g$ and $R_h$ values were determined under a set of different experimental conditions (Table 75) and found similar trends were observed (Figs. 57C,D; 58C,D).

The graft parameters such as % grafting and % efficiency were determined and found that they show different behaviour with Wt. of nylon 6. The % grafting increase initially and then it falls (Table 76), but % efficiency steadily increase with increase in the amount of backbone material nylon 6.
n_g and n_h values were determined separately and observed that both n_g and n_h decrease with the amount of backbone material (Table 77). Log n_g Vs log [Wt. of nylon 6] (Fig. 59A) and log n_h Vs log [Wt. of nylon 6] (Fig. 59B) were drawn and found to give a slope of negative 0.5 indicating inverse square root order dependences of n_g and n_h on Wt. of nylon 6. Direct plots n_g Vs [Wt. of nylon 6]^{-1/2} (Fig. 59C) and n_h Vs [Wt. of nylon 6]^{-1/2} (Fig. 59D) were also drawn in order to confirm the order dependences.

Effect of Temperature on Graft Parameters

The effect of temperature on R_g and R_h was determined under the conditions mentioned in Table 78 and found that the values increase steadily with temperature. Arrhenius plots of log R_g Vs 1/T (Fig. 60A) and log R_h Vs 1/T (Fig. 60B) were drawn. The energy of activation E_a values were determined for R_g and R_h and found to be 4.06 and 5.90 Kcal/mol respectively. The graft parameters such as % grafting and % efficiency increase with temperature (Table 79). n_g and n_h were determined separately and found that they increase with temperature (Table 79). Arrhenius plots of log n_g Vs 1/T (Fig. 60C) and log n_h Vs
1 (Fig. 60D) were also drawn and the \( E_g \) values were calculated to be 8.61 and 10.9 Kcal/mol respectively.

4.2.1.2 Discussion on Results

It is quite interesting to know that even though the results obtained in this system of graft copolymerization of MMA onto nylon 6 with PMS-H_2A redox pair are similar with regards to \( R_g \) and \( n_g \) measurement as in the earlier systems with AN as monomer, \( R_h \) and \( n_h \) are found to have different behaviour.

Hence, grafting reactions now with MMA may have the same sequence as in the previous system with AN as the monomer.

Selected Reaction Scheme

Initiation

\[
PMS + H_2A \quad \overset{K_1}{\rightleftharpoons} \quad PMS - H_2A
\]

Complex \(_1\), \( C_1 \)

\[
C_1 + \text{nylon 6} \quad \overset{K_3}{\rightleftharpoons} \quad PMS - H_2A - \text{nylon 6}
\]

Complex \(_3\), \( C_3 \)

\[
C_3 \overset{k_{12}}{\longrightarrow} \quad \text{nylon 6}^+ + H_2O + H^+ + SO_4^{2-}
\]

\[
\text{nylon 6}^+ + M \overset{k_{20}}{\longrightarrow} \text{(nylon 6)}^+ M^-
\]
SO₄²⁻ + H₂O  \xrightarrow{k₂}  \cdot OH + HSO₄⁻
\cdot OH + H₂A  \xrightarrow{k₃}  H₂O + A⁻ + H⁺
C₃ + A⁻  \xrightarrow{k₄}  SO₄²⁻ + 2HA⁻ + H₂O + H⁺

Propagation

\text{nylon 6} M⁺ + M  \xrightarrow{k'₉}  \text{nylon 6} M⁺ (where \( k'₉ \) is the rate constant for the propagation in grafting with MMA as monomer)

Termination

2\text{nylon 6} M⁺ \xrightarrow{k₅₉} \text{graft copolymer}

For the above mechanism of grafting, the expression for \( R_g \) and \( n_g \) would be written based on the discussion in 4.1.2.

\begin{align*}
R_g &= k'₉ \left( \frac{k'₁₂k'₁k'₃}{k₅₉} \right)^{1/2} \cdot [M]\cdot[\text{nylon 6}]^{1/2}[\text{PMS}]^{1/2}[\text{H}_2\text{A}]^{1/2} \\
&= E_{₉₄} \\

n_g &= \frac{k'₉ \cdot [M]}{(k₅₉)^{1/2} \cdot (2k'₁₂k'₁k'₃)^{1/2} \cdot [\text{nylon 6}]^{1/2}[\text{PMS}]^{1/2}[\text{H}_2\text{A}]^{1/2}} \\
&= E_{₉₅}
\end{align*}
In $E_{48}$, all the experimental observations such as first power dependence on [MMA] (Figs. 48A,C) square root order dependences on $[\text{PMS}]^{1/2}$ (Figs. 51A,C), $[\text{H}_2\text{A}]^{1/2}$ (Figs. 55A,C), and [nylon 6]$_{1/2}$ (Figs. 58A,C) towards $R_y$ can be seen.

In $E_{45}$, all the experimental observations such as first power dependence on [M] (Fig. 49C), inverse square root order dependences on $[\text{PMS}]^{-1/2}$ (Fig. 53C), $[\text{H}_2\text{A}]^{-1/2}$ (Fig. 56C) and on [nylon 6]$_{-1/2}$ (Fig. 59C) towards $n_g$ could be seen.

$R_h$ was found to have first power dependence when MMM was monomer (Figs. 48B,D) in this present case in contrast to the three halfth order dependence when the monomer was [AN] (Figs. 3B,D; 18B,D; 33B,D) in earlier cases. This necessitates to identify new mechanism for homopolymerization in this case. Obviously, the half order dependences on nylon 6, PMS and $H_2A$ predicts the mutual termination. Hence, it is worthwhile to think about new initiation for homopolymerization. This can be, by the reaction with the monomer and the primary radical generated from the decomposition of the complex PMS-$H_2A$-nylon 6 in contrast to the homopolymerization with AN monomer through a direct interaction between complex PMS-$H_2A$- and monomer.
Initiation

\[
\begin{align*}
PMS + H_2A & \xrightleftharpoons{K_1} PMS - H_2A \\
\text{Complex } C_1
\end{align*}
\]

\[
C_1 + \text{nylon 6} \xrightleftharpoons{K_4} PMS - H_2A - \text{nylon 6} \text{ Complex, } C_3
\]

\[
C_3 \xrightarrow{k_{12}} \text{nylon 6}^* + H_2O + H^+ + SO_4^- \\
SO_4^- + H_2O \xrightarrow{k_2} \cdot OH + HSO_4^- \\
\cdot OH + H_2A \xrightarrow{k_3} H_2O + A^+ + H^+ \\
C_1 + A^+ \xrightarrow{k_7} SO_4^- + 2HA^- + H_2O + H^+
\]

\[
M + A^+ \xrightarrow{k_{20}} M_1^*
\]

Propagation with usual propagation

\[
M_1^* + M \xrightarrow{k_{p1}} M_2^* \\
M_{n-1}^* + M \xrightarrow{k_{p2}} M_n^*
\]

Termination by mutual type

\[
M_n^* + M_n^* \xrightarrow{k_{16}} \text{homopolymer}
\]

Applying stationary state approximation to all radicals, a derivation for \( R_{1i} \) can be arrived at as
\[
\begin{align*}
\frac{d[SO_4]}{dt} &= k_{12} K_1 K_3 [\text{nylon 6}] [H_2A] [\text{PMS}] - k_2 [SO_4]^2 + k_7 K_1 [H_2A] [\text{PMS}] [A^+] = 0 \quad \cdots E_{56} \\
\frac{d[A^+]}{dt} &= k_3 [\text{OH}] [H_2A] - k_7 K_1 [H_2A] [\text{PMS}] [A^+] - k_{20} [A^+] [M] = 0 \quad \cdots E_{57} \\
\frac{d[\text{OH}]}{dt} &= k_2 [SO_4]^2 - k_3 [\text{OH}] [H_2A] = 0 \quad \cdots E_3 \\
\frac{d[M^+]}{dt} &= k_{12} K_1 K_3 [\text{nylon 6}] [H_2A] [\text{PMS}] + k_{20} [A^+][M] - k_{16} [M^+]^2 = 0 \quad \cdots E_{58} \\
[M^+]^{1/2} &= \left(\frac{k_{12} K_1 K_3}{k_{16}}\right)^{1/2} [\text{nylon 6}]^{1/2} [H_2A]^{1/2} [\text{PMS}]^{1/2} \quad \cdots E_{59} \\
\text{Knowing,} \\
R_h &= k_p^i [M^+] [M] \quad \cdots E_{60} \\
R_h &= k_p^i \left(\frac{k_{12} K_1 K_3}{k_{16}}\right) [\text{nylon 6}]^{1/2} [H_2A]^{1/2} [\text{PMS}]^{1/2} [M] \quad \cdots E_{61}
\end{align*}
\]
Here in $E_{61}$, all the experimental observations such as first power dependence on [MMA] (Figs. 48B,D), square root order dependence on [PMS] (Figs. 51B,D), [H$_2$A] (Figs. 55B,D), and [nylon 6] (Figs. 58B,D) related to $R_h$ can be clearly accounted.

For the above scheme, an expression for $n_h$ can be arrived at as

$$n_h = \frac{\text{rate of homopolymerization}}{\text{rate of termination}}$$

$$= \frac{k_p [M]}{k_{t6} [M^*]}$$

$$n_h = \frac{k_p [M]}{(k_{t6})^{1/2} (k_{12} K_1 K_3) [\text{nylon 6}]^{1/2} [H_2A]^{1/2} [\text{PMS}]^{1/2}}$$

$E_{62}$ clearly accounts for all the observed experimental results with respect to $n_h$ such as first power dependence on [MMA] (Fig. 49D), inverse square root order dependences on [nylon 6] (Fig. 59D), [PMS] (Fig. 53D) and [H$_2$A] (Fig. 56D).

These two expressions for $R_h$ and $n_h$ adequately explain all the experimental observations related to $R_h$ and $n_h$. 
Hence, \( E_{44}, E_{45}, E_{61}, \) and \( E_{62} \) are the most suitable expressions for \( R_g, n_g, R_h, \) and \( n_h \) respectively.

### 4.3.3 Evaluation of Composite Rate Constants for the System and Test for their Invariance

The rate expression as given by \( E_{44} \) is the correct selection for \( R_g \), is further confirmed by the fact that the composite rate constant

\[
k_g \left( \frac{k_{12} K_1 K_3}{k_{16}} \right)^{1/2}
\]

remains invariant for all the variations of MMA, \( H_2A \), PMS and nylon 6. The values so obtained can be seen in Table 80A.

This composite rate constant was evaluated from the slope of the plots \( R_g \) vs [MMA] (Figs. 48A,C), \( R_g \) vs [PMS] \(^{1/2}\) (Figs. 51A,C), \( R_g \) vs \([H_2A]^{1/2}\) (Figs. 55A,C) and \( R_g \) vs [Wt. of nylon 6] \(^{1/2}\) (Figs. 58A,C) and using the conditions maintained in Tables 62, 63, 66, 67, 70, 71, 74 and 75. The average value of the composite rate constant in \( E_{44} \), viz.,

\[
k_g \left( \frac{k_{12} K_1 K_3}{k_{16}} \right)^{1/2}
\]

was calculated to be \( 3.39 \times 10^{-3} \text{ mol}^{-1} \text{ l g}^{-1/2} \text{ sec}^{-1} \).
From the slopes of the plots \( n_g \) Vs \([\text{MMA}]\) (Fig. 48C), \( n_g \) Vs \([\text{PMS}]^{-1/2}\) (Fig. 53), \( n_g \) Vs \([\text{H}_2\text{A}]^{-1/2}\) (Fig. 56C) and \( n_g \) Vs \([\text{Wt. of nylon 6}]^{-1/2}\) (Fig. 59C) and using the conditions maintained in Tables 65, 69, 73 and 77, the average value of the composite rate constant in E_{45}^k \[
\frac{k_g}{(k_{t1})^{1/2}(2k_{12}K_1K_3)^{1/2}}
\] was calculated to be 25.2 mol^{-1} l sec^{-1} and the values obtained from different plots are given in Table 80A. The constancy found in the value of the composite rate constant for all the variations of MMA, PMS, H_2A and nylon 6 shows that the correct selection of the rate expression for \( n_g \) is \( E_{45}^k \).

Multiplying the composite rate constant values obtained from \( R_g \) and \( n_g \) measurements \( (k_g/k_t^{1/2}) \) value was obtained as 0.292 mol^{-1/2} l^{1/2} sec^{-1}. This value was found to be higher than \( (k_g/k_t^{1/2}) \) obtained with AN as monomer. It can be inferred therefore that MMA can better be grafted than AN.

Taking the ratio of the composite rate constant values from \( R_g \) and \( n_g \) measurements at 45^\circ C, the value \( k_{12}K_1K_3 \) was obtained as \( 1.34 \times 10^{-4} \) mol^{-1} l sec^{-1}. 
That the rate expression as given by $E_{61}$ for $R_h$,

$$k_p^t \left( \frac{k_{12} K_1 K_3}{k_{t6}} \right)$$

is the correct selection is further confirmed by the fact that the composite rate constant

$$k_p^t \left( \frac{k_{12} K_1 K_3}{k_{t6}} \right)$$

remains invariant for all the variations of MMA, PMS, H$_2$A and nylon 6. The values can be seen in 80B.

This composite rate constant was evaluated from the slopes of plot $R_h$ Vs [MMA] (Figs. 48B,D), $R_h$ Vs [PMS]$^{1/2}$ (Figs. 51B,D), $R_h$ Vs [H$_2$A]$^{1/2}$ (Figs. 55B,D), and $R_h$ Vs [Wt. of nylon 6]$^{1/2}$ (Figs. 58B,D) and using the conditions maintained in Tables 62, 63, 66, 67, 70, 71, 74 and 75. The average value of the composite rate constant in $E_{61}$, viz.,

$$k_p^t \left( \frac{k_{12} K_1 K_3}{k_{t6}} \right)$$

was calculated to be $3.77 \times 10^{-2} \text{ mol}^{-1} \text{ g}^{-1/2} \text{ sec}^{-1}$ at 40$^\circ$C.
From the slopes of the plots $n_h$ Vs [MMA] (Fig. 49D), $n_h$ Vs [PMS]$^{-1/2}$ (Fig. 53D), $n_h$ Vs [H$_2$A]$^{-1/2}$ (Fig. 56D) and $n_h$ Vs [Wt. of nylon 6]$^{-1/2}$ (Fig. 59D) and using the conditions maintained in Tables 65, 69, 73 and 77, the average value of the rate constant in $E_{62}$

$$k_p^{1/2}$$

$$(k_{16})^{1/2} (k_{12} K_1 K_3)$$

was calculated to be 247 mol$^{-1}$ l sec$^{-1}$ and the values obtained from different plots are given in Table 80B. The constancy found in the value of the composite rate constant for all the variations of MMA, PMS, H$_2$A and nylon 6 shows that the right choice of the rate expression for $n_h$ is $E_{62}$.

Multiplying the composite rate constant values from $R_h$ and $n_h$ measurements, $(k_p^{1/2} / k_t^{1/2})$ value was obtained as 3.05 mol$^{-1/2}$ l$^{-1/2}$ g$^{-1/2}$ sec$^{-1}$.

Taking the ratio of the composite rate constant values obtained from $R_h$ and $n_h$ measurements at 45°C, the value $k_{12} K_1 K_3$ was calculated to be $1.52 \times 10^{-2}$ mol$^{-1}$ l sec$^{-1}$.

The $k_p / k_t^{1/2}$ value obtained here in this work for MMA can be compared with the value available in the published literature.
Boxendale, Evans and Kilhan [202] using the redox initiator Fe$^{2+}$-$\text{H}_2\text{O}_2$ in aqueous medium have found the value for the ratio $k_p/k_t^{1/2}$ to be 12.3 at $25^\circ$C for MMA polymerization in the presence of emulsifier. Similarly Evans, Santappa and Uri [203] obtained the value 0.27 for MMA polymerization using Fe$^{3+}$-Cl$^-$ as photosensitizer in precipitating media. Atkino and Cotton [204] using Fe$^{3+}$-OH$^-$ as initiator reported a value of 0.56 at $25^\circ$C for MMA in aqueous medium.

The $k_p/k_t^{1/2}$ value for MMA with different initiating systems in aqueous medium were reported by Santappa and coworkers.

<table>
<thead>
<tr>
<th>Reference</th>
<th>$k_p/k_t^{1/2}$ mol$^{-1/2}$ sec$^{-1/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>205</td>
<td>0.60</td>
</tr>
<tr>
<td>206</td>
<td>1.42</td>
</tr>
<tr>
<td>207</td>
<td>1.13</td>
</tr>
<tr>
<td>208</td>
<td>1.25</td>
</tr>
<tr>
<td>This work</td>
<td>2.29</td>
</tr>
</tbody>
</table>

For the selected reaction scheme, an expression for $-\text{R}_{\text{PMS}}$ can be written as

$$-\text{R}_{\text{PMS}} = \frac{k_{12} K_1 K_3 [\text{PMS}] T [H_2A] [\text{nylon 6}]}{1 + K_1 [H_2A] + K_1 K_3 [H_2A] [\text{nylon 6}]}$$
under the conditions $K_1 K_3 [H_2A] [nylon 6] \gg 1 + K_1 [H_2A]$, 

$$-R_{PMS} = K_{12} [PMS]_T$$

The observed results are in agreement with $E_{63}$. From the slope of the plot, $k_{12}$ value was determined as $4.2 \times 10^{-4} \text{ sec}^{-1}$ and $k_{12} K_1 K_3$ value obtained from $R_h$ and $n_h$ measurements was $1.52 \times 10^{-4} \text{ mol}^{-1} \text{ l sec}^{-1}$. Hence, the ratio $K_1 K_3$ was obtained as $0.357 \text{ mol l}^{-1}$. This fact also supports the proposed mechanism and consequent derivation.

The increase in % grafting with increase in monomer, MMA, can be explained by the same reason as reported earlier [197, 198]. Similar effect on % grafting with $[M]$ was found by Shukla and coworkers [109, 111], Horoshi [185] and Varma and Ray [93]. Varma and Ravisankar [94] reported that the grafting efficiency was good only at low monomer concentration by another system and that sometimes it decreases with increase in $[M]$. The increment in % grafting with $[M]$ could be associated with the gel effect [197, 198] brought about by the solubility of the polymer PMMA in its own monomer. As a result, termination of the growing grafted chain radical by coupling is prevented. Further, the gel effect causes swelling of PET fiber and
facilitates diffusion of monomer to the growing grafted chains and active sites on the PET backbone thereby increasing % grafting.

The increase in % grafting and % efficiency by the parameters such as $[M]$ (Table 64), $[\text{PMS}]$ (Table 68), $[\text{H}_2\text{A}]$ (Table 72) and $[\text{nylon 6}]$ (Table 76) could be due to the involvement all these components in the grafting initiating step.

4.2.2 PMS-$\text{H}_2\text{A}$ Redox Initiated Graft Copolymerization of MMA onto nylon 66

The kinetic results obtained in this system are similar to the one with PMS-$\text{H}_2\text{A}$ redox initiated graft copolymerization of MMA onto nylon 6 but with a change in the backbone material as nylon 66.

4.2.2.1 Results on PMS-$\text{H}_2\text{A}$ Redox Initiated Graft Copolymerization of MMA onto nylon 66

Effect of Time on Graft Parameters

Both $R_g$ and $R_h$ values show an increasing trend initially and thereafter they fall (Table 81). Hence, a reaction time more than five hours was selected for this system to follow smooth kinetics. The plots $R_g$ Vs time (Fig. 61A) and $R_h$ Vs time (Fig. 61B) were drawn.
Other graft parameters like % grafting and % efficiency show an increasing trend initially and then they fall (Table 81).

$n_g$ and $n_h$ values increase with time initially and thereafter they fall (Table 81). Plots of $n_g$ Vs time (Fig. 61C) and $n_h$ Vs time (Fig. 61D) were also drawn.

**Effect of [MMA] on Craft Parameters**

A look at Table 82 clearly shows that both $R_g$ and $R_h$ values increase with MMA. Plots of log $R_g$ Vs log [MMA] (Fig. 62A) and log $R_h$ Vs log [MMA] (Fig. 62B) were drawn and found to give a slope of unity showing first power dependence of $R_g$ and $R_h$ on MMA. Direct plots $R_g$ Vs [MMA] (Fig. 63A) and $R_h$ Vs [MMA] (Fig. 63B) were drawn in order to confirm the order dependences.

The effect of MMA on $R_g$ and $R_h$ was also studied under a set of different experimental conditions as specified in Table 83. Both the values increase with MMA. Plots of log $R_g$ Vs log [MMA] (Fig. 62C) and log $R_h$ Vs log [MMA] (Fig. 62D) were drawn and found to give a slope of unity indicating a first power dependence on $R_g$ and $R_h$. Direct plots $R_g$ Vs [MMA] (Fig. 63C) and $R_h$ Vs [MMA] (Fig. 63D) were also drawn to confirm the order dependences.
The effect of change in [MMA] on % grafting and % efficiency under the conditions specified in Table 84 was tabulated and observed that both the values increase with [MMA].

n_g and n_h values were determined separately and it was found that both the values increase with increase in [MMA] under the conditions specified in Table 85. Plots of log n_g Vs log [MMA] (Fig. 64A) and log n_h Vs log [MMA] (Fig. 64B) were drawn and found to give a slope of unity thus showing first power dependence on n_g and n_h. Direct plots R_g Vs [MMA] (Fig. 64C) and R_h Vs [MMA] (Fig. 64D) were drawn to further support the order dependences.

It was found that -R_{PMS} values remain almost constant for the conditions mentioned in Table 83.

**Effect of [PMS] on Graft Parameters**

Both R_g and R_h values increase with [PMS] under the conditions mentioned in Table 86. Log R_g Vs log [PMS] (Fig. 65A), and log R_h Vs log [PMS] (Fig. 65B) plots were drawn and found to give a slope of 0.5 indicating half order dependence on R_g and R_h. Direct plots R_g Vs [PMS]^{1/2} (Fig. 66A) and R_h Vs [PMS]^{1/2} (Fig. 66B) were drawn in order to confirm the order dependences.
To ascertain the above order dependences of $R_g$ and $R_h$ on PMS, $R_g$ and $R_h$ values were determined under a set of different experimental conditions specified in Table 87 and found that both the values increase with PMS. Log $R_g$ Vs log [PMS] (Fig. 65C) and log $R_h$ Vs log [PMS] (Fig. 65D) plots were drawn and found to give a slope of 0.5 showing half order dependences on PMS. Direct plots $R_g$ Vs [PMS]$^{1/2}$ (Fig. 66C) and $R_h$ Vs [PMS]$^{1/2}$ (Fig. 66D) were drawn to confirm the order dependences.

Other graft parameters such as % grafting and % efficiency increase steadily with [PMS] under the conditions specified in Table 88.

$n_g$ and $n_h$ values were determined separately and found that the values decrease with PMS (Table 89). Log $n_g$ Vs log [PMS] (Fig. 68A) and log $n_h$ Vs [PMS] (Fig. 68B) plots were drawn and found to be straight lines with slopes of negative 0.5 indicating inverse square root order dependences of $n_g$ and $n_h$ as PMS. Direct plots $n_g$ Vs [PMS]$^{-1/2}$ (Fig. 68C) and $n_h$ Vs [PMS]$^{-1/2}$ (Fig. 68D) were drawn to further support the order dependences.

Effect of [PMS] on $-R_{PMS}$

$-R_{PMS}$ values were determined and found to increase
with PMS under the conditions specified in Tables 86 and 87. Log \((-\text{R}_{\text{PMS}})\) Vs log [PMS] (Fig. 67A) plot was drawn and found to give a slope of unity showing first power dependence of \(-\text{R}_{\text{PMS}}\) on PMS. Direct plot \(-\text{R}_{\text{PMS}}\) Vs [PMS] (Fig. 67C) was also drawn to support the order dependences.

To ascertain the order dependence of \(-\text{R}_{\text{PMS}}\) on PMS, \(-\text{R}_{\text{PMS}}\) values were determined under a set of different experimental conditions as given in Table 87. Similar trends were observed with regard to \(-\text{R}_{\text{PMS}}\) on PMS (Fig. 67B,D).

**Effect of \([\text{H}_2\text{A}]\) on Graft Parameters**

\(R_g\) and \(R_h\) values were determined under the conditions given in Table 90 and found that both the values increase with \([\text{H}_2\text{A}]\). Log \(R_g\) Vs log \([\text{H}_2\text{A}]\) (Fig. 69A) and log \(R_h\) Vs log \([\text{H}_2\text{A}]\) (Fig. 69B) plots were drawn and found to give a slope of 0.5 showing half order dependences of \(R_g\) and \(R_h\) on \([\text{H}_2\text{A}]\) respectively. Direct plots \(R_g\) Vs \([\text{H}_2\text{A}]^{1/2}\) (Fig. 70A) and \(R_h\) Vs \([\text{H}_2\text{A}]^{1/2}\) (Fig. 70B) were drawn to confirm the order dependences.

To ascertain the above order dependences, \(R_g\) and \(R_h\) values were determined under a set of different experimental conditions mentioned in Table 91. It was
observed that $R_g$ and $R_h$ values increase with $[H_2A]$. Log $R_g$ Vs log $[H_2A]$ (Fig. 69C) and log $R_h$ Vs log $[H_2A]$ (Fig. 69D) plots were drawn and found to give a slope of 0.5 showing half order dependences on $R_g$ and $R_h$. Direct plots $R_g$ Vs $[H_2A]^{1/2}$ (Fig. 70C) and $R_h$ Vs $[H_2A]^{1/2}$ (Fig. 70D) plots were drawn and found to confirm the order dependences.

Other graft parameters such as % grafting, and % efficiency were found to increase with $H_2A$ under the conditions specified in Table 92.

$n_g$ and $n_h$ measurements were carried out separately under the conditions mentioned in Table 93 and found that both $n_g$ and $n_h$ decrease with $H_2A$. Log $n_g$ Vs log $[H_2A]$ (Fig. 71A) and log $n_h$ Vs log $[H_2A]$ (Fig. 71B) plots were drawn and found to give a slope of negative 0.5 showing inverse square root order dependences on $n_g$ and $n_h$. Direct plots $n_g$ Vs $[H_2A]^{-1/2}$ (Fig. 71C) and $n_h$ Vs $[H_2A]^{-1/2}$ (Fig. 71D) were also drawn in order to confirm the order dependences of $n_g$ and $n_h$ on $H_2A$.

**Effect of Weight of nylon 66 on Graft Parameters**

For the variation of backbone material from 0.21 to 0.35 g and under the conditions mentioned in Table 94,
$R_g$ and $R_h$ values were determined and found to increase with the backbone. Log $R_g$ Vs log [Wt. of nylon 66] (Fig. 72A) and log $R_h$ Vs log [Wt. of nylon 66] (Fig. 72B) plots were drawn and found to give a slope of 0.5 indicating half order dependence of $R_g$ and $R_h$. Direct plots $R_g$ Vs [Wt. of nylon 66]^{1/2} (Fig. 73A) and $R_h$ Vs [Wt. of nylon 66]^{1/2} (Fig. 73B) were drawn to confirm the order dependences.

In an attempt to have further confirmation on the order dependences, $R_g$ and $R_h$ values were determined under a set of different experimental conditions given in Table 95 and found that both $R_g$ and $R_h$ values increase with the backbone amount. Log $R_g$ Vs log [Wt. of nylon 66] and log $R_h$ Vs log [Wt. of nylon 66] (Figs. 72C,D) plots were drawn and found to give a slope of 0.5 showing half order dependences of $R_g$ and $R_h$ on the Wt. of nylon 66. Direct plots $R_g$ Vs [Wt. of nylon 66]^{1/2} and $R_h$ Vs [Wt. of nylon 66]^{1/2} (Figs. 73C,D) were also drawn to confirm the order dependences.

Other graft parameters such as % grafting and % efficiency were determined under the conditions mentioned in Table 96. While % grafting increase initially with [Wt. of nylon 66] and then falls afterwards, the % efficiency increases with the amount of backbone.
Both $R_g$ and $R_h$ values increase with temperature under the conditions mentioned in Table 98. Arrhenius plots of $\log R_g$ vs $1/T$ (Fig. 75A) and $\log R_h$ vs $1/T$ (Fig. 75B) were drawn and the $E_a$ values for $R_g$ and $R_h$ were calculated to be 5.49 and 3.49 Kcal/mol respectively. The % grafting and % efficiency increase with the amount of backbone (Table 99).

$n_g$ and $n_h$ values were also found to increase with the Wt. of nylon 66 (Table 99). $\log n_g$ vs $1/T$ (Fig. 75C) and $\log n_h$ vs $1/T$ (Fig. 75D) plots were also drawn and the $E_a$ values for $n_g$ and $n_h$ were determined and found to be 14.9 and 15.2 Kcal/mol respectively.
4.2.2.2 Discussion on Results

It is observed that the results obtained in this system is similar to the one as seen in graft copolymerization of MMA initiated by PMS-H$_2$A redox pair onto nylon 6. The probable reaction schemes would then be similar to the one discussed as in the previous case (4.2.1.2).

Hence, a similar sequence of reaction in Scheme VIII for the graft copolymerization of MMA initiated by PMS-H$_2$A] pair onto nylon 6 with a change in backbone as nylon 66 may be selected as the most probable scheme for this system.

4.2.2.3 Selected Reaction Scheme

Initiation

\[
\begin{align*}
PMS + H_2A & \overset{K_1}{\rightleftharpoons} PMS - H_2A \\
\text{Complex}_1 \text{ C}_1
\end{align*}
\]

\[
\begin{align*}
C_1 + \text{nylon 66} & \overset{K_4}{\rightleftharpoons} PMS - H_2A - \text{nylon 66} \\
\text{Complex}_4 \text{ C}_4
\end{align*}
\]

\[
\begin{align*}
\text{C}_4 & \overset{k_{16}}{\rightarrow} (\text{nylon 66})^\cdot + H_2O + H^+ + SO_4^-
\end{align*}
\]

\[
\begin{align*}
\text{nylon 66}^\cdot + M & \overset{k_{21}}{\rightarrow} (\text{nylon 66}) M^-
\end{align*}
\]

\[
\begin{align*}
SO_4^- + H_2O & \overset{k_2}{\rightarrow} OH + HSO_4^-
\end{align*}
\]
\[ \text{OH} + H_2A \xrightarrow{k_3} H_2O + A^- + H^+ \]
\[ C_n + A^- \xrightarrow{k_{18}} 50^+ + 2HA^- + H_2O + H^+ \]

Propagation

\[(\text{nylon 66}) M^\cdot + M \xrightarrow{k'} (\text{nylon 66}) M^\cdot_2 \] (where \(k_g\) is the rate constant for the propagation in grafting with MMA as monomer)

Termination

\[2(\text{nylon 66}) M^\cdot_n \xrightarrow{k_{t5}} \text{graft copolymer} \]

For the above mechanism of grafting, the expression for \(R_g\) and \(n_g\) can be written based on the discussion

\[ R_g = k_g \left( \frac{k_{16}K_1K_4}{k_t} \right)^{1/2} [M]^{1/2} \text{[nylon 66]}^{1/2} \text{[PMS]}^{1/2} \text{[H}_2\text{A]}^{1/2} \]

\[ n_g = \frac{k_g [M]}{(k_{t1})^{1/2} (2k_{16}K_1K_4)^{1/2} [\text{nylon 66}]^{1/2} \text{[PMS]}^{1/2} \text{[H}_2\text{A]}^{1/2}} \]
In $E_{50}$, all the experimental observations such as first power dependence on [MMA] (Figs. 63A,C), square root order dependences on $[\text{PMS}]^{1/2}$ (Figs. 66A,C), $[\text{H}_2\text{A}]^{1/2}$ (Figs. 70A,C) and [nylon 66]$^{1/2}$ (Figs. 73A,C) towards $R_g$ can be seen.

All the experimental observations such as first power dependence on [M] (Fig. 64C), inverse square root order dependences on $[\text{PMS}]^{1/2}$ (Fig. 68C), $[\text{H}_2\text{A}]^{1/2}$ (Fig. 71C) and on [nylon 66]$^{1/2}$ (Fig. 74C) towards $n_g$ could be seen in $E_{51}$.

The observations made in the form of experimental dependences on [PMS], [H$_2$A], [nylon 66] and [MMA] towards $R_h$ was similar to the one observed with nylon 6 as backbone. Hence, a mechanism for homopolymerization may involve initiation by the reaction with the monomer and the primary radical generated from the decomposition of the complex PMS-H$_2$A-nylon 66.

\textbf{Initiation}

\[ \begin{align*}
\text{PMS} + \text{H}_2\text{A} & \overset{k_1}{\underset{K_1}{\rightleftharpoons}} \text{PMS - H}_2\text{A} \quad \text{Complex } C_1 \\
C_1 + \text{nylon 66} & \overset{k_2}{\underset{K_2}{\rightleftharpoons}} \text{PMS - H}_2\text{A - nylon 66} \quad \text{Complex } C_4 \\
C_4 & \overset{k_{15}}{\underset{K_{15}}{\rightleftharpoons}} \text{nylon 66}^+ + \text{H}_2\text{O} + \text{H}^+ + \text{SO}_4^{2-}
\end{align*} \]
\[ \text{SO}_4^- + \text{H}_2\text{O} \xrightarrow{k_1} \text{OH} + \text{HSO}_4^- \]
\[ \text{OH} + \text{H}_2\text{A} \xrightarrow{k_3} \text{H}_2\text{O} + \text{A}^- + \text{H}^+ \]
\[ \text{C}_1 + \text{A}^- \xrightarrow{k_4} \text{SO}_4^- + 2\text{HA}^- + \text{H}_2\text{O} + \text{H}^+ \]
\[ \text{M} + \text{A}^- \xrightarrow{k_{28}} \text{M}^* \]

**Propagation**

\[ \text{M}_1^* + \text{M} \xrightarrow{k_{11}} \text{M}_2^* \]
\[ \text{M}_{n-1}^* + \text{M} \xrightarrow{k_{12}} \text{M}_n^* \]

**Termination**

\[ \text{M}_n^* + \text{M}_n^* \xrightarrow{k_{15}} \text{homopolymer} \]

The expression for \( R_h \) will be similar to \( E_{61} \) with a replacement of suitable rate constants and backbone. Then,

\[ R_h = k_p \left( \frac{k_{16}k_1k_4}{k_{15}} \right) \left( \text{nylon 66} \right)^{1/2} \left( \text{H}_2\text{A} \right)^{1/2} \left( \text{PMS} \right)^{1/2} \left( \text{M} \right) \]

All the experimental observations such as first power dependence on \([\text{MMA}]\) (Figs. 63B,D), square root order dependences on \([\text{PMS}]\) (Figs. 66B,D), \([\text{H}_2\text{A}]\) (Figs. 70B,D) and \([\text{nylon 66}]\) (Figs. 73B,D) related to \( R_h \) can be clearly accounted in \( E_{67} \).
For the above scheme, an expression for $n_h$ can be arrived at as,

$$n_h = \frac{k_p [M]}{(k_{16}^{1/2} k_{16} k_{94}) [nylon 66]^{1/2} [H_2A]^{1/2} [PMS]^{1/2}}$$

Clearly, $E_{68}$ accounts for all the observed experimental results with respect to $n_h$ such as first power dependence on [MMA] (Fig. 64D), inverse square root order dependences on [nylon 66] (Fig. 74D), [H$_2$A] (Fig. 71D), and [PMS] (Fig. 68D).

These two expressions $R_h$ and $n_h$ adequately explain all the experimental observations related to $R_h$ and $n_h$.

Hence, $E_{50}$, $E_{51}$, $E_{67}$ and $E_{68}$ are the most suitable expressions for $R_g$, $n_g$, $R_h$ and $n_h$ respectively.

4.2.2.4 Evaluation of Composite Rate Constants for the System and Test their Invariance

From the slope of the plots $R_g$ Vs [MMA] (Figs. 63A,C), $R_g$ Vs [PMS]$^{1/2}$ (Figs. 66A,C), $R_g$ Vs [H$_2$A]$^{1/2}$ (Figs. 70A,C) and $R_g$ Vs [nylon 66]$^{1/2}$ (Figs. 73A,C) and using the conditions mentioned in Tables 82, 83, 86, 87, 90, 91, 94 and 95 the average value of the composite rate
constant in $E_{50}$, viz.,

\[
\frac{k_g}{k_{16} K_1 K_q} \left( \frac{1}{k_{15}} \right)^{1/2}
\]

was calculated to be $2.39 \times 10^{-3}$ mol$^{-1}$ l g$^{-1/2}$ sec$^{-1}$. The values obtained from different plots are given in Table 100A. The constancy found in the value of the composite rate constant shows that the right choice of the rate expression is $E_{50}$.

That the rate expression as given by $E_{51}$ as the right selection for $n_g$ is further confirmed by the fact that the composite rate constant

\[
\frac{k_g}{(k_{15})^{1/2} (2k_{16} K_1 K_q)^{1/2}}
\]

remains invariant for all the variations of MMA, PMS, $H_2A$ and nylon 66. The values so obtained are given in Table 100A.

This composite rate constant was evaluated from the slopes of the plots $n_g$ Vs $[\text{MMA}]$ (Fig. 64C), $n_g$ Vs $[\text{PMS}]^{-1/2}$ (Fig. 68C), $n_g$ Vs $[H_2A]^{-1/2}$ (Fig. 71C) and $n_g$ Vs $[\text{nylon 66}]^{-1/2}$ (Fig. 74C) and using the conditions mentioned in Tables 85, 89, 93 and 97. The average value
of the composite rate constant was calculated to be 18.2 mol\(^{-1}\) l sec\(^{-1}\).

Multiplying the composite rate constant values obtained from \(R_g\) and \(n_g\) measurements, \((k'/k_t^{1/2})\) value was obtained as \(0.208 \text{ mol}^{1/2} \text{l}^{1/2} \text{sec}^{-1}\).

The closeness of \((k'/k_t^{1/2})\) value determined for grafting reaction with nylon 6 (0.292 mol\(^{-1/2}\) l\(^{1/2}\) sec\(^{-1}\)) and nylon 66 (0.208 mol\(^{-1/2}\) l\(^{1/2}\) sec\(^{-1}\)) as backbone materials supports the assumption made in the mechanism and consequent derivation.

Taking the ratio of the composite rate constant values obtained from \(R_g\) and \(n_g\), at 45\(^\circ\)C, the value \(k_1k_4\) was obtained as \(1.31 \times 10^{-4} \text{ mol}^{-1} \text{l sec}^{-1}\).

From the slopes of the plots \(R_h\) Vs [MMA] (Figs. 63B,D), \(R_h\) Vs [PMS]\(^{1/2}\) (Figs. 66B,D), \(R_h\) Vs \([H_2A]\)^{1/2} (Figs. 70B,D) and \(R_h\) Vs [nylon 66]\(^{1/2}\) (Figs. 73B,D) and the conditions mentioned in Tables 82, 83, 86, 87, 90, 91, 94 and 95, the average value of the composite rate constant in \(E_{g-7}\), viz.,

\[
\frac{\gamma_p}{k_t} \left( \begin{array}{c} k_{16} \quad k_1 \quad k_4 \\ k_{16} \quad k_t \quad k_4 \end{array} \right)
\]

was calculated to be \(3.20 \times 10^{-2} \text{ mol}^{-1} \text{l g}^{-1/2} \text{sec}^{-1}\) at
The values obtained from different plots are given in Table 100B. The constancy found in the value of the composite rate constant shows that the right choice of the rate expression for $R_h$ is $E_{67}$.

That the rate expression as given by $E_{68}$ is the right selection for $n_h$ is further confirmed by the fact that the composite rate constant

$$\frac{k'}{p} = \left(\frac{k_{16}}{k_1 k_6}\right)^{1/2}$$

remains invariant for all variations of MMA, PMS, $H_2A$ and nylon 66. The values so obtained are given in Table 100B.

This composite rate constant was evaluated from the slope of the plots $n_h$ Vs [MMA] (Fig. 64D), $n_h$ Vs [PMS]$^{-1/2}$ (Fig. 68D), $n_h$ Vs [$H_2A$]$^{-1/2}$ (Fig. 71D) and $n_h$ Vs [nylon 66]$^{-1/2}$ (Fig. 74D) and using the conditions maintained in Tables 85, 89, 93 and 97. The average value of the composite rate constant for $n_h$ was calculated to be $164 \text{ mol}^{-1} \text{ I sec}^{-1}$.

Multiplying the composite rate constant values from $R_h$ and $n_h$ measurements, the value ($k'/k_{16}$) was obtained as $2.29 \text{ mol}^{-1/2} \text{ I}^{1/2} \text{ g}^{-1/2} \text{ sec}^{-1}$. 
The closeness of the two values (k'/k_16) obtained from previous study (3.05 mol⁻¹/² g⁻¹/² sec⁻¹) with nylon 6 as backbone and (2.29 mol⁻¹/² g⁻¹/² sec⁻¹) with nylon 66 as backbone material support the proposed mechanism and consequent derivation.

Dividing the composite rate constant values obtained from R_h and n_h measurements, the value k_16 K_1 K_4 was obtained as 1.95 x 10⁻⁴ mol⁻¹ l sec⁻¹.

For the selected reaction scheme, an expression for -R_{PMS} can be written as

\[ -R_{PMS} = \frac{(k_{16} K_1 K_4) [PMS]^T [H_2A] [nylon 66]}{1 + K_1 [H_2A] + K_4 [H_2A] [nylon 66]} \]

when K_1 K_4 [H_2A] [nylon 66] \gg 1 + [H_2A], the expression for -R_{PMS} becomes -R_{PMS} = k_{16} [PMS]^T.

The observed results are in agreement with E_69. From the slope of the plot, (k_{16}) was determined to be 4.17 x 10⁻⁴ sec⁻¹ and k_{16} K_1 K_4 value obtained from R_h and n_h measurements was calculated to be 1.95 x 10⁻⁴ mol⁻¹ l sec⁻¹. Hence, the ratio K_1 K_4 was obtained as 0.468 mol l⁻¹. This fact also favours the proposed mechanism.

The effect of % grafting and % efficiency can have relevant explanation as discussed in 4.2.1.
4.3.1 PDS-H\textsubscript{2}A Redox Initiated Graft Copolymerization of MMA onto PET

In all the earlier cases of graft copolymerization, H\textsubscript{2}A was combined with the peroxosalt, PMS to form a redox initiating system. Graft copolymerization studies involving vinyl monomers using PDS-thiourea [108], potassium permanganate-thiolic acid [110] and PDS-thiolic acid as redox initiating pairs were already known. In the present study, H\textsubscript{2}A was combined with PDS to form a redox pair for the graft copolymerization of MMA onto PET.

4.3.1.1 Results on PDS-H\textsubscript{2}A Redox Initiated Graft Copolymerization of MMA onto PET

Effect of Time on Graft Parameters

Both $R_g$ and $R_h$ values smoothly fall after five hours under the conditions mentioned in Table 101 and hence for a smooth kinetics, a reaction time more than five hours is required for this system. Plots of $R_g$ Vs time (Fig.76A) and $R_h$ Vs time (Fig. 76B) were drawn.

The % grafting and % efficiency increase upto five hours and then they fall (Table 101).

$n_g$ and $n_h$ values show similar trend with increase
in time (Table 101). $n_g$ Vs time (Fig. 76C) and $n_h$ Vs time (Fig. 76D) plots were also drawn.

**Effect of [MMA] on Graft Parameters**

It was observed that both $R_g$ and $R_h$ increase with [MMA] in the range from $7.60 \times 10^{-3}$ mol l$^{-1}$ to $76.0 \times 10^{-3}$ mol l$^{-1}$ (Table 102). Log $R_g$ Vs log [MMA] (Fig. 77A) and log $R_h$ Vs log [MMA] (Fig. 77B) plots were drawn and found to be straight lines with a slope of unity indicating a first power dependence of $R_g$ and $R_h$ on MMA. Direct plots $R_g$ Vs [MMA] (Fig. 78A) and $R_h$ Vs [MMA] (Fig. 78B) were also drawn and found to confirm the order dependences.

Similar trends were observed under a different set of experimental conditions with a change in [MMA] in the range from $1.90 \times 10^{-2}$ to $8.74 \times 10^{-2}$ mol l$^{-1}$ (Table 103). Plots of log $R_g$ Vs log [MMA] and log $R_h$ Vs log [MMA] (Figs. 77C,D) were found to give a slope of unity indicating first power dependence on MMA. Direct plots of $R_g$ Vs [MMA] and $R_h$ Vs [MMA] (Figs. 78C,D) were drawn to confirm the order dependences.

The values of other graft parameters like % grafting and % efficiency were given in Table 104. It was observed that % grafting steadily increases with MMA but % efficiency show increasing trend initially but decreases afterwards.
n_g and n_h values were determined and found that both the values decrease with MMA (Table 105). Log n_g Vs log [MMA] (Fig. 79A) and log n_h Vs log [MMA] (Fig. 79B) plots were drawn and found to give a slope of unity indicating first order dependence on MMA. Direct plots n_g Vs [MMA] (Fig. 79C) and n_h Vs [MMA] (Fig. 79D) were drawn.

### Effect of [PDS] on Graft Parameters

R_g and R_h values were determined under the conditions mentioned in Table 106. It was observed that both the values increase with PDS. Plots of log R_g Vs log [PDS] and log R_h Vs log [PDS] (Figs. 80A,B) were drawn and found that the slopes gave 0.5 order dependence of R_g and R_h on PDS. Direct plots R_g Vs [PDS]^{1/2} and R_h Vs [PDS]^{1/2} (Figs. 81A,B) were also drawn to confirm the order dependences.

In order to have further confirmation on the order dependences, R_g and R_h values were determined under different experimental conditions (Table 107). It was observed that both the values increase with PDS. Log R_g Vs log [PDS] and log R_h Vs log [PDS] (Figs. 80C,D) plots were drawn and found to give a slope of 0.5 indicating 0.5 order dependence of R_g and R_h on PDS. Direct plots R_g
Vs [PDS] and $R_n$ Vs [PDS] (Figs. 81C,D) were also drawn and found to confirm the order dependences.

Other graft parameters like % grafting and % efficiency increase with [PDS] under the conditions mentioned in Table 108.

$n_g$ and $n_h$ values were determined independently under the conditions given in Table 109 and found that both the values decrease with [PDS]. Log $n_g$ Vs log [PDS] and log $n_h$ Vs log [PDS] (Figs. 83A,B) plots were drawn and found to give negative 0.5 slope indicating inverse square root order dependences of $n_g$ and $n_h$ on PDS. Direct plots $n_g$ Vs $[H_2A]^{-1/2}$ and $n_h$ Vs $[H_2A]^{-1/2}$ (Figs. 83C,D) were also drawn to further support the order dependences of $n_g$ on PDS.

**Effect of [PDS] on $-R_{PDS}$**

$-R_{PDS}$ values were determined volumetrically and found to increase under the conditions mentioned in Tables 106 and 107. Log $-R_{PDS}$ Vs log [PDS] (Fig. 82A) plot was drawn and found to give a slope of unity indicating first power dependence of $-R_{PDS}$ on PDS. Direct plot $-R_{PDS}$ Vs [PDS] (Fig. 82C) was also drawn to further support order dependence.
To ascertain the order dependence of $-R_{\text{PDS}}$ on PDS, $-R_{\text{PDS}}$ values were determined under a set of different experimental conditions as given in Table 107. Similar trends were observed with regard to the order dependences of $-R_{\text{PDS}}$ on PDS (Figs. 82B,D).

Effect of $[H_2A]$ on Graft Parameters

$R_g$ and $R_h$ values increase with $[H_2A]$ under the conditions mentioned in Table 110. Plots of $\log R_g$ vs $\log [H_2A]$ and $\log R_h$ vs $\log [H_2A]$ (Figs. 84A,B) were drawn and found to give a slope of 0.5 showing half order dependence of $R_g$ and $R_h$ on $H_2A$. Direct plots $R_g$ vs $[H_2A]^{1/2}$ and $R_h$ vs $[H_2A]^{1/2}$ (Figs. 84A,B) were also drawn in order to confirm the order dependence.

Similar trends were observed with a change in $[H_2A]$ in the range from $10.0 \times 10^{-8}$ to $70.0 \times 10^{-8}$ mol l$^{-1}$ (Table 111). Log $R_g$ vs $\log [H_2A]$ and log $R_h$ vs log $[H_2A]$ (Figs. 84C,D) plots were drawn and found to give a slope of 0.5 indicating half order dependence of $R_g$ and $R_h$ on $H_2A$. Direct plots $R_g$ vs $[H_2A]^{1/2}$ and $R_h$ vs $[H_2A]^{1/2}$ (Figs. 85C,D) were also drawn in order to confirm the order dependences.

Other graft parameters like % grafting and % efficiency increase with $[H_2A]$ (Fig. 112).
n\text{g} and n\text{h} values were determined separately under the conditions given in Table 113.

It was observed that both the values decrease with \([H_2A]\). Log \(n_g \text{ vs } \log [H_2A]\) and log \(n_h \text{ vs } \log [H_2A]\) (Figs. 86A,B) plots were drawn and found to give slopes of negative 0.5 indicating inverse square root order dependences of \(R_g\) and \(R_h\) on \(H_2A\). Direct plots \(R_g \text{ vs } [H_2A]^{-1/2}\) and \(R_h \text{ vs } [H_2A]^{-1/2}\) (Figs. 86C,D) were also drawn to support the order dependences.

**Effect of Weight of PET on Graft Parameters**

For the variation of the backbone material from 0.05 to 0.35 g under the conditions mentioned in Table 114 \(R_g\) and \(R_h\) values increase gradually with PET. Log \(R_g \text{ vs } \log \text{ Wt. of PET}\) and log \(R_h \text{ vs } \log \text{ Wt. of PET}\) (Figs. 87A,B) plots were drawn and found to give a slope of 0.5 showing half order dependences of \(R_g\) and \(R_h\). Direct plots \(R_g \text{ vs } \text{ Wt. of PET}^{1/2}\) and \(R_h \text{ vs } \text{ Wt. of PET}^{1/2}\) (Figs. 88A,B) were also drawn to further support the order dependences.

To ascertain the order dependences, \(R_g\) and \(R_h\) measurements were carried out under a set of different experimental conditions (Table 115). Log \(R_g \text{ vs } \log \text{ Wt.}...\)
of PET) (Fig. 87C) and log $R_h$ Vs log [Wt. of PET] (Fig. 87D) plots were drawn and found to give a slope of 0.5 showing half order dependences of $R_g$ and $R_h$. Direct plots $R_g$ Vs [Wt. of PET]$^{1/2}$ (Fig. 88C) and $R_h$ Vs [Wt. of PET]$^{1/2}$ (Fig. 88D) were also drawn to further support the order dependences.

For the variation of the backbone amount under the conditions given in Table 116, the % grafting increases initially and then it falls, but % efficiency increases with the backbone amount.

$n_g$ and $n_h$ measurements were carried out under the conditions specified in Table 117 and observed that both the values decrease with the backbone amount. Log $n_g$ Vs log [Wt. of PET] (Fig. 89A) and log $n_h$ Vs log [Wt. of PET] (Fig. 89B) plots were drawn and found to give a slope of negative 0.5 pointing out inverse square root order dependences of $n_g$ and $n_h$ on the Wt. of PET. Direct plots $n_g$ Vs [Wt. of PET]$^{-1/2}$ (Fig. 89C) and $n_h$ Vs [Wt. of PET]$^{-1/2}$ (Fig. 89D) were also drawn to support the order dependences.

**Effect of Temperature on Graft Parameters**

$R_g$ and $R_h$ measurements were carried out under the conditions given in Table 118. It was observed that
both $R_g$ and $R_h$ increase with temperature. Log $R_g$ Vs $1/T$ (Fig. 90A) and log $R_h$ Vs $1/T$ (Fig. 90B) plots were drawn. The energy of activation ($E_a$) values were determined and found to be 5.4 and 6.0 Kcal/mol. Other graft parameters like % grafting and % efficiency gradually increase initially and then they fall (Table 119).

$n_g$ and $n_h$ values increase with increase in temperature (Table 119). Log $n_g$ Vs $1/T$ (Fig. 90C) and log $n_h$ Vs $1/T$ (Fig. 90D) plots were drawn and the energy of activation $E_a$ values were determined and found to be 6.10 and 7.70 Kcal/mol respectively.

4.3.1.2 Discussion on Results

In all the above systems of graft copolymerization, $H_2A$ was combined with the peroxosalt PMS, to form a redox pair. In this study, the effect of changing of PMS to PDS in the graft copolymerization of MMA onto PET was brought out using PDS-$H_2A$ redox pair.

The results obtained are similar with respect to $R_g$ and $n_g$ as in the graft copolymerization of MMA onto nylon 6 using PMS-$H_2A$ redox pair, with a change in the backbone as PET. Hence, grafting reactions may have the
same sequence as 4.1.1.2 with grafting onto nylon 6 using MMA as monomer.

### 4.1.3.3 Selected Reaction Scheme

**Initiation**

\[
PDS + H_2A \xrightleftharpoons[K_5]{} PDS - H_2A \quad \text{Complex } C_5
\]

\[
C_5 + PET \xrightarrow[K_6]{} PDS - H_2A - PET \quad \text{Complex } C_6
\]

\[
C_6 \xrightarrow{k_2} PET' + H_2O + HSO_4^- + H^+ + SO_4^2-
\]

\[
PET' + M \xrightarrow[k_2']{} PET M'
\]

\[
SO_4^2- + H_2O \xrightarrow[K_2]{} OH + HSO_4^-
\]

\[
OH + H_2A \xrightarrow[K_3]{} H_2O + A^+ + H^+
\]

\[
C_6 + A^+ \xrightarrow{k_22} SO_4^2- + 2HA^- + HSO_4^- + H^+
\]

**Propagation**

\[
(PET) M' + M \xrightarrow[k_2]{} PET M'_2
\]

\[
(PET) M'_{n-1} + M \xrightarrow[k_2]{} PET M'_n
\]

**Termination**

\[
2(PET) M'_n \xrightarrow[k_{15}]{} \text{graft copolymer}
\]
For the above mechanism of grafting, the suitable expression for $R_g$ and $n_g$ can be written based on the discussion 3.1.3.2.

\[
R_g = k_g \left( \frac{k_{22}k_5k_6}{k_{15}} \right)^{1/2} [M][PET]^{1/2}[PDS]^{1/2}[H_2A]^{1/2} \quad E_{70}
\]

\[
n_g = \frac{k'_{15} \left( 2k_{22}k_5k_6 \right)^{1/2} [PET]^{1/2}[PDS]^{1/2}[H_2A]^{1/2}}{(k'_{15})^2} \quad E_{71}
\]

In $E_{70}$, all the experimental observations such as first power dependence on [MMA] (Figs. 78A,C), square root order dependences on [PDS] $^{1/2}$ (Figs. 81A,C), $[H_2A]^{1/2}$ (Figs. 85A,C) and [PET]$^{1/2}$ (Figs. 88A,C) towards $R_g$ can be seen.

All the experimental observations made such as first power dependence on [MMA] (Fig. 79C), inverse square root order dependences on [PDS] (Fig. 82C), $[H_2A]$ (Fig. 86C) and on [PET] (Fig. 89C) towards $n_g$ could be accounted for in $E_{71}$.

$R_{tg}$ was found to have first power dependence on [MMA] in this present case in contrast to the three halfth order dependence on [AN] as in earlier cases. This necessitates to identify new mechanism for homopolymerization.
in this case. Obviously, the half order dependences [PET] (Figs. 88B,D), [PDS] (Figs. 81B,D) and [H₂A] (Figs. 85B,D) predicts that mutual termination is dominant.

The experimental observations related to $R_h$ indicate that the mechanism for homopolymerization would be similar to the one discussed in $4.1.\text{...}$

The mechanism is now written with suitable replacement of the redox pair.

Initiation

\[ PDS + H₂A \xrightarrow{K₅} PDS - H₂A \]
\[ Complex \ Cₛ \]

\[ Cₛ + PET \xrightarrow{K₆} PDS - H₂A - PET \]
\[ Complex \ C₆ \]

\[ C₆ \xrightarrow{k_22} PET' + H₂O + HSO₄⁻ + H⁺ + SO₄⁻ \]

\[ SO₄⁺ + H₂O \xrightarrow{k_2} OH + HSO₄⁻ \]

\[ OH + H₂A \xrightarrow{k_3} H₂O + A⁺ + H⁺ \]

\[ C₅ + A⁺ \xrightarrow{k_{23}} SO₄⁺ + 2HA⁻ + HSO₄⁻ + H⁺ \]

\[ C₆ + M \xrightarrow{k_{25}} M₁⁺ + SO₄⁻ + H⁺ + H₂O + (PET) \]

\[ M + A⁺ \xrightarrow{k_{10}} M₁⁺ \]
Propagation

\[
M_1^* + M \xrightarrow{k_D^*} M_2^*
\]

\[
M_n^* + M \xrightarrow{k_D} M_n^*
\]

Termination

\[
M_n^* + M_n \xrightarrow{k_{TE}} \text{homopolymer}
\]

For the above mechanism of homopolymerization, the suitable expression for \( R_n \) and \( n_n \) would then be written by recollecting \( E_{40} \).

\[
R_n = k_p^* \left( \frac{k_{22} K_5 K_6}{k_{16}} \right) [\text{PET}]^{1/2} [H_A]^{1/2} [\text{PDS}]^{1/2} [M] \quad E_{72}
\]

\[
n_n = \frac{k_p^* [M]}{(k_{16})^{1/2} (k_{22} K_5 K_6) [\text{PET}]^{1/2} [H_A]^{1/2} [\text{PDS}]^{1/2}} \quad E_{73}
\]

In \( E_{72} \), all the experimental observations such as first power dependence on \([\text{MMA}] \) (Figs. 78B,D), square root order dependences on \([\text{PDS}] \) (Figs. 81B,D), \([H_A] \) (Figs. 85B,D) and \([\text{PET}] \) (Figs. 88B,D) related to \( R_n \) could be seen.

All the experimental observations such as first power dependence on \([\text{MMA}] \) (Fig. 79D) inverse square root...
order dependences on [PET] (Fig. 89D), [H\textsubscript{2}A] (Fig. 86D), and [PDS] (Fig. 82D) with regard to \(n\) could be accounted for in \(E\).

Hence, \(E\), \(E\), \(E\), and \(E\) are the most suitable expressions for \(R\), \(n\), \(R\), and \(n\), respectively.

### 4.3.1.4 Evaluation of Composite Rate Constant for the System and test their Invariance

From the slope of the plots \(R\) Vs \([\text{MMA}]\) (Figs. 78A,C), \(R\) Vs \([\text{PDS}]^{1/2}\) (Figs. 81A,C), \(R\) Vs \([\text{H\textsubscript{2}A}]^{1/2}\) (Figs. 85A,C) and \(R\) Vs \([\text{PET}]^{1/2}\) (Figs. 88A,C) and using the conditions mentioned in Tables 102, 103, 106, 107, 110, 111, 114 and 115, the average value of the composite rate constant in \(E\), viz.,

\[
\frac{k_{2}}{k_{t5}} \left( \frac{k_{22} k_{b} k_{6}}{k_{t5}} \right)^{1/2}
\]

was calculated to be \(3.58 \times 10^{-3}\) mol\(^{-1}\) l\(^{-1/2}\) sec\(^{-1}\). The values obtained from different plots are given in Table 120A. The constancy found in the value shows that the right choice of the rate expression is \(E\).

That the rate expression as given by \(E\) as the right choice for \(\gamma\) is further confirmed by the fact that the composite rate constant,
remains invariant for all the variations of MMA, H\textsubscript{2}A and PET. The values so obtained are given in Table 120A.

This composite rate constant was evaluated from the slopes of the plots \( n_g \) Vs [MMA] (Fig. 79C), \( n_g \) Vs \([\text{PDS}]^{-1/2}\) (Fig. 82C), \( n_g \) Vs \([\text{H}_{2}\text{A}]^{-1/2}\) (Fig. 86C) and \( n_g \) Vs \([\text{PET}]^{-1/2}\) (Fig. 89C) and using the conditions specified in Tables 105, 109, 113 and 117. The average value of the composite rate constant was calculated to be 15.8 mol\(^{-1}\) l sec\(^{-1}\).

Multiplying the composite rate constant values obtained from \( R_g \) and \( n_g \) measurements \((k'_g/k_{g^t})\) value was obtained as 0.238 mol\(^{-1}\) l\(^{1/2}\) sec\(^{-1}\).

The closeness of the value \((k'_g/k_{g^t})\) with nylon 6 (0.292 mol\(^{-1}\) l\(^{1/2}\) sec\(^{-1}\)) and PET (0.238 mol\(^{-1}\) l\(^{1/2}\) sec\(^{-1}\)) as backbone materials further support the proposed mechanism.

Taking the ratio of the composite rate constant values obtained from \( R_g \) and \( n_g \) measurements at 45\(^\circ\)C, the value \( k_{22}K_5K_6 \) was obtained as \(2.26 \times 10^{-4}\) mol\(^{-1}\) l sec\(^{-1}\).
The comparison of the values \( k_{16} K_{5} K_{6} (1.31 \times 10^{-2} \text{ mol}^{-1} \text{ l sec}^{-1}) \) using nylon 66 as backbone and with the value \( k_{22} K_{5} K_{6} (2.26 \times 10^{-3} \text{ mol}^{-1} \text{ l sec}^{-1}) \) with PET as backbone suggest that both were in good agreement with the earlier observation and that PET can better be grafted than nylon 66.

From the slope of the plots \( R_{h} \text{ Vs [MMA]} \) (Figs. 7B,D), \( R_{h} \text{ Vs [PDS]}^{1/2} \) (Figs. 8B,D), \( R_{h} \text{ Vs [H2A]} \) (Figs. 85B,D) and \( R_{h} \text{ Vs [PET]}^{1/2} \) (Figs. 88B,D) and the conditions mentioned in Tables 102, 103, 106, 107, 110, 111, 114 and 115, the average value of the composite rate constant \( \frac{k'}{p} \) was calculated to be \( 4.55 \times 10^{-2} \text{ mol}^{-1} \text{ l}^{-1/2} \text{ sec}^{-1} \) at \( 45^\circ \text{C} \). The constancy found in the value shows that the right selection of the rate expression for \( R_{h} \) is \( E_{72} \).

That the rate expression by \( E_{73} \) is the right selection for \( n_{h} \) is further confirmed by the fact that the composite rate constant

\[
\frac{k'}{p} = \left( \frac{k_{22} K_{5} K_{6}}{k_{16}} \right) \left( \frac{1}{(k_{16})^{1/2}} \right) \left( k_{22} K_{5} K_{6} \right)
\]
remains invariant for all variations of MMA, PDS, H$_2$A and PET. The values so obtained are given in Table 120B.

This composite rate constant was evaluated from the slope of the plots $n_h$ Vs [MMA] (Fig. 79D), $n_h$ Vs [PDS]$^{-1/2}$ (Fig. 82D), $n_h$ Vs [H$_2$A]$^{-1/2}$ (Fig. 86D) and $n_h$ Vs [PET]$^{-1/2}$ (Fig. 89D) and using the conditions specified in Tables 105, 109, 113 and 117. The average value of the composite rate constant was calculated to be 154 g$^{-1/2}$.

Multiplying the composite rate constant values from $R_h$ and $n_h$ measurements, the value $(k'_1/k_{16})$ was calculated to be 2.68 mol$^{-1/2}$ l$^{1/2}$ g$^{-1}$ sec$^{-1}$.

Dividing the composite rate constant values from $R_h$ and $n_h$, the value $k_{22} K_5 K_6$ was obtained as $2.95 \times 10^{-4}$ mol$^{-1}$ l sec$^{-1}$.

For the selected reaction scheme, an expression for $-R_{PDS}$ can be written as,

$$-R_{PDS} = \frac{(k_{22} K_5 K_6) [PDS] [H_2A] [PET]}{1 + K_5 [H_2A] + K_5 K_6 [H_2A] [PET]}$$

when $K_5 K_6 [H_2A] [PET] \gg 1 + K_5 [H_2A]$, the expression for $-R_{PDS}$ becomes,

$$-R_{PDS} = k_{22} [PDS]$$
The observed results are in agreement with $E_{74}$ from the slope of the plot ($k_{22}$) was determined as $4.13 \times 10^{-4} \text{ sec}^{-1}$ and $k_{22} K_5 K_6$ from $R_h$ and $n_h$ measurements was calculated to be $2.95 \times 10^{-4} \text{ mol}^{-1} \text{sec}^{-1}$. Hence, the ratio $(K_5 K_6)$ was obtained as $0.707 \text{ mol l}^{-1}$.

The closeness of the values obtained from grafting reactions with nylon 6 (0.357), nylon 66 (0.468 mol l$^{-1}$) and PET (0.707 mol l$^{-1}$) as backbone materials also support the proposed mechanism.

The effect of % grafting and % efficiency can have relevant explanations as discussed earlier in 4.3.1.

### 4.3.2 PDP-H$_2$A Redox Initiated Graft Copolymerization of MMA onto PET

Graft copolymerization studies of vinyl monomer using PDP-2 amine ethane thiol redox pair [106] and PDP-fructose redox initiated system pair [107] were already reported. In the present study, H$_2$A was coupled with PDP to form a redox pair for the graft copolymerization of MMA onto PET.

#### 4.3.2.1 Results on PDP-H$_2$A Redox Initiated Graft Copolymerization of MMA onto PET

**Effect of Time on Graft Parameters**
Both $R_g$ and $R_h$ values decrease after five hours under the experimental conditions mentioned in Table 121. Hence, for smooth kinetics, a reaction time more than five hours is needed for this system. The plots of $R_g$ Vs time (91A) and $R_h$ Vs time (91B) were drawn.

The other graft parameters such as % grafting and % efficiency decrease after five hours (Table 121).

$n_g$ and $n_h$ values were determined under the experimental conditions given in Table 121 and found that both values increase with time upto five hours and then they fall. The plots of $n_g$ Vs time (91C) and $n_h$ Vs time (91D) were drawn.

**Effect of [MMA] on Graft Parameters**

It was observed that both $R_g$ and $R_h$ values increase with [MMA] in the range from $7.60 \times 10^{-3}$ to $95.0 \times 10^{-3}$ mol l$^{-1}$ (Table 122). Log $R_g$ Vs log [MMA] (Fig. 92A) and log $R_h$ Vs log [MMA] (Fig. 92B) plots were drawn and found to give a slope of unity in each case suggesting a first power dependence of $R_g$ and $R_h$ on MMA respectively. Direct plots $R_g$ Vs [MMA] and $R_h$ Vs [MMA] (Figs. 93A,B) were drawn to confirm the order dependences.

Under a set of different experimental conditions mentioned in Table 123, $R_g$ and $R_h$ values were found to
increase with MMA. Log $R_g$ Vs log [MMA] and log $R_h$ Vs [MMA] (Fig. 92C,D) plots were drawn and found to give a slope of unity in each case indicating first power dependence of $R_g$ and $R_h$ on MMA. Direct plots $R_g$ Vs [MMA] and $R_h$ Vs [MMA] (Figs. 93C,D) were drawn to further support order dependences.

While % grafting gradually increases with MMA under the conditions mentioned in Table 124, % efficiency initially show an increasing trend and thereafter they fall.

$n_g$ and $n_h$ values were determined under the conditions mentioned in Table 125 and found to decrease with MMA. Log $n_g$ Vs log [MMA] and log $n_h$ Vs log [MMA] (Figs. 94A,B) plots were drawn and found to give a slope of unity indicating first order dependence of $n_g$ and $n_h$ on MMA. Direct plots $n_g$ Vs [MMA] and $n_h$ Vs [MMA] (Figs. 94C,D) were drawn to further support order dependences.

Effect of [PDP] on Graft Parameters

Both $R_g$ and $R_h$ values were found to increase with [PDP] under the conditions mentioned in Table 126. Log $R_g$ Vs log [PDP] and log $R_h$ Vs log [PDP] (Figs. 95A,B) plots were drawn and found to give a slope of 0.5 indicating half order dependences of $R_g$ and $R_h$ respectively. Direct
254 plots $R_g$ vs $[PDP]^{1/2}$ and $R_h$ vs $[PDP]^{1/2}$ (Figs. 96A,B) were drawn to confirm the order dependences.

To ascertain the above order dependences, $R_g$ and $R_h$ values were determined under a set of experimental conditions mentioned in Table 127. Log $R_g$ vs log $[PDP]$ and log $R_h$ vs log $[PDP]$ (Figs. 95C,D) plots were drawn and found to give a slope of 0.5 suggesting half order dependences of $R_g$ and $R_h$ on PDP. Direct plots $R_g$ vs $[PDP]^{1/2}$ and $R_h$ vs $[PDP]^{1/2}$ (Figs. 96C,D) were drawn to further support order dependences.

Other graft parameters such as % grafting and % efficiency increase with PDP under the conditions mentioned in Table 128.

$n_g$ and $n_h$ values were determined under the experimental conditions given in Table 129 and found that both values decrease with PDP. Log $n_g$ vs log $[PDP]$ and log $n_h$ vs log $[PDP]$ (Figs. 98A,B) plots were drawn and found to give a slope of inverse square root order dependences in each case suggesting negative $0.5^{-1}$ order dependences. Direct plots $n_g$ vs $[PDP]^{-1/2}$ and $n_h$ vs $[PDP]^{-1/2}$ (Figs. 98C,D) were drawn to further support order dependences.
Effect of PDP on $-R_{PP}$

$-R_{PP}$ values were determined volumetrically under the conditions specified in Tables 126 and 127 and found to increase with [PDP]. Log $-R_{PP}$ Vs log [PDP] (Fig. 97A) plot was drawn and found to give a slope of unity indicating first order dependence of PDP on $-R_{PP}$. Direct plot $-R_{PP}$ Vs [PDP] (Fig. 97C) was also drawn to further support the order dependence.

To ascertain the above order dependence, $-R_{PP}$ values were determined under a set of different experimental conditions given in Table 127 and found to increase with PDP. Log $-R_{PP}$ Vs log [PDP] (Fig. 97B) plot was drawn and found to give a slope of unity indicating first order dependence of $-R_{PP}$ on PDP. Direct plot $-R_{PP}$ Vs [PDP] (Fig. 97D) was also drawn to confirm order dependence.

Effect of [H₂A] on Graft Parameters

It was observed that both $R_g$ and $R_h$ values increase with [H₂A] under the conditions specified in Table 130. Plots of log $R_g$ Vs log [H₂A] (Fig. 99A) and log $R_h$ Vs log [H₂A] (Fig. 99B) were drawn and found to be straight lines with a slope of 0.5 indicating half order dependences of $R_g$ and $R_h$ on H₂A. Direct plots $R_g$ Vs [H₂A]^{1/2} (Fig. 100A) and $R_h$ Vs [H₂A]^{1/2} (Fig. 100B) were also drawn to further support the order dependences.
To add further evidence to the above order dependences of $R_g$ and $R_h$ on $H_A$, $R_g$ and $R_h$ values were determined under a set of different experimental conditions as specified in Table 131. Log $R_g$ Vs log $[H_A]$ and log $R_h$ Vs log $[H_A]$ (Figs. 99C,D) plots were drawn and found to be straight lines with a slope of 0.5 indicating half order dependence of $R_g$ and $R_h$ on $H_A$. Direct plot $R_g$ Vs $[H_A]^{1/2}$ and $R_h$ Vs $[H_A]^{1/2}$ (Figs. 100C,D) were drawn to give support to the order dependences.

Both % grafting and % efficiency values increase with increase in [PDP] under the conditions mentioned in Table 132.

$n_g$ and $n_h$ values were determined separately under a set of experimental conditions given in Table 133. It was observed that both the values decrease with $[H_A]$. Log $n_g$ Vs log $[H_A]$ (Fig. 101A) and log $n_h$ Vs log $[H_A]$ (Fig. 101B) plots were drawn and found to be straight lines with a slope of negative 0.5 indicating inverse square root order dependence of $n_g$ and $n_h$ respectively. Direct plot $n_g$ Vs $[H_A]^{-1/2}$ (Fig. 101C) and $n_h$ Vs $[H_A]^{-1/2}$ (Fig. 101D) were also drawn to further support the order dependences.

Effect of Weight of PET on Graft Parameters

For the variation of backbone amount from
5.0 \times 10^{-2} \text{ to } 35.0 \times 10^{-2} \text{ g under the conditions given in Table 134, } R_g \text{ and } R_h \text{ values increase with PET. Log } R_g \text{ Vs log [Wt. of PET] (Fig. 102A) and log } R_h \text{ Vs log [Wt. of PET] (Fig. 102B) plots were drawn and found to be straight lines with a slope of 0.5 in each case suggesting half order dependences of } R_g \text{ and } R_h \text{ on the Wt. of PET.}

Direct plots } R_g \text{ Vs [Wt. of PET]^{1/2} (Fig. 103A) and } R_h \text{ Vs [Wt. of PET]^{1/2} (Fig. 103B) were also drawn to further support order dependences.

To add evidence to the above order dependences, } R_g \text{ and } R_h \text{ values were determined under a set of different experimental conditions given in Table 135. It was observed that both values increase with Wt. of PET. Log } R_g \text{ Vs log [Wt. of PET] and log } R_h \text{ Vs log [Wt. of PET] (Figs. 102C,D) plots were drawn and found to be straight lines with a slope of 0.5 suggesting half order dependence of } R_g \text{ and } R_h .

Direct plots } R_g \text{ Vs [Wt. of PET]^{1/2} (Fig. 103C) and } R_h \text{ Vs [Wt. of PET]^{1/2} (Fig. 103D) were drawn to further support the order dependences.

Other graft parameters like % grafting and % efficiency increase with Wt. of PET under the conditions specified in Table 136.
Kinetic chain length values for $n_g$ and $n_h$ were determined separately under the conditions mentioned in Table 137 and found that both values decrease with the backbone material. Plots of $\log n_g$ Vs $\log$ [Wt. of PET] (Fig. 104C) and $\log n_h$ Vs $\log$ [Wt. of PET] (Fig. 105D) were drawn and found to give a slope of negative 0.5 indicating square root order dependences of $R_g$ and $R_h$ on the Wt. of PET. Direct plots $n_g$ Vs [Wt. of PET]$^{-1/2}$ (Fig. 104C) and $n_h$ Vs [Wt. of PET]$^{-1/2}$ (Fig. 104D) were drawn to confirm the order dependences.

Effect of Temperature on Graft Parameters

Both $R_g$ and $R_h$ values increase with increase in temperature under the conditions specified in Table 138. Log $R_g$ Vs $T$ (Fig. 105A) and log $R_h$ Vs $T$ (Fig. 105B) plots were drawn and the energy of activation $E_a$ were determined and the values were found to be 5.03 and 6.54 Kcal/mol. The other graft parameters such as % grafting and % efficiency gradually increase with temperature (Table 139).

$n_g$ and $n_h$ values were determined separately and found that both the values increase with temperature (Table 139). Log $n_g$ Vs $T$ (Fig. 105C) and log $n_h$ Vs $T$ (Fig. 105D) plots were also drawn and the $E_a$ values were calculated to be 15.0 and 14.1 Kcal/mol respectively.
4.3.2.2 Discussion on Results

The observation made on $R_q$, $n_q$, $R_h$, and $n_h$ with PDP-H$_2$A redox pair during grafting are similar to observations made in 4.3.1. Hence, the sequence of reactions with the graft copolymerization of MMA onto PET using PDP-H$_2$A redox pair can be taken by replacing PDS by PDP.

4.3.2.3 Selected Reaction Scheme

Initiation

\[
\begin{align*}
PDP + H_2A & \xrightarrow{K_7} PDP - H_2A \\
C_7 + PET & \xrightarrow{K_8} PDP - H_2A - PET \\
C_8 & \xrightarrow{k_5} PET' + H_2O + H^+ + HPO_4^- + PO_4^{2-} \\
PET' + M & \xrightarrow{k_9} PET'M' \\
PO_4^{2-} + H_2O & \xrightarrow{k_7} HPO_4^- + \cdot OH \\
\cdot OH + H_2A & \xrightarrow{k_2} H_2O + A^- + H^+ \\
C_8 + A^- & \xrightarrow{k_8} HPO_4^- + PO_4^{2-} + H^+ + PET' \\
M + A^- & \xrightarrow{k_{10}} M_1^- 
\end{align*}
\]

Propagation

\[
(PET) M' + M \xrightarrow{k_9} PET M_2^-
\]

\[\]
Termination

\[
(PET)_n^* + M \xrightarrow{k_{t5}} PET_n^* \]

The reactions with \( P0^T \) in the initiation step are in accordance with earlier reports by Nayak and coworkers [107] of graft copolymerization of MMA onto wool using PDP-fructose redox system, by Nayak and coworkers [209] of graft copolymerization of MMA onto wool using PDP as initiator, by Lenka and coworkers of graft copolymerization of MMA onto nylon 6 using PDP as initiator and by Lenka and coworkers of vinyl polymerization of acrylamide and acrylic acid using PDP-sodium thiosulphate redox system [210] and Hariharan and coworker [54] in the vinyl polymerization of AN using PDP-H\(_2\)A redox pair.

For the above mechanism of grafting, the suitable expression for \( R_g \) and \( n_g \) would be written based on the discussion 4.1.2.

\[
R_g = k_g \left( \frac{k_{28}K_gK_8}{k_{t5}} \right)^{1/2} [M][PET]^{1/2}[PDP]^{1/2}[H_2A]^{1/2} \quad E_{75}
\]

\[
n_g = \frac{k_g [M]}{k_{t5} (2K_{28}K_gK_8)^{1/2}[PET]^{1/2}[PDP]^{1/2}[H_2A]^{1/2}} \quad E_{76}
\]
In E\textsubscript{75}, all the experimental observations such as first power dependence on [MMA] (Figs. 93A,C), square root order dependences on [PDP]\textsuperscript{1/2} (Figs. 96A,C), [H\textsubscript{2}A]\textsuperscript{1/2} (Figs. 100A,C) and [PET]\textsuperscript{1/2} (Figs. 103A,C) towards R\textsubscript{g} can be seen.

All the experimental results related to n\textsubscript{g} such as first power dependence on [MMA] (Fig. 94C), inverse square root order dependences on [PDP]\textsuperscript{-1/2} (Fig. 98C), [H\textsubscript{2}A]\textsuperscript{-1/2} (Fig. 101C) and on [PET]\textsuperscript{-1/2} (Fig. 104C) could be accounted for in E\textsubscript{76}.

The results related to R\textsubscript{h} and n\textsubscript{h} measurements are also similar to the observations made in 4.2.1.2 using PDS as one component. Therefore the mechanism for homopolymerization becomes,

\textbf{Initiation}

\[ \text{PDP + H}_2\text{A} \xrightleftharpoons[K_7]{K_8} \text{PDP - H}_2\text{A} \]

\[ \text{Complex C}_7 \]

\[ \text{C}_7 + \text{PET} \xrightleftharpoons[K_8]{K_9} \text{Complex C}_8 \]

\[ \text{C}_8 \xrightleftharpoons[k_{26}]{k_{29}} \text{PET}^- + \text{HPO}_4^- + \text{PO}_4^7 - \text{H}^+ + \text{H}_2\text{O} \]

\[ \text{PO}_4^7 - + \text{H}_2\text{O} \xrightleftharpoons[k_{29}]{k_{29}} \text{HPO}_4^- + \text{OH}^- \]
\[
\text{OH}^- + \text{H}_2\text{A} \xrightarrow{k_3} \text{H}_2\text{O} + \text{A}^\ddagger + \text{H}^+
\]

\[
\text{C}_7 + \text{A}^\ddagger \xrightarrow{k_{30}} \text{HPQ}_4^- + \text{PO}_4^\ddagger + \text{H}^+ + \text{PET}^\ddagger + \text{H}_2\text{O}
\]

\[
\text{M} + \text{A}^\ddagger \xrightarrow{k_{10}} \text{M}_1^*
\]

**Propagation**

\[
\text{M}_1^* + \text{M} \xrightarrow{k_P} \text{M}_2^*
\]

\[
\text{M}_{n-1}^* + \text{M} \xrightarrow{k_P} \text{M}_n^*
\]

**Termination**

\[
\text{M}_n^* + \text{M}_n^* \xrightarrow{k_{t6}} \text{homopolymer}
\]

For the above mechanism of homopolymerization, the suitable expression for \( R_h \) and \( n_h \) can be written using \( E_{72} \) by proper replacements.

\[
R_h = k' \left( \frac{k_{26} K_6 K_8}{k_{t6}} \right)^{1/2} [\text{PET}]^{1/2} [\text{H}_2\text{A}]^{1/2} [\text{PDP}]^{1/2} [\text{M}]
\]

.. \( E_{77} \)

\[
n_h = \frac{k'_p [\text{M}]}{(k_{t6})^{1/2} (k_{26} K_6 K_8) [\text{PET}]^{1/2} [\text{H}_2\text{A}]^{1/2} [\text{PDP}]^{1/2}}
\]

.. \( E_{78} \)

All the experimental results related to \( R_h \) such as first power dependence on [MMA] (Figs. 93B,D), square
root order dependences on [PDP] (Figs. 96B,D) on [H₂A] (Figs. 100B,D) and on [PET] (Figs. 103B,D) could be accounted for in E₇₇.

In E₇₇, all experimental observations towards n₉ such as first power dependence on [MMA] (Fig. 94D), inverse square root order dependences on [PET] (Fig. 104D), [H₂A] (Fig. 101D) and on [PDP] (Fig. 98D) can be seen.

Hence, E₇₅, E₇₆, E₇₇ and E₇₈ are the most suitable expressions for R₉, n₉, R₉ and n₉ respectively.

4.2.2 Evaluation of Composite Rate Constants for the System and Test their Invariance

From the slope of the plots R₉ Vs [MMA] (Figs. 93A,C), R₉ Vs [PDP]¹/² (Figs. 96A,C), R₉ Vs [H₂A]¹/² (Figs. 100A,C), and R₉ Vs [PET]¹/² (Figs. 103A,C) and using the conditions in Tables 122, 123, 126, 127, 130, 131, 134 and 135, the average value of the composite rate constant in E₇₅,

$$k_9 \left( \frac{k_{26} K_7 K_8}{k_{15}} \right)^{1/2}$$

was obtained as 3.49 x 10⁻³ mol⁻¹ l g⁻¹/² sec⁻¹. The values obtained from different plots are given in Table 140A. The constancy found in the value shows that the right choice of the rate expression is E₇₅.
That the rate expression as given by $E_{76}$ is the right selection for $n_g$ is further confirmed by the fact that the composite rate constant

$$k'_g = \frac{k'_5}{(k_{26}K_7K_8)^{1/2}}$$

remains invariant for all the variations of MMA, PDP, $H_2A$ and PET. The values so obtained are given in Table 140A.

This composite rate constant was evaluated from the slopes of the plots $n_g$ Vs $[MMA]$ (Fig. 94C), $n_g$ Vs $[PDP]^{-1/2}$ (Fig. 98C), $n_g$ Vs $[H_2A]^{-1/2}$ (Fig. 101C) and $n_g$ Vs $[PET]^{-1/2}$ (Fig. 104C) and using the conditions specified in Tables 125, 129, 133 and 137.

The average value of the composite rate constant was calculated to be 23.1 mol$^{-1}$ l sec$^{-1}$.

Multiplying the composite rate constant values obtained from $R_g$ and $n_g$ measurements, $(k'_g/k'_5)^{1/2}$ value was obtained as 0.284 mol$^{-1/2}$ l$^{1/2}$ sec$^{-1}$.

Taking the ratio of the composite rate constant values obtained from $R_g$ and $n_g$, the value $k_{26}K_7K_8$ was calculated to be $1.51 \times 10^{-4}$ mol$^{-1}$ l sec$^{-1}$. 
From the slope of the plots \( R_h \) vs [MMA] (Figs. 93B,D), \( R_h \) vs \([\text{PDP}]^{1/2}\) (Figs. 96B,D), \( R_h \) vs \([\text{H}_2\text{A}]^{1/2}\) (Figs. 100B,D) and \( R_h \) vs \([\text{PET}]^{1/2}\) (Figs. 103B,D) and the conditions mentioned in Tables 122, 123, 126, 127, 130, 131, 134 and 135. The average value of the composite rate constant in \( E_{77'} \), viz.,

\[
\begin{pmatrix}
  k_{26} & k_7 & k_8 \\
  k_{16}
\end{pmatrix}
\]

was calculated to be \( 3.51 \times 10^{-2} \text{ mol}^{-1} \text{ l g}^{-1/2} \text{ sec}^{-1} \). The values obtained from different plots are given in Table 140B. The constancy found in the value shows that right selection of the rate expression for \( R_h \) is 77.

That the rate expression for \( n_h \) is \( E_{78} \) is the right choice is further confirmed by the fact that the composite rate constant,

\[
\frac{k_i}{\left(k_{16}\right)^{1/2} \left(2k_{26}k_7k_8\right)}
\]

remains invariant for all variations of MMA, PDP, H\(_2\)A and PET. The values so obtained are given in Table 140B.

This composite rate constant was evaluated from the slope of the plots \( n_h \) vs [MMA] (Fig. 94D), \( n_h \) vs
[PDP] (Fig. 98D), $n_h$ Vs $[H_2A]$ (Fig. 101D) and $n_h$ Vs [PET] (Fig. 104D) and using the conditions mentioned in Tables 125, 129, 133 and 137.

The average value of the composite rate constant was calculated to be 229 g$^{-1/2}$.

Multiplying the composite rate constant values from $R_h$ and $n_h$, the value $(k'_P/k_{1/2})$ was calculated to be 2.83 mol$^{-1/2}$ l$^{1/2}$ g$^{-1}$ sec$^{-1}$.

Dividing the composite rate constant values from $R_h$ and $n_h$ measurements, the value $k_{26} K_7 K_8$ was calculated to be $1.53 \times 10^{-8}$ mol l$^{-1}$ sec$^{-1}$.

From a comparison of the value $k_{22} K_5 K_6$ ($2.95 \times 10^{-8}$ mol l$^{-1}$ sec$^{-1}$) obtained from PDS-$H_2A$-MMA-PET system with the value $k_{26} K_7 K_8$ ($1.53 \times 10^{-8}$ mol l$^{-1}$ sec$^{-1}$) obtained from PDP-$H_2A$-MMA-PET system, it is observed that grafting initiation with PDP as oxidant is less effective than when PDS is used as oxidant.

For the selected reaction scheme, an expression for $-R_{PDP}$ can be written as,

$$-R_{PDP} = \frac{(k_{26} K_7 K_8) [PDP] [H_2A] [PET]}{1 + K_7 [H_2A] + K_8 [H_2A] [PET]}$$
When \( K_7 K_8 [H_2A] [PET] \gg 1 + K_7 [H_2A] \), the expression for \( -R_{PDP} \) becomes,

\[ -R_{PDP} = k_{26} [PDP] \]

The observed results are in agreement with \( E_{79} \). From the slope of the plot \( (k_{26}) \) was determined as \( 4.22 \times 10^{-4} \) sec\(^{-1}\) and \( k_{26} K_7 K_8 \) value obtained from \( R_h \) and \( n_h \) measurements was calculated to be \( 1.53 \times 10^{-4} \) mol\(^{-1}\) l sec\(^{-1}\), the ratio \( (K_7 K_8) \) was obtained as 0.363 mol l\(^{-1}\). This fact supports the grafting reactions.

The effect of graft parameters on % grafting and % efficiency can have the relevant explanation as discussed earlier in 4.2.1

### 4.3.3 PDP-H_2A Redox Initiated Graft Copolymerization of AN onto PET

The observations made in this system are similar to the previous one of graft copolymerization of MMA onto PET using PDP-H_2A redox pair but with a different monomer AN.

#### 4.3.3.1 Results on PDP-H_2A Redox Initiated Graft Copolymerization of AN onto PET

**Effect of Time on Graft Parameters**

Both \( R_g \) and \( R_h \) values shows a decreasing trend
after five hours under the experimental conditions specified in Table 141. Hence, for smooth kinetics study, a reaction time more than five hours is needed for this system. Plots of $R_g$ Vs time (Fig. 106A) and $R_h$ Vs time (Fig. 106B) were drawn.

The other graft parameters such as % grafting and % efficiency also decrease after five hours (Table 141).

The kinetic chain length values for $n_g$ and $n_h$ were determined and found that both the values decrease after five hours suggesting a reaction time more than five hours is needed for this system. Plots of $n_g$ Vs time (Fig. 106C) and $n_h$ Vs time (Fig. 106D) were drawn.

Effect of [AN] on Graft Parameters

It was observed from the $R_g$ and $R_h$ measurements under a set of experimental conditions specified in Table 142, that both $R_g$ and $R_h$ values increase with AN. Log $R_g$ Vs log [AN] (Fig. 107A) and log $R_h$ Vs log [AN] (Fig. 107B) plots were drawn and found to give straight lines with a slope of unity in the case of $R_g$ and a slope of 1.5 with respect to $R_h$ suggesting a first power dependence on $R_g$ and three halfth order dependence on $R_h$ respectively. Direct plots $R_g$ Vs [AN] (Fig. 108A) and $R_h$ Vs [AN]$^{1.5}$ (Fig. 108B) were drawn to confirm the order dependences.
In order to ascertain the above order dependences of $R_\theta$ and $R_\phi$ on AN, $R_\theta$ and $R_\phi$ values were determined under a set of different experimental conditions as given in Table 143 and found that both the values increase with AN. Log $R_\theta$ Vs log [AN] (Fig. 107C) and log $R_\phi$ Vs log [AN] (Fig. 107D) plots were drawn and found to give a slope of unity with respect to $R_\theta$ and 1.5 with regard to $R_\phi$ suggesting first order dependence of $R_\theta$ on AN and 1.5 order dependence of $R_\phi$ on AN respectively. Direct plots $R_\theta$ Vs [AN] (Fig. 108C) and $R_\phi$ Vs [AN]$^{1.5}$ (Fig. 108D) were drawn to confirm the order dependences.

While % grafting gradually increases with [AN], % efficiency increases initially and then falls thereafter, under the conditions specified in Table 144.

$n_\theta$ and $n_\phi$ values were determined separately under the conditions mentioned in Table 145 and found that both the values increase with AN. Log $n_\theta$ Vs log [AN] (Fig. 109A) and log $n_\phi$ Vs log [AN] (Fig. 109B) plots were drawn and found to be straight lines with a slope of unity in the case of $n_\theta$ and 0.5 with respect to $n_\phi$ respectively suggesting a first order dependence of $n_\theta$ on AN and half order dependence on $n_\phi$ respectively. Direct plots of $n_\theta$ Vs [AN] (Fig. 109C) and $n_\phi$ Vs [AN]${^{1/2}}$ (Fig. 109D) were also drawn to confirm the order dependences.
Effect of [PDP] on Craft Parameters

It was observed from the $R_g$ and $R_h$ measurements under the experimental conditions mentioned in Table 146, that both the values increase gradually with [PDP]. Log $R_g$ Vs log $[PDP]$ (Fig. 110A) and log $R_h$ Vs log $[PDP]$ (Fig. 110B) plots were drawn and found to be straight lines with a slope of 0.5 pointing out a half order dependence of $R_g$ and $R_h$ on PDP. Direct plots $R_g$ Vs $[PDP]^{1/2}$ (Fig. 111A) and $R_h$ Vs $[PDP]^{1/2}$ (Fig. 111B) were drawn to confirm the order dependences.

To add evidence to the above order dependences, $R_g$ and $R_h$ values were determined under a set of different experimental conditions given in Table 147. It was observed that both the values increase with PDP. Log $R_g$ Vs log $[PDP]$ (Fig. 110C) and log $R_g$ Vs log $[PDP]$ (Fig. 110D) plots were drawn and found to be straight lines with a slope of 0.5 suggesting half order dependences on $R_g$ and $R_h$. Direct plots of $R_g$ Vs $[PDP]^{1/2}$ (Fig. 111C) and $R_h$ Vs $[PDP]^{0.5}$ (Fig. 111D) were drawn in order to confirm the order dependences.

It was observed that both % grafting and % efficiency increase gradually with PDP under the conditions given under Table 148.
**Effect of PDP on \(-R_{pd}\)**

\(-R_{pd}\) values were determined volumetrically under a set of different experimental conditions mentioned in Tables 145 and 147 and found that both the values increase with PDP. Log \(-R_{pd}\) Vs log [PDP] (Figs. 112A, B) plots were drawn separately and found to be straight lines with a slope of unity indicating first power dependence. Direct plots \(-R_{pd}\) Vs [PDP] (Figs. 112C, D) were also drawn to further support the order dependences.

**Effect of \([H_2A]\) on Graft Parameters**

Both \(R_g\) and \(R_h\) values increase with \([H_2A]\) under the conditions mentioned in Table 150. Log \(R_g\) Vs log \([H_2A]\) (Fig. 114A) and log \(R_h\) Vs log \([H_2A]\) (Fig. 114B) plots were drawn and found to be straight lines with a slope of 0.5.
indicating half order dependence of \( R_g \) and \( R_h \) on \( H_A \).

Direct plots \( R_g \) Vs \( \sqrt{H_A} \) (Fig. 115A) and \( R_h \) Vs \( \sqrt{H_A} \) (Fig. 115B) were drawn to confirm the order dependence.

To ascertain the order dependences, \( R_g \) and \( R_h \) values were determined under the conditions specified in Table 151, it was observed that both the values increase with \( H_A \). Log \( R_g \) Vs log \( H_A \) (Fig. 114C) and log \( R_h \) Vs log \( H_A \) (Fig. 114D) plots were drawn and found to give a slope of 0.5 in each case thus showing half order dependence of \( R_g \) and \( R_h \) on \( H_A \) respectively. Direct plots \( R_g \) Vs \( \sqrt{H_A} \) (Fig. 115C) and \( R_h \) Vs \( \sqrt{H_A} \) (Fig. 115D) were also drawn to confirm the order dependences.

Other graft parameters like % grafting and % efficiency increase with increase in \( H_A \) under the conditions specified in Table 152.

\( n_g \) and \( n_h \) values were determined under the conditions mentioned in Table 153 and found that both the values decrease with \( H_A \). Log \( n_g \) Vs log \( H_A \) (Fig. 116A) and log \( n_h \) Vs log \( H_A \) (Fig. 116B) plots were drawn and found to give straight lines with a slope of negative 0.5 in each case, thus indicating inverse square root order dependence of \( n_g \) and \( n_h \) on \( H_A \). Direct plots \( n_g \) Vs \( \sqrt{H_A} \) (Fig. 116C) and \( n_h \) Vs \( \sqrt{H_A} \) (Fig. 116D) were drawn to confirm the order dependences.
Effect of Weight of PET on Craft Parameters

\( R_g \) and \( R_h \) values were determined under the conditions mentioned in Table 154 and found that both the values increase with Wt. of PET. Log \( R_g \) Vs log [Wt. of PET] (Fig. 117A) and log \( R_h \) Vs log [Wt. of PET] (Fig. 117B) plots were drawn and found to give straight lines with a slope of 0.5 in each case thus pointing out half order dependence of \( R_g \) and \( R_h \) on the Wt. of PET. Direct plots \( R_g \) Vs [Wt. of PET]^{1/2} (Fig. 118A) and \( R_h \) Vs [Wt. of PET]^{1/2} (Fig. 118B) were also drawn to confirm the order dependences.

In order to ascertain the above order dependences, \( R_g \) and \( R_h \) values were determined under the conditions specified in Table 155. It was found that both the values increase with the Wt. of PET. Log \( R_g \) Vs log [Wt. of PET] (Fig. 117C) and log \( R_h \) Vs log [Wt. of PET] (Fig. 117D) plots were drawn and found to be straight lines with a slope of 0.5 in each case thus showing half order dependence of \( R_g \) and \( R_h \) on the Wt. of PET. Direct plots \( R_g \) Vs [Wt. of PET]^{1/2} (Fig. 118C) and \( R_h \) Vs [Wt. of PET]^{1/2} (Fig. 118D) were drawn to confirm the order dependences.

It was observed that while % grafting increases initially and then falls afterwards under the conditions
mentioned in Table 156, % efficiency gradually increases.

Kinetic chain length values for $n_g$ and $n_h$ were determined under the conditions specified in Table 157. It was observed that both the values decrease with the amount of backbone material. Log $n_g$ Vs log [Wt. of PET] (Fig. 119A) and log $n_h$ Vs log [Wt. of PET] (Fig. 119B) plots were drawn and found to give straight lines with a slope of negative 0.5 in each case showing inverse square root order dependences on $n_g$ and $n_h$. Direct plots $n_g$ Vs [Wt. of PET]$^{-1/2}$ (Fig. 119C) and $n_h$ Vs [Wt. of PET]$^{-1/2}$ (Fig. 119D) were also drawn to confirm the order dependences.

**Effect of Temperature on Graft Parameters**

Both $R_g$ and $R_h$ values increase with temperature under the conditions mentioned in Table 158. Arrhenius plots log $R_g$ Vs $1/T$ (Fig. 120A) and log $R_h$ Vs $1/T$ (Fig. 120B) were drawn. The $E_a$ values for $R_g$ and $R_h$ were determined and found to be 5.49 and 7.63 Kcal/mol.

Other graft parameters such as % grafting and % efficiency increase with temperature under the conditions specified in Table 159.

Kinetic chain length values $n_g$ and $n_h$ were determined under the conditions mentioned in Table 159 and
found that both the values increase with increase in temperature. Arrhenius plots $n_0$ Vs $T$ (Fig. 120C) and $\log n_h$ Vs $T$ (Fig. 120D) were drawn and the $E_a$ values were determined and found to be 8.72 and 7.32 Kcal/mol respectively.

4.3.3.2 Discussion on Results

It was observed that the results obtained in this system was similar to the one as seen in graft copolymerization of AN onto PET initiated by PMS-H$_2$A redox pair (4.1.1) but with a different oxidant PDF. This suggests that the probable reaction scheme would be similar as in the earlier study (4.1.2).

4.3.3.3 Selection Reaction Scheme

Initiation

\[
\begin{align*}
PDP + H_2A & \xrightleftharpoons{K_7} PDP - H_2A \\
\text{Complex } C_7 & \\
C_7 + PET & \xrightarrow{K_9} PDP - H_2A - PET \\
\text{Complex } C_8 & \\
C_8 & \xrightarrow{k_{26}} PET' + H_2O + H^+ + HPO_4^- + PO_4^- \\
PET' + M & \xrightarrow{k_5} PET M^+
\end{align*}
\]
PO₄³⁻ + H₂O $\overset{k_{27}}{\longrightarrow}$ HPO₄²⁻ + OH⁻

OH⁻ + H₂A $\overset{k_3}{\longrightarrow}$ H₂O + A⁺ + H⁺

C₈ + A⁺ $\overset{k_{28}}{\longrightarrow}$ HPO₄²⁻ + PO₄³⁻ + H⁺ + PET⁺

M + A⁺ $\overset{k_{10}}{\longrightarrow}$ M⁺

Propagation

$M_1^* + M \overset{k_9}{\longrightarrow} M_2^*$

$M_{n-1}^* + M \overset{k_9}{\longrightarrow} M_n^*$

Termination

$M_n^* + M_n^* \overset{k_{11}}{\longrightarrow}$ graft copolymer

For the above mechanism of grafting, the suitable expression for R₉ and n₉ would be written based on the discussion at 4.7.1.2.

$R_9 = k_9 \left( \frac{k_{26} K_7 K_8}{k_{k_{11}}} \right)^{1/2} (M)(PET)^{1/2}(PDP)^{1/2}(H₂A)^{1/2}$

$\therefore E_{80}$

$n_9 = \frac{k_9 (M)}{(k_{k_{11}}) (2 k_{26} K_7 K_8)^{1/2} (PET)^{1/2} (PDP)^{1/2} (H₂A)^{1/2}}$

$\therefore E_{81}$
All the experimental results such as first power dependence on [AN] (Figs. 108A,C), square root order dependences on [PDP]^{1/2} (Figs. 111A,C), [H_A]^{1/2} (Figs. 115A,C), and [PET]^{1/2} (Figs. 118A,C) towards R can be seen in $E_0$.

In $E_0$, the experimental observations related to n such as first power dependence on [AN] (Fig. 109C), inverse square root order dependences on [PDP]^{-1/2} (Fig. 113C), [H_A]^{-1/2} (Fig. 116C) and [PET]^{-1/2} (Fig. 119C) could be accounted.

$R_n$ was found to have three halfth order dependence on [AN] (Figs. 108B,D), half order dependences on [PET] (Figs. 118B,D), [H_A] (Figs. 115B,D) and [PDP] (Figs. 111B,D) suggesting mutual termination as predicted in earlier study. Hence, it is worthwhile to have the following mechanism for homopolymerization.

\[
\begin{align*}
\text{Initiation} \\
\text{PDP + H}_2\text{A} \xrightleftharpoons{K_7} \text{PDP - H}_2\text{A} \\
\text{Complex C}_7 \\
\text{C}_7 + \text{PET} \xrightleftharpoons{K_8} \text{PDP - H}_2\text{A - PET} \\
\text{Complex C}_8 \\
\text{C}_8 \xrightleftharpoons{k_{26}} \text{PET}^+ + \text{HPO}_4^+ + \text{PO}_4^{2-} + \text{H}^+ + \text{H}_2\text{O}
\end{align*}
\]
\[
\begin{align*}
\text{PO}_4^{3-} + H_2O & \xrightarrow{k_{2g}} HPO_4^- + 3H^+ \\
\text{OH}^- + H_2A & \xrightarrow{k_3} H_2O + A^+ + H^+
\end{align*}
\]

\[
\begin{align*}
C_7 + A^+ & \xrightarrow{k_{31}} HPO_4^- + PO_4^{3-} + H^+ + \text{PET}^+ + H_2O \\
C_8 + M & \xrightarrow{k_{31}} M_1^+ + H_2O + PO_4^{3-} + H^+ + \text{(PET)} \\
M + A^+ & \xrightarrow{k_{10}} M_1^+
\end{align*}
\]

Propagation

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

Termination

\[
M_n^+ + M_n^+ \xrightarrow{k_{t4}} \text{homopolymer}
\]

For the above mechanism of homopolymerization, the suitable expression for \( R_h \) and \( n_h \) would then be written using \( E_{40} \) and \( E_{41} \).

\[
R_h = k_p \left( \frac{k_{31} K_1 K_2 K_4}{k_{t4}} \right)^{1/2} \frac{[\text{PET}]}{[H_2A]}^{1/2} \frac{[\text{PET}]}{[\text{PET}]}^{1/2} \frac{[M]}{3^{3/2}} \]

\( \cdots \ E_{82} \)

\[
n_h = \frac{k_p^{1/2} [M]}{(k_{t4})^{1/2} (2k_{31} K_1 K_2)^{1/2} [\text{PET}]}^{1/2} [H_2A]^{1/2} [\text{PET}]}^{1/2} \frac{[M]}{3^{3/2}} \]

\( \cdots \ E_{83} \)
All the experimental results such as three halfth order dependences on [AN] (Figs. 108B,D), square root order dependences on [PET]^{1/2} (Figs. 118B,D) [PDP]^{1/2} (Figs. 111B,D) and [H_A]^{1/2} (Figs. 115B,D) towards R_n can be seen in E_82.

In E_83, all the experimental observations related to n_h such as half order dependences on [M] (Fig. 109D), inverse square root order dependences on [H_A]^{-1/2} (Fig. 116D), [PET]^{-1/2} (Fig. 119D), and [PDP]^{-1/2} (Fig. 113D) could be seen.

Hence, E_80, E_81, E_82, and E_83 are the most suitable expressions for R_g, n_g, R_n and n_h respectively.

4.3.3.4 Evaluation of Composite Rate Constants for the System and Test their Invariance

From the slope of the plots R_g Vs [AN] (Figs. 108A,C), R_g Vs [PDP]^{1/2} (Figs. 111A,C), [H_A]^{1/2} (Figs. 115A,C) and [PET]^{1/2} (Figs. 118A,C) and using the conditions in Tables 142, 143, 146, 147, 150, 151, 154 and 155, the average value of the composite rate constant in E_80,

\[
k_g \left( \frac{k_26 K_y K_6}{k_{t1}} \right)^{1/2}
\]
was obtained as $4.38 \times 10^{-4} \text{ mol}^{-1} \text{ l g}^{-1/2} \text{ sec}^{-1}$. The values obtained from different plots are given in Table 160A. The constancy found in the value shows that right choice of the rate expression is $E_{80}$.

That the rate expression as given by $E_{81}$ as the right choice for $n_g$ is further confirmed by the fact that the composite rate constant

$$k'_g = \frac{k'_g}{k_{11} (2 k_g k_7 k_8)^{1/2}}$$

remains invariant for all the variations of AN, PDP, $H_2A$ and PET. The values so obtained are given in Table 160A.

This composite rate constant was evaluated from the slopes of the plots $n_g$ Vs [AN] (Fig. 109C), $n_g$ Vs [PDP]$^{-1/2}$ (Fig. 113C), $n_g$ Vs $[H_2A]^{-1/2}$ (Fig. 116C) and $n_g$ Vs [PET]$^{-1/2}$ (Fig. 119C) and using the conditions mentioned in Tables 145, 149, 153 and 157. The average value of the composite rate constant was calculated to be $21.2 \text{ g}^{-1/2}$.

Multiplying the composite rate constant values obtained from $R_g$ and $n_g (k'_g/k_t^{1/2})$ value was obtained as $0.096 \text{ mol}^{-1/2} \text{ l}^{1/2} \text{ sec}^{-1/2}$. 
It is interesting to note that \( \left( \frac{k_g}{k_t^{1/2}} \right) \) value with AN as monomer as determined with this system (0.096 mol\(^{-1/2}\) sec\(^{-1/2}\)) is close to the value determined earlier in PMS-H\(_2\)A-AN-PET system (0.117 mol\(^{-1/2}\) sec\(^{-1/2}\)), PMS-H\(_2\)A-AN-nylon 6 (0.108 mol\(^{-1/2}\) sec\(^{-1/2}\)) and PMS-H\(_2\)A-AN-nylon 66 (0.098 mol\(^{-1/2}\) sec\(^{-1/2}\)) systems, thereby supporting the proposed scheme.

Taking the ratio of the composite rate constant values obtained from \( k_g \) and \( n_g \), the value \( k_{26} K_7 K_8 \) was calculated to be \( 2.0 \times 10^{-5} \) mol\(^{-1}\) sec\(^{-1}\).

From the slope of the plots \( R_h \) Vs [AN]\(^{1.5}\) (Figs. 108B,D), \( R_h \) Vs [PDP]\(^{1/2}\) (Figs. 111B,D), \( R_h \) Vs [H\(_2\)A]\(^{1/2}\) (Figs. 115B,D), and \( R_h \) Vs [PET]\(^{1/2}\) (Figs. 118B,D) and the conditions mentioned in Tables 112, 143, 146, 147, 150, 151, 154 and 155, the average value of the composite rate constant in \( E_{82} \) is

\[
k' = \left( \frac{k_{31} K_7 K_8}{k_{14}} \right)^{1/2}\]

was calculated to be \( 1.46 \times 10^{-2} \) mol\(^{-1/2}\) sec\(^{-1/2}\). The values so obtained from different plots are given in Table 160B. The constancy found in the values shows that the right selection of the rate expression for \( R_h \) is \( E_{82} \).
That the right choice for \( n_h \) is \( E_{33} \) is further confirmed by the fact that the composite rate constant

\[
\frac{k'_{p}}{(k_{t}^{1/2})} \equiv \left( \frac{2 k_{31} K_{7} K_{8}}{k_{7}^{1/2}} \right)
\]

remains invariant for all the variations of \( AN \), \( PDP \), \( H_{2}A \) and PET. The values so obtained are given in Table 160B.

This composite rate constant was evaluated from the slope of the plots \( n_{h} \) Vs \( [AN]^{1/2} \) (Fig. 109D), \( n_{h} \) Vs \( [PDP]^{1/2} \) (Fig. 113D), \( n_{h} \) Vs \( [H_{2}A]^{1/2} \) (Fig. 116D) and \( n_{h} \) Vs \( [PET]^{1/2} \) (Fig. 119D) and using the conditions specified in Tables 145, 149, 153 and 157. The average value of the composite rate constant was calculated to be 193 mol\(^{-1}\) l sec\(^{-1}\).

Multiplying the composite rate constant value from \( R_{h} \) and \( n_{h} \), the value \( (k'_{p}/k_{t}^{1/2}) \) was calculated to be 1.68 mol\(^{-3/4}\) l\(^{-3/4}\) g\(^{-1/2}\) sec\(^{-1/2}\).

During the composite rate constant values obtained from \( R_{h} \) and \( n_{h} \) measurements, the value \( k_{31} K_{7} K_{8} \) was calculated to be \( 7.56 \times 10^{-5} \) mol\(^{-3/2}\) l\(^{3/2}\) sec\(^{-1}\).

Knowing \( k_{26} K_{7} K_{8} \) value from \( R_{g} \) and \( n_{g} \) measurements as \( 2.07 \times 10^{-5} \) mol\(^{-1}\) l sec\(^{-1}\) and \( k_{31} K_{7} K_{8} \)
value from \( R_H \) and \( n_H \) measurements as \( 7.56 \times 10^{-5} \) mol\(^{-3/2}\) l\(^{3/2}\) sec\(^{-1}\) the ratio of the two values \((k_{26}/k_{31})\) was obtained as 0.273 mol\(^{1/2}\) l\(^{-1/2}\). The very low value for the ratio predicts the predominance of homopolymerization in over grafting than in PMS-H\(_2\)A-AN-PET system.

For the selected reaction scheme, an expression for \(-R_{PDP}\) can be written as

\[
-R_{PDP} = \frac{(k_{31}K_7K_8)[M][PDP]_T[H_2A][PET]+(k_{26}K_7K_8)[PDP][H_2A][PET]}{(1 + K_7[H_2A]) + K_7K_8[H_2A][PET]} \tag{E84}
\]

where \([PDP]_T = \text{initial [PDP]} \) taken.

When \( K_7K_8[H_2A][PET] \gg 1 + K_7[H_2A] \), the expression becomes,

\[
-R_{PDP} = (k_{31}[M] + k_{26})[PDP] \tag{E85}
\]

The values obtained for \( k_{31} \), \( K_7 \), \( K_8 \) and \( k_{26} \), \( K_7 \), \( K_8 \) from the slopes of the plots \(-R_{PDP} \) vs \([PDP] \) (Figs. 112C,D) are \( 3.44 \times 10^{-4} \) mol\(^{-1}\) l\(^{-1}\) sec\(^{-1}\) and \( 3.0 \times 10^{-4} \) mol\(^{-1}\) l\(^{-1}\) sec\(^{-1}\) respectively for two different \([M]\). Using the slopes and knowing \(-R_{PDP}\) was invariant to the change in \([H_2A]\) and \([PET]\), the two equations \((k_{31}[M] + k_{26})K_7K_8\) with two different \([M]\) as in Tables 146 and 147 are solved to obtain the ratio \((k_{26}/k_{31})\). The calculated value was
found to be 0.162. This again supports that $k_{26} \ll k_{31}$ as it was inferred through grafting measurements.

The effect of % grafting and % efficiency by the parameters can have all relevant explanation as discussed earlier in 4.1.1.

4.4. Evidences for Grafting

4.4.1 Thermal Analysis

Thermogravimetric analysis of polymer samples gives thermograms which shows the weight loss of the samples at various temperatures. Derivative thermogravimetry (DTG) gives the change of mass with respect to time and this will be more useful in deriving thermal characteristics of the samples though it gives the same information as obtained from thermogravimetric curve.

Thermograms were recorded for the following samples with a heating rate of 10°C/min starting from room temperature to 700°C.

1. Parent PET
2. PET grafted with PAN
3. PET grafted with PMMA
4. Parent nylon 6
The % weight loss at different temperatures, initial decomposition temperature (IDT), final decomposition temperature (FDT) for the different grafted samples are tabulated as follows (Page 286).

From the table, it can be seen that the % weight loss increases with temperature for all the samples. The thermal behaviour of PET and its grafted sample with PAN were found to be similar. On the other hand, the thermal behaviour of PET and its grafted sample with PMMA were found to be different. For PET-g-MMA sample, the decomposition begins even at lower temperature. This may be due to the decomposition of the side chain polymer at lower temperature. IDT was found to be lowered for the grafted samples and indicating the above possibility. IDT of PMMA grafted sample was found to be higher than the PAN grafted sample. The higher FDT value for PET-g-PMMA gives an idea that the thermal stability for the grafted sample is high at higher temperature. The difference in thermal behaviour of the grafted samples in comparison with
1. THERMOGRAM OF PURE PET
2. THERMOGRAM OF PET GRAFTED WITH AN USING PMS-H₂ A REDOX PAIR
3. THERMOGRAM OF PET GRAFTED WITH MMA USING PDP-H₂ A REDOX PAIR
1, 1a. THERMOGRAM OF PURE NYLON 6
2, 2a. THERMOGRAM OF NYLON 6 GRAFTED WITH AN USING PMS-H₂A REDOX PAIR
3, 3a. THERMOGRAM OF NYLON 6 GRAFTED WITH MMA USING PMS-H₂A REDOX PAIR
1. THERMOGRAM OF PURE NYLON 66
2. THERMOGRAM OF NYLON 66 Grafted with an Using PMS-\text{H}_2\text{A} Redox Pair
3. THERMOGRAM OF NYLON 66 Grafted with MMA Using PMS-\text{H}_2\text{A} Redox Pair
the backbone adds evidence for the grafting. The similar
trend of thermal behaviour can also be seen in the cases of nylon 6/nylon 66 and their grafted samples. This adds
evidence for the grafting onto nylon 6/nylon 66 and their grafted samples.
<table>
<thead>
<tr>
<th>Sample</th>
<th>% grafting</th>
<th>IDT*^(_{\circ C})</th>
<th>FDT#^(_{\circ C})</th>
<th>% weight loss at (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Parent PET</td>
<td>Nil</td>
<td>380</td>
<td>470</td>
<td>5 30 55</td>
</tr>
<tr>
<td>2 PET grafted with PAN</td>
<td>25</td>
<td>350</td>
<td>440</td>
<td>5 10 60</td>
</tr>
<tr>
<td>3 PET grafted with PMMA</td>
<td>62</td>
<td>320</td>
<td>530</td>
<td>5 8 15</td>
</tr>
<tr>
<td>4 Parent nylon 6</td>
<td>Nil</td>
<td>350</td>
<td>500</td>
<td>4 5 8 20</td>
</tr>
<tr>
<td>5 Nylon 6 grafted with PAN</td>
<td>12.5</td>
<td>300</td>
<td>480</td>
<td>4 5 11 46</td>
</tr>
<tr>
<td>6 Nylon 6 grafted with PMMA</td>
<td>48</td>
<td>325</td>
<td>525</td>
<td>5 26 56</td>
</tr>
<tr>
<td>7 Parent nylon 66</td>
<td>Nil</td>
<td>350</td>
<td>500</td>
<td>4 5 8 20</td>
</tr>
<tr>
<td>8 Nylon 66 grafted with PAN</td>
<td>20.1</td>
<td>290</td>
<td>500</td>
<td>4 4 4 5 8 24</td>
</tr>
<tr>
<td>9 Nylon 66 grafted with PMMA</td>
<td>40</td>
<td>335</td>
<td>520</td>
<td>6 6 8 48</td>
</tr>
</tbody>
</table>

* IDT - Initial decomposition temperature
# FDT - Final decomposition temperature
4.4.2 Infrared Spectra

The infrared spectra of the following samples were recorded to identify the grafted side chains.

PET, PET-g-PMMA, PET-g-PAN, nylon 6, nylon 6-g-PMMA, nylon 6-g-PAN, nylon 66, nylon 66-g-PMMA, and nylon 66-g-PAN.

In the spectra of the grafted samples few peaks characteristic of PMMA or PAN side chain appear besides the peaks corresponding to the backbone. The grafted polymer with PAN shows two peaks at 2262 and 1613 cm\(^{-1}\) characteristic of the nitrile group. This gives an idea that the backbone were modified during grafting reactions.

The following assignments are made from the infrared spectra of the samples.

PET

1712 cm\(^{-1}\) (C = O str.), 1504 cm\(^{-1}\) (aromatic C = C str.)
1200 cm\(^{-1}\) (carboxylate C-O str.), 1241 cm\(^{-1}\) (CH\(_2\)-O-str.),
850 cm\(^{-1}\) (CH out of plane def.,) 1100 cm\(^{-1}\) and 1280 cm\(^{-1}\)
(C=O str. bond is aryl carboxylate ester).

nylon 6/nylon 66

1710 cm\(^{-1}\) (C=O str.), 1130 cm\(^{-1}\) (-C-N str.in sec. amide),
700 cm\(^{-1}\) (C-c bending vibrations for the groups (CH\(_2\))\(_n\)) where n ≥ 4.
INFRARED SPECTRA OF PURE PET
INFRARED SPECTRA OF PET GRAFTED WITH ① AND ② MMA
The IR spectra of the grafted polymer with PMMA could not be differentiated from the IR spectra of the backbone due to the presence of ester C=O group in the backbone and in the grafted side chain.

4.4.3 Dye Uptake

The grafted and ungrafted samples were dyed for 2% shade with 30% acetic acid with a dye in open bath at boil for 1 hr. keeping the liquor ratio 1:200.

Lanasyn 5 C.L. dye was used for nylon 6/nylon 66 samples.

Foron scarlet E-2 CFL dye was used for PET samples.

After dyeing was over, the amount of dye absorbed by the fibers were determined spectrophotometrically using spectronic 20. $\lambda_{\text{max}}$ was fixed at 440 nm for the dyes used for nylon 6/nylon 66 samples and 500 nm for the dye used for PET samples.

The optical density of the residual mother liquor was measured and used to find the amount of dye uptake by the filter using calibrated curve.
Dye uptake values for different samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>% grafting</th>
<th>% of dye uptake</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Pure nylon 66</td>
<td>-</td>
<td>52.5</td>
</tr>
<tr>
<td>2 Nylon 66 grafted with PAN</td>
<td>40.5</td>
<td>57.6</td>
</tr>
<tr>
<td>3 nylon 66 grafted with PMMA</td>
<td>60.1</td>
<td>60.8</td>
</tr>
<tr>
<td>4 Pure nylon 6</td>
<td>-</td>
<td>56.2</td>
</tr>
<tr>
<td>5 Nylon 6 grafted with PAN</td>
<td>13</td>
<td>53.2</td>
</tr>
<tr>
<td>6 nylon 6 grafted with PMMA</td>
<td>48</td>
<td>58.3</td>
</tr>
<tr>
<td>7 Pure PET</td>
<td>-</td>
<td>38.9</td>
</tr>
<tr>
<td>8 PET grafted with PAN</td>
<td>30</td>
<td>47.6</td>
</tr>
<tr>
<td>9 PET grafted with PMMA</td>
<td>62</td>
<td>59.5</td>
</tr>
</tbody>
</table>

From the above table, it is clear that the increase in % grafting increases the dye uptake for all the three synthetic fibers viz., PET, nylon 6 and nylon 66. The dyeability of the textile fiber can be increased by introducing suitable functional group in the fiber structure so that it becomes center of absorption. The dyeability can also be enhanced by bringing about opening up of the fiber structure, thus creating additional accessibility for the dye molecules.

The present observation may be due to both the above mentioned criteria [211] for the synthetic fibers. The change in dye uptake gives supporting evidence for grafting.
4.5. Conclusions

A mechanism which agrees well with all experimental observations related to $R_g$, $n_g$, $R_h$ and $n_h$ was given in graft copolymerization of AN onto PET using PMS-H$_A$ redox pair. This was arrived after analysing the other possible reaction paths.

In the mechanism, active site generation was proposed to involve the decomposition of the initial complex formed between PMS-H$_A$ and backbone. This novel type of grafting step is given for the first time. The simultaneous homopolymerization is being initiated by the direct interaction between monomer and the complex between PMS, H$_A$ and backbone. The observed half order dependence of the backbone both in graft copolymerization and homopolymerization strongly favours this proposal.

Suitable rate expressions were derived for $R_g$, $n_g$, $R_h$ and $n_h$ with the proposed mechanism. The invariance in the composite rate constants present in those expressions under different experimental conditions adds support to the proposed mechanism. The rate constants evaluated showed that the rate of grafting would follow the order $P_{ET} > n_{y/ony} > P_{ET} > n_{y/ony}$ on nylon 66.
A comparison of the composite rate constants in graft copolymerization studies involving MMA onto nylon 6/nylon 66 and graft copolymerization studies involving AN onto nylon 6/nylon 66 indicates that the rate of grafting may be better with MMA as monomer in comparison with AN as monomer.

While changing the redox pair from PMS-H₂A to PDS-H₂A or PDP-H₂A, the mechanism for grafting and homopolymerization could be the same when the graft copolymerization was carried out with MMA.

$k_{g}/k_{t}^{1/2}$ and $k_{p}/k_{t}^{1/2}$ values were determined using PDS-H₂A and PDP-H₂A systems and compared. The values were found to be close to the one obtained in graft copolymerization of AN onto PET/nylon 6/nylon 66 using PMS-H₂A redox initiating system.

The grafted samples showed different thermal characteristics from the pure backbone. This indicates that the pure backbone has been modified during grafting.

The infrared spectra for the pure backbone and the isolated backbone were recorded and the presence of PAN or PMMA in the isolated grafted backbone was confirmed.
The increase in dye uptake for the grafted sample in comparison with parent backbone also favours grafting.