4.1. Introduction

In this chapter the effect of methylene blue (MB) chloride in the free radical polymerization of various monomers such as methyl methacrylate (MMA), acrylonitrile (AN), methyl acrylate (MA), acrylamide (AA), methacrylonitrile (MAN) and styrene (St) has been studied by measuring the rates of polymerization ($R_p$) of the above monomers both in the presence or absence of MB. The $R_p$ data have been used to evaluate the rate constants for the reaction of MB with the above polymer radicals on the basis of a reaction scheme and the kinetic equation derived therefrom.

All of the above monomers barring styrene and so also the radicals derived from them have electron withdrawing substituents. Only polystyrene radical has the phenyl group (which is an electron releasing substituent) at the alpha position. Kochi observed selectivity in the electron-transfer oxidation of small carbon radicals by metal ions. Those radicals having electron withdrawing substituents were found to be resistant to electron-transfer oxidation by Cu(II) ion.
The reversible decolorisation of MB by water soluble small carbon radicals such as $\alpha$-cyano alkyl radicals observed by Haines and Waters indicate that radicals having electron withdrawing substituents such as $\text{-CN}$ at the $\alpha$ position are in fact oxidized by MB. The reversible nature of oxidation also indicates that the oxidation follows electron-transfer route. In this perspective it would be worthwhile to determine quantitatively the rate constants of the oxidation of various polymer radicals with MB.

In addition, apart from electronic effects such as reactivity and polarity of the radicals steric effect may play a big role in radical-substrate reactions. In recent years Bamford demonstrated that the $\alpha$ methyl group of the penultimate unit in the PMA radical offers considerable steric hindrance in the reaction of this radical with a substrate ca. CBr$_4$ where the transfer of Br atom which has a considerably big size is involved. Methylene blue ion also has a large size. The reaction of MB with radicals may also exhibit steric hindrance with certain radicals and may thus bring in selectivity in reactions with radicals. All these aspects of the reaction will be considered in this chapter.
4.2. Effect of Methylene Blue Chloride in the Polymerization of Methyl Methacrylate (MMA)

Polymerization of methyl methacrylate is carried out both in the presence and absence of MB with AIBN as initiator and the rate of polymerization ($R_p$) was measured (vide experimental section 2.2.4, chapter-2). The results of the experiments with the following concentrations of different reagents are plotted in the figure-16 as percent conversion vs. time (min.)

\[ [\text{MMA}] = 3.12 \text{ mole l}^{-1}, \quad [\text{AIBN}] = 8.02 \times 10^{-3} \text{ mole l}^{-1} \]

and \[ [\text{MB}] \text{ varied from } 5.9 \times 10^{-4} \text{ to } 1.18 \times 10^{-3} \text{ mole l}^{-1} \]

DMF was used as solvent and the reaction temperature was 60°C.

Figure-16 shows that polymerization in presence of MB is preceded by an induction period (i.p). The steady state rate obtained after the induction period was over almost equals the rate observed under similar conditions in the absence of the dye (Table-9).
Fig-16. Plot of % conversion vs. time for M'A polymerization in the presence or absence of MBC1. 

\[
\begin{align*}
[M\text{MA}] &= 3.12 \text{ mole/1}, \\
[A\text{IBN}] &= 8.02 \times 10^{-3} \text{ mole/1}, \\
\text{Temp.} &= 60^\circ\text{C}, \text{Solvent-DMF} \\
[M\text{BC}] &= 0.0; \\
\Phi &= 5.3 \times 10^{-4}; \\
\Delta &= 8.85 \times 10^{-4}; \\
\square &= 1.18 \times 10^{-3} \text{ mole/1}.
\end{align*}
\]
Table-9

Polymerization of methylmethacrylate in the presence and absence of MBC1. Solvent - DMF, Temp. 60°C;

\[ [\text{AIBN}] = 8.02 \times 10^{-3} \text{ mole}^{-1}, \quad [\text{MMA}] = 3.12 \text{ mole}^{-1} \]

<table>
<thead>
<tr>
<th>([\text{MBC1}] \times 10^4 \text{ mole}^{-1})</th>
<th>Induction period (min)</th>
<th>(R_p \times 10^4) in mole (-1)sec(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>1.3</td>
</tr>
<tr>
<td>5.9</td>
<td>2</td>
<td>1.2</td>
</tr>
<tr>
<td>8.85</td>
<td>2</td>
<td>1.2</td>
</tr>
<tr>
<td>11.80</td>
<td>2.6</td>
<td>1.2</td>
</tr>
</tbody>
</table>

It may be inferred that MB is not a retarder for MMA polymerization. The slight induction period observed is quite unexpected. However, in these series of experiments a high concentration of the initiator was used. It would be worthwhile to examine whether any retardation is noticeable at low initiator concentration. With this end in view another series of experiments were conducted at a low initiator concentration. The results of these experiments are represented in figure-17 and table-10.
Fig-17. Plot of per cent conversion Vs. time for MMA polymerization in the presence or absence of Methylene Blue Chloride. $[\text{AIBN}] = 1.15 \times 10^{-3}$ mole l$^{-1}$; $[\text{MMA}] = 1.404$ mole l$^{-1}$, Temp. 60°C
Solvent-DMF. MBCl concentration for curves 1 through 5 are indicated.
Table-10

Polymerization of MMA in the presence and absence of MBC1.

Solvent DMF, Temp. 60°C, \([\text{AIBN}] = 1.15 \times 10^{-3} \text{ mole l}^{-1}\)
\([\text{MMA}] = 1.404 \text{ mole l}^{-1}\)

<table>
<thead>
<tr>
<th>([\text{MBCl}] \times 10^4) mole l(^{-1})</th>
<th>Induction period (i.p) min</th>
<th>Consumption of AIBN during i.p mole l(^{-1})</th>
<th>([\text{Inhibitor impurity}] \times 10^{-5}) mole l(^{-1})</th>
<th>Steady state rate (R_p \times 10^5) mole l(^{-1}) sec(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.59</td>
</tr>
<tr>
<td>6.16</td>
<td>42.5</td>
<td>2.27 \times 10^{-5}</td>
<td>6 \times 10^{-5}</td>
<td>2.51</td>
</tr>
<tr>
<td>9.24</td>
<td>48</td>
<td>2.5 \times 10^{-5}</td>
<td>6.6 \times 10^{-5}</td>
<td>2.45</td>
</tr>
<tr>
<td>12.32</td>
<td>46.5</td>
<td>2.42 \times 10^{-5}</td>
<td>6.4 \times 10^{-5}</td>
<td>2.20</td>
</tr>
<tr>
<td>18.48</td>
<td>33</td>
<td>1.74 \times 10^{-5}</td>
<td>4.6 \times 10^{-5}</td>
<td>1.90</td>
</tr>
</tbody>
</table>

*Calculations based on the assumption that during i.p one molecule of inhibitor impurity is removed by each chain radical. \(k_d\) for AIBN = 1.01 \times 10^{-5} sec\(^{-1}\) at 60°C;
(Ref.31) efficiency of initiation = 0.66 (Ref.79).
Here the presence of distinct i.p. is clearly evident. The i.p., however, is not proportional to the dye concentration as would be evident from the data in Table-10 and cannot be correlated with any known parameter. The i.p. was determined from the extrapolation of the steady state portion of the curve to the time axis as is shown in figure-17 by dotted lines.

The i.p. is not due to MB. Had it been so, the color of the dye would have disappeared at the end of i.p. But no perceptible diminution of color intensity was observed. It may be inferred that the induction period is due to some trace quantity inhibitor which got introduced into the system in some unknown way. Assuming that one inhibitor molecule is removed by each chain radical during i.p. it would be possible to calculate the amount of inhibitor impurity present in the system. Table-10 includes such data. The calculation was made in the following way. The amount of initiator decomposed during i.p. was obtained from the relation

\[
\ln C_t = \ln C_0 - k_d t
\]

where

- \( C_t \) = concentration of initiator at the end of i.p.
- \( C_0 \) = initial initiator concentration
- \( k_d \) = rate constant for the 1st order decomposition of AIBN
The value of $2f (C_0 - C_t)$ gives the amount of inhibitor present in the system ($f =$ efficiency of initiation). The relevant data for $f$ and $k_d$ were obtained from the literature. It may be noted here that the retardation observed following the i.p. is not due to the reaction products obtained during the impurity scavenging process. Because had it been so, the retarded rate of polymerization observed using the highest dye concentration would not have been lower than the retarded rate observed using the lowest dye concentration, the i.p. being shorter in the former system than in the latter. The retardation observed at the end of i.p. is therefore attributed to MB itself.

Nevertheless, it would be desirable to check directly if the impurity comes with the dye. A program for further purification of the dye was then undertaken. Literature reveal that impurities in MB are generally thionines of various degrees of methylation. Trimethylthionine is the most probable one.
Purification by column chromatography over basic aluminium oxide or removal of incompletely methylated thionines by quick extraction into thiophene free benzene from ammoniacal solutions of MB and subsequently lowering the pH followed by recovery of MB from the aqueous solution are the two important methods of purification suggested in the literature. Accordingly, one sample of MB was purified by each of the two above mentioned methods (vide experimental section 2.1.4. chapter 2).

Polymerization of MMA with fixed monomer (1.4 mole l\(^{-1}\)) and initiator concentration (1.1 \(\times\) 10\(^{-3}\) mole l\(^{-1}\)) was carried out in presence of MB thus purified. A sample of MB purified by recrystallization from alcohol was also used. Figure-18 shows the results obtained in each case along with a control experiment (absence of dye). It would be evident from the figure-18 that the i.p. persisted in each of these systems containing samples of MB purified by different methods. The cause of this i.p. could not be ascertained decisively. The experiments and arguments presented above indicate that the impurity did not come directly with the dye, although it was somehow connected with the presence of the dye. The source of the inhibitor impurity remained obscure. Since the i.p. was erratic and not proportional to the dye concentration, it may be presumed that the inhibitor was generated in the system.
Fig-15. Percent conversion vs. time plot for PVF polymerization in DMF at 60 °C in presence of
VBC1 purified by different methods. x = 0 for curve 1 and 10 for others Curves 1, [VBC1] = 0;
curve 2, VBC1 purified by extraction method; curve 3, VBC1 recrystallized; curve 4, VBC1 purified
by column chromatography [VBC1] = 2.55 x 10^{-3} mole l^{-1} for curve 2. [VBC1] = 1 x 10^{-3} mol l^{-1}.
from the interaction of the dye with the trace impurities that might be present in the solvent and/or monomer. The solvent and the monomer were, however, pure enough because in the absence of the dye no i.p. was observed. However, some trace reducing substances e.g. amines, organic acids etc. that may be present in DMF may interact with the dye to generate the inhibitor impurity. But these are mere speculations.

Nevertheless, since we have seen that the steady state rate attained after the i.p. was over, is not affected by the inhibitor impurity it would be possible to study the retarding effect of MB by measuring the initial steady state rates attained after the i.p. was over. Again, since the figure-18 shows that no improvement occurs following attempts at the purification of the dye (which is a specially pure sample marketed by E. Merck), in subsequent phases of the work the dye after two crystallization from ethyl alcohol was used. The retarded rate of polymerization is taken as equal to the initial steady rate of polymerization attained after the i.p. was over. Table-10 shows that MB retards rather weakly the polymerization of M4A. The data will be processed in section 4.8.5.2 of this chapter.
4.3. Effect of Methylene Blue Chloride in the Polymerization of Acrylonitrile (AN)

Methylene blue retards the polymerization of acrylonitrile. The effect of MB in acrylonitrile polymerization has been studied by measuring the rates of polymerization of AN under various conditions in the presence and absence of MB.

Figure-19 shows the effect of varying amounts of MBC1 in the polymerization of AN in DMF at 60°C at a fixed concentration of initiator (1.97x10⁻³ mole ⁻¹) and monomer (2.27 mole ⁻¹). MB concentrations were varied from 6.82x10⁻⁴ to 3.41x10⁻³ mole ⁻¹. Figure-19 shows that, as in case of MMA, polymerization of AN is preceded by an induction period (i.p) when MB is present in the polymerization medium. Table-11 shows that the i.p. is erratic and again not proportional to the dye concentration as was found in the case of MMA polymerization. A steady state rate period is rapidly established at the end of i.p. The \( R_p \) values recorded in table-11 show that MBC1 significantly retards the polymerization of AN. The \( R_p \) data were evaluated from the slope of percent conversion vs. time plot in the steady state region established after i.p. was over. The \( R_p \) data have
Fig. 10. De-cort conversion vs. time plot for the polymerization of acrylonitrile in presence or absence of VCl in DMSO at 80°C. [AN] = 2.87 mole l⁻¹, [VCl] = 1.17 x 10⁻³ mole l⁻¹, VCl concentration for curves 1 through 5 are 0, 6.84 x 10⁻⁵, 13.68 x 10⁻⁵, 20.47 x 10⁻⁵, 3 x 2 x 10⁻⁴ mole l⁻¹ respectively.
been used in section 4.8.5.1 to determine quantitatively the dependence of $R_p$ on MB concentration from a kinetic analysis of polymerization reaction.

**Table 11**

Results of polymerization of acrylonitrile in the presence of methylene blue chloride. Dye variation, $[\text{AIBN}] = 1.97 \times 10^3$ mole $\text{l}^{-1}$. $[\text{AN}] = 2.27$ mole $\text{l}^{-1}$, Solvent-DMF, Temp. 60°C.

<table>
<thead>
<tr>
<th>$[\text{MBCl}] \times 10^4$ mole $\text{l}^{-1}$</th>
<th>i.p. (min)</th>
<th>$R_p \times 10^5$ mole $\text{l}^{-1}$ sec $^{-1}$</th>
<th>$1/R_p \times 10^{-4}$ 1 mole $\text{l}^{-1}$ sec $^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-</td>
<td>2.76</td>
<td>3.62</td>
</tr>
<tr>
<td>6.82</td>
<td>15</td>
<td>1.36</td>
<td>7.35</td>
</tr>
<tr>
<td>13.65</td>
<td>13</td>
<td>1.00</td>
<td>10</td>
</tr>
<tr>
<td>20.47</td>
<td>27</td>
<td>0.75</td>
<td>13.33</td>
</tr>
<tr>
<td>34.12</td>
<td>27</td>
<td>0.504</td>
<td>19.84</td>
</tr>
</tbody>
</table>
Figure-20a shows the results of polymerization as percent conversion vs. time plot when polymerization was conducted at a fixed concentration of monomer (2.27 mole l\(^{-1}\)) and methylene blue (1.14x10\(^{-3}\) mole l\(^{-1}\)) and varying concentration of initiator. The AIBN concentration varied from 1.52x10\(^{-3}\) to 4.06x10\(^{-3}\) mole l\(^{-1}\). As before polymerization was preceded by induction periods and the rates of polymerization were calculated from the slopes of the plots in the steady state region established after the i.p was over. The data are recorded in table-12 and analysed in section 4.8.5.1. It would be evident from the figure-20a for the two higher concentrations of AIBN that the steady state rate period established after the i.p was over do not continue for a long time. After 20-30 min the rate drops as would be apparent from the lowering of the slope of the % conversion vs. time plot from its value in the initial steady state rate period. This lowering of the rate has been ascribed to the products of the reaction being more efficient retarder than MB itself. This phenomenon has been discussed in the section 4.8.7.

Figure-20b shows the plot of percent conversion vs. time for the AN polymerization in the absence of the dye at a fixed concentration of the monomer (2.27 mole l\(^{-1}\)) and varying concentration of initiator (from 1x10\(^{-3}\) to 4x10\(^{-3}\) mole l\(^{-1}\)). The \(R_p\) values for these systems are recorded in table-13.
Fig-20a. Percent conversion vs. time plot for AN polymerization in presence of MBG1 in DMF at 60°C at fixed monomer and dye concentration, initiator concentrations varied and indicated in the figure: 

\[
\begin{align*}
\text{[MB]} &= 11.4 \times 10^{-4} \text{ mole/l} \\
\text{[Monomer]} &= 2.27 \text{ mole/l} \\
\text{[AIBN]} &= 1.4 \times 10^{-3} \text{ mole/l} \\
\end{align*}
\]

Fig-20a. Percent conversion vs. time plot for AN polymerization in presence of MBG1 in DMF at 60°C at fixed monomer and dye concentration, initiator concentrations varied and indicated in the figure: 

\[
\begin{align*}
\text{[MB]} &= 11.4 \times 10^{-4} \text{ mole/l} \\
\text{[Monomer]} &= 2.27 \text{ mole/l} \\
\text{[AIBN]} &= 1.4 \times 10^{-3} \text{ mole/l} \\
\end{align*}
\]
Fig-20b. Percent conversion vs. time plot for the polymerization of AN in DMF at 60°C in absence of NEC. 

\[ [AN] = 2.27 \text{ mole} \text{ l}^{-1} \], AIBN concentrations for curves 1 to 3 are \( 4 \times 10^{-3}, 2 \times 10^{-3} \text{ and } 1 \times 10^{-3} \text{ mole} \text{ l}^{-1} \) respectively.
From figure-26b it is clear that $R_p$ in the absence of dye is proportional to the square root of the initiator concentration as is normally observed in a conventional free radical polymerization. The values of $R_{p,0}$ at various AIBN concentrations could be obtained from figure-26b and were used for the application of equation 90 (vide section 4.8.5.1).

**Table-12**

Results of polymerization of AIBN in presence of methylene blue chloride. Initiator variation. $[AN] = 2.27$ mole $l^{-1}$, $[MBCl] = 1.14 \times 10^{-3}$ mole $l^{-1}$, Solvent-DMF, Temp. 60°C.

<table>
<thead>
<tr>
<th>$[\text{AIBN}] \times 10^3$ mole/l</th>
<th>i.p. min</th>
<th>$R_p \times 10^5$ mole $l^{-1}$</th>
<th>$1/R_p \times 10^{-4}$ (mole/l)$^{1/2}$</th>
<th>$\sqrt{[\text{MBCl}]} \times 10^{-3}$ mole $l^{-1}$ sec$^{-1}$</th>
<th>$\frac{1}{R_p} \times 10^5$ mole $l^{-1}$ sec$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.06</td>
<td>2.5</td>
<td>2.23</td>
<td>4.48</td>
<td>6.37</td>
<td>2.46</td>
</tr>
<tr>
<td>3.04</td>
<td>5</td>
<td>1.74</td>
<td>5.74</td>
<td>5.51</td>
<td>3.29</td>
</tr>
<tr>
<td>2.03</td>
<td>17.5</td>
<td>1.24</td>
<td>8.06</td>
<td>4.5</td>
<td>4.93</td>
</tr>
<tr>
<td>1.52</td>
<td>21</td>
<td>0.945</td>
<td>10.58</td>
<td>3.89</td>
<td>6.58</td>
</tr>
</tbody>
</table>
Table-13

Results of polymerization of acrylonitrile in the absence of methylene blue. Initiator variation. 
\([AN] = 2.27 \text{ mole } l^{-1}, \text{ Solvent-DMF, Temp. } 60^\circ \text{C.}\)

<table>
<thead>
<tr>
<th>[AIBN] mole l(^{-1})</th>
<th>(R_p^0 \times 10^5)</th>
<th>(1/R_p^0 \times 10^{-4})</th>
<th>([\text{AIBN}]^{1/2} \times 10^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(4 \times 10^{-3})</td>
<td>4.36</td>
<td>2.29</td>
<td>6.32</td>
</tr>
<tr>
<td>(2 \times 10^{-3})</td>
<td>2.90</td>
<td>3.45</td>
<td>4.47</td>
</tr>
<tr>
<td>(1 \times 10^{-3})</td>
<td>1.89</td>
<td>5.29</td>
<td>3.16</td>
</tr>
</tbody>
</table>
4.4. Effect of Methylene Blue Chloride in the Polymerization of Methyl Acrylate (MA)

Polymerization of methyl acrylate was carried out at 60°C using variable dye concentrations and fixed monomer and initiator concentrations. The monomer and AIBN concentrations used were 1.63 mole \(-1\) and \(1.98 \times 10^{-3} \text{ mole } \cdot \text{mol}^{-1}\) respectively. The results are shown in figure-21. Figure-21 shows that in presence of MBCl polymerization is preceded by an i.p., following which there is an acceleratory rate period, then a steady state period of about 25 minutes duration under the reaction conditions. Thereafter ensues a deceleratory rate period. The deceleratory rate period is possibly the result of reaction of polymer radical with the products of reaction which function as more efficient retarders than MB itself. This effect was also observed in styrene polymerization and to a markedly lower extent in AN polymerization. Thus the rate at any stage after the i.p. was over was the consequence of two effects superimposed: (a) decreased MB concentration and (b) increased secondary retarder concentration with the progress of reaction. This secondary retarder has not been identified. However, some possibility has been discussed in section 4.8.7 of this chapter. In view of the complex nature of the reaction the
Fig. 21. Percent conversion vs. time plot for the polymerization of MA in presence or absence of MBG in DMS at 60°C. [MA] = 1.63 mole l⁻¹ [AIBN] = 1.976x10⁻³ mole l⁻¹. MBG concentration for the curves 1 through 4 are 0, 5.66x10⁻⁴, 8.34x10⁻⁴, 16.68x10⁻⁴ mole l⁻¹ respectively.
rates of polymerization measured in the small steady state region succeeding i.p. were used to evaluate the rate constant for the reaction of MB with PMA radical. These rates are recorded in table-14. The rates of polymerization calculated from the steady state region in the percent conversion vs. time plot are tabulated below (Table-14).

Table-14

Results of polymerization of methyl acrylate in the presence and absence of methylene blue chloride. Dye variation: [AIBN] = 1.98x10^-3 mole l^-1, [MA] = 1.63 mole l^-1, Solvent- DMF, Temp. 60°C.

<table>
<thead>
<tr>
<th>[MBCl]x 10^4 mole l^-1</th>
<th>i.p.(min)</th>
<th>R_p x 10^5 mole l^-1 sec^-1</th>
<th>1/R_p x 10^-4 mole^-1 l. sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>10.5</td>
<td>0.952</td>
</tr>
<tr>
<td>5.56</td>
<td>19</td>
<td>4.46</td>
<td>2.24</td>
</tr>
<tr>
<td>8.34</td>
<td>19</td>
<td>3.38</td>
<td>2.96</td>
</tr>
<tr>
<td>16.68</td>
<td>30</td>
<td>2.08</td>
<td>4.81</td>
</tr>
</tbody>
</table>
The data in the table-14 shows that polymerization of MA is retarded in the presence of MB. The results, however, are analysed in section 4.8.5.3 of this chapter.

4.5. Effect of Methylene Blue Chloride in the Polymerization of Methacrylonitrile (MAN)

Methacrylonitrile was polymerized at 60°C at constant monomer and AIBN concentration and at varying dye concentrations. The monomer and initiator concentrations used were 7.76 mole l^{-1} and 5x10^{-3} mole l^{-1} respectively and the dye concentration varied from 1.10 x 10^{-3} to 2.20 x 10^{-3} mole l^{-1}. The results are shown in the figure-22. Figure-22 shows that as with other monomers polymerization is preceded by an induction period followed by an acceleratory rate period which culminates into a steady state rate period. The i.p. is, however, small about 6 min under the experimental conditions used. The rather high concentrations of initiator used in this case is responsible for low i.p.. Table-15 includes the rate data evaluated from the slope of percent conversion vs. time plot in the steady state rate region marked as AB in the curves.
Fig. 22. Percent conversion vs. time plot for the polymerization of MA in presence or absence of MBC1 in DMF at 60°C. $[\text{MA}] = 7.76 \text{ mole} \cdot \text{l}^{-1}$; $[\text{DIB}] = 5 \times 10^{-3} \text{ mole} \cdot \text{l}^{-1}$. MBC1 concentration for curves 1 through 4 are 0, $1.102 \times 10^{-3}$, $1.65 \times 10^{-3}$, $2.204 \times 10^{-3}$ respectively. $x = 0$ for curve 1 and 6 min for others.
Results of polymerization of methacrylonitrile in the presence and absence of methylene blue chloride. Dye variation:

\[ [\text{AIBN}] = 5 \times 10^{-3} \text{ mole l}^{-1} \quad [\text{MAN}] = 7.76 \text{ mole l}^{-1}, \text{ Solvent-DMF, Temp. 60}^\circ\text{C}. \]

| [MBCl] \( \times 10^3 \) mole l\(^{-1} \) | i.p. | \( R_p \times 10^5 \) mole l\(^{-1}\) sec\(^{-1} \) | \( 1/R_p \times 10^{-4} \) 1 mole\(^{-1}\) sec |  
|-----------------|------|----------------|-----------------|----------|
| 0               | 0    | 1.38           | 7.25            |          |
| 1.10            | 6    | 1.16           | 8.62            |          |
| 1.65            | 6    | 1.08           | 9.28            |          |
| 2.20            | 9    | 0.099          | 10.03           |          |

It is evident from the figure-22 that MB retards the rate of polymerization of MAN. The results are analysed in section 4.8.5.4 of this chapter.
4.6. Effect of Methylene Blue Chloride in the Polymerization of Styrene (St)

Styrene was polymerized both in the presence and absence of MB in the dark at 60°C. For these sets of experiments monomer and AIBN concentration were kept constant at 4.31 mole l\(^{-1}\) and 6.0 x 10\(^{-3}\) mole l\(^{-1}\) respectively. The dye concentration was varied from 1.53 x 10\(^{-4}\) to 9.21 x 10\(^{-4}\) mole l\(^{-1}\). The results are shown in the figure-23 in the form of percent conversion vs. time plots. It is clear from the figure-23 that MB has a substantial retarding influence on the polymerization of styrene and the degree of retardation depends on the concentration of MB used. Induction period (i.p.) was not observed presumably because comparatively high concentration of initiator was used so that the inhibitor was consumed during the time thermal equilibrium was established in the dilatometers. The high initiator concentration had to be used in order to be able to measure the rates with reasonable accuracy. As in the case of methyl acrylate the initial steady state period of about 20-25 min duration is followed by a fall off of the rate and then as most of the dye is consumed acceleration in rate sets in and finally as all the dye is consumed the rate approaches close to that of the unretarded
Fig-23. Plot of % conversion vs. time for styrene polymerization in presence or absence of MBC1. $[\text{Styrene}] = 4.3 \text{ mole l}^{-1}$, $[\text{AIBN}] = 6 \times 10^{-3} \text{ mole l}^{-1}$, Temp. 60°C. Solvent-DMF. MBC1 concentrations for the curves 1 through 6 are 0, $1.53 \times 10^{-3}$, $3.07 \times 10^{-4}$, $4.65 \times 10^{-4}$, $7.67 \times 10^{-4}$, $9.21 \times 10^{-4}$ mole l$^{-1}$ respectively.
rate. The fall off of the initial rate is caused probably by the reaction of polymer radical with the reaction products (secondary retarder). Thus the rate at any stage other than the initial is the consequence of two effects superimposed: (a) decreased MB concentration and (b) increased secondary retarder concentration with the progress of reaction. The acceleration of the rate at later stages is caused by the decrease of both dye and secondary retarder concentration. In view of the complex nature of the reaction use was made of the initial $R_p$ for the purposes of the evaluation of the rate constant of PS radical with MB. With the progress of polymerization the color of MB fades and almost disappears when the rate of polymerization approaches the rate value close to that obtained in the absence of the dye. Only with this monomer has it been possible to follow the entire course of retardation reaction because it occurred during a reasonable period of time. The initial $R_p$ data are recorded in table-16 and the data have been analysed in section 4.8.5.6 of this chapter.
Results of the polymerization of styrene in the presence and absence of methylene blue chloride. Dye variation: \([\text{AIBN}] = 6.0 \times 10^{-3} \text{ mole l}^{-1}, [\text{St}] = 4.31 \text{ mole l}^{-1}\), Solvent - DMF, Temp. 60°C.

<table>
<thead>
<tr>
<th>([\text{MBCl}] \times 10^4)</th>
<th>(\frac{R \times 10^5}{\text{mole l}^{-1} \text{sec}^{-1}})</th>
<th>(\frac{1/R_p \times 10^4}{\text{1 mole}^{-1} \text{sec}^{-1}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.28</td>
<td>3.05</td>
</tr>
<tr>
<td>1.53</td>
<td>1.34</td>
<td>7.50</td>
</tr>
<tr>
<td>3.07</td>
<td>0.826</td>
<td>12.10</td>
</tr>
<tr>
<td>4.65</td>
<td>0.496</td>
<td>20.10</td>
</tr>
<tr>
<td>7.67</td>
<td>0.312</td>
<td>32.05</td>
</tr>
<tr>
<td>9.21</td>
<td>0.237</td>
<td>42.3</td>
</tr>
</tbody>
</table>
4.7. Effect of Methylene Blue Chloride in the Polymerization of Acrylamide (AM)

For this monomer ethylene glycol was used as the solvent instead of DMF. This is because DMF is a nonsolvent for polyacrylamide and polymerization in DMF would be heterogeneous. Chen showed that methylene blue does not aggregate in this solvent medium. Furthermore, ethylene glycol is a solvent for polyacrylamide and therefore this solvent allows homogeneous polymerization of this monomer. Hence ethylene glycol was chosen as the solvent and in order to keep the parity in working temperature used for the polymerization of other monomers polymerization was conducted at 60°C. Furthermore, since AIBN is not soluble in ethylene glycol, 4,4'-azobis 4-cyanopentanoic acid (AZP) was used as the initiator. Polymerization could not be followed dilatometrically because of experimental difficulties. Ethylene glycol being a very viscous solvent nitrogen evolved due to the decomposition of the azo initiator appeared as big bubbles. This upset the dilatometric work. The sealed dilatometers were therefore kept for a definite period of time in the thermostat at 60°C. At the end of which they were taken out and immediately chilled in ice-cold water. The dilatometers were broken open
and the contents quantitatively removed with the aid of a springe and the polymer precipitated in ice-cold ethanol. The polymers were purified by dissolving them in minimum amount of distilled water and precipitating them into cold methanol. The polymers were filtered through tared gooch crucibles, washed thoroughly with methanol and dried in a vacuum oven at 50°C. Table-17 records the yield of polyacrylamide under varying experimental conditions.

It is clear from the data in the table-17 that MB strongly retards the polymerization of acrylamide. Since MB exists as a monomer in this solvent, the present results disagree with the conclusion of Chen\textsuperscript{94,95} that MB monomer is not a chain terminator in acrylamide polymerization. It should be noted here that Chen's inference was based on indirect experimentation. \( R_p \) data reported in the table-17 have been analysed in section 4.8.5.5 of this chapter.
Table 17

Results of polymerization of acrylamide in presence and absence of methylene blue chloride. $[AZP] = 4.44 \times 10^{-3}$ mole $l^{-1}$, $[AA] = 1$ mole $l^{-1}$, Solvent- Ethylene Glycol, Temp. 60°C.

<table>
<thead>
<tr>
<th>$[MBCl] \times 10^4$ (mole $l^{-1}$)</th>
<th>Reaction volume ml</th>
<th>Weight of polymer formed in gm</th>
<th>Time of polymerization in hrs</th>
<th>$R_p$ (1/mole $l^{-1}$ sec)</th>
<th>$1/R_p \times 10^4$ (1/mole sec$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>19.0</td>
<td>6.68</td>
<td>0.0289</td>
<td>6</td>
<td>$2.8 \times 10^{-6}$</td>
<td>35.7</td>
</tr>
<tr>
<td>15.2</td>
<td>7.00</td>
<td>0.0362</td>
<td>6</td>
<td>$3.3 \times 10^{-6}$</td>
<td>30.29</td>
</tr>
<tr>
<td>11.4</td>
<td>7.03</td>
<td>0.0350</td>
<td>5</td>
<td>$3.8 \times 10^{-6}$</td>
<td>26.31</td>
</tr>
<tr>
<td>7.6</td>
<td>6.86</td>
<td>0.0506</td>
<td>4½</td>
<td>$6.4 \times 10^{-6}$</td>
<td>15.62</td>
</tr>
<tr>
<td>5.7</td>
<td>6.69</td>
<td>0.0668</td>
<td>4</td>
<td>$9.7 \times 10^{-6}$</td>
<td>10.31</td>
</tr>
<tr>
<td>3.8</td>
<td>7.07</td>
<td>0.1092</td>
<td>3½</td>
<td>$1.7 \times 10^{-5}$</td>
<td>5.9</td>
</tr>
<tr>
<td>0</td>
<td>6.86</td>
<td>0.2449</td>
<td>1/3</td>
<td>$4.18 \times 10^{-4}$</td>
<td>0.24</td>
</tr>
</tbody>
</table>
4.8. Discussions

4.8.1. Methylene Blue Monomer as a Retarder of Free Radical Polymerization

It is established in chapter 3 that MB exists as a monomer in the solvent mixtures consisting of DMF and monomers. Results reported in the sections 4.2 through 4.6 of this chapter show that MB retards the polymerization of monomers such as St, AN, MA, MAN and MMA respectively in DMF solution of course to different extents for each monomer. Results presented in section 4.7 show that MB retards the polymerization of acrylamide as well. The solvent used in the latter case was ethylene glycol and Chen showed that MB exists as a monomer in this solvent. These facts prove that MB monomer is an effective retarder in vinyl polymerization. Earlier, Chen from the study of the photopolymerization of acrylamide in water using MB as a photosensitizer concluded that MB dimer and multimers and not the MB monomer are effective in so far as oxidation of poly(acrylamide) radicals is concerned. Chen's conclusion follows from indirect experimentation discussed in a following section. In contrast, our results indicate that MB monomer also is a chain terminator not only in acrylamide polymerization but in the polymerization of a host of other vinyl monomers as
well. However, the degree of retardation varies from monomer to monomer. Furthermore, Beardwell observed that MB inhibits polymerization of 9-vinyl carbazole in methyl alcohol solution. It is known that MB exists as a monomer in methyl alcohol. Beardwell's results thus also indicate MB monomer is an effective chain terminator.

4.8.2. Interpretation of Chen's Results

It is desirable to discuss the results of Chen on the basis of which she concluded that MB monomer is not a chain terminator in acrylamide polymerization. Chen studied the photopolymerization of acrylamide in aqueous medium using MB as a photosensitizer. The relevant points of her results are mentioned below and reproduced in figure-24.

1) The plot of $R_p$ vs. MB concentration in water was a curve passing through a maximum. Similar results were anticipated also in ethylene glycol medium wherein MB exists as a monomer. However, in the latter case the maximum in the $R_p$ vs. $[MB]$ curve was not experimentally obtained in the concentration range of MB used in her work. It was, however, argued that a rate maximum would appear at a higher MB concentration in ethylene glycol than were used in the experiments.
Fig-24. Effect of Methylene Blue concentration on the photopolymerization of acrylamide in water at 25°C using triethanolamine as activator. O rate, □ mol. wt. (Taken from Ref.94)
(ii) Variation of $R_p$ with $[MB]$ with change in total dye concentration was similar to the variation of the concentration of MB monomer with total dye concentration.

(iii) The molecular weights of the polymers decreased with increase in $[MB]$. The concentration of MB aggregates increases with increase in concentration of MB.

Thus, according to Chen, at the lower MB concentration region where MB aggregate concentration is low the termination of polymer radicals by MB and consequent retardation of $R_p$ does not occur. On the other hand, at the higher MB concentration the chains are terminated by MB aggregates. And, furthermore, because MB monomer concentration which is responsible for initiation, is not proportionally increased with increase in total dye concentration rate of initiation of polymerization is also not proportionally increased.

However, the above results may be interpreted in another way. Let us consider the variation of $R_p$ with $[MB]$. This kind of result is commonly achieved in systems where the initiator acts also as a chain terminator. For example, Mandal observed similar variation of $R_p$ with $Fe(Clo_4)_3$ concentration in the polymerization of styrene in the mixed solvent of t-butyl alcohol and water using $Fe(Clo_4)_3$ and
thiourea as initiator system. Fe(C104)3 acts also as a chain terminator in the free radical polymerization of styrene. The fact that the variation of \( R_p \) with \([I]\) is a curve having a maximum may be proved mathematically for systems where the catalyst acts both as an initiator and chain terminator. This is proved below.

<table>
<thead>
<tr>
<th>Reaction Scheme</th>
<th>Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>( I \rightarrow 2R^* )</td>
<td>( R_i = k \ [I] [M] ) Initiation</td>
</tr>
<tr>
<td>( R^* + M \rightarrow M_1^* )</td>
<td></td>
</tr>
<tr>
<td>( M_n^* + M \rightarrow M_{n+1}^* )</td>
<td>( R_p = k_p [M]^* [M] ) Propagation</td>
</tr>
<tr>
<td>( M_n^* + M_m^* \rightarrow \text{Polymer} )</td>
<td>( R_t = 2k_t [M]^*^2 ) Termination</td>
</tr>
<tr>
<td>( M_n^* + I \rightarrow \text{Polymer} )</td>
<td>( R_c = k_c [M]^* [I] ) Termination</td>
</tr>
</tbody>
</table>

where "I" represents the initiator which acts also as a chain terminator, \( R^* \) the primary radical, \( M_n^* \) the chain radical and

\[
[M^*] = \sum_{n=1}^{\infty} [M_n^*]
\]
Application of steady state condition provides

\[ 2k_t [M^*]^2 + k_c [M^*] [I] - R_1 = 0 \]  
(57)

\[ M^* = \frac{-k_c [I] \pm \sqrt{k_c^2 [I]^2 + 8 R_1 k_t}}{4k_t} \]

\[ = \frac{-k_c [I] + k_c [I] \sqrt{1 + \frac{8 R_1 k_t}{k_c^2 [I]^2}}}{4k_t} \]  
(58)

(The negative value of \([M^*]\) was discarded because of being unreal)

Now \( R_p = k_p [M^*] [M] \)  
(59)

Substituting the value of \([M^*]\) from equation 58 into 59 one gets

\[ R_p = -\frac{k_p k_c [I] [M]}{4k_t} + \frac{k_p k_c [I] [M]}{4k_t} \sqrt{1 + \frac{8 k_t R_1}{k_c^2 [I]^2}} \]  
(60)

Now since \( R_1 \propto [I] \)

or \( R_1 = K [I] \) where \( K \) is a constant
\[ R_p = -\frac{k_p k_c [I] [M]}{4k_t} + \frac{k_p k_c [I] [M]}{4k_t} \sqrt{1 + \frac{8Kk_t}{k_c^2 [I]}} \]  

(61)

Thus at a constant \([M]\)

\[ R_p = -a [I] + b [I] \sqrt{1 + \frac{c}{[I]}} \]  

(62)

where \(a\), \(b\) and \(c\) are constants

In order to find out whether the curve of \(R_p\) vs. \([I]\) would have a maximum it is necessary to find out the value of

\[ \frac{dR_p}{d[I]} \quad \text{and} \quad \frac{d^2 R_p}{d[I]^2} \]

Differentiation gives the following values

\[ \frac{dR_p}{d[I]} = -a + b \sqrt{1 + \frac{c}{[I]}} \quad - \quad \frac{bc}{2[I] \sqrt{1 + \frac{c}{[I]}}} \]  

(63)

and

\[ \frac{d^2 R_p}{d[I]^2} = -\frac{bc^2}{4[I]^3} \quad \frac{1}{\left\{ 1 + \frac{c}{[I]} \right\}^{3/2}} \]  

(64)

At the maximum \( \frac{dR_p}{d[I]} = 0 \) and \( \frac{d^2 R_p}{d[I]^2} = -\text{ve} \).
Examination of the equation 63 reveals that there exists a catalyst concentration where \( \frac{d R_p}{d [I]} = 0 \). This concentration is obtainable from the relation

\[
b\sqrt{1 + \frac{c}{[I]}} = a + \frac{bc}{2[I]\sqrt{1 + \frac{c}{[I]}}}
\]

Thus it is clear that there exists an extremum in the curve and since the 2nd derivative is always negative it is evident that the extremum is a maximum.

It is thus evident that the rate variation results obtained by Chen can be explained in a way different from that given by her. However, the system investigated by Chen is more complex than the one assumed here because of the aggregation of MB with increasing concentration. Nevertheless, in view of the arguments presented above the conclusions reached by Chen do not have unequivocal basis. The other result of Chen viz. the decrease of DP with \([MB]\) is an expected one if MB acts also as a chain terminator.

4.8.3. Reaction Scheme of the Present Work

Having thus established that MB monomer is a chain terminator in the polymerization reactions investigated in this work we proceed to formulate a reaction scheme on the basis of which the rate constants of the oxidation of various
polymer radicals by MB may be evaluated. The reaction scheme we considered is given below.

**Reaction Scheme**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Type</th>
<th>Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. $\text{I} \xrightarrow{k_d} 2\text{R}^*$</td>
<td>Initiation</td>
<td>$2f k_d [\text{I}]$ (1-4)</td>
</tr>
<tr>
<td>$\text{R}^* + \text{M} \rightarrow \text{M}_1^*$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B. $\text{M}<em>n^* + \text{M} \rightarrow \text{M}</em>{n+1}$</td>
<td>Propagation</td>
<td>$k_p [\text{M}^*] [\text{M}]$ (5)</td>
</tr>
<tr>
<td>C. $\text{M}_n^* + \text{M}_m^* \rightarrow \text{P}_n + \text{P}_m$</td>
<td>Homoterminal by either disproportionation or combination</td>
<td>$2 k_t [\text{M}^*]^2$ (6)</td>
</tr>
<tr>
<td>$\text{P}_{n+m}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D. $\text{M}_n^* + \text{MB}^+ \rightarrow \text{P}_n + \text{MB} + H^+$</td>
<td>Termination by electron transfer to MB</td>
<td>$k_x [\text{M}^*] [\text{MB}]$ (65)</td>
</tr>
<tr>
<td>or</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\sim \text{CH}_2 - \text{CHX} + \text{MB}^+ \rightarrow \sim \text{CH} = \text{CHX} + \text{MB} + H^+$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>E. $\text{M}_n^* + \text{MB}^* \rightarrow \text{P}_n + \text{MB}$</td>
<td>Termination by either H atom transfer or addition to MB semiquinone</td>
<td>$k_y [\text{M}^*] [\text{MB}]$ (66)</td>
</tr>
<tr>
<td>$\text{P}_n \text{MB}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>or</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\sim \text{CH}_2 - \text{CHX} + \text{MB}^* \rightarrow \sim \text{CH} = \text{CHX} + \text{MB}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\sim \text{CH}_2 - \text{CH(X)MB}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F. $2 \text{MB} + H^+ \rightarrow \text{MB}^+ + \text{MBH}$</td>
<td>Dismutation</td>
<td>$2 k_z [\text{MB}^*]^2$ (67)</td>
</tr>
</tbody>
</table>
The factor 2 in the rate equations 6 and 67 comes in because two similar radicals are terminated in the respective reactions.

In the above scheme I represents the initiator, M the monomer, R* primary radical, M_n* the polymer radical having n monomer units, P_n the polymer molecule with DP = n, MB the methylene blue semiquinone, P_nMB the polymer molecule attached to MB and MBH the leuco MB. The chemical structure of MB, MB and MBH are represented below.

![Chemical structures]

The rate equation for each reaction is given in the right hand side of the above scheme. It should be noted that [M'] represents the total chain radical concentration present in the system at any moment or in other words

\[ [M'] = \sum_{n=1}^{\infty} [M_n^*] \]

The principle of equal reactivity of all chain radicals of a given monomer has been followed.
The proton required for the formation of leuco MB in reaction 67 in the aprotic solvent DMF would be available from reaction 65. Haines and Waters\(^8\) in their study of the reaction of MB with α-cyanoalkyl radicals and also Beardwell\(^122\) in his study of the reaction of MB with poly(9-vinyl carbazole) radical found the decolorisation of MB to be reversible which indicate that reaction 65 is an electron transfer one rather than addition of the free radicals to the aromatic nucleus of the dye ion. Also, it has been established\(^124\) that MB semiquinones undergo disproportionation reaction to yield leuco MB and MB\(^+\). That leuco MB is one of the products of the reaction has been confirmed from oxidation experiments discussed later in this chapter.

In the above reaction scheme reinitiation of polymerization by the semiquinone radical has not been taken into account on the presumption that there will be considerable steric hindrance in the reaction. The adherence of the experimental results to the rate expression obtained without considering reinitiation by MB supports this view. Also, the mode of termination represented in reaction 6 and 66 respectively is unimportant for kinetic analysis. The rate expression will be independent of the mode of reaction. Similarly kinetic expression will not be altered if reaction 65 is an addition reaction instead of electron transfer.
4.8.4. Derivation of the Expression for Rate of Polymerization

The expression for the rate of polymerization in the presence of MB was derived following Kice\textsuperscript{36} as illustrated below. It was assumed that the usual steady state condition with regard to the concentration of radicals applies. One may, therefore, write

\[
\frac{d[M^*]}{dt} = R_i - 2k_t[M^*]^2 - k_x[M^*][MB] - k_y[M^*][MB^*] = 0
\]

or

\[
R_i = 2k_t[M^*]^2 + k_x[M^*][MB] + k_y[M^*][MB^*] \tag{68}
\]

and

\[
\frac{d[MB^*]}{dt} = k_x[M^*][MB] - k_y[M^*][MB^*] - 2k_z[MB^*]^2 = 0
\]

or

\[
k_x[M^*][MB] = k_y[M^*][MB^*] + 2k_z[MB^*]^2 \tag{69}
\]
Addition of equations 68 and 69 gives

\[ R_1 = 2 k_t [M']^2 + 2 k_y [M'] [MB'] + 2 k_z [MB']^2 \]  

(70)

An examination of the reaction scheme reveals that of the total MB produced in reaction 65 some disappear by reaction 66 and the rest by reaction 67. The fraction \( \alpha \) which disappear by reaction 66 may be expressed as

\[ \alpha = \frac{k_y [M'] [MB']}{k_x [M'] [MB]} \]  

(71)

Combining equations 69 and 71 one obtains

\[ \alpha = \frac{k_y [M'] [MB']}{k_y [M'] [MB'] + 2 k_z [MB']^2} \]  

(72)

\[ = \frac{k_y [M']}{k_y [M'] + 2 k_z [MB']} \]  

(73)

Similarly the fraction \( \beta \) which disappears by reaction 67 is given by
\[
\beta = \frac{2k_z [MB^*]^2}{k_x [M^*][MB]} \tag{74}
\]

\[
\alpha = \frac{2k_z [MB^*]}{k_y [M^*] + 2k_z [MB^*]} \tag{75}
\]

Combining equations 70, 71 and 74 one obtains

\[
R_1 = 2k_t [M^*]^2 + 2\alpha k_x [M^*][MB] + \beta k_x [M^*][MB] \tag{76}
\]

Substitution of the expressions 73 and 75 for \(\alpha\) and \(\beta\) into equation 76 gives the following equation.

\[
R_1 = k_x [M^*][MB] \left[ \frac{2k_y [M^*] + 2k_z [MB^*]}{k_y [M^*] + 2k_z [MB^*]} \right]
\]

\[
+ 2k_t [M^*]^2 \tag{77}
\]

The rate of polymerization \(R_p\) may be expressed as

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

or \([M^*] = \frac{R_p}{k_p [M]} \tag{78}\)
Furthermore, in the absence of MB the steady state assumption would give at the same initiator concentration

$$R_i = R_t = 2 k_t [M^*]^2_o$$

(79)

where $[M^*]_o$ is the stationary chain radical concentration obtainable in the absence of MB. Again since the rate of polymerization in the absence of MB may be expressed as

$$R_{p,o} = k_p[M^*]_o[M]$$

(80)

one obtains combining equation 79 and 80

$$R_i = 2 k_t R_{p,o}^2 / k_p^2 [M]^2$$

(81)

Substitution of equation 78 and 81 into 77 gives

$$
\frac{2 k_t R_{p,o}^2}{k_p^2 [M]^2} = \frac{k_x R_p [MB]}{k_p[M]} \left[ \frac{2 k_y R_p}{k_p[M]} + \frac{2 k_z [MB^*]}{k_p[M]} \right] + \frac{2 k_t R_p^2}{k_p^2 [M]^2}
$$

(82)

or

$$
\frac{k_x R_p [MB]}{[M]} \left[ \frac{2 k_y R_p}{k_p[M]} + \frac{2 k_z [MB^*]}{k_p[M]} \right] = \frac{2 k_t}{k_p^2 [M]^2} (R_{p,o}^2 - R_p^2)
$$

(83)
Thus equation 83 expresses the $R_p$ in an implicit way and it is now necessary to replace $[MB^*]$ in terms of experimentally measurable quantities. This is done in the following way. Solution of the quadratic equation 70 for $[MB^*]$ gives

$$[MB^*] = \frac{-2 k_y [M] + \sqrt{4 k_y^2 [M]^2 - 16 k_t k_z [M]^2 + 8 k_z R_p}}{4 k_z}$$

(84)

Substitution of equations 78 and 81 into 84 gives

$$[MB^*] = \frac{k_y}{2 k_p k_z [M]} \left[ \sqrt{R_p^2 + \frac{4 k_t k_z}{k_y^2} (R_p - R_p^2)} - R_p \right]$$

(85)

Now if we define two new symbols

$$\mu = \frac{R_p}{R_p, o} \quad \text{and} \quad \Phi = \frac{k_y}{\sqrt{2 k_t k_z}}$$

Equation 85 may be rewritten as

$$[MB^*] = \frac{k_y R_p}{2 k_p k_z [M]} \left\{ \sqrt{1 + \frac{(1 - \mu^2)}{\Phi^2 \mu^2}} - 1 \right\}$$

(86)
Substitution of equation 86 into 88 gives

\[
\frac{k_x R_p \ [MB]}{[M]} = \frac{2 k_y R_p}{k_p [M]} + \frac{2 k_z k_y R_p}{2k_p k_z [M]} \left\{ \frac{1}{\sqrt{1 + \frac{(1-\mu^2)}{\phi^2 \mu^2}}} - 1 \right\}
\]

Algebraic manipulation yields

\[
\frac{R_p [MB]}{R_p, o^2 - R_p^2} \left[ 1 + \sqrt{1 + \frac{(1-\mu^2)}{\phi^2 \mu^2}} \right] = \frac{2 k_t}{k_p k_x [M]} \sqrt{1 + \frac{1-\mu^2}{\phi^2 \mu^2}}
\]

or

\[
\frac{\mu^2 [MB]}{1-\mu^2} \left[ 1 + \sqrt{1 + \frac{(1-\mu^2)}{\phi^2 \mu^2}} \right] = \frac{2 k_t}{k_p k_x [M]} \sqrt{1 + \frac{1-\mu^2}{\phi^2 \mu^2}}
\]

From an examination of equation 89 it is apparent that a plot

\[
\frac{\mu^2 [MB]}{1-\mu^2} \left[ 1 + \sqrt{1 + \frac{1-\mu^2}{\phi^2 \mu^2}} \right] \text{ vs. } \frac{R_p}{[M]} \sqrt{1 + \frac{1-\mu^2}{\phi^2 \mu^2}}
\]
should be a straight line for an appropriate value of $\phi^2$.
The slope of the line yields the value of $2k_x/k_p$ $k_x$ from
which the value of $k_x$ may be obtained since $k_p$ and $k_t$ values
are obtainable from the literature. In order to make the
said plot it is necessary to assume different values of $\phi$
ranging from one to infinity and see for which values of $\phi$
the equation 89 fits the experimental results best. The lower
limit of one for the value of $\phi$ is chosen because work in the
field of copolymerization has shown that cross termination is
usually a rather favoured mode of termination for dissimilar
radicals.$^{38,69,70}$ A high value of $\phi$ makes the term containing
it negligibly small.

When $\phi = 1$ the cross termination rate constant becomes
the geometric mean of the homotermination rate constant. Under
this condition equation 89 reduces to

$$\frac{1}{R_p} = \frac{1}{R_p^0} + \frac{k_x [MB]}{R_t k_p [M]}$$

(90)

$(R_p^0 = R_p, 0)$

or

$$\frac{1}{R_p} = \frac{1}{R_p^0} + \frac{k_v [MB]}{2f k_d [T] k_p [M]}$$
4.8.5. Rate Constants \( (k_x) \) for the Reaction of Polymer Radicals with MB monomer

We shall now analyse the rate of polymerization data on the basis of the kinetic equation derived in the section 4.8.4 and evaluate the rate constants for the oxidation of polymer radicals effected by methylene blue (chloride) monomer.

4.8.5.1. Acrylonitrile-Methylene Blue Chloride (MBC1) System

Figure-25 shows that the plot of reciprocal rate of retarded polymerization vs. MBC1 concentration (vide Table-11) is linear with an intercept at \( 1/R_p \) axis corresponding to the reciprocal rate of unretarded polymerization \( (1/R_p^0) \) observed in the absence of MB. This is in agreement with equation 90 which is obtained from the general equation 89, as a special case \( (\phi = 1) \). The slope of the line has the value \( \boxed{k_x/R_i k_p [M]} \) which therefore is also the value of \( k_x/ (R_i k_p [M]) \). From this value \( k_x \) can be evaluated since \([M]\) is known and the value of \( R_i \) as well as \( k_p \) may be obtained from literature.
Fig-25. Test of equation 90. Plot of $\frac{1}{R_p}$ vs. $[\text{MBC}]$ for Acrylonitrile polymerization. $[\text{AIBN}] = 1.97 \times 10^{-3}$ $[n] = 2.27$ mole l$^{-1}$, Temp. 60°C. Solvent-DMF.
\[ R_p = 1.42 \times 10^{-5} [\text{AIBN}] \text{ mole/liter sec}^{-1} \] (Ref. 79)
and \[ k_p = 1960 \text{ liter mole}^{-1} \text{ sec}^{-1} \] (Ref. 125)

\[ [\text{AIBN}] = 1.97 \times 10^{-3} \text{ mole} \text{ l}^{-1} \] and \[ [\text{AN}] = 2.27 \text{ mole} \text{ l}^{-1} \]
(used in experiment). From these data \( k_x \) is determined to be 5800 liter mole\(^{-1}\) sec\(^{-1}\) at 60°C.

Figure 26a shows that a plot of \((1/R_p - 1/R_p^0)\) vs. \([\text{AIBN}]^{-1}\) at a fixed concentration of dye and monomer (vide Table-12) is linear as is expected if equation 90 is obeyed. The value of \( R_p^0 \) required for the plots in figure 26a were obtained from figure 26b. The slope of the line in figure 26a gives the value of \( k_x [\text{MBC}] / 2k_d k_p [M] \) from which \( k_x \) is determined to be 5340 liter mole\(^{-1}\) sec\(^{-1}\).

A value of \( 1.42 \times 10^{-5} \text{ sec}^{-1} \) was used for \( 2f k_d \) (Ref. 79) and that of \( k_p \) mentioned above. \( k_x \) thus evaluated is in reasonable agreement with that reported in the previous paragraph.

4.8.5.2. Methyl Methacrylate-Methylene Blue Chloride (MBC1) System

Figure 27 shows a plot of \( 1/R_p \) vs \([\text{MBC1}]\) at a fixed initiator \( (1.15 \times 10^{-3} \text{ mole/l}) \) and monomer \( (1.4 \text{ mole/l}) \) concentration, the dye concentration being varied (vide Table-10). The straight line was drawn using least square
Fig. 26a. Test of equation 90. Plot of \( \frac{1}{R_p} - \frac{1}{R_p^0} \) vs. 
\([\text{AIBN}]^{-1}\) in Acrylonitrile polymerization. 
\([\text{MBC}] = 1.14 \times 10^{-3} \text{ mole l}^{-1}\), 
\([\text{AN}] = 2.27 \text{ mole l}^{-1}\), Solvent-DMF 
Temp. 60°C.
Fig-26b. Plot of $R_p^0$ vs. $\sqrt{[\text{AIBN}]} \times 10^2$ in Acrylonitrile polymerization in absence of MBCl. Temp. 60°C, Solvent-DMF.
Fig. 27. Test of equation 90. Plot of $1/R_p$ vs. $[\text{MBCl}]$ in Methyl methacrylate polymerization in DMF at 60°C. $[\text{MMA}] = 1.4 \text{ mole l}^{-1}$; $[\text{AIBN}] = 1.15 \times 10^{-3} \text{ mole l}^{-1}$. 
Equation 90 may be considered to apply for this system also. As in the case of AN the rate constant \( k_x \) is evaluated from the slope of the line using equation 90. The following values of \( R_1 \) and \( k_p \) at 60°C are used.

\[
R_1 = 1.34 \times 10^{-5} \left[ \text{AIBN} \right] \text{ mole/liter sec}^{-1} \quad (\text{Ref 79})
\]

\[
k_p = 734 \text{ liter mole}^{-1} \text{ sec}^{-1} \quad (\text{Ref 126.83})
\]

From the slope of the line

\[
\frac{k_x}{R_1k_p [M]} = 7.73 \pm 1.78 \times 10^6
\]

From which \( k_x \) was determined to be 123 ± 28 \( \text{l mole}^{-1} \text{ sec}^{-1} \) at 60°C.

It is obvious from a comparison of the figures 25 and 27 respectively that equation 90 does not fit as good for MMA as for AN. It is therefore worth checking whether the general equation 89 with higher values of \( \phi^2 \) fit the MMA results any better. Figure 28 shows plot of the general equation 89 for various values of \( \phi^2 \) viz 1, 2, 5, 10, 100, 1000, \( \infty \) (data included in appendix Table XII). When \( \phi^2 = 1 \), a straight line parallel to the ordinate is obtained. The validity of the condition \( \phi^2 = 1 \) would have reduced the
Fig-28. Plot of general equation 89 for various values of $\varphi^2$ in Methyl methacrylate polymerization in DVP at 60°C. Data given in Table-10 and also in Table-XII in the appendix.
line to a point. This follows from the fact that for
\( \phi^2 = 1 \) the R.H.S of equation 89 has the constant value
equal to \( R_p^0/[M] \). So if equation 89 is obeyed the L.H.S
of the equation will also have a constant value for various
values of \([M]\) and the corresponding \( R_p \)'s. Thus the plot of
the experimental data according to equation 89 should yield
only a point if the condition \( \phi^2 = 1 \) is obeyed. The slope
of the line passing through the origin and the said point
would have given the value of \( 2 k_t/k_p k_x \) from which \( k_x \) could
be calculated provided \( k_t \) and \( k_p \) are known. Either experimental
error or the invalidity of the condition \( \phi^2 = 1 \), however,
may cause a spread of the points over a straight line parallel
to the ordinate as is obtained for the MMA-MBCI system.

As would be evident from figure 28 values of \( \phi^2 \)
greater than 1 do not improve the situation as far as the
fitting of the general equation 89 is concerned. We therefore
held that the spread of the points in figure-28 for \( \phi = 1 \)
is due to experimental error.

We came across a similar situation in the styrene MBCI
system as will be discussed later where the fitting of the
equation 89 for \( \phi^2 = 1 \) is similar to that observed with
MMA. However, in the former system it was found that a large
value of \( \phi^2 \) fit the data much better with the general
equation 89.
4.8.5.3. Methyl Acrylate-Methylene Blue Chloride (MBC1) System

Figure 29 shows a plot of $1/R_p$ vs. $[\text{MBC1}]$ concentration based on the data presented in table-14 for methyl acrylate-MBC1 system at the fixed concentration of AIBN, $1.98 \times 10^{-3}$ mole/l and monomer $1.63 \text{ mole} \, l^{-1}$ but varying concentrations of MBC1. It is evident from the figure that equation 90 is obeyed as in the case of the previous two systems. Accordingly, the rate constant $k_x$ is evaluated from the slope of the line given by $k_x / (R_1 k_p [M])$ (vide equation 30). The slope has the value $2.37 \times 10^7$. Thus

$$\frac{k_x}{R_1 k_p [M]} = 2.37 \times 10^7$$

and $k_x$ is equal to $2120 \text{ mole}^{-1} l^{-1} \text{ sec}^{-1}$ at $60 \degree C$.

For calculating $k_x$ the following literature data for $R_1$ and $k_p$ were used

$$R_1 = 1.33 \times 10^{-5} \text{ mole} \, l^{-1} \text{ sec}^{-1} (\text{Ref 79})$$

$$k_p = 2090 \text{ mole}^{-1} \text{ sec}^{-1} (\text{Ref 103})$$

and $[M] = 1.63 \text{ mole} \, l^{-1}$ (used in the experiment)

$$[[\text{AIBN}]] = 1.98 \times 10^{-3} \text{ mole} \, l^{-1} (\text{used in the experiment})$$
Fig-29. Test of equation 90. Plot of \(1/R_p\) vs. \([\text{MBC}]\) in Methyl acrylate polymerization in DMF at 60°C, \([\text{MA}] = 1.63\) mole l\(^{-1}\), \([\text{AIBN}] = 1.98 \times 10^{-3}\) mole l\(^{-1}\).
4.8.5.4. Methacrylonitrile-Methylene Blue Chloride (MBC1) System

Figure 30 shows a plot of $1/R_p$ vs $[MBCl]$ based on the data presented in table-15 for the methacrylonitrile-MBC1 system at a fixed concentration of initiator and monomer and varying concentration of MBC1. It is evident from the figure that equation 90 is obeyed for this system also. The rate constant $k_x$ for the reaction of poly-MAN radical with MBC1 is derived from the slope of the line shown in figure 30. The slope has the value $1.28 \times 10^7$. Thus

$$\frac{k_x}{R_1 k_p [M]} = 1.28 \times 10^7$$

and $k_x$ is found to be 1390 liter mole$^{-1}$ sec$^{-1}$ at 60°C. For calculating $k_x$ from the above equation the following data from the literature were used

$$R_1 = 1.4 \times 10^{-5} \text{ mole l}^{-1} \text{ sec}^{-1} \quad \text{(Ref 79)}$$

$$k_p = 200 \text{ l mole}^{-1} \text{ sec}^{-1} \quad \text{(Ref 102)}$$

The AIBN and monomer concentrations used in this system were $5 \times 10^{-3}$ and 7.76 mole/l respectively.
Fig-30. Test of equation 90. Plot of \(1/R_p\times10^4\) mole sec. vs. in Methacrylonitrile polymerization in DMF at 60°C. 
\([\text{MAN}] = 7.76\ \text{mole l}^{-1};\ [\text{AIBN}] = 5\times10^{-3}\ \text{mole l}^{-1}.\)
The low \( k_p \) value of this monomer necessitated the use of a higher monomer concentration than is used in the previous three systems.

4.8.5.5. Acrylamide-Methylene Blue Chloride (MBC1) System

Figure 31 shows the plot of \( 1/B_p \) vs. \([\text{MBC1}]\) on the basis of the data presented in table-17 for the acrylamide-MBC1 system in ethylene glycol medium at 60°C at the fixed concentration of 4,4'-azobis-4-cyanopentanoic acid \( 4.44 \times 10^{-3} \) mole/l and monomer 1 mole l\(^{-1}\), the MBC1 concentrations being varied. It is evident from the plot that equation 90 is obeyed for this system also. The slope of the line has the value \( 1.91 \times 10^8 \).

Thus

\[
\frac{k_x}{R_1 k_p [M]} = 1.91 \times 10^8
\]

However, \( k_p \) and \( R_1 \) values are not directly available for this system. The only data available for \( k_p \) is that of Dainton et al.\(^{28}\) who reported a value of 18,000 l/mole/sec at 25°C in water for \( k_p \). Assuming that the value would be independent of solvent and also assuming an activation energy of 4 K cal mole\(^{-1}\) \( k_p \) at 60°C turns out to be 36,570 l mole\(^{-1}\) sec\(^{-1}\).
Fig-31. Test of equation 90. Plot of $1/R_p$ vs $[\text{MBC}]$ in Acrylamide polymerization in ethylene glycol at 60°C. 

$[\text{[AA]}] = 1$ mole $l^{-1}$; $[\text{[A7]}] = 4.44 \times 10^{-3}$ mole $l^{-1}$. 
Furthermore, $R_1$ is difficult to estimate. The rate of decomposition of 4,4'-azobis-4-cyanopentanoic acid is found to be solvent dependent. The available literature values of the first order rate constant for the decomposition of 4,4'-azobis-4-cyanopentanoic acid (AZP) in various solvents at 60°C is given in the Table-18.

**Table-18**

First order rate constant for the decomposition of 4,4'-azobis-4-cyanopentanoic acid in various solvents at 60°C.

<table>
<thead>
<tr>
<th>Sample description</th>
<th>$k_d \times 10^5$ sec$^{-1}$</th>
<th>Solvent</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixed isomers</td>
<td>0.49</td>
<td>Water</td>
<td>8</td>
</tr>
<tr>
<td>Meso</td>
<td>1.21</td>
<td>N,N-Dimethyl acetamide</td>
<td>127</td>
</tr>
<tr>
<td>±</td>
<td>1.30</td>
<td>&quot;</td>
<td></td>
</tr>
<tr>
<td>Mixed isomers</td>
<td>1.56</td>
<td>N,N-Dimethyl formamide</td>
<td>123</td>
</tr>
</tbody>
</table>

Taking the lowest value of $k_d$ and assuming the efficiency of initiation to be 0.5

$$R_1 = 2 f k_d [AZP] = 2 \times 0.5 \times 0.49 \times 10^{-5} [AZP]$$
Putting these values in the above equation $k_x$ turns out to be $1.52 \times 10^5$ l mole$^{-1}$ sec$^{-1}$ at 60°C. The value of $k_x$ is found to be very large and there is a considerable degree of uncertainty in the value due to the uncertainties involved in the values derived for $k_p$ and $R_1$ as discussed in the preceding paragraphs. Also, since the $R_p$ data for this system were obtained from the yield of polymer obtained after a long time, there is every possibility that the present high result may also be a consequence of secondary retardation as was observed with MA and styrene respectively. For this reason this value is not considered in the subsequent discussions of this chapter.

4.8.5.6. Styrene-Methylene Blue Chloride (MBCl) System

Thus far we have seen that the assumption that the cross termination rate constant involving the polymer radical and MB semiquinone is the geometric mean of the homotermination rate constants ($\phi = 1$) is obeyed for the polymer radicals discussed in the preceding sections. All these radicals have electron withdrawing substituents such as -CN, -COOCH$_3$, -CONH$_2$ etc. in the alpha position. It would be expected that for a radical having electron-releasing substituent at the alpha position this relation would no longer hold good. Because of opposite polarity $\phi$ is expected to have a value
greater than 1. Polystyryl radical is a radical of this latter type. The data for this system is now analysed.

Figure 32 shows a plot of $1/R_p$ vs. $[MBCl]$ based on the data presented in table-16 for styrene-MBCl system at the fixed concentration of AIBN $6 \times 10^{-3}$ mole $^{-1}$ and styrene $4.31$ mole $^{-1}$, the dye concentrations being varied.

The straight line drawn through $1/R_p^0$ is shown in the figure as a full line. The slope of the line has a value $3.75 \times 10^8$. Thus,

$$\frac{k_x}{R_1 k_p [M]} = 3.75 \times 10^8$$

from which $k_x$ was determined to be $2.38 \times 10^4$ mole$^{-1}$ sec$^{-1}$.

The values of $R_1$ and $k_p$ at $60^\circ$C were obtained from the literature:

$$k_p = 176 \text{ mole}^{-1} \text{ sec}^{-1} \quad \text{(Ref 27)}$$

$$R_1 = 1.4 \times 10^{-5} [\text{AIBN}] \text{ mole}^{-1} \text{ sec}^{-1} \quad \text{(Ref 79,129)}$$

The dotted line in the figure is drawn following the least square treatment of the data. The slope was found to be $(4.23 \pm 0.25) \times 10^8$ which can be compared with the value reported above. However, this least square line leaves an intercept at the $1/R_p$ axis which is one third the theoretical value of $1/R_p^0$. Hence, it is considered that the condition $\phi = 1$ is not well obeyed for styrene. This would be more clear from the plot according to
Fig-32. Test of equation 90. Plot of $1/R_p$ vs. $[\text{MBC}]$ for Styrene polymerization in DMF at 60°C. $[S_H] = 4.31$ mole l$^{-1}$; $[\text{AIBN}] = 6 \times 10^{-3}$ mole l$^{-1}$. The dotted line represents the least square plot.
The plot results in a line parallel to the ordinate axis for $\phi^2 = 1$ as shown in the figure 33. As discussed in section 4.8.5.2 while analysing the data for MMA the validity of the condition $\phi = 1$ would have reduced the line to a point. Either experimental error or the invalidity of the condition $\phi = 1$ yields a line parallel to the ordinate axis. It is therefore worth checking whether other values of $\phi$ results in a better fit of the data to the general rate equation 89. Figures 33 and 34 show such plots for $\phi^2 = 10, 100, 10^4$. It is evident from the figure 34 that at high values of $\phi^2$ viz $10^4$, the equation fits the data very well to the general equation. Under these conditions the term under the square root in the general equation becomes very close to 1.

The slope of the plot in figure 34 for the line obtained when $\phi^2 = 10^4$ gives

$$2 \frac{k_t}{k_p} k_x = 19.52$$

from which $k_x$ is determined to be $20,900 \text{ mole}^{-1} \text{ sec}^{-1}$. 

\[
\frac{2}{\mu} \left[ \frac{\text{MB}}{1 - \mu^2} \left( 1 + \left( 1 + \frac{1}{\phi^2 \mu^2} \right)^{\frac{1}{2}} \right) \right] \quad \text{vs.} \quad \frac{R_P}{[I]} \left( 1 + \frac{1}{\phi^2 \mu^2} \right)^{\frac{1}{2}}
\]
Fig-33. Test of general equation 89 for various values in Styrene polymerization in DMF at 60°C. $\Phi^2$ values indicated in the figure. Data given in Table-16 and also in Table-XII in the appendix.
Fig-34. Test of general equation 89 for $\varphi^2 = 10^4$ in 
Styrene polymerization in DMF at 60 °C. Data 
given in Table-16 and also in Table-XIII in the 
appendix.
The necessary values of $k_p$ and $k_t$ are obtained from the literature. $k_p = 176 \text{ mole}^{-1}\text{ sec}^{-1}$ and $k_t = 3.6\times10^7 \text{ mole}^{-1}\text{ sec}^{-1}$ at 60°C.

The value of $k_x$ thus obtained is somewhat lower than the value 23,900 obtained by applying the condition $\phi = 1$ as discussed earlier in this section.

It thus follows that the rate of polymerization data for radicals having electron withdrawing groups in the alpha position fit the general rate equation 89 when the cross termination constant factor $\phi$ has a value equal to unity. While for $PS$tr radical having a electron releasing substituent (phenyl group) the equation fits best when $\phi$ is large which indicates that the cross termination is favoured in this case. This difference in behaviour between these two types of radicals (electron withdrawing substituent vs. electron releasing substituent) is quite in line with the expectations when one considers the role of polar factors in radical termination reactions. The general observation is that cross termination rate constant is a geometric mean of the homotermination rate constants when radicals of similar polarity are involved. On the other hand, cross termination is very much favoured over homotermination when radicals of opposite polarity are involved (vide section 1.6.9).
4.8.6. Reversibility of the Decolourization of Methylene Blue

During the course of retardation of polymerization, the colour of MB fades. Haines and Water as well as Beardwell noted that the decolourization of MB following reactions with free radicals is reversible i.e. the leuco MB could be oxidized back to MB. The reversibility of the process is tested in this work. The styrene system is chosen because the decolourization of MB is fastest in this system and substantial decrease in MB colour occurs in a reasonable time.

If the reaction between polymer radical and MB (reaction 65) is an electron transfer one and if the subsequent reaction between the polymer radical and MB semiquinone (reaction 66) is not a combination one, then it should be possible to get back MB to its initial concentration level on oxidizing the leuco dye at the end of the reaction. This conclusion, however, assumes that the mutual reaction between MB semiquinones (reaction 67) is a disproportionation one.

The reversibility test was carried out in the following way. Appropriate amounts of monomer, solvent, initiator and dye were mixed in a vessel and then put in sealing tubes.
provided with A-10 standard joints. The tubes were then
degassed in a vacuum line through three freeze-thaw cycles
and then sealed under vacuum. The absorption spectra of the
reaction mixtures in the visible region were recorded after
suitable dilution before they were put into the sealing tubes.
The sealed tubes were then placed in a thermostatic bath
maintained at 60°C. After a suitable time interval the tubes
were taken out of the thermostat, broken open and the
absorption spectra were again recorded after suitable dilution.
The diluted solutions were taken in volumetric flasks, kept
open to atmosphere for about a week and the spectra were again
recorded after the necessary volume adjustments. In some of
the tubes small quantity of FeCl₃ was added at the end of air
oxidation in order to insure complete oxidation of the leuco
dye. The absorption data of the systems are reproduced in
table-19. These data allow us to determine the amount of leuco
MB formed in the system during the reaction. This value is
equal to that of the MB that was regenerated by means of
oxidation after the reaction time interval. These data are
summarised in table-20.
Table-19

Absorption data of polymerization reaction mixture before and after polymerization. \([\text{Styrene}] = 4.31 \text{ mole l}^{-1}\), \([\text{AIBN}] = 5.27 \times 10^{-3} \text{ mole l}^{-1}\), Solvent-DMF, Temp. 60°C.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Polymerization time min</th>
<th>Original value</th>
<th>After reaction</th>
<th>After Air oxidation following polymerization</th>
<th>After air and FeCl₃ oxidation following polymerization</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>120</td>
<td>0.122</td>
<td>0.0085</td>
<td>-</td>
<td>0.022</td>
</tr>
<tr>
<td>2</td>
<td>190</td>
<td>0.186</td>
<td>0.0145</td>
<td>0.024</td>
<td>0.027</td>
</tr>
<tr>
<td>3</td>
<td>240</td>
<td>0.249</td>
<td>0.0185</td>
<td>0.038</td>
<td>0.050</td>
</tr>
</tbody>
</table>

a - Absorbance at 653 nm in 1 cm cell of 0.5 ml reaction mixture diluted to 100 ml with methanol.

b - Readings taken immediately after opening the reaction tubes.

c - Kept open to atmosphere for 5 days and then volume adjusted. No change with any further time was noted.
Test of reversibility of decolourization of MB in case of styrene polymerization in DMF at 60°C. \([\text{Styrene}] = 4.31 \text{ mole l}^{-1}, [\text{AIBN}] = 5.27 \times 10^{-3} \text{ mole l}^{-1}\)

<table>
<thead>
<tr>
<th>Serial No.</th>
<th>([\text{MB}] \times 10^4) mole l(^{-1})</th>
<th>Reaction time (t) min at 60°C</th>
<th>([\text{MB}] \times 10^4) mole l(^{-1}) after oxidation</th>
<th>([\text{MB}] \times 10^4) mole l(^{-1})</th>
<th>Regenerated MB %</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>2.49</td>
<td>120</td>
<td>0.17</td>
<td>0.45</td>
<td>12.1</td>
</tr>
<tr>
<td>II</td>
<td>3.79</td>
<td>190</td>
<td>0.29</td>
<td>0.55</td>
<td>7.4</td>
</tr>
<tr>
<td>III</td>
<td>5.08</td>
<td>240</td>
<td>0.38</td>
<td>1.02</td>
<td>13.6</td>
</tr>
</tbody>
</table>

It would be evident from table 20 that only about 10% of the dye colour that was reduced could be regained on oxidation of the polymerized solution. These results indicate that

(i) leuco MB is one of the products of the reaction
(ii) decolourization of MB is not completely reversible which means that leuco MB is not the only product of the reaction or in other words even if reaction 65 is an electron transfer one, reaction 66 substantially leads to combination of the semiquinone with polystyrene radical.

4.8.7. The Phenomenon of Secondary Retardation

It has been mentioned in sections 4.3, 4.4 and 4.6 that the rate of polymerization in presence of MB falls off after the reaction progressed for a while. This indicated that the product of the reaction is a more powerful retarder than MB. This phenomenon is referred to here as secondary retardation. It would be pertinent here to comment on the possible nature of this secondary retarder. In the preceding section it has been established that leuco MB is one of the products of the reaction. The reverse of the dismutation reaction 67 becomes important as leuco MB is formed with the progress of reaction. It is known that in partly reduced MB solution a few percent of the total dyestuff can be present as the semiquinone due to the reaction of MB with leuco MB.\textsuperscript{124,130} Such reactions would result in an increase in MB semiquinone concentration over that existing in the initial stages. The MB semiquinone is expected to be a stronger retarder than MB itself. The retardation of polymerization at any stage is effected by (i) the MB and (ii) the MB
semiquinone. With progress of reaction the former decreases and the latter increases (due to reaction 65). This process continues for a while and then when the MB concentration falls off, that of the semiquinone follows suit and the acceleration in $R_p$ occurs due to the decrease of both MB and the semiquinone. This latter phenomenon has been observed in the styrene system (vide section 4.6) where it was possible to follow the reaction up to complete decolourization of MB within a reasonable time period. The secondary retardation was significant in styrene and MA polymerization. It was also discernible in AN polymerization (Figures 20a); but was not observed in MMA and MAN polymerization respectively. A longer reaction time might have been necessary for these two latter systems in order to be able to observe the secondary retardation. The low reactivity of these radicals with MB may be the reason for this.

4.8.8. Correlation of the Rate Constant $k_\alpha$ with the Radical Reactivity and Polarity

The rate constants for the reaction between polymer radicals and MB as determined in the present work are assembled in table-21 along with the Q and e values of the respective monomers vis-a-vis radicals.
Table-21

Values of $k_x$ for the reaction of polymer radicals with MB along with their $Q$ and $e$ values of respective monomers

<table>
<thead>
<tr>
<th>Polymer radical</th>
<th>$k_x$ at 60°C</th>
<th>$e$</th>
<th>$Q$</th>
</tr>
</thead>
<tbody>
<tr>
<td>St</td>
<td>20,900</td>
<td>-0.80</td>
<td>1.00</td>
</tr>
<tr>
<td>MA</td>
<td>2,120</td>
<td>0.60</td>
<td>0.42</td>
</tr>
<tr>
<td>MAN</td>
<td>1,390</td>
<td>0.81</td>
<td>1.12</td>
</tr>
<tr>
<td>MMA</td>
<td>123</td>
<td>0.40</td>
<td>0.74</td>
</tr>
<tr>
<td>AN</td>
<td>5,800</td>
<td>1.20</td>
<td>0.80</td>
</tr>
</tbody>
</table>
In this type of oxidative termination one would expect that a radical having electron releasing substituent in the alpha position should react with MB at a faster rate than a radical having electron withdrawing substituent. The highest rate constant observed in this work for polystyrene radical is therefore expected. Previously, Beardwell noted that MB inhibits the AIBN initiated polymerization of N-vinyl carbazole. This is in line with the greater electron donating ability of the poly(NVC) radical than that of the PST radical as would be revealed from the e values of Alfrey Price Q-e scheme. The values are e = -1.40 for NVC and e = -0.8 for styrene. However, the value of the rate constant does not depend only on e but also on Q value.

It would be worthwhile to examine whether the Q-e scheme of Alfrey Price or the pattern scheme of Bamford, Jenkins and Johnston (BJJ) could quantitatively account for the rate constant data.

4.8.8.1. Correlation of $k_x$ According to the Q-e Scheme

From the discussions presented in section 1.6.2 regarding application of Q-e scheme in chain transfer, it follows, that for the two reactions under consideration here, viz.
we have
\[ \frac{k_x}{k_p} = \frac{PRQ_{MB} \exp(-e_{MB}e_R)}{PRQ_m \exp(-e_mE_R)} \]  
(91)

where \( PR \) is the reactivity parameter of the radical \( M^* \), \( Q_{MB} \) and \( Q_m \) are those for \( MB \) and the monomer \( M \) respectively. \( e_{MB} \) and \( e_m \) are the polarity parameters of \( MB \) and the monomer \( M \) respectively and \( e_R \) is that of the radical. It is a common practice to consider \( e_R = e_m \), whereupon equation 91 reduces to

\[ \frac{k_x}{k_p} = \frac{Q_{MB}}{Q_m} \exp(e_m^2-e_mE_{MB}) \]  
(92)

This gives rise to the equation

\[ \ln Q_{MB} = \ln (Q_m k_x/k_p) - e_m^2 + e_mE_{MB} \]  
(93)

The 1st and 2nd term of the R.H.S of equation 93 can be calculated for a given system of monomer-\( MB \). Thus for some arbitrary \( e_{MB} \) values \( \ln Q_{MB} \) can be calculated and a plot of \( \ln Q_{MB} \) vs. \( e_{MB} \) may be obtained. For every monomer-\( MB \) system one such line would be obtained. If the Q-e scheme is obeyed,
Fig. 35. Test of Q-e scheme for the k_x data determined in this work. Plot of equation 93.
all such lines would intersect at a point or over a narrow region and from the co-ordinate of the point of intersection \( Q_{MB} \) and \( e_{MB} \) may be evaluated. However, from the figure 35 it is evident that the lines intersect each other at a large number of points. The lines for MMA and MA in particular are quite off from which it is concluded that the Q-e scheme is not obeyed or in other words the rate constant data can not be explained taking into account only the polarity and reactivity of the radicals. Some other factor has to be taken into consideration for any correlation of the data. The reason for such behavior is discussed in the following sections.

4.8.8.2. Correlation of \( \ln k \) According to the Pattern Scheme

The rate constant data were also analysed according to the BJJ pattern scheme as described in the section 1.6.3. The pattern scheme leads to the following equation \(^{37,46}\) (see section 1.6.3)

\[
\log_{10} k = \log_{10} k_{T} + \alpha \sigma + \beta
\]

The quantities in the above equation have been defined earlier.

A plot of \( \log_{10} k_{x} - \log_{10} k_{T} \) vs. \( \sigma \) (where \( \sigma \) is the Hammett parameter) should be a straight line if pattern scheme holds good. Such an attempt is made in figure 36a. In drawing the figure \( k_{T} \) and \( \sigma \) values were obtained from the literature.
Fig-36a. Test of BJJ pattern scheme for the $k_x$ data determined in this work. Plot of $\log_{10} k_x - \log_{10} t_{\tau T}$ vs. $\sigma$ according to equation 44.
Fig-36b. Test of EJJ pattern scheme for FeCl₃ and CuCl₉, respectively. Data given in Tables XIV and XV in the appendix.
and are given in table-22. Figure 36a shows that the data for St, MAN and AN fall on a straight line. The $k_x$ values for MMA and MA are far too low. We have argued in the subsequent discussion that the low value for MMA is a result of steric hindrance. As for the MA data, it needs to be increased 40-fold in order to get it on the line. This is too big to be considered an experimental error. However, in many oxidative terminations the MA data are found to be much lower than the value predicted on the basis of the $Q$-e or the pattern scheme. For example, figure 36b shows the pattern plot for the reaction of polymer radicals with FeCl$_3$ and CuCl$_2$ respectively (based on the data in tables XIV and XV of Appendix). In both cases the MA data lie well below the expected values. Thus in order to bring the MA data on the line it has to be increased about 80 times for CuCl$_2$ and 9 times for FeCl$_3$ respectively. Thus disregarding the data for MMA and MA the line shown in figure 36a was drawn from which the $\alpha$ and $\beta$ values for MBC1 turn out to be -4.6 and 6.9 respectively. The $\alpha$ and $\beta$ values so obtained are compared in the table 23 with those for FeCl$_3$ and CuCl$_2$ respectively. The lower $\beta$ value for MBC1 than CuCl$_2$ or FeCl$_3$ points to the lower reactivity of MBC1 compared to the other two. Furthermore the lower $|\alpha|$ values for MBC1 indicates that the polar contribution is somewhat less than offered by FeCl$_3$ or CuCl$_2$. 
### Table-22

Values of $k_x$, $k_{t,T}$ and $\sigma$ for various polymer radicals

<table>
<thead>
<tr>
<th>Polymer radical</th>
<th>$k_x$ at 60°C</th>
<th>$k_{t,T}$ at 60°C</th>
<th>$\log_{10}k_x - \log_{10}k_{t,T}$</th>
<th>$\sigma$ b</th>
</tr>
</thead>
<tbody>
<tr>
<td>St</td>
<td>20,900</td>
<td>2.11x10^{-3}</td>
<td>6.9958</td>
<td>- 0.01</td>
</tr>
<tr>
<td>MA</td>
<td>2,120</td>
<td>0.56</td>
<td>3.5781</td>
<td>0.385</td>
</tr>
<tr>
<td>MAN</td>
<td>1,390</td>
<td>2.0x10^{-2}</td>
<td>4.8420</td>
<td>0.49</td>
</tr>
<tr>
<td>MMA</td>
<td>123</td>
<td>1.25x10^{-2}</td>
<td>3.9930</td>
<td>0.215</td>
</tr>
<tr>
<td>AN</td>
<td>5,800</td>
<td>0.785</td>
<td>3.8685</td>
<td>0.66</td>
</tr>
</tbody>
</table>

a - Ref. 37, 46

b - J. Hine, Physical Organic Chemistry, McGraw-Hill, 2nd ed. p 87 (1962). For radicals having two alpha substituents, the algebraic sum of para $\sigma$-values has been used (vide section 1.6.3).
Table-23

\( \alpha \) and \( \beta \) values for MBCl, CuCl\(_2\) and FeCl\(_3\)

<table>
<thead>
<tr>
<th></th>
<th>( \alpha )</th>
<th>( \beta )</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MBCl</td>
<td>- 4.6</td>
<td>6.9</td>
<td>This work</td>
</tr>
<tr>
<td>FeCl(_3)</td>
<td>- 5.66</td>
<td>7.4</td>
<td>46</td>
</tr>
<tr>
<td>CuCl(_2)</td>
<td>- 5.4</td>
<td>9.0</td>
<td>77</td>
</tr>
</tbody>
</table>
4.8.3. Steric Effect

The failure of both the Q-e and the BJJ pattern scheme to accommodate all the data induced us to look for a possible explanation. To this end we confine our discussion with the rate constants obtained for PSt, PAN and PMMA radicals as given in table-22. Previous studies on oxidative termination of polymer radicals with transition metal salts revealed that PAN radical is only about 1.5 times as reactive as PMMA towards FeCl₃ and PMMA radical is 5 times as reactive as PAN radical towards CuCl₂ (vide Table-3). On the other hand, PMMA radical is not oxidized by Fe³⁺ ion, while PAN radical is so oxidized (Table-3). These data are summarized in table 24 for convenience. Dainton and Seaman attributed this difference in behaviour between PMMA and PAN radical towards Fe³⁺ ion to the steric hindrance exerted in the reaction with PMMA radical. Recently Bamford demonstrated that the alpha methyl group in the penultimate unit of PMMA radical imposes a considerable steric hindrance in transfer reactions involving large atoms such as bromine in CBr₄ (vide section 1.6.8). Considering the large size of MB⁺ the sluggish reaction of MB⁺ with PMMA radical in comparison to PAN radical may also be attributed to steric hindrance. It should be noted here that the steric effect while influences the transfer reaction when Br atom transfer from CBr₄ does not seem to
Rate constants \( k_x \) for reaction between polymer radicals and Methylene Blue chloride at 60°C and the \( Q \) and \( e \) values of the respective monomer.

<table>
<thead>
<tr>
<th>Polymer radical</th>
<th>( k_x \times 10^{-3} ) l mole(^{-1} ) sec(^{-1} )</th>
<th>( Q )</th>
<th>( e )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \text{MBCl}^a )</td>
<td>( \text{Fe}^{3+}^b )</td>
<td>( \text{FeCl}_3^c )</td>
</tr>
<tr>
<td>PST</td>
<td>20.9</td>
<td>-</td>
<td>5.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0</td>
<td>3.0</td>
</tr>
<tr>
<td>PMMA</td>
<td>0.12</td>
<td>0</td>
<td>3.0</td>
</tr>
<tr>
<td>PAN</td>
<td>5.8</td>
<td>13.0</td>
<td>4.5</td>
</tr>
</tbody>
</table>

\( a \) - this work at 60°C in DMF

\( b \) - ref. 74 at 25°C in water

\( c \) - ref. 79 at 60°C in DMF
operate when Cl atom transfer from FeCl₃ is involved. This follows from the fact that the reaction rate between FeCl₃ and the same polymer radicals as are used in this work such as PSt, PMMA, PAN and PMAN could be correlated using Q-e scheme. It thus follows that a critical substrate size exists below which the influence of steric effect in the reaction with the above mentioned polymer radicals particularly PMMA radical becomes insignificant. The failure of both Q-e scheme and the BJJ pattern scheme to account for the rate constant data for PMMA radical may thus presumably be attributed to the steric hindrance. Considering the large size of MB⁺ such a contention is not at all unjustified. Steric hindrance in the reaction of PMMA radical with chloranil has also been presumed to be the reason as to why the reaction is slow. However, if only the alpha methyl group of the penultimate unit is mainly responsible (see section 1.6.8) for steric hindrance, then one would expect that the data for MAN would also be much lower than predicted from Q-e or pattern treatment. However, as shown in figure 36a and discussed in section 4.8.8.2 the MAN data turns out to be normal. This fact tends to indicate that for the steric effect to be important the sizes of both the alpha substituents of the penultimate unit of a radical must be considered. The CN group is of considerably
smaller size than COOCH₃ and perhaps for this reason PMAN radical does not appear to impose any significant steric hindrance in spite of having the alpha methyl group. As for the low value for MA we have already discussed that this is a general trend for MA with many a substrates e.g. FeCl₃, CuCl₂. An explanation for this is not apparent.