

Methylene blue as a retarder of free radical polymerization:

1. Polymerization of acrylonitrile, methyl methacrylate and styrene*

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Methylene blue (MB), a redox dye, in monomeric form significantly retards the free radical polymerization of styrene (ST) and acrylonitrile (AN) in *N,N*-dimethyl formamide solvent. The effect is small in methyl methacrylate (MMA) polymerization. Partly reduced MB is found to be a stronger retarder than MB. The rate constants for the oxidation of the polymer radicals by MB at 60°C follows the order ST > AN > MMA. The results cannot be explained when only taking into consideration the reactivity and polarity parameters of the radicals and the substrate, as is done in the Q-e scheme. The low rate constant with the PMMA radical is attributed to steric effects. The current work has shown that single molecules of MB are effective chain terminators and this is in sharp contrast with the conclusion reached by Chen who postulated that only the aggregates of MB are the chain terminators in the polymerization of acrylamide in water.

Keywords Retarder; inhibitor; free radical; vinyl polymerization; methylene blue; redox dye

INTRODUCTION

Methylene blue (MB), a redox dye of the thiazine class, is frequently used as a photosensitizer in free radical polymerizations¹. The use of MB as a polymerization inhibitor of several vinyl monomers has been mentioned in the patent literature²⁻⁵. A short review on the use of MB as a redox stabilizer has been published recently⁶. Haines and Waters⁷ observed that MB is reversibly decolorized by α -cyano alkyl radicals.

The interaction of this dye with polymer radicals has not been quantitatively studied. The dye forms aggregates of two or more than two molecules in the aqueous phase depending on its concentration⁸. Chen¹ inferred that the monomeric MB does not oxidize the polyacrylamide (PAA) radical, but the dimer does so and the dimer thus decreases the molecular weight of PAA. This claim seemed to have insufficient experimental validity. In this paper the interaction of MB with poly(methylmethacrylate) (PMMA), polystyrene (PS) and poly(acrylonitrile) (PAN) radicals has been quantitatively studied.

EXPERIMENTAL

Materials

MMA, AN and St were washed free from inhibitors,

dried and distilled under reduced pressure. The middle fraction was used for the experimental investigations. *N,N*-Dimethylformamide (DMF) (BDH) was distilled under reduced pressure. The first fraction ~15% of the total charge was rejected. The middle fraction comprising 70% of the total charge was collected. DMF so obtained was reported to be sufficiently dry for polymerization studies⁹.

Methylene blue (MB) of specially pure quality for microscopy (E. Merck) was used after recrystallization twice from ethanol. 2,2'-Azobisisobutyronitrile (AIBN) was recrystallized twice from absolute ethanol and dried in a vacuum desiccator. The dye concentrations used in the experiments were determined spectrophotometrically using ethanol as the diluent. The molar absorptivity index value in ethanol was obtained from the literature⁸ as $98 \times 10^4 \text{ dm}^2 \text{ mol}^{-1}$. Basic aluminum oxide (Sarabhai Merck) was used for column chromatography of the dye.

Method

The rates of polymerization (R_p) were followed dilatometrically. The reaction mixtures in the dilatometers were freed from air in a vacuum line by standard freeze-thaw techniques and sealed in vacuum. The experiments were carried out in the absence of light. The percentages of volume contraction for one hundred per cent conversion were taken as 16.5, 23.4 and 29.7 for the styrene¹⁰, MMA¹¹ and AN¹² polymerizations respectively.

Absorption spectra were recorded partly in a Hilger Uvispek spectrophotometer and partly in a CARY 17D spectrophotometer.

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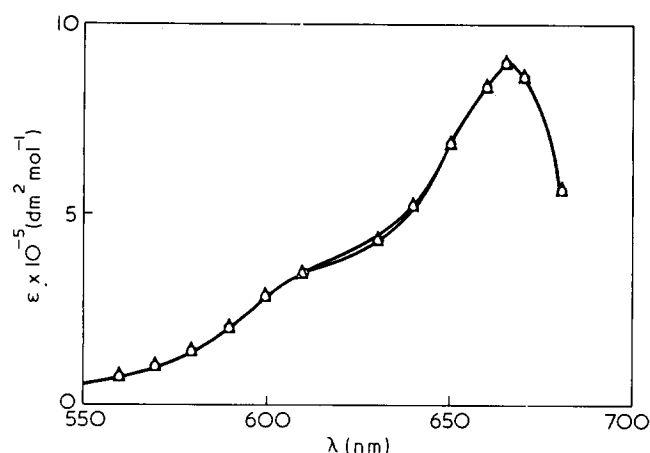


Figure 1 Plot of molar absorptivity index vs. wavelength for MB in a mixture of acrylonitrile (15% by volume) and DMF. [MB] varied from 0.87×10^{-5} to 1.74×10^{-4} mol dm⁻³

RESULTS

Molecular state of methylene blue in reaction medium

As has been mentioned in the introduction MB in aqueous solution undergoes reversible aggregation to dimers or multimers depending on its concentration⁸. This is manifested in the absorption spectra of MB in water. Aggregation induces metachromacy, i.e. new bands appear on the short wavelength side of the main band which diminishes with increasing concentration and consequently Beer's law is not obeyed¹³⁻¹⁸. Metachromacy is also observed in some low dielectric constant organic solvents¹⁹. Alcohols especially methanol and ethanol are solvents where the dye does not form aggregates and consequently Beer's law is obeyed in these solvents. In view of Chen's inference¹¹ that MB in its monomeric form is inefficient so far as oxidation of polyacrylamide radical is concerned, it was pertinent to determine the state of methylene blue in the mixture of vinyl monomer and the solvent (DMF) used in this work. Figure 1 shows the absorption spectra of methylene blue in a mixture of DMF and acrylonitrile (15% by volume) at various dye concentrations in the range 8.7×10^{-6} to 1.74×10^{-4} mol dm⁻³. The spectra show a maximum at 665 nm with a shoulder around 615 nm. The spectra remain unchanged over the concentration range mentioned above. Hence it can be concluded that the dye exists as a monomer in this solvent mixture. Similarly, it has been observed that the dye obeys Beer's law in the solvent mixture consisting of DMF and styrene (1:1 V/V) when the dye concentration is increased 30-fold from 0.97×10^{-5} to 2.9×10^{-4} mol dm⁻³. This indicates that MB exists as a monomer in this solvent mixture also.

It was reported for another strongly metachromatic dye, pinacyanol, that a benzene solution of the dye containing at least 30 volume per cent DMF eliminates the metachromatic phenomenon which is very strong in pure benzene²⁰.

General features of polymerization

In general, the polymerization was followed up to a conversion of about 2%. In order to insure the existence of MB as a monomer in the polymerizing solution the MB concentration was kept low. The maximum MB concentration used was 3.4×10^{-3} mol dm⁻³. A low initiator concentration *ca.* 1 to 2×10^{-3} mol dm⁻³ was

used in AN as well as MMA polymerization so that no significant decrease in MB concentration occurs during a run. However, induction periods (i.p.) appeared at such comparable initiator and dye concentrations*. The i.p.'s are attributed to some unidentified impurity in MB which could not be removed either by recrystallization or by column chromatography over basic aluminium oxide¹⁸. The steady state rates of polymerization achieved after the i.p. was over remained constant for a sufficient length of time and these were used to calculate the rate constants for the reaction of the polymer radicals with MB.

With styrene the retardation effect is greatest and for this monomer a lower MB concentration and a higher AIBN concentration had to be used in order to make the rate measurements possible with any reasonable accuracy. The course of the polymerization was followed until the disappearance of the MB colour in some experiments. Figure 2 shows the % conversion vs. time plot for the polymerization of styrene at the fixed AIBN concentration of 6.0×10^{-3} mol dm⁻³ while the concentration of MB varied from 1.53×10^{-4} to 9.21×10^{-4} . An induction period was not observed under these conditions. Presumably the impurity in MB was scavenged during the time required for thermal equilibration of the contents of the dilatometers with the thermostat temperature at the higher initiator and lower MB concentration used in this case than were used in the AN or MMA polymerizations. It is clear from Figure 2 that the initial R_p decreases after a few minutes and then at later stages acceleration in the rate sets in. At the lowest MB concentration an increase in R_p over the initial value precedes the decrease. This increase is caused by the depletion of MB which can be significant at this lowest dye concentration. Finally as all the dye is consumed the rate attains a value close to that of the unretarded rate

* See Figures 3-5 for the concentrations used in AN and MMA polymerizations.

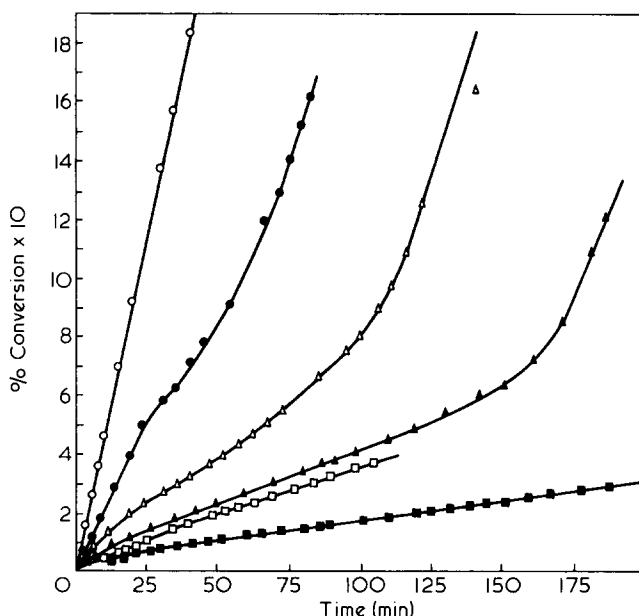
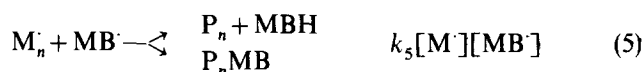
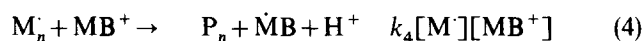


Figure 2 Plot of % conversion vs. time for styrene polymerization in DMF at 60°C. [St] = 4.31 mol dm⁻³, [AIBN] = 6.0×10^{-3} mol dm⁻³. MB concentrations in mol dm⁻³ are \circ , zero; \bullet , 1.53×10^{-4} ; Δ , 3.07×10^{-4} ; \blacktriangle , 4.65×10^{-4} ; \square , 7.67×10^{-4} and \blacksquare , 9.21×10^{-4}

observed in the absence of MB. The fall off of the rate below the initial value indicates that the product of the reaction is a more efficient retarder than MB itself. This effect was also observed in AN polymerization although to a markedly lower extent. Thus the rate at any stage other than the initial is the consequence of two effects superimposed on each other: (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. No attempt has been made to identify this secondary retarder generated in the reaction. However one possibility has been discussed in the next section. 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 for the reaction of the polymer radical with MB.

Reaction scheme and kinetic equations

The rate constants for the reaction between polymer radicals and MB could be evaluated by considering the following reaction scheme.



where MB and MBH represent the MB semiquinone and leuco-MB respectively. The proton required for the formation of leuco-MB in reaction (6) in the aprotic solvent DMF would be available from reaction (4). Haines and Waters⁷ in their study of the reaction of MB with α -cyanoalkyl radicals and also Beardwell²¹ in his study of the reaction of MB with a poly(9-vinyl carbazole) radical found the decolouration of MB to be reversible which indicates that reaction (4) is an electron transfer reaction rather than an addition of the free radicals to the aromatic nucleus of the dye ion. Also, it has been established that MB semiquinones undergo a disproportionation reaction²² to yield one molecule of leuco-MB and one molecule of MB^+ . That leuco-MB is one of the products of the reaction has been confirmed from reoxidation experiments for the styrene system discussed later in this work. The reverse of the dismutation reaction (6) is also an important reaction to be considered as leuco-MB is formed with the progress of reaction. It is known that in partly reduced MB solution a few per cent of the total dye stuff can be present as the semiquinone due to the reaction of MB with leuco-MB^{22,23}. Such reactions would result in an increase in MB semiquinone concentration over that existing in the

initial stages. This may explain the decrease in R_p observed after the reaction had progressed for a few minutes.

In the above reaction scheme, reinitiation of polymerization by the semiquinone radical has not been taken into consideration 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 $\text{MB} \cdot$ supports this view.

The expression for the rate of polymerization could be derived following Kice²⁴ to be as follows

$$\begin{aligned} \frac{\mu^2[\text{MB}^+]}{1-\mu^2} \left[1 + \left\{ 1 + \frac{1(1-\mu^2)}{\phi^2 \mu^2} \right\}^{1/2} \right] \\ = \frac{k_3 R_p}{k_2 k_4 [\text{M}]} \left\{ 1 + \frac{(1-\mu^2)}{\phi^2 \mu^2} \right\}^{1/2} \end{aligned} \quad (7)$$

$$\text{where } \mu = \frac{R_p}{R_p^0} = \frac{\text{Rate of retarded polymerization}}{\text{Rate of unretarded polymerization}}$$

$$\text{and } \phi = k_5 / (k_3 k_6)^{1/2}$$

When $\phi = 1$, i.e. cross termination rate constant is the geometric mean of the rate constants for the homotermination reactions. Equation (7) reduces to

$$\frac{1}{R_p} = \frac{1}{R_p^0} + \frac{k_4[\text{MB}^+]}{R_i k_2 [\text{M}]} \quad (8)$$

It is evident from the results presented below that equation (8) is applicable for polymer radicals having electron withdrawing groups such as those present in AN and MMA, while a large ϕ value provides a good fit for equation (7) to the data obtained for the polystyryl radical which has an electron releasing substituent. This difference in behaviour is expected considering the opposite polarity of the two sets of radicals.

Acrylonitrile

Figure 3 shows that the plot of reciprocal rate of retarded polymerization vs. MB concentration is linear with an intercept at the $1/R_p^0$ 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 (8) which is obtained from the general equation (7) in a special case ($\phi = 1$). The slope of the line as obtained from equation (8) allows evaluation of k_4 . The following values of R_i and k_2 are obtained from literature^{25,26} and used to calculate k_4 at 60°C.

$$R_i = 1.42 \times 10^{-5} [\text{AIBN}] \text{ mol dm}^{-3} \text{ s}^{-1}$$

and

$$k_2 = 1960 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

The value of k_4 is thus determined to be $5800 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 60°C.

Figure 4 shows that a plot of $(1/R_p - 1/R_p^0)$ vs. $[\text{Initiator}]^{-1}$ at fixed concentrations of dye and monomer is linear as is expected if equation (8) is obeyed. The slope of the line gives $k_4[\text{MB}]/2fk_d k_2$ from which k_4 is determined to be $5340 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. This value is in

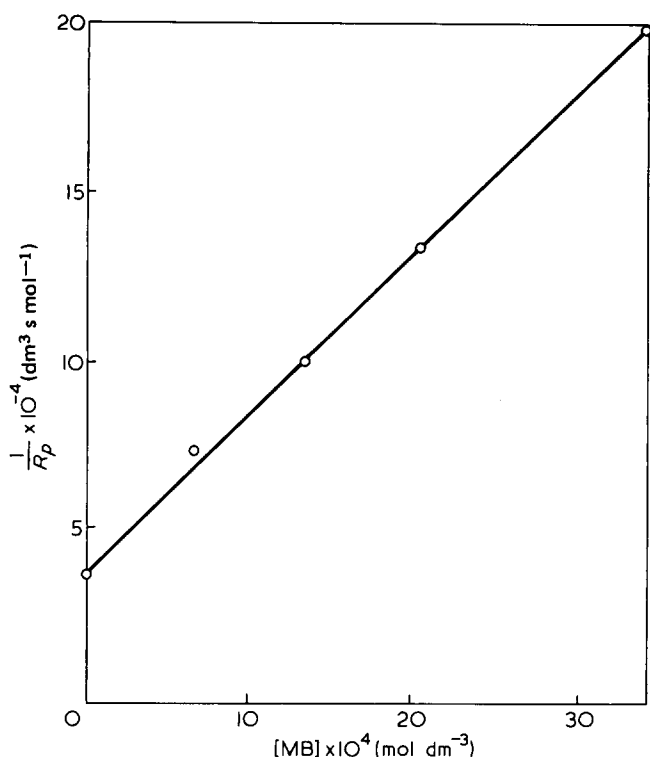


Figure 3 Plot of $1/R_p$ vs. $[MB]$ in AN polymerization. $[AN] = 2.27 \text{ mol dm}^{-3}$, $[AIBN] = 1.97 \times 10^{-3} \text{ mol dm}^{-3}$, solvent DMF, temperature 60°C

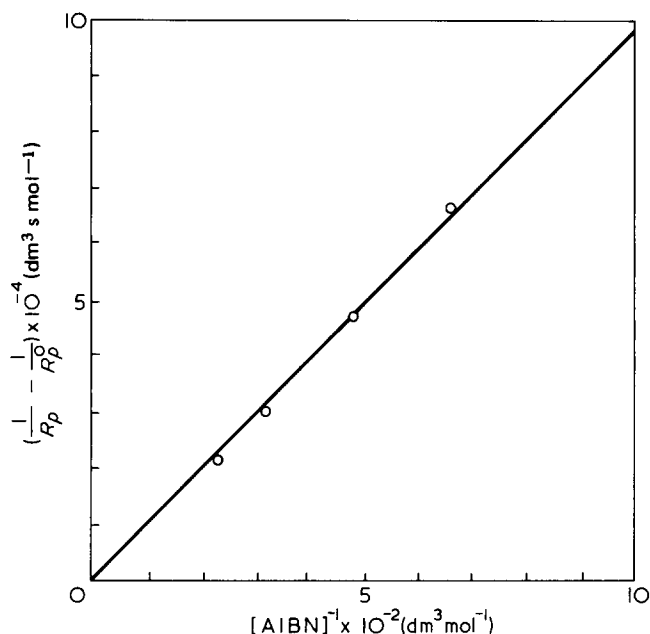


Figure 4 Plot of $(1/R_p - 1/R_p^0)$ vs. $[AIBN]^{-1}$ in AN polymerization. $[AN] = 2.27 \text{ mol dm}^{-3}$, $[MB] = 1.14 \times 10^{-3} \text{ mol dm}^{-3}$

reasonable agreement with that determined from Figure 3 as reported above.

MMA

Figure 5 shows a plot of $1/R_p$ vs. $[MB]$ at fixed initiator and monomer concentrations. The straight line was drawn using the least square method. Equation (8) may be considered to apply for this system also. As in the case of AN the rate constant k_4 is evaluated from the slope of the line using equation (8). The following values of R_i and k_2

at 60°C are used^{25,27}:

$$R_i = 1.34 \times 10^{-5} [AIBN] \text{ mol dm}^{-3} \text{ s}^{-1}$$

$$k_2 = 734 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

k_4 is thus determined to be $120 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 60°C .

Styrene

MB strongly retards the polymerization of this monomer. The values of R_p at a fixed AIBN concentration and varying MB concentration are given in Table 1. For this monomer, equation (7) fits the results quite well using a value of ϕ sufficiently large to make the second term under the square root in equation (7) negligible. Figure 6 shows such a plot for $\phi = 100$. Further increase in the value of ϕ does not affect the result. The slope of the line yields the value of k_3/k_2k_4 from which k_4 is estimated to be $20900 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 60°C . The values of k_3 and k_2 used for the calculation as obtained from the literature²⁸ are 7.2×10^7 and $176 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ respectively.

Reversibility of the decolourization of methylene blue

During the course of retardation of polymerization the colour of MB fades. Haines and waters⁷ as well as Beardwell²¹ noted that the decolouration of MB following reactions with free radicals is reversible, i.e. the leuco-methylene blue formed could be oxidized back to MB. The reversibility of this process is tested here. If the reaction between the polymer radical and MB is an electron transfer one and if the subsequent reaction between the polymer radical and the MB semiquinone is

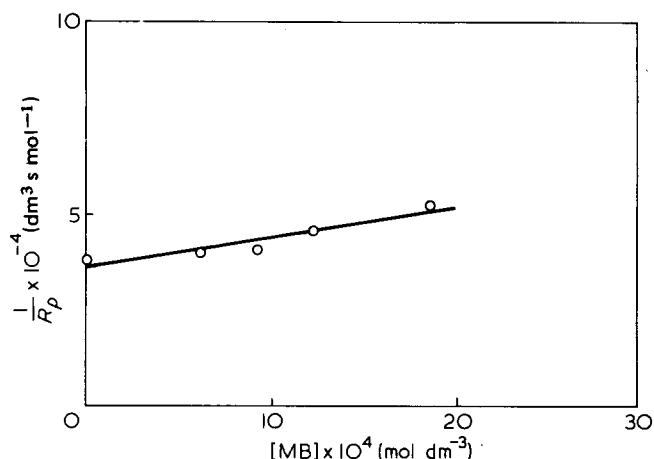


Figure 5 Plot of $1/R_p$ vs. $[MB]$ in MMA polymerization. $[MMA] = 1.4 \text{ mol dm}^{-3}$, $[AIBN] = 1.15 \times 10^{-3} \text{ mol dm}^{-3}$, solvent DMF, temperature 60°C

Table 1 Rates of polymerization of styrene in DMF both in the presence and absence of MB. Reaction conditions: $[Styrene] = 4.31 \text{ mol dm}^{-3}$; $[AIBN] = 6.0 \times 10^{-3} \text{ mol dm}^{-3}$; temperature = 60°C

$[MB] \times 10^4 \text{ (mol dm}^{-3}\text{)}$	Initial value of $R_p \times 10^5 \text{ (mol dm}^{-3} \text{ s}^{-1}\text{)}$
0	3.28
1.53	1.34
3.07	0.83
4.65	0.50
7.67	0.31
9.21	0.24

not a combination one, then it should be possible to get MB back to its initial concentration level on oxidizing the leuco-dye at the end of a reaction. This conclusion however assumes that the mutual reaction between MB semiquinones (reaction (6)) is a disproportionation reaction. Table 2 shows the results of oxidation of some reaction mixtures in the case of styrene polymerization. It is evident that only ~10% of the reduced dye could be oxidized back to MB on oxidation of the reaction mixture after the colour of MB had faded substantially. The oxidation was carried out by keeping the reaction mixture open to the atmosphere for about a week after diluting the reaction mixture with methyl alcohol followed by oxidation with FeCl₃. These results show that the decolouration process is not completely reversible which means that even if reaction (4) is an electron transfer one, reaction (5) may substantially lead to combination of the semiquinone with polystyryl radical.

DISCUSSION

The rate constants for the reaction between polymer radicals and MB as determined here are given in Table 3 along with the rate constants for reactions with Fe_{aq}³⁺ and FeCl₃. The *Q* and *e* values of the respective monomers are also included.

In this type of oxidative termination one would expect that a radical with an electron releasing substituent should react with MB at a faster rate than a radical with an electron withdrawing substituent. The highest rate constant observed in this work for a polystyrene radical is therefore expected. Previously, Beardwell²¹ noted that MB inhibits the AIBN initiated polymerization of 9-vinyl

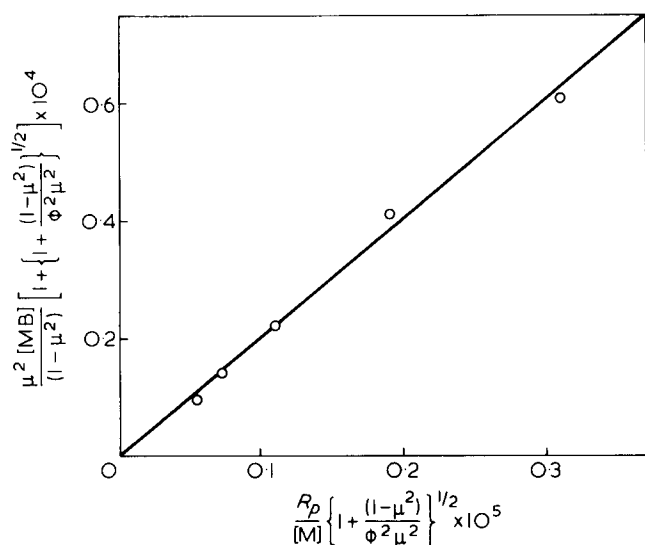


Figure 6 Plot according to equation (7) for styrene polymerization in presence of MB. $\phi = 100$

Table 2 Test of reversibility of the decolouration of MB in case of styrene polymerization in DMF at 60°C. [Styrene] = 4.31 mol dm⁻³; [AIBN] = 5.27 × 10⁻³ mol dm⁻³

Serial No.	[MB] _i × 10 ⁴ (mol dm ⁻³)	Reaction time (t) min at 60°C	[MB] _f × 10 ⁴ (mol dm ⁻³)	[MB] × 10 ⁴ after oxi- dation (mol dm ⁻³)	MB regenerated (%)
I	2.49	120	0.17	0.45	12.1
II	3.79	190	0.29	0.55	7.4
III	5.08	240	0.38	1.02	13.6

carbazole. This is in line with the greater electron donating ability of the poly(NVC) radical than that for the PSt radical as would be revealed from the *e* values of the Alfrey-Price *Q-e* scheme. The values are *e* = -1.40 for NVC and, *e* = -0.8 for styrene²⁹.

The low value of the rate constant for the PMMA radical with MB is rather unexpected. Previous studies on oxidative termination of polymer radicals with transition metal salts revealed that the PAN radical is only about 1.3 times as reactive as PMMA towards FeCl₃²⁵ and the PMMA radical is 4 times as reactive as the PAN radical towards CuCl₂¹².

However, the PMMA radical is not oxidized by the Fe³⁺ ion³⁰⁻³² while the PAN radical is³²⁻³⁴ (Table 3). However, the difference in behaviour of the two polymer radicals PMMA and PAN towards MB or Fe_{aq}³⁺ is not immediately apparent. This cannot be explained only in terms of the reactivity and polarity. Application of the *Q-e* scheme to the reaction of MB with polymer radicals gives rise to the following equation³⁵:

$$\ln Q_{MB} = \ln(Q_m k_4 / k_2) - e_m^2 + e_m e_{MB}$$

where *Q*_{MB} and *e*_{MB} are respectively the reactivity and polarity parameters of MB; *Q*_{*m*} and *e*_{*m*} are those parameters for the polymer radical; *k*₄ and *k*₂ having been defined earlier. Using the *k*₄ values for the PSt and PAN radicals as determined here and the *k*₂, *e*_{*m*} and *Q*_{*m*} values for these two radicals from the literature, *Q*_{MB} and *e*_{MB} were calculated to be 8.46 and 2.50 respectively. From these data and the values of *k*₂, *Q*_{*m*} and *e*_{*m*} applicable for MMA, *k*₄ was calculated to be 3617 with the PMMA radical. The measured value is way below this. This suggests that apart from reactivity and polarity some other factor must play a role. Recently Bamford³⁶⁻³⁸ demonstrated that the α -methyl group in the penultimate unit of the PMMA radical imposes a considerable steric hindrance in transfer reactions involving large atoms such as Br in CBr₄. Considering the large size of MB⁺ and also Fe_{aq}³⁺, the sluggish reaction of both of these with PMMA radical is therefore not unexpected on steric grounds. It

Table 3 Rate constants (*k*₄) for the reaction between polymer radicals and methylene blue at 60°C and the *Q* and *e* values for the respective monomers

Polymer radical	<i>k</i> ₄ × 10 ⁻³ (dm ³ mol ⁻¹ s ⁻¹)			<i>Q</i>	<i>e</i>
	MB ^a	Fe ³⁺ +b _{aq}	FeCl ₃ ^c		
PSt	20.9	—	54	1.00	-0.80 (assumed)
PMMA	0.12	~0	3.0	0.74	0.40
PAN	5.8	13.0	4.5	0.60	1.20

^a This work at 60°C in DMF

^b Refs. 32, 33 at 25°C in water

^c Ref. 25 at 60°C in DMF

should be noted in this connection that the steric effect as mentioned above, while it operates when a Br atom transfer from CBr_4 is involved, does not seem to do so when Cl atom transfer from FeCl_3 is involved. This follows from the fact that the reaction between FeCl_3 and polymer radicals obeys the $Q-e$ scheme³⁵. That steric hindrance may be responsible for the unexpected resistance towards oxidation of PMMA radical by $\text{Fe}_{\text{aq}}^{3+}$ has also been postulated earlier by Dainton and Seaman³².

Finally, studies of absorption spectra showed that MB exists as a monomer in the mixture of DMF and monomers. Therefore, we conclude that the MB monomer is an effective retarder in vinyl polymerization. This is in sharp contrast to the inference made by Chen¹ that only MB aggregates and not the MB monomer are effective in so far as oxidation of polymer radicals is concerned. Furthermore, Beardwell²¹ observed that MB inhibits polymerization of 9-vinylcarbazole in methyl alcohol solution. It is known that MB exists as a monomer in methyl alcohol. Beardwell's results thus show also that MB monomer is an effective chain terminator. Preliminary studies of acrylamide polymerization in presence of MB in an ethylene glycol medium indicate that the MB monomer is an effective chain terminator in acrylamide polymerization also. These and results with other monomers will be dealt with in a separate publication.

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