

Polymerization of vinyl acetate using visible radiation and a dye-reducing agent sensitizer:

2. Kinetic studies and polymerization mechanism*

D. R. Pemberton

Napier College, Colinton Road, Edinburgh EH10 5DT, UK

and A. F. Johnson

University of Bradford, Bradford, W. Yorkshire, BD7 1DP, UK

(Received 11 October 1982; revised 17 June 1983)

The polymerization of vinyl acetate photosensitized by ethyl eosin and ascorbic acid in aqueous methanol shows a marked induction period before polymerization commences, but thereafter, irradiation does not affect the rate of polymerization. Both dissolved oxygen and water are essential for polymerization, and the rate passes through a maximum as the concentration of dye or reducing agent is increased. A mechanism for the reaction is proposed involving initiation of polymerization by hydroxyl radicals. Polymerization initiated by reaction between hydrogen peroxide and ascorbic acid is also studied as this system is thought to participate in the photochemical system.

Keywords Photosensitized polymerization; visible radiation; kinetics; vinyl acetate; ethyl eosin; ascorbic acid

INTRODUCTION

Part 1 of this report examined the photochemistry of reactions which lead to the initiation of polymerization when visible radiation is used to induce reaction between ethyl eosin, ascorbic acid and dissolved oxygen in the presence of vinyl acetate monomer in aqueous methanol as solvent.

The investigations showed that in anaerobic conditions a relatively simple reaction occurred on irradiation in which the dye was reduced. In aerobic conditions, however, the reduction of the dye was retarded, and a complex reaction occurred involving dye, reducing agent and oxygen in which the overall effect in the early part of the reaction was reduction of oxygen to hydrogen peroxide and oxidation of ascorbic acid. When all dissolved oxygen had reacted, then the dye was reduced rapidly by reaction with any remaining ascorbic acid. The end products of reduction of ethyl eosin and oxidation of ascorbic acid were assumed to be leuco dye and dehydroascorbic acid, respectively, although the presence of these products was not confirmed, and they may undergo further reaction.

On irradiation of air saturated solutions it was shown that approximately 0.5 mol of hydrogen peroxide was produced for each mol of ascorbic acid consumed at low ascorbic acid concentrations ($<1.6 \times 10^{-3}$ mol dm⁻³) whilst in the presence of higher concentrations of ascorbic acid the final peroxide concentration was approximately 8×10^{-4} mol dm⁻³ and independent of the initial ascorbic acid concentration. The hydrogen peroxide then reacted very slowly with any remaining ascorbic acid. This process continued after irradiation ceased and has been shown to initiate the polymerization of vinyl acetate.

EXPERIMENTAL

Materials

The sources of the materials used and their purification have been reported in part 1¹.

Methods

Polymerization was followed in an irradiated dilatometer. The rate of polymerization was calculated from a knowledge of the density of monomer and polymer in solution² and the dimensions of the dilatometer. The rate data were cross-checked by gravimetry after each reaction and good agreement was found between the two techniques. The induction period before measurable polymerization was taken as the point of intersection of the extrapolation of the rectilinear part of the monomer conversion-time graphs with the time axis (see Figure 1, Part 1).

Polymerizations initiated by hydrogen peroxide with ascorbic acid were followed in a similar manner to that described previously except that the dilatometer was not irradiated. As the redox reaction between ascorbic acid and hydrogen peroxide begins as soon as the reactants are mixed the following procedure was adopted for preparing the reaction mixtures:

A 25 cm³ stoppered flask was prepared containing a known amount of ascorbic acid dissolved in methanol and vinyl acetate. In a second flask a solution containing hydrogen peroxide, water and methanol was prepared. The volume of the two solutions was adjusted by addition of methanol to give a total volume of 25 cm³. The flasks were deoxygenated separately with oxygen-free nitrogen for 30 min, the gas having been passed previously through

a similar solvent mixture to reduce excessive evaporation. The solutions were rapidly and thoroughly mixed in a nitrogen filled glove box and immediately transferred to a dilatometer which was stoppered and placed in a thermostatically controlled bath maintained at 30°C ($\pm 0.01^\circ\text{C}$) as quickly as possible.

RESULTS AND DISCUSSIONS

Photo-initiated polymerization

The variation of rate of reaction with dye concentration is given in Figure 1. No detectable polymerization occurred at initial dye concentrations $> 3 \times 10^{-4}$ mol dm $^{-3}$ or $< 1 \times 10^{-6}$ mol dm $^{-3}$. The maximum yield of polymer (up to 35% conversion to polymer) was obtained within this range, i.e. 1.15×10^{-5} mol dm $^{-3}$ dye. At lower dye concentrations a prolonged induction period was observed before polymerization occurred. It was also noticeable that at low dye concentrations the polymerization mixture and the polymer isolated were almost colourless, but at high dye concentrations the

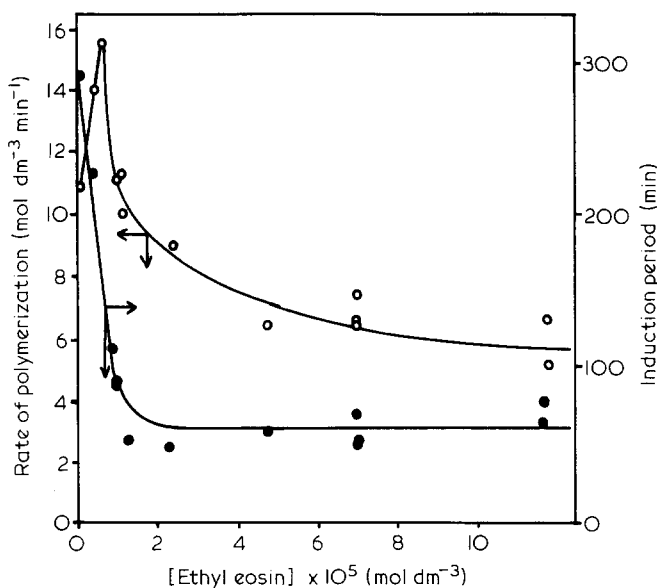


Figure 1 Effect of ethyl eosin concentration on the rate of polymerization and length of the induction period before the start of polymerization. [ascorbic acid] = 4.5×10^{-3} mol dm $^{-3}$; [vinyl acetate] = 2.17 mol dm $^{-3}$; [water] = 4.44 mol dm $^{-3}$

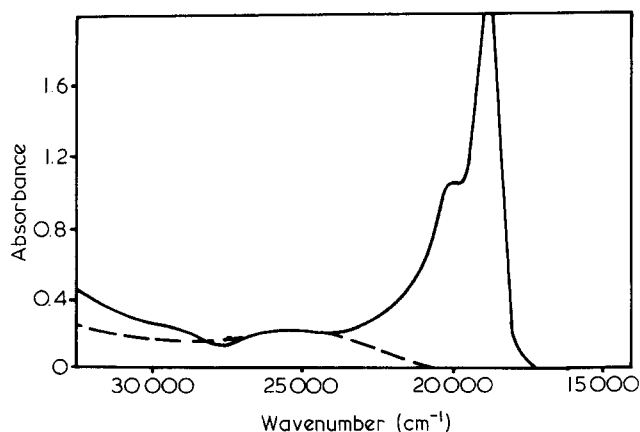


Figure 2 Spectrum of reaction mixture in methanol before irradiation (—) and after irradiation (---) and polymerization

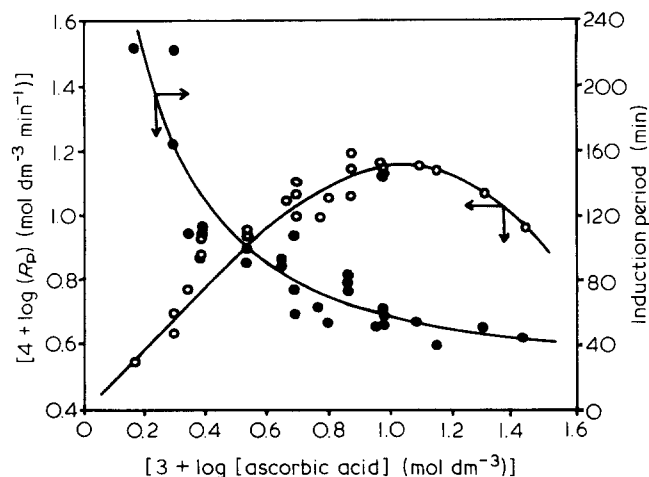


Figure 3 Effect of initial ascorbic acid concentration on the rate of polymerization and length of the induction period. [ethyl eosin] = 2.27×10^{-5} mol dm $^{-3}$; [vinyl acetate] = 2.17 mol dm $^{-3}$; [water] = 4.44 mol dm $^{-3}$

solution remained coloured throughout the polymerization and the polymer retrieved was yellow. The absorption spectrum of the final reaction solution was different from that of the dye (Figure 2).

The influence of reducing agent was similarly determined by varying its concentration. At low initial ascorbic acid concentrations ($< 10^{-3}$ mol dm $^{-3}$), no polymerization occurred, and the dye colour did not fade completely. At higher concentrations the rate of polymerization was approximately proportional to the ascorbic acid concentration, the slow reaction given at initial ascorbic acid concentrations of $\approx 2 \times 10^{-3}$ mol dm $^{-3}$ showing a marked increase in rate as the reaction progressed. The rate of reaction attained a maximum at an ascorbic acid concentration of approximately 1×10^{-2} mol dm $^{-3}$, above which the rate again decreased (Figure 3). The length of the induction period was reduced by increasing the ascorbic acid concentration (Figure 3).

The polymerization has an order of approximately 3/2 with respect to the vinyl acetate concentration (Figure 4), and 0.7 with respect to the water concentration (Figure 5). Increasing the monomer concentration increased the induction period, whereas an increase in water concentration decreased the induction period. At low water concentrations the reaction, although slower, continued for a much longer period. For example, at a water concentration of 2.2 mol dm $^{-3}$, the reaction continued at a steady rate for three days after irradiation for 7 h. With very low water concentrations no polymer was produced although the dye fading reaction did occur slowly.

Variations in the light intensity had little or no effect on the rate of polymerization, although it did influence the induction period (Table 1).

A qualitative study was carried out into the effect of oxygen on the polymerization reaction. If the reaction mixture was carefully deoxygenated by passing nitrogen through the mixture in the dilatometer for 30 min prior to irradiation, no polymerization occurred, although the dye faded rapidly during irradiation. Inefficient oxygen removal (passing nitrogen through the solution for 5 min) gave enhanced polymerization rates and shorter induction periods, although the polymerization reaction was short lived, and the final yield of polymer was small (Figure 6).

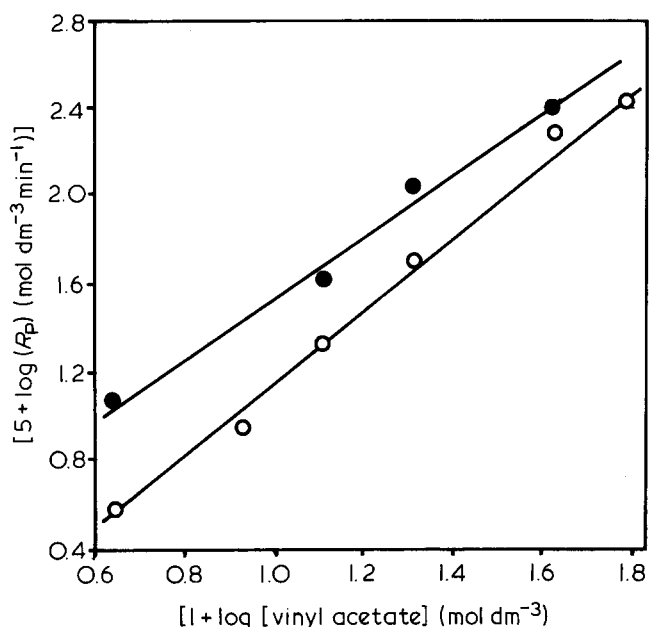


Figure 4 Rate of polymerization (R_p) with vinyl acetate concentration. ●, [ethyl eosin] = 1.15×10^{-5} mol dm $^{-3}$; [ascorbic acid] = 4.5×10^{-3} mol dm $^{-3}$; [water] = 4.44 mol dm $^{-3}$. ○, [ethyl eosin] = 2.27×10^{-5} mol dm $^{-3}$; [ascorbic acid] = 1.96×10^{-3} mol dm $^{-3}$; [water] = 4.44 mol dm $^{-3}$

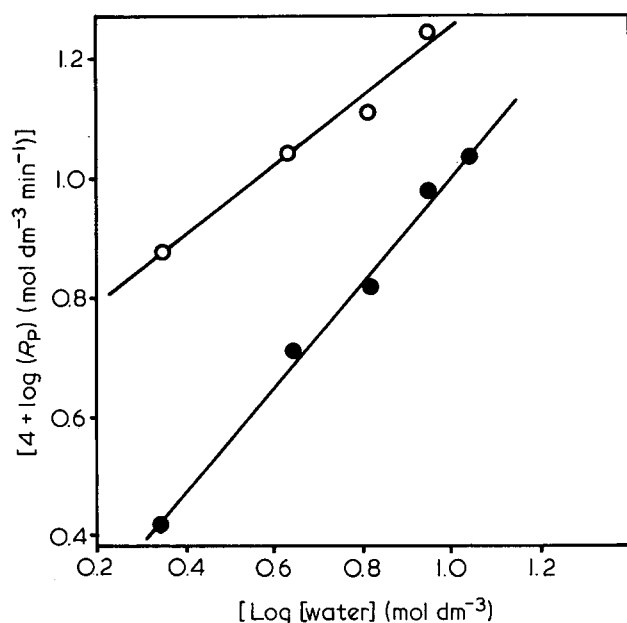


Figure 5 Rate of polymerization (R_p) with water concentration. ●, [ethyl eosin] = 2.27×10^{-5} mol dm $^{-3}$; [ascorbic acid] = 1.96×10^{-3} mol dm $^{-3}$; [vinyl acetate] = 2.17 mol dm $^{-3}$. ○, [ethyl eosin] = 1.15×10^{-5} mol dm $^{-3}$; [ascorbic acid] = 4.5×10^{-3} mol dm $^{-3}$; [vinyl acetate] = 2.17 mol dm $^{-3}$

The results of this study, although similar in some respects to those of other investigators of dye/reducing agent-initiation, have some distinctive features. The most clear difference is the fact that in the work reported here, the rate of polymerization is unaffected by light intensity, and the polymerization reaction does not occur until all the dye has been destroyed. A further pointer to a distinctive and complex reaction sequence is the fact that the rate of polymerization is almost independent of the dye concentration.

The course of the polymer reaction is much more sensitive to the ascorbic acid concentration. The fact that with low ascorbic acid concentrations no polymerization occurs (although it may be present in higher concentration than the dye), indicates its involvement not only in the photo-initiated reaction sequence, but also in the subsequent reactions leading directly to the initiation of polymerization. The fact that there is no polymerization at low concentrations of ascorbic acid could be attributed to its complete consumption in side reactions in the initial stages of the reaction sequence.

It has been shown¹ that hydrogen peroxide is generated in the photo-initiated reaction between the dye, reducing agent and oxygen. It is probable that this hydrogen peroxide subsequently undergoes a redox reaction with ascorbic acid producing free radical species which could initiate polymerization. To test whether this reaction is responsible for initiation of polymerization a brief study has been made of the direct polymerization of vinyl acetate using the redox system without involving radiation sources.

Initiation of polymerization by hydrogen peroxide and ascorbic acid

Before exploring this reaction in some detail, it is interesting to note that if a typical reaction mixture for

Table 1 Influence of light intensity on initial polymerization rate. All samples contain ethyl eosin (2.27×10^{-5} mol dm $^{-3}$) ascorbic acid (3.93×10^{-3} mol dm $^{-3}$), vinyl acetate (2.17 mol dm $^{-3}$) and water (4.44 mol dm $^{-3}$)

Relative light intensity	Polymerization rate $\times 10^4$ (mol dm $^{-3}$ min $^{-1}$)	Induction period (min)
1.0	7.1	117
1.0	6.2	122
0.48	7.5	140
0.48	7.1	162
0.26	6.4	214
0.12	7.6	322

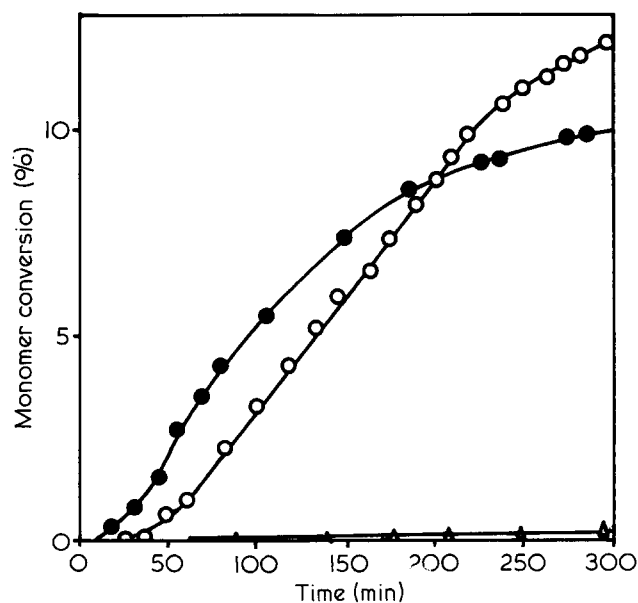


Figure 6 Effect of oxygen on the rate of polymerization. ○, Air saturated; ●, purged with nitrogen for 5 min; △, purged with nitrogen for 30 min. [ethyl eosin] = 2.27×10^{-5} mol dm $^{-3}$; [vinyl acetate] = 2.17 mol dm $^{-3}$; [ascorbic acid] = 1.96×10^{-3} mol dm $^{-3}$; [water] = 4.44 mol dm $^{-3}$

photochemical initiation studies (see Table 1) is taken, thoroughly deoxygenated, and irradiated for 2 h, no polymerization occurs but the dye colour is completely discharged. If a small quantity of deoxygenated hydrogen peroxide is then introduced to the reaction mixture, polymerization commences immediately and at a similar rate to that normally observed in the photo-initiated polymerizations.

A separate series of experiments was carried out in which the hydrogen peroxide concentrations used were approximately the same as those produced in a typical photo-initiated polymerization reaction, e.g. 9×10^{-4} mol dm⁻³. Similar vinyl acetate and water concentrations were also used to those in the photopolymerization reactions. The results obtained by varying the ascorbic acid concentrations only are given in Table 2.

With water, hydrogen peroxide and monomer concentrations maintained constant, the initial rate of polymerization was proportional to the square root of the ascorbic acid concentration for low values of the concentration, with a maximum rate in the reaction with 5×10^{-3} molar ascorbic acid. The overall conversion of monomer increased with increasing ascorbic acid concentrations to a peak value when the concentrations of ascorbic acid and hydrogen peroxide were equal, decreasing when the ascorbic acid was present in excess. The monomer conversion time curves show the following features:

(1) Unlike the photo-initiated processes, the redox initiated polymerization started immediately the reagents were mixed. Short induction periods were observed in some cases but the phenomenon was irreproducible and can be attributed probably to small quantities of oxygen present as impurity.

(2) The rate of polymerization decreases with time, unlike the case of the photo-initiated reactions where the rate of reaction remains essentially unchanged over a wide range of conversion. At low ascorbic acid concentrations where the hydrogen peroxide concentration greatly exceeds that of the acid, a plot of log (rate of polymerization) against log (concentration of monomer less concentration remaining when reaction ceased) reveals an overall reaction order of 0.4 with respect to

monomer. When the ascorbic acid was in large excess with respect to the hydrogen peroxide an overall order of reaction of 0.8 with respect to monomer is observed.

The initial rates of reaction in these experiments are approximately ten times greater than the initial rates of the photo-initiated reactions. Although not the only explanation, it could be that the photo-initiated reactions are retarded by other components in the reaction mixture. In an attempt to substantiate this postulate two experiments were carried out. In the first, a small quantity of ethyl eosin solution was added to the reaction mixture. Reaction was slightly retarded but the effect was small (Table 2). The dye colour faded during the first 5–10 min of the reaction, and the solution became yellow despite the fact that the reaction mixture was not exposed to light.

In the second, a mixture of ethyl eosin and an excess of ascorbic acid in methanol was deoxygenated and irradiated until the dye colour was just destroyed. A solution of monomer and hydrogen peroxide were added and the mixture then transferred to the dilatometer. The initial rate of polymerization observed was substantially reduced as compared with the rate expected in the absence of dye. Apparently the products of the dye/reducing agent reaction can retard polymerization although these experiments give no information concerning the precise nature of the retarder. Neither does the experiment truly mimic the likely course of the photo-initiated reaction. For example, the solution used in this experiment had been deoxygenated before irradiation. If dehydroascorbic acid is the retarder more of this compound would be produced by photo-reaction in the presence of oxygen leading to greater retardation as ascorbic acid is oxidized in the dye/reducing agent/oxygen reaction. This latter comment is explored further later.

What the results clearly indicate is that the polymerization of vinyl acetate can be initiated by a redox system consisting of ascorbic acid and hydrogen peroxide. Furthermore, as hydrogen peroxide has been identified as a product of the photochemically-induced reaction in the presence of oxygen, and because no polymerization could be detected in the photo-initiated process unless an excess of ascorbic acid was present, then it can be inferred that a similar mechanism to that for the non-photochemical processes must be operative in the latter case.

Table 2 Hydrogen peroxide/ascorbic acid initiated polymerization. All solutions contained: vinyl acetate (2.17 mol dm⁻³) and water (4.44 mol dm⁻³), solvent methanol

Ascorbic acid concentration $\times 10^4$ (mol dm ⁻³)	Hydrogen peroxide concentra- tion $\times 10^4$ (mol dm ⁻³)	Initial rate of polymerization $\times 10^3$ (mol dm ⁻³ min ⁻¹)	Reaction order	Final yield of polymer (%)
1.96	9.0	4.0	0.4	20
3.93	9.0	5.9	0.7	38
5.89	9.0	7.4	0.8	43
9.82	9.0	11.9	0.8	41
19.64	9.0	13.1	0.9	40
39.28	9.0	14.8	0.8	30
78.56	9.0	14.6	0.8	34
196.40	9.0	6.7	0.9	14
196.40	9.0	6.4	1.0	12
19.64	9.0	10.1 ^a	—	32
19.64	9.0	5.0 ^b	—	—
9.89	7.0	1.11 ^c	—	—
9.89	7.0	12.6	—	—

^a Ethyl eosin (2.27×10^{-3} mol dm⁻³)

^b Ethyl eosin (2.27×10^{-3} mol dm⁻³). The mixture of ethyl eosin and ascorbic acid was deoxygenated and irradiated to destroy the dye before addition of hydrogen peroxide and monomer

^c The mixture was saturated with air. There was an induction period of approximately 330 min before the reaction started

It is noteworthy that although the redox initiated reaction is much faster than the photo-initiated reaction, the effect of ascorbic acid on the rate of reaction is similar in both systems as shown in Figure 7. In both cases the rate of reaction passes through a maximum as the ascorbic acid concentration is increased, although the maximum occurs at higher ascorbic acid concentrations in the photo-initiated reaction than in the case of redox initiation. This is entirely consistent with the view expressed earlier that the photochemical process may be retarded. A retarder might be expected to have greater influence on the reaction with low ascorbic acid concentrations, thus shifting the observed maximum to higher concentrations of ascorbic acid.

REACTION MECHANISM

The major observations which any reaction scheme must explain are as follows:

(1) There is an induction period prior to polymerization during which time the dye colour fades completely.

(2) Polymerization continues for a long period after irradiation has been discontinued indicating that the radicals produced during irradiation, i.e. the semiquinone dye and semi-reduced ascorbic acid are not responsible for the initiation of polymerization.

(3) Dye, reducing agent, oxygen and water are all necessary for polymerization to occur. The oxygen, similar to the dye, is consumed during the induction period. There is an optimum ascorbic acid concentration for effective photo-induced polymerization: Too high a concentration gives low polymerization rates. Too low a concentration will give no polymerization at all. Water is necessary for polymerization to occur, although its addition can be effective even after the dye has faded.

(4) The light intensity has no effect on the rate of polymerization although increasing its intensity does increase the length of the induction period.

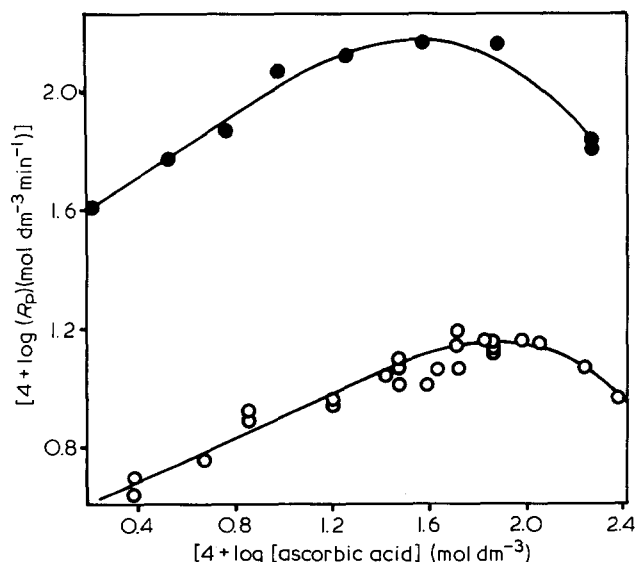
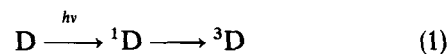


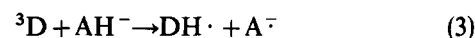
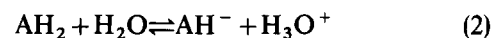
Figure 7 Effect of ascorbic acid concentration on the rate of polymerization. ●, Redox [hydrogen peroxide/ascorbic acid] initiation. [hydrogen peroxide] = 9.0×10^{-4} mol dm $^{-3}$; [vinyl acetate] = 2.17 mol dm $^{-3}$; [water] = 4.44 mol dm $^{-3}$. ○, Photo-initiation (ascorbic acid concentrations corrected to allow for that used in the initial dye fading reaction). [ethyl eosin] = 2.27×10^{-5} mol dm $^{-3}$; [vinyl acetate] = 2.17 mol dm $^{-3}$; [water] = 4.44 mol dm $^{-3}$.

A possible mechanism which explains these observations can be arrived at as follows:

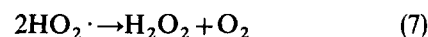
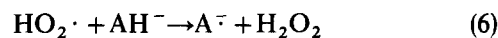
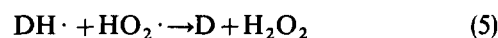
In the first instance, light is almost certainly absorbed by the monomeric form of the dye ethyl eosin (D) giving the excited triplet form of the dye (3D) via the singlet state (1D) as shown in equation (1)



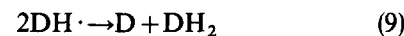
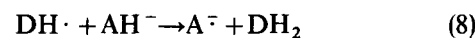
The excited triplet may react with ascorbic acid producing the semiquinone dye ($DH\cdot$) and semi-oxidized ascorbic acid (A^-). The species that undergoes this reaction is the mono-ion of ascorbic acid (AH^-)¹:



where AH_2 represents undissociated ascorbic acid. Direct reaction between the triplet dye and oxygen has been excluded as no reaction was observed in the absence of reducing agent. In the presence of oxygen the semiquinone dye can react to form hydrogen peroxide by the route outlined in equations (4)–(7).



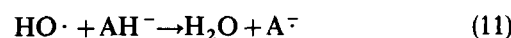
When all the oxygen has been consumed by the above reactions, the dye is reduced to the leuco form either by reaction with ascorbic acid (equation (8)) or disproportionation of the semiquinone radicals (equation (9)):



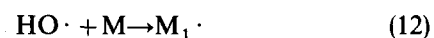
It did not prove possible to recover the dye once the colour had been destroyed, and it is probable that the leuco dye undergoes further reaction. The semi-oxidized ascorbate ion (A^-) will similarly undergo further reaction being oxidized to dehydroascorbic acid by reaction with 3D or $HO_2\cdot$ analogous to equations (3) and (6), or by disproportionation (equation (16)).

Both the $DH\cdot$ and A^- radicals are stabilized by delocalization of the unpaired electron, and are not sufficiently reactive to act as initiators for polymerization. Their presence, together with unreacted oxygen, will inhibit polymerization during this initial phase of the reaction sequence. Changing the intensity of irradiation will affect the rate of these reactions but will not affect the amount of hydrogen peroxide generated. As subsequent reactions of the peroxide are very slow in comparison with these reactions, rates of the following processes (equations (10)–(19)) will be independent of the intensity of irradiation used, and will continue after irradiation has been discontinued.

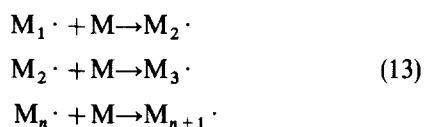
Any ascorbic acid which might remain after these reactions have taken place can react with the hydrogen peroxide to produce free radicals, equations (10) and (11):



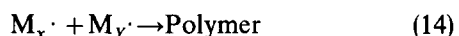
The precise nature of the radicals which initiate polymerization has not been established but $A^{\cdot-}$ radicals, in which the unpaired electron is delocalized in the highly conjugated tricarbonyl system, is unlikely to act as initiator, whereas the hydroxyl radicals are very reactive and are known to initiate the polymerization of vinyl acetate (equation (12)):



The usual propagation reactions would follow initiation, equation (13):



Termination of the growing chains may occur by combination or disproportionation reactions, equation (14)



or by reaction with the relatively stable $A^{\cdot-}$ radical:



There would be competition for the $A^{\cdot-}$ species which are probably removed in the bimolecular reaction shown in equation (16) or the unimolecular process shown later (equation (19)):

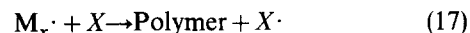


(A^{2-} represents the dianion of ascorbic acid and A represents dehydroascorbic acid).

The fact that the rate of polymerization in the photo-initiated reactions is much less than in the direct ascorbic acid/hydrogen peroxide initiated reactions merits further comment. This observation, together with the fact that the rate of reaction frequently increased in the latter stages,

often long after irradiation had ceased, suggests that some species is formed in the photo-initiated reaction sequence which is also acting as a chain terminator.

The reaction can be schematically represented by equation (17):



where X represents the retarder molecule. The identity of X is not clear but could be either the leuco dye or the dehydroascorbic acid. It has been shown that the photo-initiated polymerization is slowed by the presence of high initial dye concentrations, but this effect is small. However, high initial rates of polymerization were achieved when the photosensitive mixture was partially deoxygenated before irradiation. Also, relatively high rates were achieved in the direct ascorbic acid/hydrogen peroxide initiated reaction in the presence of deoxygenated, irradiated ascorbic acid/dye mixture. In the latter cases the main effect would be to produce lower concentrations of dehydroascorbic acid than in the standard photo-initiated polymerization. This suggests that the retarder is dehydroascorbic acid. The retarder, as well as reacting with the growing polymer chains, may also remove other free radicals from the reaction sequence:



The changes in concentration of the main reactants during the reaction sequence due to these reactions are summarized diagrammatically in Figure 8.

Kinetic analysis

It is possible to apply the conventional steady-state hypothesis to the redox initiated polymerization sequence which has been postulated if it is assumed that polymerization takes place by a free radically induced chain mechanism. If the pre-initiation processes are ignored and attention is focused on the polymerization

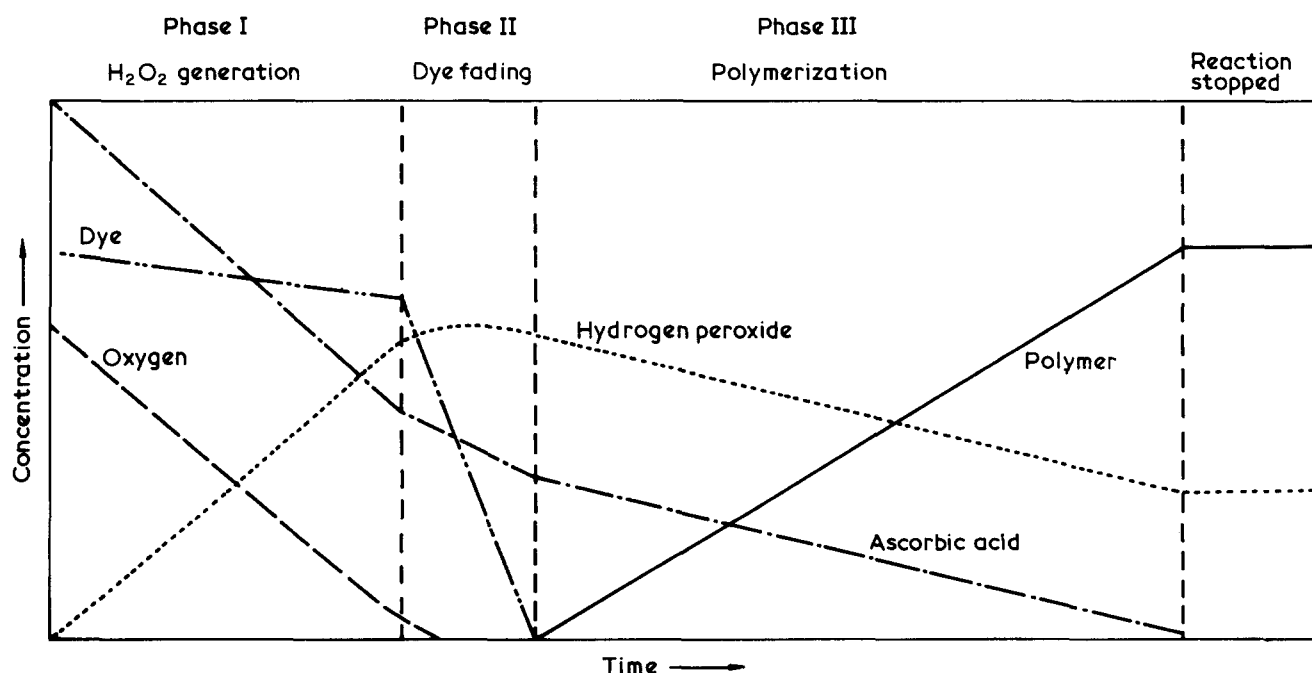


Figure 8 Diagrammatic representation of the changes in concentration of the various species in the overall reaction mechanism

stage of the reaction only, then two sets of conditions can be distinguished, i.e. reactions where the ascorbic acid concentrations is either low or high in relation to that of the dye in the reaction mixture.

When ascorbic concentrations are low most of the acid will be used in the initial photoreaction leaving very little residual acid present at the start of the polymerization reaction. The concentration of retarders however, will be just as great as in experiments where the initial ascorbic concentrations were higher. Consequently, the rate of reaction (11) is probably low and negligible in comparison with other reactions involving HO· radical (i.e. reactions (12) and (18)). Termination of the growing chains is also more likely by reaction with the retarder than by mutual reaction or with semi-reduced ascorbic acid. Thus by taking into account reactions (2), (10), (12), (13) and (17)–(19) and neglecting reactions (11) and (14)–(16), the rate of polymerization is:

$$\frac{-d[M]}{dt} = \frac{K^{1/2}k_{10}k_{12}k_{13}[M][H_2O_2][AH_2]^{1/2}[H_2O]^{1/2}}{k_{17}[X](k_{12}[M] + k_{18}[X])} \quad (20)$$

where K is the first dissociation constant for ascorbic acid, and k is the rate constant for the reaction indicated by the subscript. Equation (20) agrees reasonable well with the experimental results. The order of reaction with respect to ascorbic acid found experimentally was close to unity, but if allowance is made for the quantity used in the photo-induced reaction with dye and oxygen, the rate of polymerization is found within experimental error at the start of the polymerization reaction to be proportional to the square root of the ascorbic acid concentration (see *Figure 7*). Similarly, the order with respect of water was found to be between 0.6 and 0.8 which allowing for experimental error and the effect of water on the first stage of the reaction sequence, represents satisfactory agreement with the chain reaction model predictions. The order with respect to monomer of 3/2 is intermediate between the values of 1 and 2, which theory predicts depending on the efficiency of the initiation reaction. Note that the order with respect to retarder is between -1 and -2 . If leuco dye was the species responsible, then excess dye added to the mixture should cause a rapid decline in

the rate of reaction. This was not found to be the case, which is further evidence that the retarder could be dehydroascorbic acid, the concentration of which would not be greatly affected by the addition of excess dye.

At high ascorbic acid concentrations reaction (11) would become more significant, leading to a higher concentration of semi-reduced ascorbic acid radicals. Hence, the most important termination reaction under these conditions is likely to be reaction (15). Taking into account reactions (10)–(13), (15) and (16), and neglecting reactions involving the retarder, i.e. reactions (17) and (18) and applying the steady-state approximation, the rate of polymerization is:

$$\frac{-d[M]}{dt} = \frac{k_{12}k_{13}[M]^2}{k_{15}} \times \left(\frac{k_{10}k_{16}[H_2O]}{k_{11}(k_{11}K^{1/2}[AH_2]^{1/2}[H_2O]^{1/2} + k_{12}[M])} \right)^{1/2} \quad (21)$$

Equation (21) could not be substantiated with the data reported, since the rates of the photo-initiated reactions remained considerably slower at all ascorbic acid concentrations than the directly initiated redox reactions. Nevertheless, this expression for the rate of loss of monomer does indicate that excess of ascorbic acid will lead to lower polymerization rates. In practice, the rates decrease more rapidly than equation (21) would suggest with increasing ascorbic acid. However, the rates of the photo-initiated reactions are predicted to be less influenced than the direct redox reaction.

ACKNOWLEDGEMENTS

The authors wish to express gratitude to the Principal and staff of Norwich City College and also to Dr W. Schmidt, formerly of Scott-Bader & Co., for support and encouragement.

REFERENCES

- 1 Pemberton, D. R. and Johnson, A. F. *Polymer* 1984, **25**, 536
- 2 Collins, E. A., Bâres, J. and Billmeyer, F. 'Experiments in Polymer Science', Wiley, 1973, p. 87