The Role of Radiolytically Generated Species in Radiation-induced Polymerization of Vinylbenzyltrimethylammonium Chloride (VBT) in Aqueous Solution: Steady-state and Pulse Radiolysis Study

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Vinylbenzyltrimethylammonium chloride/Pulse radiolysis/Radiation polymerization/Cross-linking/Degradation.

Radiation-induced polymerization of vinylbenzyltrimethylammonium chloride (VBT) in aqueous solution has been investigated by steady-state and pulse radiolysis techniques. The effects of dose, dose rate, monomer concentration, pH, and ambient conditions on steady state polymerization were investigated. The reactions of primary radicals of water radiolysis, such as OH radical, e\textsubscript{aq}, and H atom, were studied. The reactions of other chemically active species such as O\textsuperscript{2–}, oxidizing radicals such as N\textsubscript{3}, Cl\textsubscript{2–}, Br\textsubscript{2–}, SO\textsubscript{4}–, and a reducing specie such as CO\textsubscript{2–} with VBT were also investigated. The reaction of VBT with OH radical and H atom were investigated by formation kinetics and by competition kinetics. The rate constant values for the reaction of OH radical with VBT were 4.7 \times 10^{9} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} and 1.7 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} by formation kinetics and by competition kinetics, respectively. The hydrated electron reacts with VBT with a rate constant of 1.9 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} to form an anion. At pH 1, H atom reaction with VBT is diffusion controlled with a rate constant of 5.1 \times 10^{9} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} as determined by formation kinetics and 1.7 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} as determined by competition kinetics. VBT radical anion reacts with VBT at a rate that is almost twice the rate at which VBT radical cation reacts with VBT, indicating anionic initiation of the polymerization of VBT. VBT undergoes very fast steady-state polymerization and dose rate; the presence of efficient radical quenchers such as oxygen and concentration of VBT in the aqueous solution affects the extent of polymerization. Typically, a dose of 4 kGy is sufficient to achieve 80–85% polymerization. The monomer solution shows a drastic increase in the viscosity of the solution, which finally gels to a soft rubbery mass.

INTRODUCTION

Synthesis and the thermochemical polymerization of styrene-based trialkyl ammonium salts of the polycationic family have been of great interest to many workers recently\textsuperscript{1–3}. Among the poly (trialkyl ammonium salts), poly (vinyl benzyl trimethyl ammonium chloride) [PVBT] has been reported to be the most chemically stable polymer\textsuperscript{4}. PVBT membranes have been proposed for the electrolysis of water at low voltage\textsuperscript{5}, as bactericidal polymer\textsuperscript{6,7}, for molecular recognition\textsuperscript{8}, and for synthesizing radiation-grafted copolymers\textsuperscript{9} with high selectivity for heavy metal ions. The thermochemical polymerization of vinyl benzyl trimethyl ammonium chloride (VBT) and similar ammonium chlorides salt has been reported earlier\textsuperscript{10}. The cross-linking of PVBT by UV and X-ray radiation\textsuperscript{10,11} has also been well documented. The pulse radiolysis technique has proven to be the most powerful technique to study the reactions of short-lived intermediates in the polymerization of synthetic monomers\textsuperscript{12}, of biopolymers\textsuperscript{13}, and of biologically important molecules\textsuperscript{14–16}. The pulse radiolysis studies of 2-[(methylacryloxy)ethyl]trimethyl ammonium chloride (MADQUAT)\textsuperscript{17} and its steady state polymerization\textsuperscript{19} has also been reported recently. To the best of our knowledge, however, neither pulse radiolysis studies nor the steady-state polymerization of VBT has been reported. In the present study we have extensively investigated the radiation polymerization of VBT, which readily ionizes to a cationic species in aqueous solution. The pulse radiolysis studies
of VBT in aqueous solution were carried out to elucidate the nature and characteristic of transient species involved in the process of its polymerization because several reactive intermediates such as ions, excited molecules, and radicals are formed during radiolysis, and any of the reactive species, viz., free radical, radical cation, or radical anion, can initiate the polymerization process. These studies were compared with the radiation chemistry of parasodium styrene sulphonate, which ionizes to an anion in aqueous medium\(^{19}\). Further steady-state radiation studies were carried out to investigate changes in the viscosity of monomer solution and to see the effect of radiation dose, dose rate, concentration, and pH on its extent of polymerization.

**MATERIALS AND METHODS**

Vinylbenzyltrimethylammonium chloride (VBT), Mol. wt. 211.74 in powder form, from Aldrich was used as received. All other chemicals were of AnalyR grade. Nanopure water (conductivity 0.6 \(\mu\)S cm\(^{-1}\)), obtained by passing distilled water through a Barnstead Nanopure purifying system, was used for preparing all solutions. The pH values of solutions were adjusted using HClO\(_4\), \(\text{KH}_2\text{PO}_4\), \(\text{Na}_2\text{HPO}_4\), \(\text{H}_2\text{O}\), and \(\text{NaOH}\) in appropriate quantities. IOLAR grade (purity 99.9\%) gases \(\text{N}_2\) or \(\text{N}_2\text{O}\) used for purging solutions were obtained from Indian Oxygen Limited. For steady-state gamma irradiation, a gamma chamber was used with suitable attenuators. A UV-Vis 2000 spectrophotometer from Shimadzu was used for monitoring absorbance. Viscometry studies were carried out with an Ubbelholde viscometer from M/s Scam India at a temperature of 25 ± 0.5°C.

**Polymerization of VBT**

The absorption spectra of aqueous solution of VBT showed strong absorption at 254 nm with molar extinction coefficient (1 \(\epsilon_{254} = 20,950 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}\)). The polymerization of VBT was followed spectrophotometrically by measuring the decrease in the absorption of monomer at this wavelength.

**Pulse radiolysis dosimetry**

Dosimetry measurements were carried out by using aerated 1 \(\times 10^{-2}\) mol dm\(^{-3}\) KSCN, and (SCN)\(_2^-\) radicals were monitored at 500 nm. The absorbed dose per pulse was calculated by using \(\Phi = 21520 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1} \text{ sec}^{-1} \times 100 \text{ eV}\) for (SCN)\(_2^-\) radicals\(^{20}\), where \(\epsilon\) is the molar absorptivity and \(G\) is the radiation chemical yield expressed as the number of molecules formed or destroyed per 100 eV of energy absorbed.

**Pulse radiolytic procedure**

Pulse radiolysis studies were carried out to determine the rate constants between radiolytic products of water and VBT, the preferential mode of reaction of \(\text{OH}\) with VBT, and to determine the rate of reactions of transient formed by the reaction of VBT with primary radiolytic products with VBT or the reaction medium by irradiating solutions in 1 cm square suprasil cuvettes with 50 ns electron pulses from a 7 MeV linear electron accelerator (LINAC). The details of the pulse radiolysis setup used are described elsewhere\(^{21,22}\).

**Pulse radiolysis experiments**

When \(\text{H}_2\text{O}\) is irradiated, the following primary radicals are produced

\[
\text{H}_2\text{O} \rightarrow \text{OH}, \text{H}^+, e^-_{\text{aq}}
\]

To study the reactions of these radiolytic products with VBT, either of them was generated selectively in the medium by methods described earlier in the literature\(^{23}\). To selectively produce OH radicals, the solutions were saturated with \(\text{N}_2\text{O}\) before pulse irradiation. This resulted in the scavenging of \(e^-_{\text{aq}}\), and under these conditions the yield of OH radicals was 90% of the total radicals \(G(\text{OH}) = 5.4 \text{ mol/100 eV}\). The remaining 10% contribution was of H atoms; \(G(\text{H}) = 0.6 \text{ mol/100 eV}\).

\[
\text{N}_2\text{O} + e^-_{\text{aq}} \rightarrow \text{N}_2 + \text{OH}^- + \text{OH}
\]

For investigating the reaction of H radicals, they were selectively generated by radiolyzing the solution at pH -1 in presence of \(t\)-butanol. At low pH, \(e^-_{\text{aq}}\) in the medium react with \(H^+\) ions to give \(H^+\) radicals, and OH radicals are scavenged by \(t\)-butanol.

\[
e^-_{\text{aq}} + \text{H}^+ \rightarrow \text{H}^+
\]

\(e^-_{\text{aq}}\) were selectively generated by pulse radiolyzing of the solutions in the presence of 0.3 mol dm\(^{-3}\) \(t\)-butanol (at near neutral pH), which scavenges the \('\text{OH}\) radicals.

\[
\text{'OH} + (\text{CH}_3)_2\text{COH} \rightarrow \text{H}_2\text{O} + (\text{CH}_3)_2\text{C(\text{CH}_3)}_2\text{OH}
\]

The rate of reaction of \('\text{OH}\) and \(H^+\) with VBT were followed by formation kinetics and by competition kinetics. The formation of the transient with OH radical was investigated by observing the absorption at 350 nm \(k_{\text{abs}}\) in an \(\text{N}_2\text{O}\)-saturated aqueous solution of VBT in the concentration range of 0.1–1 \(\times 10^{-3}\) mol dm\(^{-3}\). Over this range, the pseudo-first order rate \(k_{\text{abs}}\) was found to increase with solute concentration. The bimolecular rate constant was determined from the slope of the linear plot of \(k_{\text{abs}}\) vs. solute concentration. In the competition kinetic study, \(\text{N}_2\text{O}\) saturated aqueous solutions containing 1 \(\times 10^{-4}\) mol dm\(^{-3}\) KSCN and different concentrations of VBT in the range (0.1–1) \(\times 10^{-4}\) mol dm\(^{-3}\) were pulsed and the absorbance at 500 because of (SCN)\(_2^-\) was measured immediately after the electron pulse.

The two competing reactions involved

\[
\text{'OH} + \text{SCN}^- \rightarrow \text{SCN}^- + (\text{SCN})_2^- \quad (5)
\]

\[
\text{'OH} + \text{VBT} \rightarrow \text{products} \quad (6)
\]

leads to relation

\[
A_o/A = 1 + \{k_{\text{VBT}} + k_{\text{OH}}[\text{VBT}] / k_{\text{SCN}}^- + k_{\text{OH}}[\text{SCN}^-]\} \quad (7)
\]

where \(A_o\) and \(A\) are the transient absorbances of the solutions.
at 500 nm in the absence and presence of VBT, respectively. The substitution of $k_{\text{SCN-OH}}$ of $1 \times 10^{10}$ dm$^3$ mol$^{-1}$ s$^{-1}$ at pH 1 was evaluated.

For a determination of the rate of reaction of H atom with VBT by transient formation, the $(0.1-1) \times 10^{-3}$ mol dm$^{-3}$ solution of VBT was pulse radiolyzed in the presence of $0.3$ mol dm$^{-3}$ $t$-butanol at pH 1. For the competition kinetics study of H, tetra-cycline was used as a reference solute. N$_2$-bubbled aqueous solutions at pH ~ 1 containing $5 \times 10^{-4}$ mol dm$^{-3}$ tetra-cycline (TC) and varying concentrations of $(0.1-1) \times 10^{-3}$ mol dm$^{-3}$ of VBT and $0.3$ mol dm$^{-3}$ $t$-butanol as ‘OH scavenger were pulsed, and absorbance at 440 nm because of the TC-H adduct was measured immediately after the electron pulse. By using $k_{\text{TC-H}}$ of $2.5 \times 10^{9}$ dm$^3$ mol$^{-1}$ s$^{-1}$, we evaluated $k_{\text{VBT-H}}$.

Secondary one-electron oxidants were produced by the reaction of ‘OH radicals with inorganic anions via the following reactions:

\begin{align}
\text{‘OH} + \text{N}_3^- & \rightarrow \text{N}_3^+ + \text{OH}^- \quad (8) \\
\text{‘OH} + \text{Cl}^- & \rightarrow \text{Cl}^+ + \text{OH}^- \quad (9) \\
\text{Cl}^- + \text{Cl}^- & \rightarrow \text{Cl}_2^- \quad (9) \\
\text{‘OH} + \text{Br}^- & \rightarrow \text{Br}^+ + \text{OH}^- \quad (10) \\
\text{Br}^- + \text{Br}^- & \rightarrow \text{Br}_2^- \\
\text{S}_2\text{O}_5^2^- + \text{e}_{\text{aq}}^- (\text{H}) & \rightarrow \text{SO}_4^{2-} + \text{SO}_3^{2-} (\text{HSO}_4^-) \quad (11)
\end{align}

The ‘OH radicals can react with VBT in three different ways, namely (i) electron transfer; (ii) addition-forming OH adduct; and (iii) abstraction of the H atom. In the first way, radical cation is produced, whereas in the latter two a radical is formed, as shown in Reactions 12–14

\begin{align}
\text{VBT} + \text{‘OH} & \rightarrow \text{VBT}^+ + \text{OH}^- \quad (12) \\
\text{VBT} + \text{‘OH} & \rightarrow \text{VBT}^- + \text{OH}^- \quad (13) \\
\text{VBT} + \text{‘OH} & \rightarrow \text{VBT}(-\text{H}) + \text{H}_2\text{O} \quad (14)
\end{align}

To distinguish between addition and the electron transfer reaction of ‘OH radicals, the reactions of VBT with various one-electron oxidants were investigated.

**Reactions with specific one-electron oxidants**

At near neutral pH, N$_3^+$ was used to bring about one-electron oxidation of VBT. The N$_3^+$ radicals (oxidation potential = +1.33 V) were generated by the pulse radiolyzing N$_2$O-saturated aqueous solution of NaN$_3$ $(4 \times 10^{-2}$ mol dm$^{-3}$) containing $5 \times 10^{-4}$ mol dm$^{-3}$ of solute.

The reaction of VBT with SO$_4^{2-}$ was followed by pulse radiolyzing of an N$_2$ purged solution containing $4 \times 10^{-2}$ mol dm$^{-3}$ K$_2$S$_2$O$_8$, $0.3$ mol dm$^{-3}$ $t$-butanol, and $1 \times 10^{-3}$ mol dm$^{-3}$ VBT at pH ~ 10.2.

The rate constant for the reaction of Br$_2^-$ with VBT was determined by following the decay of Br$_2^-$ at 320 nm at neutral pH, whereas the reaction of Cl$_2^-$ with VBT followed by a study of the decay of Cl$_2^-$ at 345 nm at pH ~ 1.

For following the reaction of O$_2^-$ with VBT, the N$_2$O-purged solution containing $1 \times 10^{-3}$ mol dm$^{-3}$ of VBT at pH 12.8 was pulse-radiolyzed. Under these conditions, the OH radical deprotonates to O$_2^-$ ($pK_{\text{OH}}$ = 11.9, reduction potential = +1.77 V) and is available for reaction with VBT.

The reaction of e$_{\text{aq}}^-$ with VBT was studied by pulse radiolyzing the N$_2$-saturated aqueous solution of $1 \times 10^{-3}$ mol dm$^{-3}$ VBT at near neutral pH containing $0.3$ mol dm$^{-3}$ $t$-butanol.

The reaction of CO$_2^-$, a specific one-electron reductant with VBT, was studied by pulse-radiolyzing a solution purged with N$_2$O containing $5 \times 10^{-4}$ mol dm$^{-3}$ VBT and $2 \times 10^{-2}$ mol dm$^{-3}$ sodium formate. Under these conditions, all ‘OH generated by Reaction 2 are converted into CO$_2^-$, which then reacts with VBT as shown in accordance with reactions

\begin{align}
\text{H}/\text{OH} + \text{HCO}_3^- & \rightarrow \text{H}_2\text{O} + \text{CO}_2^- \quad (15) \\
\text{CO}_2^- + \text{VBT} & \rightarrow \text{VBT}^- + \text{CO}_2 \quad (16)
\end{align}

**Reduction of VBT by e$_{\text{aq}}^-$ and the ability of its reduced intermediate to react with solvent**

The reduced transient generated by the reaction of VBT with e$_{\text{aq}}^-$ can abstract an H atom to give a species that is generated by the direct reaction of VBT with H atom. This possibility was probed by studying the electron transfer from anion to the efficient oxidizing agent methyl violoeng (MV$^{2+}$) and by monitoring the formation of its reduced form at 605 nm

\begin{align}
\text{VBT}^- + \text{MV}^{2+} & \rightarrow \text{VBT}^- + \text{MV}^{4+} \quad (17)
\end{align}

Oxygen has high reactivity toward free radicals; therefore the influence of O$_2$ on the decay behavior of ‘OH adduct of VBT was studied. The ‘OH adduct reactivity toward oxygen was investigated by varying oxygen concentration in a pulsed solution of an O$_2$ purged, an aerated and an N$_2$-purged solution. Under this condition, O$_2$ concentration varies from $1.3 \times 10^{-3}$ mol dm$^{-3}$ to $1 \times 10^{-3}$ mol dm$^{-3}$.

**Steady-state radiation effect on monomer solution**

For studies of the effect of monomer concentration on polymerization reaction, studies at three different monomer concentrations $(1 \text{ mol dm}^{-3}$, $0.5 \text{ mol dm}^{-3}$, and $0.25 \text{ mol dm}^{-3}$) at a dose rate of 2 kGy h$^{-1}$ were carried out under aerated conditions.

The effect of ambience on the radiation polymerization of VBT was seen by monitoring the polymerization extent of aerated, N$_2$-purged, and O$_2$-purged monomer solution for a solution of monomer concentration $0.25 \text{ mol dm}^{-3}$ at a dose rate of 2 kGy h$^{-1}$. The polymerization of ionic monomers such as VBT can get affected by pH of the medium; therefore the effect of pH on polymerization at pH 11.5, 9.0, and 4.5 with a dose rate of 4 kGy h$^{-1}$ for monomer concentration of $0.25 \text{ mol dm}^{-3}$ in an aerated solution was investigated.

The monomer VBT is hygroscopic in nature. To see the effect of moisture on its polymerization, two samples of VBT—one as received and the other vacuum dried—were irradiated, and poly-
merization followed for both samples.

When an aqueous monomer solution is irradiated, an appreciable change in the viscosity is expected as polymerization proceeds. The viscosity change of aerated and N₂-purged 1 mol dm⁻³ solutions were observed at a dose rate of 4 kGy h⁻¹.

RESULTS

The reaction rate constant of various species with VBT is given in Table 1.

Reaction of 'OH radical with VBT

Figure 1a shows the transient absorption spectra 2 µS after the electron pulse of 50 ns was delivered to N₂O-saturated 1 × 10⁻³ mol dm⁻³ near neutral pH. It exhibits absorption bands with λ_max at 275 nm and 350 nm with broad absorption in the 300–330 nm region. The absorption at 275 nm decayed by first-order kinetics with k = 5.6 × 10⁷ s⁻¹ and 350 nm with second-order kinetics with 2k = 4.9 × 10⁹ dm³ mol⁻¹ s⁻¹ (inset, Fig. 1), resulting in the formation of some monomeric or dimeric phenolic product (Scheme 1) as time resolved studies showed no new band with the decay of this one. The bimolecular rate constant at 350 nm was found to be 4.7 × 10⁹ dm³ mol⁻¹ s⁻¹. Neither absorption band was observed in the presence of t-butanol (0.3 mol dm⁻³) (Fig. 1c), an efficient OH radical scavenger, indicating that the bands are due to the reaction of OH radicals with the solute. A rate constant value of 1.7 × 10¹⁰ dm³ mol⁻¹ s⁻¹ was determined by competition kinetics. Figure 2 shows the variation in transient absorbance with a change in the ratio VBT/SCN⁻.

Figure 1b shows the transient spectra when the solution was purged in the presence of NaN₃. It exhibits an absorption band with λ_max = 275 nm with a broad absorption shoulder in the 300–320 nm region. The absorption over the entire spectrum decayed by first order kinetics with k = 5.3 × 10³ s⁻¹. N₃ radical in the absence of any added solute shows absorption maxima at 277 nm (ε = 1,400 dm³ mol⁻¹ cm⁻¹) and decay by a second order mechanism with 2k = 8 × 10⁸ dm³ mol⁻¹ s⁻¹. In the presence of solute, these radicals would react to give solute radical cation. The absorption in the presence of solute was quite high and was observed to build up slowly, reaching completion in about 30 μs. Because N₃⁻ radicals are much more specific in their reaction in comparison to OH radicals and predominantly undergo electron

| Table 1. Rate constant of radiolytically generated species with VBT. |
| Species | pH | Rate constant (dm³ mol⁻¹ s⁻¹) |
| Oxidizing species | | |
| OH | 6.3 | 4.7 × 10⁹ |
| 'OH | 6.3 | 1.7 × 10¹⁰ |
| N₃⁻ | 6.3 | 3.6 × 10⁸ |
| Br₂⁻ | 6.3 | 4.1 × 10⁷ |
| Cl₂⁻ | 1.2 | 2.3 × 10⁸ |
| SO₄⁻ | 10.2 | 3.7 × 10⁷ |
| O⁻ | 12.8 | 1.5 × 10⁹ |
| Reducing species | | |
| e⁻ | 6.3 | 1.9 × 10¹⁰ |
| CO₂⁻ | 6.3 | 4.4 × 10⁸ |
| H⁺ | 1.2 | 5.1 × 10⁹ |
| H₂⁺ | 1.2 | 1.7 × 10¹⁰ |

By competition kinetics.
transfer reaction, the observed spectrum (Fig. 1b) can be attributed to solute radical cation formed on the reaction of N$_3^\cdot$ with the solute (Reaction 18).

$$\text{N}_3^\cdot + \text{VBT} \rightarrow \text{VBT}^{+\cdot} + \text{N}_3^-$$  \hspace{1cm} (18)

The bimolecular rate constant for the reaction of N$_3^\cdot$ with VBT at 275 nm was determined to be $3.6 \times 10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$. Under the experimental conditions, the entire OH radicals would first react with N$_3^\cdot$, and the N$_3^\cdot$ radicals formed would then react with VBT. The formation of radical cation was confirmed by pulsing an N$_2$O saturated solution containing $5 \times 10^{-10}$ mol dm$^{-3}$ VBT, $2 \times 10^{-2}$ mol dm$^{-3}$ NaN$_3$, and $6 \times 10^{-6}$ mol dm$^{-3}$ ABTS [2,2'-Azinobis(3-ethyl benzothiazoline-6-sulfonate)], an efficient reducing agent, and by monitoring the formation of ABTS$^{+\cdot}$ because of the Reaction 19 at 645 nm$^{28}$.

$$\text{VBT}^{+\cdot} + \text{ABTS}^{2-} \rightarrow \text{VBT} + \text{ABTS}^{+\cdot}$$  \hspace{1cm} (19)

The reaction of radical cation with monomer was studied by varying the VBT monomer concentration in the concentration range (0.1–1) $\times 10^{-3}$ mol dm$^{-3}$ and following the decay of radical action at $\lambda = 310$ nm. The bimolecular rate constant of radical cation with the solute (Reaction 20) was found to be $5.7 \times 10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$.

$$\text{VBT}^{+\cdot} + \text{VBT} \rightarrow \text{Dimer radical cation}$$  \hspace{1cm} (20)

The transient absorption spectra of the species formed by the reaction of VBT with SO$_4^{2-}$ Br$_2^-$, and Cl$_2^-$ were similar to that obtained by the reaction of N$_3^\cdot$ with VBT.

Figure 3 shows transient optical absorption spectra species formed by the reaction of O$^-$ with VBT of this solution. The absorption spectra exhibit an absorption band with $\lambda_{\text{max}}$ at 275 nm. The rate constant for the reaction was found to be $1.5 \times 10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$. The species formed decayed by second order kinetics with a rate constant of $3.8 \times 10^4$ s$^{-1}$.

**Reaction of e$_{aq}^-$ with VBT**

The bimolecular rate constant for the Reaction 21 was found to be $1.9 \times 10^{10}$ dm$^3$ mol$^{-1}$ s$^{-1}$. Because chloride ions do not react with hydrated electrons$^{29}$, the calculated rate constant can be considered as the rate constant of the addition of e$_{aq}^-$ to VBT. The absorption spectrum of the transient observed 2 $\mu$s after the pulse (Fig. 4a) shows the presence of one optical absorption band with $\lambda_{\text{max}} = 300$ nm and an extinction coefficient ($\varepsilon$) = $3.9 \times 10^4$ dm$^3$ mol$^{-1}$ cm$^{-1}$. The transient species at 300 nm decayed by second order kinetics with $2k = 3.9 \times 10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$.

The reaction of radical anion with monomer was studied by varying the VBT monomer concentration in the concentration range of (0.1–1) $\times 10^{-3}$ mol dm$^{-3}$ and following the decay of radical anion at $\lambda = 300$ nm. The bimolecular rate constant for the reaction of radical anion with the solute (Reaction 22) was found to be $1.2 \times 10^7$ dm$^3$ mol$^{-1}$ s$^{-1}$.

$$\text{VBT}^- + \text{VBT} \rightarrow \text{Dimer radical anion}$$  \hspace{1cm} (22)

Figure 4c shows the absorption spectrum of species formed by a reaction of CO$_2^{2-}$, a specific one-electron reductant with VBT, 40 $\mu$s after the pulse ($\lambda_{\text{max}}$ at 300 nm). The spectrum is similar to that obtained by the reaction of e$_{aq}^-$, except that lower OD values for the transient were obtained. The bimolecular rate constant for the reaction was found to be $4.4 \times 10^8$ dm$^3$ mol$^{-1}$ s$^{-1}$, and the species decayed by second order kinetics with $2k = 9.3 \times 10^7$ dm$^3$ mol$^{-1}$ s$^{-1}$.

**Reaction of H atom with VBT**

Figure 4b shows transient absorption spectra of the species formed as a result of the reaction of H atom with the solute. The transient absorption spectra shows two absorption peaks: one at
\[ \lambda = 280 \text{ nm} \] with an extinction coefficient of \( (\varepsilon) = 4.3 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1} \) and the band decays by second order kinetics with \( 2k = 4.0 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \), and the other at \( \lambda = 325 \text{ nm} \) with an extinction coefficient \( (\varepsilon) = 4.3 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1} \) and the band decays by second order kinetics with \( 2k = 7.2 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \).

Effect of \( O_2 \) on \( OH \) adduct

Figure 5 shows the plot of rate constant values for the reaction of \( OH \) adduct with \( O_2 \), at different \( O_2 \) concentrations. It was seen that \( OH \) adduct reacts very slowly with \( O_2 \), and the rate constant value was determined to be \( 6.7 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \).

Steady-state polymerization of \( VBT \)

Figure 6 shows the effect of irradiation on the extent of the polymerization of aqueous \( VBT \) solution. It can be seen that at all dose rates the polymerization starts as soon as the radiation dose is delivered to the solution without any induction period. The concentration and ambience affect the extent of polymerization is clear from the profiles in Figs. 7 and 8; however, Fig. 9 clearly indicates that no significant change in polymerization extent takes place with \( \text{pH} \) of the medium. (The \( VBT \) in the text of the paper indicates the cation moiety generated due to ionization of monomer in aqueous solution whereas \( VBT \) cation \( (VBT^+) \) stands for the \( VBT \) cation radical generated by reaction of this parent cation \( (VBT) \) with chemically reactive species of water radiolysis.)

On irradiation of vacuum-dried monomer up to a dose of 10
Fig. 10. Effect of irradiation on viscosity of 1 mol dm$^{-3}$ aqueous para-sodium styrene sulphonate (SSS)\textsuperscript{19}, which ionizes to an aerated solution at a dose of 1.3 kGy, no polymerization was observed. Table 2 shows the effect of irradiation on nondried monomer.

Table 2. Radiation polymerization of nondried solid VBT.

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<th>Dose (kGy)</th>
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</table>

Figure 10 shows changes in the viscosity of the monomer solution (a) N$_2$-purged solution; (b) aerated solution. Inset: viscosity change at lower doses for aerated solution.

Fig. 10. Effect of irradiation on viscosity of 1 mol dm$^{-3}$ aqueous monomer solution: (a) N$_2$-purged solution; (b) aerated solution. Inset: viscosity change at lower doses for aerated solution.

DISCUSSION

Rate constant values obtained by two methods for the reaction of OH radical with VBT are quite different. A higher rate constant value was obtained by competition kinetics because the competition kinetics method gives the overall rate constant value, whereas the formation kinetics for that transient gives it only for which the measurement is carried out. This indicates that some other species besides that with $\lambda_{\text{max}} = 350$ nm is also formed. The rate constant value obtained by competition kinetics is the same as that for 2-[(methacryloyloxy)ethyl]trimethyl ammonium chloride (MADQUAT)\textsuperscript{17} obtained by competition kinetics. However, the value obtained by transient formation is slightly lower than that obtained for the reaction of OH with para-sodium styrene sulphonate (SSS)\textsuperscript{19}, which ionizes to an anion in aqueous medium.

Hydroxyl radicals can react with organic molecules by addition to the unsaturated bond or by the abstraction of the H atom. By proper selection of the experimental conditions, it is possible to find out which the predominant route of reaction is because OH radical typically behaves as an electrophile in its reaction with organic compounds, whereas its conjugate form O$^-$ is a nucleophile\textsuperscript{30}. Therefore, whereas OH readily adds to the double bonds, O$^-$ does not, and thus its rate constants for addition reactions are generally much slower than those of OH. But both forms of radical can abstract H atom from C--H bond almost equally efficiently. To investigate whether OH radical is predominantly undergoing an addition or abstraction reaction, the reaction of O$^-$ with VBT was carried out. The rate constant of VBT with O$^-$ was found to be about 3 times lower than that of OH at near neutral pH (Table 1), indicating that OH preferentially adds on to the molecule, whereas O$^-$ reacts by H$^+$ abstraction. Also, because the rate of reaction of VBT with SO$_4^{2-}$ (3.7 $\times$ 10$^{-10}$ dm$^3$ mol$^{-1}$ s$^{-1}$) is about 2.5 times higher than that of O$^-$ (1.5 $\times$ 10$^{-10}$ dm$^3$ mol$^{-1}$ s$^{-1}$), it can be said that SO$_4^{2-}$ does not react with VBT by H atom abstraction, but by electron transfer.

The rate constant for the reaction of eaq with VBT is almost the same as that of the reaction of eaq with SSS\textsuperscript{19}, indicating that the reactivity of eaq with vinyl monomeric salts, such as VBT and SSS having a pendant-substituted aromatic ring, is independent of whether they ionize to cationic or anionic species in an aqueous solution. The spectra because of the reaction of CO$_2$ with the solute are similar to that of the reaction of solute with eaq (inset Fig. 4), indicating that similar transient species are generated as a result of their reactions. However, the lower OD values and a rate constant that is approximately 45 times lower for the reaction of CO$_2$ with the solute indicate that a complete electron transfer is not taking place and that the redox potential for the VBT/VBT$^+$ couple may be high. Based on the molar absorptivity of the transient VBT$^+$, formed on the reaction with eaq, the yield of the transient was estimated to be only 5%, and this supports the low rate constant value.

The bimolecular rate constant values for the reaction of radical cation and radical anion with VBT were found to be 5.7 $\times$ 10$^6$ dm$^3$ mol$^{-1}$ s$^{-1}$ and 1.2 $\times$ 10$^6$ dm$^3$ mol$^{-1}$ s$^{-1}$, respectively. The second value is twice that of the first, indicating that the polymerization of VBT is initiated by radical anion.

For H atom reaction with VBT, the rate constant values obtained by absorption kinetics and competition kinetics were different; this indicates the formation of more than one species because of this reaction. The spectra and the kinetic parameter of the transient resulting from the reaction of solute with eaq and H atom are different, indicating that different species are formed because of their interaction with solute. This observation was confirmed because no signal as a result of MV$^{2+}$ at 605 nm was seen when the electron transfer studies from VBT$^+$ to MV$^{2+}$ were carried out.

A rate constant value of 6.7 $\times$ 10$^6$ dm$^3$ mol$^{-1}$ s$^{-1}$ for a reaction of species formed by the reaction of OH with VBT with O$_2$ sig-
ifies that if the polymerization is initiated by a species generated by a reaction of OH radical with VBT, which occurs in aerated solution at neutral pH, the rate of polymerization will not be appreciably affected by the presence of O₂.

Steady state polymerization
For technological applications, the monomers are polymerized under the different conditions of radiation dose, dose rate, concentration, ambience, and others; therefore the effect of these variables on the extent of polymerization was investigated.

Radiation-induced ionic polymerization reactions are not influenced by the presence of efficient radical quenchers, such as oxygen. The polymerization of VBT starting immediately on irradiation indicates that it proceeds via an ionic mechanism. But because the polymerization yields in N₂-purged solution were always higher than in the aerated solution (inset, Fig. 6), the indication was that to some extent free radical mechanism contributed to polymerization. This contribution can be said to be marginal because no sharp acceleration in polymerization rates were observed as a result of the depletion of dissolved oxygen in the medium after irradiating for some time. There are contributions by the ionic and the free radical mechanisms. This was further established because in the dose range studied, the polymer yields decreased as the dose rate increased, indicating that polymerization does not strictly follow a free radical path because the rate of propagation varies as the square root of the dose rate for free radical process. These steady-state radiation studies are in agreement with the pulse radiolysis studies, where the radical-anion initiation of polymerization of VBT was predicted.

The increase in polymer yields with the increase in monomer concentration can be attributed to two factors. First is the decrease in the electrostatic repulsion of ionized monomer from the ionized-growing polyelectrolyte chain favoring propagation. Second, at low concentration more growing chains are getting terminated by combining with the radiolysis product of water (H⁺·OH), more often yielding telomers instead of reacting with monomer molecules to form long-chain polymers.

Although the polymer yields for the N₂-purged solution and the aerated solution are more or less the same, the purging O₂ causes a decrease in the polymer yields (Fig. 8). This again confirms the role of the free radical path in the polymerization of VBT.

No significant change in polymer yields at three different pH indicates that either the change in pH does not affect the extent of the ionization of VBT or that its extent of ionization does not affect its tendency to polymerize.

Many monomers show ultrafast polymerization in solid state. VBT in dried state showed no polymerization, even when a radiation dose 10 times higher than that required for its polymerization in the aqueous solution was delivered; however, nondried VBT polymerized on irradiation. VBT is hygroscopic in nature; therefore it can be said that it polymerizes on irradiation only in the presence of water, i.e., when it is ionized.

Assuming that an increase in viscosity of the VBT solution during irradiation indicates the polymerization of VBT, a comparatively slower increase in viscosity of the aerated solution indicates that the presence of air hinders the process of the polymerization of VBT. Moreover, as finally the monomer forms a soft gel mass this shows polymer formed predominantly undergoes cross-linking on irradiation in aqueous solutions.

CONCLUSION
The present investigation shows that the radiation polymerization of VBT in aqueous solution is initiated by a radical-anionic species. The radiolytically generated OH and H⁺ atom react with VBT to give more than one species. Dose, dose rate, concentration of monomer, and ambience of polymerization affect the polymerization of VBT, which undergoes very fast radiation polymerization, but only in an ionized state. The poly (VBT) formed during the radiation polymerization of VBT is soluble in water and predominantly undergoes cross-linking to form a gel.

REFERENCES


