Radiation Effect on Poly(vinylbenzyltrimethylammonium chloride) in Aqueous Solution: Pulse Radiolysis and Steady-state Study

Virendra KUMAR, Yatendra K. BHARDWAJ*, Sunil SABHARWAL and Hari MOHAN1

Pulse radiolysis/Poly(vinylbenzyltrimethylammonium chloride)/Radiation/Polymerization/Degradation/ Cross-linking.

Poly(vinylbenzyltrimethylammonium chloride) (PVBT) has been synthesized by radiation-induced polymerization of Vinylbenzyltrimethylammonium chloride (VBT). The viscosity average molecular weight of synthesized polymer was estimated to be ~10^5 by viscosity measurements. The radiation-induced affects on PVBT have been investigated by steady-state and pulse radiolysis (PR) techniques. The reactions of primary radicals •OH, eaq–, and H generated by the radiolysis of water with PVBT were studied. The reactions of some other species such as N3, Cl2–, Br2–, SO4–, and CO2– with PVBT were also investigated. The results indicate that the reactivity of these species toward PVBT is lower than that with the monomer VBT. The rate constants for the reactions of OH radical and H atom with PVBT were evaluated both by competition kinetics and by direct observation of the buildup of transient species. The difference in the rate constant values evaluated by the two methods indicated that 'OH and H' react with PVBT to give more than one species. It was observed that the OH radical and H atom react with PVBT in different manners. Near neutral pH, the OH radicals react to form an adduct and to generate a radical by abstracting methylenic H atom. The H atom, however, also abstracts the H atom from the PVBT backbone. The rate constant value for the reaction of hydrated electron with PVBT was found to be 3.1 × 10^9 dm^3 mol^–1 s^–1. Steady-state irradiation studies of the aqueous PVBT solution indicated that PVBT predominantly undergoes cross-linking on irradiation. Cross-linking is a function of dose rate, concentration, and ambient of irradiation. At concentrations < 2%, only intramolecular cross-linking takes place, whereas beyond this concentration, the intermolecular cross-linking of polymer chains takes place to form a soft gel. The gel dose (Dgel) is a function of the ambient of irradiation.

INTRODUCTION

Water-soluble cationic polymers are of great industrial importance because they have been used for years for fines retention in paper, as flocculants, as stabilizers for emulsion polymerization, in cosmetics and pharmaceuticals, and in general wherever aqueous solid-liquid separation is required. Among the ammonium, sulphonium, and phosphonium of the cationic family, ammonium-based polymers have been the most popular because of the ready availability of their monomers and their higher chemical stability. In recent years, there has been great interest in the study of a tri-alkyl ammonium chloride, poly(vinylbenzyltrimethylammonium chloride) (PVBT), probably because of its versatility. PVBT has amphiphilic nature because it contains hydrophobic groups (methyl groups and backbone chains) and a hydrophilic group (positively charged tertiary amine group) in very elementary unit, and for this reason it has been successfully tried as a drug delivery system, as a swelling kinetics modifier, and as a selective adsorbent. PVBT membranes have been proposed for the electrolysis of water at low voltage, as a bactericidal polymer, for molecular recognition, and for synthesizing radiation-grafted copolymers with high selectivity for heavy metal ions. The cross-linking of PVBT by UV and X-ray radiation has also been well documented. However to the best of our knowledge; the effect of high-energy radiation such as gamma radiation on PVBT has not been reported. In the present study we have extensively investigated the radiation effect on PVBT in an aqueous solution. The effect of radiation dose, dose rate, concentration, and ambient on the viscosity and cross-linking of PVBT has been studied. Furthermore, the pulse radiolysis technique, which has proven to be a powerful technique for studying the reactions of short-lived intermediates in the polymerization of synthetic monomers, biopolymers, and biologically im-

*Corresponding author: Fax: +91-22-25505151,
E-mail: ykbhard@magnum.barc.ernet.in
E-mail: kbhardwaj2001@yahoo.co.in
Radiation Technology Development Section and Radiation Chemistry and Chemical Dynamics Division, Bhabha Atomic Research Centre, Trombay, Mumbai-400 085, India.
portant molecules\(^{16,17}\) was used to elucidate the nature and characteristic of transient species produced during radiolysis, which are involved in the process of its cross-linking. The results of the study have been compared with that of poly(\textit{para}-sodium styrene sulphonate), which ionizes to a polyanion in aqueous medium.\(^{18}\)

**MATERIALS AND METHODS**

Vinylbenzyltrimethylammonium chloride (VBT) molecular weight 211.74 in powder form, from Aldrich, was used as received. All other chemicals were of AnalaR 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 by using HClO\(_4\) acid, KH\(_2\)PO\(_4\), Na\(_2\)HPO\(_4\), 2H\(_2\)O, and NaOH in appropriate quantities. IOLAR grade (purity 99.9\%) gases N\(_2\), N\(_2\)O, and O\(_2\) used for purging solutions were obtained from Indian Oxygen Ltd. For steady-state gamma irradiation, a gamma camera having a dose rate 8 kGy hr\(^{-1}\), as measured by Fricke dosimeter, was used with suitable attenuators. Viscosity measurements for molecular weight determination and other studies were carried out with an Ubbelholde viscometer from M/s Scam India at a temperature of 25 ± 0.5°C. The polymer prepared was estimated for its Cl\(^{-}\) content by using a DIONEX-500 ion chromatograph system (DX-500, Dionex) in suppressed conductivity mode. This system consists of a separating column AS11 coupled with AG11, an ASRS-II suppressor, and an ED40 detector in conductivity mode. A 3 \(\times\) 10\(^{-3}\) mol dm\(^{-3}\) NaOH with a flow of 1 ml/min was used as the mobile phase in the isocratic mode.

**Radiation-induced polymer synthesis and characterization of polymer**

We synthesized PVBT \((M_r = 1.0 \times 10^{5})\) by radiation polymerization of 1 mol dm\(^{-3}\) aqueous solution of VBT by using gamma radiation from a gamma chamber (GC-5000) at a dose rate of 4 kGy hr\(^{-1}\) for a total dose of 1.67 kGy. The PVBT in solution was then precipitated out by pouring it into the excess of acetone. Polymer obtained in this way was redissolved in minimum amount of water and reprecipitated in excess of acetone. The dissolution and precipitation was carried out several times to remove any free monomer. The PVBT was then vacuum dried at 30°C and ground into powder form. The molecular weight of polymerized VBT was estimated by using the Mark-Houwink equation \([\eta] = K M^\alpha\), where \([\eta]\) is the limiting viscosity number, \(K\) and \(\alpha\) are constants, and \(M\) is the molecular weight. The values of \(K = 5.77 \times 10^{-3}\) and \(\alpha = 0.88\) were used.\(^{19}\) The ion chromatography studies indicated that only about 50% of the monomer units incorporated in the polymer have attached Cl\(^{-}\) ions, indicating that during the radiation polymerization of VBT some of the chloride ions are sacrificed.

**Pulse radiolysis dosimetry**

The dosimetry measurements were carried out using aerated \(1 \times 10^{-2}\) mol dm\(^{-3}\) KSCN solution and absorption due to (SCN\(_2\))\(^{-}\) radical were monitored at 500 nm. The absorbed dose per pulse was calculated by using \(G=21,520\) dm\(^{-3}\) mol\(^{-1}\) cm\(^{-1}\) per 100 eV for (SCN\(_2\))\(^{-}\) radical,\(^{20}\) where \(G\) is the radiation chemical yield expressed as the number of molecules formed or destroyed per 100 eV of energy absorbed and \(\varepsilon\) is the molar absorptivity.

**Pulse radiolytic procedure**

Pulse radiolysis studies were carried to determine the rate constants between radiolytic products of water and PVBT to characterize the transients formed by these reactions and to study the preferential mode of reaction of OH and H\(^{•}\) with PVBT. To carry out pulse radiolysis studies, polymer solutions of suitable concentrations in 1 cm\(^2\) suprasil cuvettes were irradiated with 50 ns electron pulses from a 7 MeV linear electron accelerator (LINAC). The details of pulse radiolysis setup used are described elsewhere.\(^{21,22}\)

**Pulse radiolysis experiments**

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

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

To study the reactions of these radiolytic products with PVBT, any one 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 N\(_2\)O prior to pulse irradiation. This resulted in scavenging of \(e_{aq}^{-}\), and under these conditions the yield of the OH radicals was 90% of the total radicals \(G (\text{OH}) = 6.1\). The remaining 10% contribution was of H\(^{\cdot}\) atoms; \(G (\text{H}) = 0.6\).

\[
\text{N}_2\text{O} + e_{aq}^{-} \rightarrow \text{N}_2 + \text{OH} + \text{\'OH}
\]

\(e_{aq}^{-}\) were selectively generated by pulse radiolysis of the solutions in the presence of 0.3 mol dm\(^{-3}\) t-butanol (at near neutral pH), which scavenges the OH radicals.

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

For investigating the reaction of H radical, we selectively generated them by radiolyzing the solution at pH ~1 in the presence of t-butanol. At low pH, \(e_{aq}^{-}\) in the medium react with H\(^{\cdot}\) ions to give H\(^{\cdot}\) radicals, and OH radicals are scavenged by t-butanol.

\[
e_{aq}^{-} + \text{H}^{\cdot} \rightarrow \text{H}^{\cdot}\n\]

The rate of reaction of \text{\'OH} and H\(^{\cdot}\) with PVBT was followed both by formation kinetics and by competition kinetics. The formation of the transient with OH radical was investigated by observing the absorption at 340 nm and 280 nm in an N\(_2\)O saturated aqueous solution of PVBT in the concentration range \((2.5-10) \times 10^{-3}\) mol dm\(^{-3}\). Over this range, the pseudo-first order rate \((k_{\text{obs}})\) was found to increase with polymer concentration. The bimolecular rate constant was determined from the slope of the linear plot of \(k_{\text{obs}}\) vs. polymer concentration. In the competition kinetic study, N\(_2\)O-saturated
aqueous solutions containing 2.9 × 10⁻³ mol dm⁻³ KSCN and different concentrations of PVBT in the range (1–10) × 10⁻³ mol dm⁻³ were pulsed, and the absorbance at 500 nm because of (SCN)₂⁻ was measured immediately after the electron pulse.

The two competing reactions involved

\[ \text{OH} + \text{SCN} \rightarrow \text{OH} + (\text{SCN})_2^- \]  \hspace{1cm} (5)

\[ \text{OH} + \text{PVBT} \rightarrow \text{products} \]  \hspace{1cm} (6)

lead to relation:

\[ A_j/A_o = 1 + \frac{k_{\text{PVBT,OH}} [\text{PVBT}]/k_{\text{SCN,OH}} [\text{SCN}]}{k_{\text{PVBT,OH}} [\text{PVBT}]/k_{\text{SCN,OH}} [\text{SCN}]} \]  \hspace{1cm} (7)

where \( A_j \) and \( A_o \) are the transient absorbances of the solution at 500 nm in the absence and presence of PVBT, respectively. Substituting \( k_{\text{SCN,OH}} \) of 1.1 × 10⁻¹⁰ dm³ mol⁻¹ s⁻¹, \( k_{\text{PVBT,OH}} \) was evaluated.

The contribution of H atom reaction to PVBT(OH) spectra was investigated by pulse radiolyzing N₂O-saturated 1 × 10⁻³ mol dm⁻³ solution of PVBT in the presence of t-butanol, a very effective OH radical scavenger.

For determination of rate of reaction of the H atom with PVBT by transient formation, (0.5–2) × 10⁻³ mol dm⁻³ solution of PVBT was pulse radiolyzed in the presence of O₂, which acts as an OH radical scavenger. The t-butanol radicals formed were found to be unreactive toward PVBT. The reaction between \( e_{\text{aq}}^- \) and PVBT was monitored by following the decay of \( e_{\text{aq}}^- \) at 700 nm.

The reaction of CO₂⁻ (Redox Pot. CO₂/CO₂⁻ = 2.0), a specific one-electron reductant with PVBT was studied by pulse radiolyzing a solution purged with N₂O containing 1 × 10⁻³ mol dm⁻³ PVBT and 2 × 10⁻² mol dm⁻³ sodium formate. Under these conditions, all ‘OH generated by reaction (2) are converted into CO₂⁻, which then reacts with PVBT as shown in accordance with reactions

\[ \text{H}^\bullet + \text{OH} + \text{HCO}_2^- \rightarrow \text{H}_2\text{O} + \text{CO}_2^- \]  \hspace{1cm} (12)

\[ \text{CO}_2^- + \text{PVBT} \rightarrow \text{PVBT}^- + \text{CO}_2 \]  \hspace{1cm} (13)

Reactivity and identification of types of radicals formed by the reaction of OH and H with PVBT

The OH radical and H atom can react with the backbone as well as with the pendant part of polymer. The abstraction reaction with the polymer backbone will lead to the generation of two types of radicals, depending on the radical being formed at \( \alpha \) or \( \beta \) position with respect to the substituted aromatic ring. \( \alpha \)-Radicals of well-defined model systems of polymers have been characterized by an absorption band at about 290–330 nm, whereas \( \beta \)-radicals have been shown to absorb at wavelengths ≤ 250 nm. The fraction of \( \alpha \)-radicals formed can be determined by using the difference in the reducing ability of \( \alpha \)- and \( \beta \)-radicals. \( \alpha \)-Radicals of polymers have been reported to be readily oxidizable as compared to the \( \beta \)-radicals. The reaction of these radicals with thionine, which readily undergoes one-electron reduction yielding semithionine (\( \lambda_{\text{max}} = 400 \text{ nm} \), \( \varepsilon_{400} = 6.826 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1} \), reduction potential value = +0.05 V vs. NHE), was tried to quantitatively determine the fraction of \( \alpha \)-radicals formed in reaction. The formation of semithionine was monitored at 400 nm by pulse radiolyzing of a 5 × 10⁻³ mol dm⁻³ PVBT, an N₂O-saturated solution containing different concentrations ([0–4] × 10⁻³ mol dm⁻³) of thionine. The matrix and pulse dose conditions were chosen to ensure that (1) all the ‘OH/H radicals predominantly react only with PVBT, and (2) the PVBT radicals that were formed react completely with thionine.

The reaction of ‘OH/H with the pendant part of a molecule may mainly lead to formation of the respective adduct with an aromatic ring, or they may abstract a methylene hydrogen atom. It is well known that carbon-centered radicals have high reactivity with O₂, whereas an aromatic ring OH adduct has poor reactivity with O₂. To study the reaction of a transient formed by the reaction of ‘OH with PVBT with O₂,
the concentration of O$_2$ was varied in $1 \times 10^{-3}$ mol dm$^{-3}$ PVBT solution in the range $(0–2) \times 10^{-4}$ mol dm$^{-3}$ by mixing N$_2$O-purged and aerated solutions in different ratios.

**Steady-state radiation effects on polymer solution**

To study the effect of radiation dose and dose rate, the viscosity of 4% aerated PVBT solution was monitored at dose rates of 8 kGy h$^{-1}$, 4 kGy h$^{-1}$, and 2 kGy h$^{-1}$.

The polymer solutions of concentration 1%–10% were irradiated at a dose rate of 8 kGy h$^{-1}$ under aerated conditions to learn the effect of irradiation as a function of polymer concentration.

The viscosity of 4% PVBT solution was monitored as a function of radiation dose at a dose rate of 4 kGy h$^{-1}$ under aerated, N$_2$ purged, and O$_2$ purged conditions in order to see the effect of ambience on the irradiation of the polymer solution.

**RESULTS**

The aqueous solution of PVBT showed absorption spectra at $\lambda_{\text{max}} = 224$ nm with a molar extinction coefficient ($\varepsilon_{224} = 6,850$ dm$^3$ mol$^{-1}$ cm$^{-1}$) and a negligible absorption at $\lambda = 254$ nm corresponding to monomer.$^{14}$ PVBT, being a highly ionizable polymer, readily ionizes in an aqueous solution. For all pulse radiolysis experiments, the PVBT solution of concentration $< 10^{-2}$ mol dm$^{-3}$ was used. At these concentrations, PVBT can be assumed to be completely ionized to a chloride ion and a polycationic species.

**Reactivity of OH radicals with PVBT**

Figure 1(a) shows the transient absorption spectra obtained by the reaction of OH radical with PVBT. The figure shows broad absorption bands extending over the region 270 nm to 360 nm with two prominent peaks at 280 and 340 nm. In the presence of 0.3 mol dm$^{-3}$ $t$-butanol, an efficient OH radical, and a weak H atom scavenger, these absorption bands were not observed, suggesting that the spectra is due to the reaction of OH with PVBT. Decay kinetics showed that the bands at 280 and 340 nm decayed by first-order kinetics with $k = 4.5 \times 10^{2}$ s$^{-1}$ and $1.3 \times 10^{2}$ s$^{-1}$, respectively. Different decay rates at these two wavelengths may suggest the presence of two different species formed on the reaction of OH radicals with polymer.

The bimolecular rate constants determined from the slope of the linear plot of $k_{\text{obs}}$ vs. solute concentration were found to be $4.3 \times 10^{7}$ dm$^{3}$ mol$^{-1}$ s$^{-1}$ and $7.2 \times 10^{6}$ dm$^{3}$ mol$^{-1}$ s$^{-1}$ at 340 nm and 280 nm, respectively. A rate constant value of $2.3 \times 10^{10}$ dm$^{3}$ mol$^{-1}$ s$^{-1}$ was obtained by competition kinetics study. Figure 1 inset shows the result of competition kinetics.

The decay of the transients formed by the reaction of OH radical with PVBT at $\lambda = 280$ nm. Figure 2 shows the decay profiles at $\lambda = 340$ nm. The reactivity of various radiolytic products of water with PVBT is described below.
Reactivity studies of PVBT with OH in the pH range 1–10 indicated that time-resolved transient spectra at pH 10 was similar to that at neutral pH, whereas the spectra at pH 1 was quite different and showed absorption in the range 280–400 nm with $\lambda_{\text{max}} = 340$ nm. Figure 3 shows the transient absorption spectrum of the reaction of PVBT with OH at different pH. The bimolecular rate constant value at pH ~1 was found to be $3.1 \times 10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$, and the species decayed by first-order kinetics with $k = 8.6 \times 10^2$ s$^{-1}$.

Figure 4 shows transient optical absorption obtained by the reaction of O$^-$ with PVBT. The absorption spectrum exhibits an absorption band with $\lambda_{\text{max}}$ at 280 nm. The rate constant for the reaction of O$^-$ with PVBT was found to be $1.1 \times 10^8$ dm$^3$ mol$^{-1}$ s$^{-1}$.

One electron oxidation of PVBT was tried by using N$_3$ at near neutral pH. The transient optical absorption spectrum recorded showed no significant absorption in the wavelength range studied in the dose range 15 Gy to 120 Gy, indicating that either electron transfer is not taking place or the oxidation potential of PVBT is quite high (>1.33 V). Similar studies with Cl$_2$-, Br$_2$-, and SO$_4$- indicated negligible reaction with these species.

The bimolecular rate constant for the reaction of $e_{\text{aq}}^-$ with PVBT was determined to be $3.1 \times 10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$. The time-resolved spectrum of the transient species formed by the reaction of $e_{\text{aq}}^-$ with PVBT is shown in Fig. 5. The transient spectra show a sharp band at 270 nm with molar extinction coefficient $\varepsilon_{270} = 9,450$ dm$^3$ mol$^{-1}$ cm$^{-1}$, and the transient decayed by first-order kinetics with $k = 8.6 \times 10^2$ s$^{-1}$.

Figure 5(d) shows an absorption spectrum of transient observed by the reaction of CO$_2^-$ with PVBT, 2.5 µs after the pulse. It is similar to the transient spectra obtained by the reaction of $e_{\text{aq}}^-$ with PVBT, but with lower OD values.

Figure 6 shows transient absorption spectra for the reaction of H atom with PVBT observed 4 µs after the pulse. The transient absorption spectra shows a sharp peak at 275 nm. The bimolecular rate constant was found to be $6.2 \times 10^7$ dm$^3$ mol$^{-1}$ s$^{-1}$. 

---

Fig. 3. Absorption spectra of PVBT radicals 8 µs after the pulse, after pulsing N$_2$O-saturated solution, [PVBT] = $1 \times 10^{-3}$ mol dm$^{-3}$ at a dose of 15 Gy (a) at pH ~1, (b) near neutral pH, (c) at pH ~10.

Fig. 4. Time resolved spectra of the transient formed, 8 µs after the pulse by reaction of O$^-$ with N$_2$O-saturated 1 $\times$ 10$^{-3}$ mol dm$^{-3}$ PVBT solution at pH 12.8. Inset: Decay of the transient formed by reaction of O$^-$ with PVBT at $\lambda = 275$ nm. (a) $[O_2] = 0 \times 10^{-3}$ mol dm$^{-3}$, (b) $[O_2] = 0.05 \times 10^{-3}$ mol dm$^{-3}$, (c) $[O_2] = 0.10 \times 10^{-3}$ mol dm$^{-3}$, (d) $[O_2] = 0.15 \times 10^{-3}$ mol dm$^{-3}$, (e) $[O_2] = 0.20 \times 10^{-3}$ mol dm$^{-3}$.

8.4 $\times$ 10$^6$ dm$^3$ mol$^{-1}$ s$^{-1}$.

Fig. 5. Time resolved spectra of the transient formed by reaction of N$_2$-saturated PVBT solution with $e_{\text{aq}}^-$, [PVBT]=1 $\times$ 10$^{-3}$ mol dm$^{-3}$, [t-butanol] = 0.3 mol dm$^{-3}$, pulse duration 50 ns, dose 15 Gy (a) 2 µs, (b) 6 µs, (c) 10 µs after the pulse, (d) one electron reduction by CO$_2^-$ containing 2 $\times$ 10$^{-5}$ mol dm$^{-3}$ sodium formate.
s\(^{-1}\). The molar extinction coefficient of the species formed by reaction of H atom with PVBT was found to be \( \varepsilon_{275} = 2,380 \) dm\(^3\) mol\(^{-1}\) cm\(^{-1}\), and the transient decayed by first-order kinetics with \( k = 3.2 \times 10^3 \) s\(^{-1}\). The rate of reaction by competition kinetics was evaluated to be \( 2.5 \times 10^8 \) dm\(^3\) mol\(^{-1}\) s\(^{-1}\). Figure 6 (inset) shows the results of these studies. Figure 6 (b) shows the time-resolved transient spectra of the species generated when \( 1 \times 10^{-3} \) mol dm\(^{-1}\) PVBT aerated solution containing 0.3 mol dm\(^{-3}\) \( t \)-butanol was pulsed at pH ~1.

**Steady-state irradiation effect on aqueous PVBT solution**

Figure 7 shows the effect of gamma irradiation on the viscosity of aerated 4% PVBT aqueous solution at different dose rates. It is evident from the profiles that changes in the viscosities of the polymer solutions depend both on the total dose imparted and on the dose rate. It was seen that for aqueous PVBT solution, a change in the viscosity on irradiation was a function of the polymer concentration. Figure 8 and inset show the results of these studies. It was observed that at concentrations < 8%, there is initially a decrease in the viscosity of the polymer solution on irradiation, whereas at higher concentrations (>8%), the solutions become viscous at the onset of irradiation and soon form a soft nonflowing gel mass. The phenomenon of gelation could be observed at a dose of as low as 0.2 kGy for an aerated solution of 10% concentration.

Figure 9 shows the results of ambient conditions on the irradiation of aqueous PVBT solution. It can be seen that there is initially a decrease in the viscosity of polymer solution in aerated and O\(_2\)-purged solution, but not in the N\(_2\)-purged solution.
DISCUSSION

The reaction of OH radical with PVBT resulting in more than one species was confirmed by three observed facts: (1) The transient spectra show two maxima corresponding to 280 nm and 340 nm that decay at different rates; (2) A decay of transient with $\lambda_{\text{max}} = 340$ nm gets affected by the presence of O$_2$, whereas with $\lambda_{\text{max}} = 280$ nm does not; (3) The rate constant values obtained by competition kinetics is much higher than that calculated by transient formation. A higher rate constant value was obtained by competition kinetics because the competition kinetics method gives the overall rate constant value, whereas formation kinetics provide the rate constant of the formation of that transient only for which the measurement is carried out. The OH radical can react with PVBT to give any of the six species, namely, $\alpha$-radical (I), $\beta$-radical (II), methylene radical (III), tetramethyl radical (IV), OH-adduct (V), and radical-cation (IV), as shown in scheme I. The formation of species III, IV, and V have been postulated for a similar compound benzyl trimethylammonium chloride by Bobrowski\textsuperscript{31). However, the formation of species (IV) has been ruled out because of low rate constant values (~1.6 × 10$^6$ dm$^3$ mol$^{-1}$ s$^{-1}$).\textsuperscript{31) On similar grounds we can also neglect its formation in regard to PVBT.

A comparison of rate constant values obtained by transient formation with rate constant values of other water-soluble high molecular weight polymers determined by the same method, viz., polyvinyl methyl ether (3.3 × 10$^8$ dm$^3$ mol$^{-1}$ s$^{-1}$),\textsuperscript{32) polyethylene oxide (5.8 × 10$^8$ dm$^3$ mol$^{-1}$ s$^{-1}$),\textsuperscript{33) polyvinyl pyrrolidone (2 × 10$^8$ dm$^3$ mol$^{-1}$ s$^{-1}$),\textsuperscript{34) polyacrylic acid (2.2 × 10$^8$ dm$^3$ mol$^{-1}$ s$^{-1}$),\textsuperscript{35) and poly (p-sodium styrene sulphonate) (5.3 × 10$^8$ dm$^3$ mol$^{-1}$ s$^{-1}$) of high molecular weight\textsuperscript{18) indicates that for water soluble polymers, the reactivity of OH radical with polymers varies with the chemical structure of the monomeric unit of the polymer and its molecular weight.

The very low absorption values for Fig. 1(b) indicate that there is no significant contribution to PVBT(OH) spectra because of the H atom reaction with PVBT.

PVBT undergoes negligible electron transfer reaction with specific one electron oxidants N$_3^\cdot$, Cl$^\cdot$, Br$^\cdot$, and SO$_4^\cdot$, indicating that OH does not undergo electron transfer reaction with PVBT to form radical-cationic species (VI) in scheme I. We have earlier reported that the monomer VBT of PVBT undergoes electron transfer reaction with OH radicals.\textsuperscript{14) This indicates that either the electron-rich centers in monomer are sacrificed as the monomer polymerizes to polymer, or they get enveloped as a result of the coiling of the polymer molecule. Similarly poor electron transfer reaction with the OH radical has recently been reported for poly (p-sodium styrene sulphonate),\textsuperscript{18) though its monomer p-sodium styrene sulphonate undergoes very efficient electron transfer reaction.\textsuperscript{36) The OH radicals are known to undergo addition reaction with the molecules having unsaturation\textsuperscript{37); therefore they may either add to the aromatic ring of PVBT to form an adduct, or they may abstract the H atom from the PVBT molecule. The H atom abstraction reaction with the polymer backbone will lead to the generation of two types of radicals, depending on the radical being formed at $\alpha$ or $\beta$ position with respect to the substituted aromatic ring (Scheme I).

However, no signal for semithionine was observed. This indicated that the $\alpha$-radicals are not formed and that $\beta$-radicals absorb at $\lambda \leq 250$ nm; thus the transient spectra obtained were for another species. To further confirm the formation of any radical species, the decays of the transient formed by a reaction of OH radical with PVBT at $\lambda = 280$ nm and 340 nm were studied by a varying O$_2$ concentration in reaction medium. The decay of species with $\lambda_{\text{max}} = 340$ nm was only affected by presence of O$_2$. This indicated that the transient corresponding to this wavelength is a carbon-centered species, whereas the one corresponding to $\lambda_{\text{max}} = 280$ nm is an OH adduct. The carbon-centered radical species that was generated may be methylenic radicals (III). As from the steady-state studies (described later in the steady-state part of the studies), it was seen that PVBT predominantly undergoes cross-linking on irradiation in an aqueous solution.

It has been reported that for systems containing an aromatic ring, the extent of OH reaction with the molecule depends on the substituent in the ring.\textsuperscript{38-40) and the transient shows an absorption in the range of 320 to 340 nm. To further analyze
the OH reactions, the PVBT reaction was studied with O\textsuperscript{•-}. OH radicals can react with organic molecules by addition to the unsaturated bond or by the abstraction of an H atom. By properly selecting the experimental conditions, we may learn which route of reaction is predominant because the OH radical typically behaves as an electrophile in its reaction with organic compounds, whereas its conjugate form O\textsuperscript{•} is a nucleophile.\textsuperscript{41} So although OH readily adds to the double bonds, O\textsuperscript{•} does not; therefore its rate constants for addition reactions are generally much slower than OH. But both forms of the radical can abstract the H atom from the C–H bond with almost equal efficiency. O\textsuperscript{•} may undergo a reaction with PVBT to yield I, II, or III in scheme I because it is known to preferentially abstract the hydrogen atom from the methyl substituents rather than add to the aromatic ring.\textsuperscript{32,43} The rate constant for the reaction of O\textsuperscript{•} with PVBT was found to be ~6 times lower than the rate of reaction of the OH radical (λ = 280 nm). As discussed above, the transient generated by the reaction of an OH radical with PVBT (λ\textsubscript{max} = 280 nm) is an OH adduct, whereas the transient formed by the abstraction reaction of O\textsuperscript{•} with PVBT (λ\textsubscript{max} = 275 nm) will be a radical species. Thus the two transients are different species, though they show their λ\textsubscript{max} at about same wavelengths. This was confirmed by our following the decay (at 275 nm) of the transient formed by a reaction of O\textsuperscript{•} with PVBT at different oxygen concentrations (Fig. 4). The rate of reaction with O\textsubscript{2} was found to be 2.2 × 10\textsuperscript{8} dm\textsuperscript{3} mol\textsuperscript{-1} s\textsuperscript{-1}.

The transient spectrum of OH radical reaction with PVBT at a lower pH is different from that at a neutral or higher pH. This may be attributed to the formation of ClOH\textsuperscript{•} as a reactive species at low pH (instead of OH radical) because of the reaction of the OH radical and Cl\textsuperscript{-} in the medium, as explained earlier by other researchers,\textsuperscript{44} or at low pH the PVBT chains may probably orient in such a way that the site or the extent of reaction of OH with PVBT changes.

The hydrated electron is known to predominantly react with benzyltrimethylammonium cation to yield benzyl radical by the elimination of tertiary amine.\textsuperscript{31} In analogy to these observations, PVBT may also be assumed to yield polymeric benzyl radical, as shown in scheme II. The reaction of hydrated electron with PVBT may proceed through the polymer radical, which ultimately decomposes to benzyl radical and tertiary amine, or the electron may be transferred directly to the benzyl group, causing a release of the benzyl radical.

The bimolecular rate constant for the reaction of e\textsubscript{aq}\textsuperscript{-} with PVBT is much lower than the bimolecular rate value of 1.9 × 10\textsuperscript{10} dm\textsuperscript{3} mol\textsuperscript{-1} s\textsuperscript{-1} for the monomer VBT. The lower rate constant value for PVBT in comparison to its monomer VBT indicates an inaccessibility of the site for e\textsubscript{aq}\textsuperscript{-} reaction in regard to polymer. The similar spectrum obtained because of the reaction of e\textsubscript{aq}\textsuperscript{-} and CO\textsubscript{2}\textsuperscript{•} indicate that similar species are formed by their reaction; however, the lower absorption values in regard to CO\textsubscript{2}\textsuperscript{•} indicate that complete reduction does not take place.

The higher rate constant value determined by competition kinetics for H atom reaction with PVBT suggest the formation of more than one transient species. The H atom may react with PVBT to produce various species, as shown in scheme III. It has been reported\textsuperscript{45,46} that the H atom preferentially undergoes addition reaction with benzyltrimethylammonium chloride cation to form a species similar to VIII in scheme III. However, because PVBT has an H atom attached to the polymer backbone, the abstraction of the H atom to generate α- and β-radiicals is also possible. On pulsing the PVBT solution containing thionine, the formation of semithionine (at 400 nm) was observed, indicating the formation of α-radicals on the reaction of H with PVBT. From the results of these experiments, the yield of α-radicals was estimated to be 26%. This
value is twice that reported for another ionizable polymer poly-(p-sodium styrene sulphonate), which ionizes to an anionic species; however it is similar to the values reported for α-radical yields of other water-soluble polymeric systems, viz., 26% for poly vinyl methylether, 33% for polyacrylic acid, and significantly lower than the reported 70% for polyvinyl alcohol. This indicates that the fraction of α-radicals generated for water-soluble polymers as a result of H-abstraction reaction depends on the type of monomeric unit of the polymer. Since only 26% of the H atoms generated resulted in α-radicals remaining may react to form other species in scheme III. To identify the transient for which spectra were obtained, pulse radiolysis studies with the H atom were carried out under aerated conditions. Under aerated conditions, the H atoms in the medium are converted to HO₂⁻. It is well documented that HO₂⁻ predominantly reacts with solutes by H atom abstraction and absorbs in range < 250 nm. Since the transient spectra obtained by the reaction of HO₂⁻ radical with PVBT is similar to that obtained by the reaction of the H atom with the polymer, it can be said that spectra 6(a) are due to species formed by an abstraction reaction of the H atom with PVBT.

**Steady state irradiation effect on PVBT solution.** Polymers undergo degradation and cross-linking simultaneously on irradiation in solvents. The net effect depends on which is predominant of the two processes. For a given system, the predominant process primarily depends on the chemical structure of monomer units constituting the polymer, the type of solvent, and the dose range of study. For aqueous PVBT solutions, an initial decrease in the viscosity of the solutions at all dose rates indicates degradation of the polymer chains to lower molecular weight fragments. For a dilute aqueous polymer solution, the initial decrease in viscosity can be attributed to the indirect effect of radiolytic products of water because the major energy deposition takes place in water. It is clear that the reaction of radiolytic products of water with the polymer results in species, which preferentially undergoes main chain scission. Similar observations have been recently reported for another ionic polymer system, namely, poly-(p-sodium styrene sulphonate). These observations suggest that at a low concentration, since the polymer chains are far apart, even at very high radiation doses when sufficient radicals are generated on polymer chains, no intermolecular cross-linking takes place. Cross-linking, if any, is of an intramolecular type, which does not result in polymer gel. On the other hand, at higher concentrations (>8%) the chains are close enough so that the radicals generated on two polymer chains interact to form intermolecular cross-links to form gel.

The ambient condition during irradiation is known to significantly affect the properties of products formed during irradiation. An initial decrease in the viscosity of polymer solution under aerated and oxygenated conditions indicates that dissolved O₂ acts as a promoter for oxidative degradation of the polymer.

**CONCLUSION**

Radiation polymerization studies indicate that high molecular weight PVBT can be obtained at a very low radiation dose under aerated conditions. Pulse radiolysis studies of PVBT show that the reactivity of radiolytic products of water with PVBT is lower than that with the monomer VBT. OH radicals react with the polymer either to give a radical species by methylene H abstraction or to form an adduct. H atom reaction with PVBT generates α-radicals to a significant extent. The aqueous electron (eₐ⁻) reacts with PVBT predominantly to give a polymeric benzyl radical.
Steady-state irradiation studies in aqueous solution show that PVBT predominantly undergoes cross-linking on irradiation in aqueous solutions. Beyond critical concentration of 2%, PVBT undergoes intermolecular cross-linking to form a soft rubbery gel. However, the gelation dose is a function of dose rate, concentration, and ambience of irradiation.

ACKNOWLEDGEMENTS

We sincerely thank Mr. Tirumalesh K. of Isotope Application Division, BARC, for carrying out the chloride estimation studies of radiation polymerized PVBT. We are also thankful to one of the referees whose comments have considerably improved the quality of the paper.

REFERENCES

1. Hukeler, D., Hamielec, A. E. and Baade, W. (1989) The polymerization of quaternary ammonium cationic monomers with acrylamide. In: Polymers in Aqueous Media, Advances in Chemistry Series J. 223, Ed. E. Glass, pp. 175–192, American Chemical Society, Washington, D.C.
2. Sata, T., Tsujimoto, M., Yamaguchi, T. and Matsusaki, K. (1996) Change of anion exchange membrane in sodium hydroxide solution at high temperature. J. Membr. Sci. 112: 161–170.
3. Konar, N. and Kim, C. (1998) Water soluble quaternary amine polymers as controlled release carriers. J. Appl. Polym. Sci. 69: 263–269.
4. Bhardwaj, Y. K., Kumar, V. and Sabharwal, S. (2003) Swelling behavior of radiation polymerized polyampholytic two component gels: dynamic and equilibrium swelling kinetics. J. Appl. Polym. Sci. 88: 730–742.
5. Tsuchida, E. and Nishide, H. (1977) Polymer metal complexes and their catalytic activity. Adv. Polym. Sci. 24: 1–87.
6. Hanada, F. and Hirayama, H. (1991) Bipolar membranes for electrolys is of water at low voltage. Chem. Abstr. 114: 124114.
7. Seckin, T., Alici, B., Cetinkaya, E. and Ozdemir, I. (1996) Synthesis and radical polymerisation of novel vinyl monomers having imidazoline and pyrimidine moieties. Polym. Bull. 37: 443–450.
8. Kanazawa, A., Ikeda, T. and Endo, T. (1993) Polymeric phosphonium salts as a novel class of cationic biocides-II Effects of counter anion and molecular weight on antibacterial activity of polymeric phosphonium salts. J. Polym. Sci. Part A: Polym. Chem. 31: 1441–1447.
9. Takeoka, Y., Berker, A. N., Du, R., Enoke, T., Grosberg, A., Kardar, M., Oya, T., Tanaka, K., Wang, G., Yu, X. and Tanaka, T. (1999) First order phase transitions and evidence for frustrations in polyampholytic gels. Am. Chem. Soc. 82: 4683–4685.
10. Nho, Y. C., Sugo, T., Makuuchi, K. and Jin, J. H. (1993) Radiation induced co-grafting of vinylbenzyltrimethylammonium chloride and hydroxethyl methacrylate onto polyethylene in the presence of solvents. Polli mo 17: 433–440.
11. Jones, R. J., Matsubayashi, Y. and Haskins N. J. (1989) Mechanism of radiation-induced crosslinking of chloromethyl styrene and methyl styrene. Eur. Polym. J. 25: 701–707.
12. Jones, R. J., Miller Tate P. C. and Bramley D. R. (1993) Excited state charge-transfer interactions in electron-beam resists based on styrene co-polymers. Polymer 34: 1768–1772.
13. Wojnarovatis, L., Takacs, E. and Biro, A. (1995) Propagation and size-dependent chain termination rate parameters in the polymerization of acrylates in aqueous solution as studied by pulse radiolysis. J. M. S. Pure Appl. Chem. A32: 443–454.
14. Kumar, V., Bhardwaj, Y. K., Sabharwal, S. and Mohan, H. (2003) Role of radiolytically generated species in radiation induced polymerization of vinylbenzyltrimethyl ammonium chloride (VBT) in aqueous solution: steady state and pulse radiolysis study. J. Radiat. Res. 44: 161–169.
15. Sonntag, C. V., Bothe, E., Ulanski, P. and Deeble, D. J. (1995) Pulse radiolysis in model studies toward radiation processing. Radiat. Phys. Chem. 46: 527–532.
16. Kuwabara, M., Ida, Y., Inamami, O., Sawamura, S., Yoko- yama, K. and Tsujitani, M. (2002) Radiation-chemical properties of the hypoxic cell radiosensitizer doranidazole (PR-350). J. Radiat. Res. 43: 77–88.
17. Kapoor, S., Mukherjee, T., Kagiya, T. V. and Nair, C. K. K. (2002) Redox reactions of tocopherol monoglucoside in aqueous solutions: a pulse radiolysis study. J. Radiat. Res. 43: 99–106.
18. Bhardwaj, Y. K., Mohan, H., Sabharwal, S. and Mukherjee, T. (2001) Radiation effect on poly (p-sodium styrene sulphonate) of different degrees of polymerization in aqueous solution: pulse radiolysis and steady state study. Radiat. Phys. Chem. 62: 229–242.
19. Higo, Y., Kato, Y., Itoh, M. and Kozuka, M. (1982) Gel-permeation chromatography and intrinsic viscosity of poly(4-vinylbenzyltrimethylammonium chloride) in aqueous solution. Polym. J. 14: 809–814.
20. Fielden, E. M. (1982) Chemical dosimetry of pulsed electron and X-ray sources in the 1–20 MeV range. In: Study of Fast Processes and Transient Species by Electron Pulse Radiolysis, Eds. J. H. Baxendale and F. Busi, pp. 49–62, D. Riedel Publishing, Dordrecht, Holland.
21. Guha, S. N., Moorthy, P. N., Kishore, K., Naik, D. B. and Rao, K. N. (1987) One electron reduction of thionine studied by pulse radiolysis. Proc. Indian Acad. Sci. (Chem. Sci.) 99: 261–271.
22. Priyadarshini, K. I., Naik, D. B., Moorthy, P. N. and Mittal, J. P. (1991) Energy transfer studies of coumarin dyes using electron pulse radiolysis. Proc. 7th Tihany Symposium on Radiation Chem, Budapest, p.105.
23. Spinks, J. W. T. and Woods, R. J. (1990) Water and Inorganic Aqueous Systems. In: An Introduction to Radiation Chemistry, Eds. J. W. T. Spinks and R. J. Woods, pp. 243–313, John Wiley, New York.
24. Ellison, D. H., Salmon, G. A. and Wilkinson, F. (1972) Nano-second pulse radiolysis of methanolic and aqueous solutions of readily oxidizable solutions. Proc. R. Soc. Lond. Ser. A. 328: 23–34.
25. Sabharwal, S. and Kishore, K. (1994) Pulse radiolysis study of reactions of tetracycline with radiolytically generated reducing species. Radiat. Phys. Chem. 44: 507–513.
26. Bensasson, R. V. L. and E. J. and Truscott, T. G. (1983) Introduction In: Flash Photolysis and Pulse Radiolysis Contributions to the Chemistry of Biology and Medicine, pp. 1–19, Pergamon Press, Oxford.

27. Neta, P., Simic, M. and Hayon, E. (1969) Pulse radiolysis of aliphatic acids in aqueous solution I. Simple monocarboxylic acids. J. Phys. Chem. 73: 4207–4213.

28. Simic, M., Neta, P. and Hayon, E. (1969) Pulse radiolysis of aliphatic acids in aqueous solution II. Hydroxy and polycarboxylic acid. J. Phys. Chem. 73: 4214–4220.

29. Sonntag, C. V., Bothe, E., Ulanski, P. and Deeble, D. J. (1995) Pulse radiolysis studies toward radiation processing. Radiat. Phys. Chem. 46: 527–534.

30. Spinks, J. W. T. and Woods, R. J. (1990) Aqueous organic systems. In: An Introduction to Radiation Chemistry, pp. 315–363, John Wiley, New York.

31. Bobrowski, K. (1981) Pulse radiolysis of aqueous solutions of benzyltrialkylammonium cations. Reactions with the primary transients from water radiolysis. J. Phys. Chem. 85: 382–388.

32. Sabharwal, S., Mohan, H., Bhardwaj, Y. K. and Majali, A. B. (1996) Structure-reactivity studies on the crosslinking of poly(vinyl methyl ether) in aqueous solution: a pulse radiolysis study. J. Chem. Soc. Faraday Trans. 92: 4401–4406.

33. Ulanski, P., Zainuddin and Rosiak, J. M. (1995) Pulse radiolysis of poly(ethylene oxide) in aqueous solution I. Formation of macroradicals. Radiat. Phys. Chem. 46: 913–916.

34. Davis, J. E., Sangster, D. F. and Senogles, E. (1981) Pulse radiolysis of aqueous solutions of N-vinylpyrrolidin-2-one and poly(N-vinylpyrrolidin-2-one). Aust. J. Chem. 34: 1423–1434.

35. Behzadi, A. and Schanbel, W. (1973) Kinetic studies on the influence of conformation and chain length on the reaction of hydroxyl radicals with poly(acrylic acid) in solution. Macromolecules 6: 824–826.

36. Bhardwaj, Y. K., Mohan, H., Sabharwal, S. and Majali, A. B. (2000) Role of radiolytically generated species in radiation polymerization of sodium p-styrene sulphonate (SSS) in aqueous solution: Steady state and pulse radiolysis study. Radiat. Phys. Chem. 58: 373–385.

37. Spinks, J. W. T. and Woods, R. J. (1990) Water and Inorganic Aqueous Systems. In: An Introduction to Radiation Chemistry, pp. 243–313, John Wiley, New York.

38. O’Neill, O., Steenken, S. and Schulte-Frohlinde, D. (1975) Formation of radical cations of methoxylated benzenes by reaction with OH radicals, Ti^+(aq), Ag^+(aq) and SO_4^− in aqueous solution. An optical and conductometric pulse radiolysis and in situ radiolysis electron spin resonance study. J. Phys. Chem. 79: 2773–2779.

39. Mc Askill, N. A. and Sangster D. F. (1984) Competition between reactive sites during the pulse radiolysis of styrene in aqueous solution. Aust J. Chem. 37: 2137–2143.

40. Behar, D. (1991) Are positive ion formed in pulse radiolysis of alkylobenzene sulfonates. J. Phys. Chem. 95: 4342–4347.

41. Buxton, G. V., Greenstock, C. L., Helman, W. P. and Ross, A. B. (1988) Critical review of rate constants of hydrated electron, hydrogen atom and hydroxyl radical (‘OH/’O’) in aqueous solution. J. Phys. Chem. Ref. Data 17: 517–751.

42. Sehested, K., Corfitzen, H., Christensen, H. C. and Hart, E. J. (1975) Rates of reaction of O·, OH and H with methylated benzenes in aqueous solution. Optical spectra of radicals. J. Phys. Chem. 79: 310–315.

43. Holckman, J. and Sehested, S. (1977) Dissociation of the OH adduct of N, N-dimethylamine in aqueous solution. J. Phys. Chem. 81: 1963–1966.

44. Jayson, G. G., Parsons, B. J. and Swallow, A. J. (1973) Some simple, highly reactive, inorganic chlorine derivatives in aqueous solution. J. Chem. Soc. Faraday Trans. 69: 1597–1607.

45. Chutny, B. (1967) Spectral correlation of transients with their parent derivatives in aqueous solution. Nature, 213: 593–594.

46. Anbar, M., Farhataziz and Ross, A. (1975) Natl. Stand. Ref. Data Ser. (U. S. Natl. Bur. Stand.), No. 51.

47. Sabharwal, S., Mohan, H., Bhardwaj, Y. K. and Majali, A. B. (1999) Radiation induced crosslinking and strand breaking of pol(vinyl methylether) in aqueous solution. Radiat. Phys. Chem. 54: 643–653.

48. Ulanski, P., Bothe, E., Hildenbrand, K., Sonntag, C. V. and Rosiak, J. M. (1997) The influence of repulsive forces on the lifetime of poly(acrylic acid) radicals an aqueous solution. Nukleonika 42: 425–436.

49. Ulanski, P., Bothe, E., Rosiak, J. M. and Sonntag, C. V. (1994) OH radical induced crosslinking and strand breaking of pol(vinyl alcohol) in aqueous solution in the absence and presence of oxygen. A pulse radiolysis and product study. Macromol. Chem. Phys. 195: 1443–1461.

50. Gordon, L. H. (1981) Optical Spectra of Non Metallic Inorganic Transient Species in Aqueous Solution, p. 20, National Standard Reference Data System (NSRDS), U.S. Dept. of Commerce.

51. Woods, R. J. and Pikaev, A. K. (1993) Polymer modification. In: Applied Radiation Chemistry, pp. 331–391, John Wiley & Sons, Inc.

52. Chapiro, A. (1962) General aspects of radiation initiated polymerization. In: Radiation Chemistry of Polymeric Systems, Ed. A. Chapiro, pp. 121–154, Interscience, New York.

53. Liu, P., Zhai, M., Li, J., Jing, P. and Wu, J. (2002) Radiation preparation and swelling behaviour of sodium carboxymethyl cellulose hydrogels. Radiat. Phys. Chem. 63: 525–528.

54. Kume, T., Nagasawa, N. and Yoshii, F. (2002) Utilization of carbohydrates by radiation processing. Radiat. Phys. Chem. 63: 625–627.

Received on October 6, 2003
1st Revision on January 30, 2004
Accepted on February 10, 2004