Radiation Chemical Studies on Thermosensitive N-isopropylacrylamide and Its Polymer in Aqueous Solutions

ANJALI ACHARYA1, HARI MOHAN2 and S. SABHARWAL1*

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The pulse radiolysis technique has been employed to determine the initiation and propagation rates of different transient species involved in the polymerization of N-isopropylacrylamide (NIPA) in aqueous solutions. Polymerization by anionic mechanism has been observed to be faster than by the free-radical mechanism. The kinetic, spectroscopic and redox properties of the transient species formed upon reaction of primary radiolytic species of water radiolysis with NIPA have been evaluated. The one-electron oxidation potential for the formation of a radical cation is quite high (>2 V), but the one-electron reduction potential is low (in the range of ~0.3 to ~0.7 V). The radical anion of NIPA is able to undergo an electron-transfer reaction with MV2+, and has a pKa value of 3.2. The tert-butyl alcohol radical was also able to initiate polymerization. Gamma radiation-induced polymerization studies showed that the reaction of H2/ OH-/ tert-butyl alcohol radicals with NIPA results in a nearly equal yield of the gel fraction. The hydrogel is observed to have very little swelling below pH 3 and above pH 10. The linear polymer of NIPA formed by irradiating dilute aqueous solution is found to be a thermosensitive polymer with lower a critical solution temperature (LCST) of ~33°C. The diameters of polymer molecules were 290 and 20 nm at temperature below and above LCST, respectively.

INTRODUCTION

Polymers that do not dissolve in water, but swell due to the presence of an elastic network are called “hydrogel.” Some of these polymer gels can respond dramatically to changes in their environment, such as the temperature, pH, solvent composition, and applied voltage. The gel synthesized from the N-isopropylacrylamide (NIPA) monomer is a well-known thermosensitive gel that shows a discontinuous volume phase transition in response to temperature changes.1–7 The lower critical solution temperature (LCST) of a linear polymer of NIPA (PNIPA) in aqueous solution and the volume phase transition temperature (VPTT) of the crosslinked PNIPA hydrogel are essentially the same phenomena, and is generally called the transition temperature (Tg). The crosslinked gel of NIPA undergoes a reversible volume transition at ~34°C. Below this temperature, the gel exhibits strong polymer-solvent interactions through hydrogen bonding between the hydrophilic groups of the polymer and the surrounding water molecules. These interactions make the gel highly solvated, contributing to a relative increase in the particle size. Above 34°C, the gel favors polymer-polymer interactions with neighboring polymer strands inside the gel, which are stronger than the polymer-solvent interactions. The polymer-polymer interactions are caused by hydrogen bonding between polymers and also hydrophobic interactions between isopropyl groups. These interactions cause the water molecule to be expelled from the gel, and the gel collapses. Because of its unique properties, PNIPA hydrogels are being investigated as a model for a theoretical examination of phase transition as well as for practical applications.8–11 Many research groups all over the world are now working on this intelligent hydrogel. Therefore, it is important to study in detail the mechanism involved in the formation of linear polymer and the crosslinked gel. Some researchers have studied the reactivity of primary reactive species of water radiolysis with acrylamide and its derivatives in dilute aqueous solution. Detailed studies about the radiation chemistry involved during hydrogel formation of the NIPA monomer have not been reported.12–15

Although polymerization could be carried out by conventional means, ionizing radiations has been preferred and recognized as a suitable tool for the synthesis of biocompatible polymers.16 It is a simple and additive free process in which no initiator or chemical accelerators are required to carry out polymerization and crosslinking reactions. In continuation of our previous work, we have now focused attention on eluci-

*Corresponding author: Fax: +91-22-2550 5151,
E-mail: sunsab@magnum.barc.ernet.in
1Radiation Technology Development Section and 2Radiation Chemistry & Chemical Dynamics Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India.
dating the characteristics of the transient species due to the reaction of 'OH and H' radicals with a monomer.\textsuperscript{17} In addition to these studies, the redox properties of the transient species have also been investigated. A linear polymer of NIPA has been prepared by steady state $\gamma$-radiolysis; its molecular weight and LCST have been determined. The PNIPA hydrogel has also been prepared separately by the reaction of $e_{aq}$, 'OH, H' and tert-butyl alcohol radicals with a monomer using a $^{60}$Co source at various doses. The pH-dependent swelling ratio of PNIPA hydrogel has been determined.

**MATERIALS AND METHODS**

**Materials**

N-isopropylacrylamide (NIPA, Scheme 1), obtained from Aldrich Chemicals, was used without any further purification. All other chemicals used were of AnalaR-grade purity. The solutions were prepared in “nanopure” water, and freshly prepared solutions were used in each experiment. The pH of the solution was adjusted using HClO$_4$ and NaOH. High-purity gases (N$_2$, N$_2$O, O$_2$) were used for purging the solutions. The optical absorption studies in the ground state were carried out with a Hitachi 330 spectrophotometer.

**Preparation of linear polymer**

A linear polymer of NIPA was synthesized by irradiating an aqueous solution of NIPA (4 wt%) in a gamma chamber to a total $\gamma$-dose of 8 kGy (dose rate = 8 kGy/h). After irradiation, the solution was diluted with water. The linear polymer was separated by the addition of methanol. The precipitated linear polymer was dissolved in water and used for further studies.

**Preparation of hydrogel**

The three dimensionally cross-linked polymer of NIPA was synthesized by irradiating an aqueous solution of NIPA (10 wt%) for different times in a gamma chamber (dose rate = 0.48 kGy/h) under experimental conditions, such that only 'OH/H'/$e_{aq}$/tert-butyl alcohol radicals react with the monomer. For sol-gel studies, the crosslinked gels were swollen in distilled water at 25$^\circ$C, and then deswelled at 45$^\circ$C to leach out the sol-fraction. The gels were again swollen at 25$^\circ$C and the process was repeated until no more sol-fraction leached out. The gels were dried to a constant weight for gel determination. The % gel formed was estimated from the weight ratio of the water-insoluble fraction to the feed monomer.\textsuperscript{41}

**pH-Dependent swelling studies**

A known weight of dried gel ($W_o$) was immersed in an aqueous solution of different pH values for equilibrium swelling studies. The hydrogel was periodically removed, and its weight was determined after removing the excess surface water. The gel sample was kept in the solution until a constant weight was attained ($W_s$), and then the swelling ratio ($S_o = W_s/W_o$) was determined.

**Determination of the molecular weight of polymer**

The molecular weight of NIPA polymer was determined by measuring the viscosity of a polymer solution in an Ubbelohde viscometer.\textsuperscript{18} The time taken for the polymer solution to flow through a constant volume in Ubbelohde viscometer was determined for different concentrations. From the intrinsic viscosity [$\eta$], the viscosity-average molecular weight ($M_v$) was determined by using the following relationship:

$$\eta = K M_v^n,\quad (1)$$

where $K$ and $\alpha$ are constants for a given polymer-solvent system at a given temperature. The particle size of the polymer was determined by a dynamic light scattering technique using a Brookhaven Instruments Corporation particle sizer (Model BI-90).

**Pulse radiolysis studies**

Pulse radiolysis experiments were carried out with high-energy electron pulses (7 MeV, 50/500 ns) obtained from a linear electron accelerator (Ray Technologies, UK), whose details are given elsewhere.\textsuperscript{19,20} The dose delivered per pulse was determined with aerated aqueous solution of KSCN (1 × 10$^{-2}$ mol dm$^{-3}$). The G denotes the number of species per 100 eV of absorbed energy ($G = 1$ corresponds to 0.1036 $\mu$mol J$^{-1}$) and $\epsilon$ is the molar absorptivity of (SCN)$_2^-$ at 500 nm. The dose per pulse was close to 12 and 30 Gy for 50 and 500 ns pulse respectively (1 Gy = 1 J kg$^{-1}$).

The radiolysis of N$_2$-saturated neutral aqueous solution leads to the formation of three highly reactive species (H', 'OH, $e_{aq}$) in addition to the formation of less reactive or inert molecular products (H$_2$, H$_2$O$_2$, H$_3$O$^+$).\textsuperscript{21}

$$\text{H}_2\text{O} \rightarrow \text{H}' + \text{OH} + e_{aq}$$

A reaction with 'OH radicals was carried out in N$_2$O-saturated solutions, where $e_{aq}$ was quantitatively converted to 'OH radicals with $G(\text{OH}) = 5.6$. The reaction with O$^-$ was carried out in N$_2$O-saturated solutions at pH = 13, where 'OH radicals were converted to O$^−$ with a $K_v$ value of 11.9. A reaction with $e_{aq}$ was carried out under N$_2$-saturated conditions in the presence of tert-butyl alcohol (0.3 mol dm$^{-3}$) to scavange 'OH radicals. The reaction with H was carried out under N$_2$-saturated conditions at pH = 1, where $e_{aq}$ was converted to H with $G(\text{H}) = 3.2$. 'OH radicals were scavenged by tert-butyl alcohol (0.3 mol dm$^{-3}$).

The reaction with Cl$_2^-$, a specific one-electron oxidant, was carried out in aerated acidic (pH = 1) aqueous solution of Cl$^-$ (1 × 10$^{-4}$ mol dm$^{-3}$) by monitoring its decay in the presence of different concentrations of NIPA. The reaction with SO$_4^{2−}$ was carried out in a N$_2$-saturated aqueous solution of S$_2$O$_4^{2−}$ (4 × 10$^{-2}$ mol dm$^{-3}$) containing tert-butyl alcohol (0.3 mol dm$^{-3}$) and a low concentration of NIPA. The reaction with COO$^-$, a specific one-electron reductant, was carried out in a N$_2$O-saturated aqueous solution of sodium formate (1 × 10$^{-3}$ mol dm$^{-3}$) containing a low concentration of NIPA (1 × 10$^{-3}$ mol dm$^{-3}$).
A reaction with hydroxy alkyl radicals [CH₂OH, CH₃CHOH, (CH₃)₂COH, CH₂(CH₃)₂COH] was carried out in N₂O-saturated solutions containing 1 mol dm⁻³ alcohol and 10⁻⁵ mol dm⁻³ NIPA.

The transient species formed upon pulse radiolysis were monitored using a 450 W pulsed xenon arc lamp as the light source, a monochromator (Kratos, GM-252), and a Hamamatsu R-955 photomultiplier as the detector. The photomultiplier output was digitized using a 100 MHz storage oscilloscope interfaced to a computer for kinetic analysis. The rate-constant values were taken from that kinetic analysis for which a very good correlation was obtained between the experimental and calculated results.²²) The bimolecular rate constant was determined from a linear-regression plot of kobs versus the solute concentration for at least three experiments. The variation was within ±10%.

RESULTS AND DISCUSSION

Ground-state optical absorption studies on the NIPA monomer

The ground-state optical absorption spectrum of an aqueous solution of NIPA (8 × 10⁻⁵ mol dm⁻³, pH = 1) shows an absorption band at 205 nm (ε = 6.5 × 10³ dm³ mol⁻¹ cm⁻¹), a shoulder in the 220–240 nm region and with negligible absorption at λ > 280 nm (Fig. 1a). The absorption spectrum remained the same in the pH 1–10 region. As the pH was increased (pH > 10), the absorption in the 200–220 nm region decreased (Fig. 1b) along with the formation of a broad band in the 220–235 nm region (Fig. 1c). At pH = 13, a sharp absorption band at 230 nm (ε = 3.2 × 10³ dm³ mol⁻¹ cm⁻¹) with negligible absorption at λ > 280 nm (Fig. 1d) was observed. The variation of the absorbance at 220 nm as a function of the pH is shown as an inset of Fig. 1. The optical absorption spectra were corrected for the background absorption of the matrix at each pH. These changes may be due to hydrolysis since amides are known to hydrolyse rapidly by acids and far more rapidly by alkalies.²³) It is clear from these results that the optical absorption detection technique can be employed for pulse radiolysis studies without any correction for the ground-state absorption in the 300–700 nm region.

Pulse radiolysis studies

Reaction of H atoms with NIPA: A pulse radiolysis of N₂-saturated acidic (pH = 1) aqueous solution of NIPA (1 × 10⁻³ mol dm⁻³) showed the formation of a transient absorption band with λmax at 410 nm (Fig 2a). The rate constant for the reaction of H⁺ with NIPA was determined by formation kinetic studies. The pseudo-first-order rate constant (kobs) increased with the solute concentration, and the bimolecular rate constant, determined from the slope of a linear plot, gave a value of 4 × 10⁹ dm³ mol⁻¹ s⁻¹. The bimolecular rate constant for the reaction of H⁺ with NIPA was also determined by competition kinetics studies using tetracycline as a reference solute (kTC+H = 2.5 × 10⁹ dm³ mol⁻¹ s⁻¹).²⁴) The transient absorbance of the TC-H⁺ adduct at 440 nm, formed upon the pulse radiolysis of a N₂-saturated acidic (pH = 1) aqueous solution, was determined for various concentrations of NIPA (0–1 × 10⁻³ mol dm⁻³ containing tetracycline (4 × 10⁻⁴ mol dm⁻³) and tert-butyl alcohol (0.3 mol dm⁻³). The bimolecular rate constant value was determined to be 2 × 10⁹ dm³ mol⁻¹ s⁻¹.

An analysis of the absorption signal at 410 nm (inset, Fig. 2) revealed that it was decaying neither by first-order nor by second-order kinetics, when the entire absorption-time signal was analyzed. This indicates that more than one process is responsible for its decay. The monomer radical (M₁⁺), formed upon a reaction of a H⁺ atom with NIPA (Reaction 3), can further propagate with other NIPA molecules to form a dimer and higher polymer radicals (Reactions 4, 5):

\[ \text{NIPA} + \text{H}^+ \rightarrow \text{M}_1^+ , \]

Fig. 1. Ground-state optical absorption spectra of an aqueous solution of NIPA (8 × 10⁻⁵ mol dm⁻³) at pH = 1 (a); 10.5 (b); 11.5 (c) and 13 (d). The inset shows the variation of absorption at 220 nm as a function of the pH.

Fig. 2. Transient optical absorption spectra obtained upon the pulse radiolysis of a N₂-saturated acidic (pH = 1) aqueous solution of NIPA (1 × 10⁻³ mol dm⁻³) 2 (a) and 40 µs (b) after the pulse. The inset shows the absorption-time profile at 410 nm.
The absorption signal at 410 nm would represent the overall decay for all of these reactions. An analysis of the initial signal (up to 100 µs) showed decay by first order with $k = 5 \times 10^3$ s$^{-1}$. The decay from 100 to 450 ms also showed first-order kinetics with $k = 2 \times 10^4$ s$^{-1}$. The decay becomes still slower with increasing time ($k = 1 \times 10^3$ s$^{-1}$ from 450 to 800 µs), which would be due to the formation of bulkier polymer radicals. These decay rates can be taken as propagation rates for the polymerization reaction. A time-resolved study (Fig. 2b) has not shown any appreciable change in $\lambda_{\text{max}}$, but the transient absorption band was broader in nature, which may be due to the formation of bulkier radicals of similar nature. The addition of H$^+$ could be at the double bond (Scheme 1), and this radical could now add to other NIPA molecules to continue propagation.

Scheme 1

Reaction with 'OH radicals: Pulse radiolysis of a N$_2$O-saturated neutral aqueous solution of NIPA (1 × 10$^{-3}$ mol dm$^{-3}$) showed the formation of a transient absorption band at 420 nm (Fig. 3a). In the presence of tert-butyl alcohol (0.3 mol dm$^{-3}$), an efficient 'OH radical and weak H$^+$ atom scavenger, small absorption was seen in the 270–550 nm region, indicating that the observed spectrum (Fig. 3a) is mainly due to the reaction of 'OH radicals with NIPA. The bimolecular rate constant for the reaction of O– with NIPA, determined by formation kinetic studies at 420 nm, gave a value of $6 \times 10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$. Competition kinetic studies using KSCN as the standard solute gave a value of $7 \times 10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$. Similar to the transient absorption signal at 410 nm, in the case of the H$^+$ atom reaction with NIPA (Fig. 2), the absorption signal at 420 nm obtained upon the reaction of 'OH radicals with NIPA, also showed neither first nor second-order kinetics. The absorption up to 100 µs decayed by first-order kinetics with $k = 5 \times 10^3$ s$^{-1}$, and that from 100 to 500 µs also decayed by first-order kinetics with $k = 2 \times 10^3$ s$^{-1}$. The decay was slower after 450 µs. These changes should be due to a propagation initiated by the monomer radical formed upon the reaction of 'OH with NIPA, similar to those shown in Reactions 4 and 5.

The transient absorption band at 420 nm decayed faster under aerated conditions (Fig. 3e), as compared to a N$_2$O-saturated solution (Fig. 3d). Fig. 3b represents the transient absorption spectrum obtained by a pulse radiolysis of an aerated aqueous solution of NIPA (1 × 10$^{-3}$ mol dm$^{-3}$), 3 µs after the pulse. The small absorption observed in the 350–450 nm region was completely scavenged under O$_2$-saturated conditions. These studies suggest that the transient species formed upon a reaction with the 'OH radical is a carbon-centered radical, which had high reactivity with oxygen. The kinetic and spectroscopic properties of the transient species formed upon a reaction of H$^+$ and an 'OH reaction with NIPA are similar, suggesting that a similar type of the transient species is formed in both cases. 'OH radicals may also add to the double bond in a similar manner as shown in Scheme 1. The nature of the transient absorption spectrum remained the same in the pH 3.5–10 region, indicating that the transient species formed upon the reaction of 'OH radicals with NIPA does not undergo any acid-base catalyzed reaction.

Reaction with O$^-$: The reaction of O$^-$ with NIPA showed the formation of a transient absorption band at 420 nm with shoulders in the 340–360 and 550–650 nm regions (Fig. 3c). The bimolecular rate constant for the reaction of O$^-$ with NIPA, determined by formation kinetic studies at 420 nm, was found to be $1 \times 10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$. In this case also, the absorption signal did not show either first or second-order decay. The absorption up to 100 µs decayed by first-order kinetics with $k = 7 \times 10^3$ s$^{-1}$, and from 100 to 500 µs also decayed by first-order kinetics with $k = 3 \times 10^3$ s$^{-1}$. These rates should be the propagation rates of the transient species formed upon reaction of O$^-$ with NIPA.

As mentioned earlier, H$^7$'OH radicals can react with NIPA either by addition to the unsaturated bond, or by abstraction of the H$^+$ atom. It may be possible to find out which is the predominant route of reaction by selecting the experimental conditions. The 'OH radical behaves as an electrophile, whereas its conjugate form, O$^-$, is a nucleophile. Therefore, 'OH radicals readily add to the double bond, and the O$^-$ reaction is by...
H-abstraction, whose rate is slower than OH radical addition and a different nature of the transient spectra (Fig. 3c) may also support the conclusion that the O– reaction with NIPA is by an abstraction mechanism, and that H/ OH radicals are involved in the polymerization of NIPA could not be determined. These results suggest that propagation by an anionic mechanism is faster. It has also been reported that eaq– adds to the vinyl double bond of NIPA.

The transient absorption of eaq– at 700 nm decayed faster and by first-order kinetics in the presence of low concentrations of NIPA (1 × 10–4 mol dm–3, pH = 10.2), indicating high reactivity of eaq– with NIPA. The bimolecular rate constant was determined to be 1 × 108 s–1. The time-resolved spectra showed the formation of a transient absorption band at 295 nm with broad absorption in the 350–450 nm region. This spectrum should be due to the transient species (radical anion) formed upon the reaction of COO– with NIPA (Reaction 6) because COO– in the absence of any added solute has λmax at 260 nm (ε = 2 × 104 dm3 mol–1 cm–1).

\[
\text{COO}^- + \text{NIPA} \rightarrow (\text{NIPA})^- + \text{CO}_2
\]

The absorption-time profile at 295 nm showed decay by first-order kinetics with k = 2 × 105 s–1. Similar to the eaq– reaction with NIPA, in this case also, the rates of different propagation steps involved in the polymerization process could not be determined. The yield of the transient absorption band at 295 nm, formed upon a reaction of COO– with NIPA, was comparable to that formed upon a reaction with eaq–.

The isopropyl ketyl radical (CH3)2COH, IP, is another specific one-electron reductant with E° = –1.05 V, and is formed by the pulse radiolysis of a N2O-saturated aqueous solution of isopropanol. Pulse radiolysis of a N2O-saturated aqueous solution (pH = 6) of isopropanol (1 mol dm–3) containing NIPA (1 × 10–3 mol dm–3) showed the formation of a transient absorption band at 285 nm with broad absorption in the 350–450 nm region. This spectrum should be due to the transient species (radical anion) formed upon the reaction of COO– with NIPA (Reaction 6) because COO– in the absence of any added solute has λmax at 260 nm (ε = 2 × 104 dm3 mol–1 cm–1).

Table 1. Kinetic and spectroscopic properties of the transient species formed upon pulse radiolysis of an aqueous solution of NIPA under different conditions.

| Reaction              | pH | λ (nm) | k (dm3 mol–1 s–1) (initiation) | ε (dm3 mol–1 cm–1) | Propagation rates (s–1) |
|-----------------------|----|--------|-------------------------------|------------------|------------------------|
| NIPA + H+             | 1  | 410    | 4 × 107 (2 × 109)             | 1350 ± 100       | 5 × 104, 2 × 105, 1 × 106 |
| NIPA + OH             | 6  | 420    | 6 × 108 (7 × 109)             | 850 ± 100        | 5 × 104, 2 × 104        |
| NIPA + O2             | 13 | 430    | 1 × 1010                     | 650 ± 100        | 7 × 104, 3 × 103        |
| NIPA + eaq–           | 10.2 | 295 | 1 × 1010 (1 × 1010)          | 7220             | 7 × 104                |
| NIPA + Cl2–           | 1  | 370–450 | 2 × 107                     | 8100             | 2 × 104                |
| NIPA + COO–           | 6  | 295    | -                             | -                | -                      |
| NIPA + IP             | 6  | 285, 410 | 5 × 109, 1 × 108             | -                | 9 × 103, 3 × 103, 1 × 103 |

The value in brackets was obtained by competition kinetic studies. *By formation kinetics at 295 nm.
reaction (a, Scheme 2):

$$(\text{CH}_3)_2\text{COH} + \text{NIPA} \rightarrow (45 \%) (\text{NIPA})^- + (\text{CH}_3)_2\text{CO} + \text{H}^+$$  

(a)

$$\rightarrow (55 \%) [\text{NIPA-}-(\text{CH}_3)_2\text{COH}]^+$$  

(b)

Scheme 2

The kinetic and spectroscopic properties of the transient absorption spectrum formed upon a reaction of the isopropyl ketyl radical with NIPA remained the same in the pH 6–10 range. However, at pH = 1, the transient absorption band at 285 nm showed a blue shift and $\lambda_{\text{max}}$ may be at wavelength <280 nm (Fig. 5). The variation of absorbance at 285 nm as a function of the pH showed an inflection point at pH = 3.2 (inset, Fig. 5). These studies show that while the nature of the transient absorption spectrum in the 370–500 nm region remained the same, the band at 285 nm showed a $pK_a$ value at 3.2 (Reaction 7). This should be due to protonation of the radical anion formed upon a reaction of the isopropyl ketyl radical with NIPA. The reaction of $e_{aq}^-$ with NIPA could not be carried out at pH < 3.5 due to its reaction with $H^+$. The isopropyl ketyl radical, which is a specific one-electron reduc-
tant, can be conveniently used to record the spectra and measure the $pK_a$ value of the radical anion in acidic solutions.

$$(\text{NIPA})^- + H^+ \rightarrow (\text{NIPA-H})^-$$  

(7)

The reactions of other hydroxy alkyl radicals [CH$_2$OH, CH$_3$CHOH, CH$_2$(CH$_3$)$_2$COH] were also carried out in N$_2$O-saturated solutions containing 1 mol dm$^{-3}$ alcohol and 1 $\times$ 10$^{-3}$ mol dm$^{-3}$ NIPA. CH$_3$CHOH radical ($E^o$ = –0.95 V) was also observed to react with NIPA, and the transient absorption spectrum was similar to that shown in Fig. 4. However, the overall yield of both transient bands at 285 and 410 nm was slightly lower (Table 2). The bimolecular rate constant for the reaction of the CH$_3$CHOH radical with NIPA was 4 $\times$ 10$^9$ dm$^3$ mol$^{-1}$ s$^{-1}$ and 1 $\times$ 10$^8$ dm$^3$ mol$^{-1}$ s$^{-1}$ at 285 and 410 nm, respectively. The yields of these transient absorption bands decreased further (Table 2) when the reaction was carried out with CH$_2$OH ($E^o$ = –0.73 V) and CH$_2$(CH$_3$)$_2$COH ($E^o$ = 0.15 V). The bimolecular rate constant for the reaction of these radicals with NIPA could not be determined accurately due to a very low absorption signal. The decreased yield should be due to the lower reduction potential values of these hydroxy alkyl radicals.

**Redox nature of transient species:** The oxidant methylviolotten (MV$^{2+}$) was used to determine the yield of reducing radical produced upon the reaction of $e_{aq}^-$ with NIPA. The reduced form (MV$^-$) has a well-defined band at 605 nm ($\varepsilon$ = 1.28 $\times$ 10$^4$ dm$^3$ mol$^{-1}$ cm$^{-1}$). Redox experiments were carried out in aqueous solutions of NIPA (1 $\times$ 10$^{-2}$ mol dm$^{-3}$), containing low concentrations (2 $\times$ 10$^{-4}$ mol dm$^{-3}$) of MV$^{2+}$. The transient species formed upon the reaction of $e_{aq}^-$ with NIPA (pH = 10.2) was observed to react with MV$^{2+}$ with a bimolecular rate constant of 5 $\times$ 10$^9$ dm$^3$ mol$^{-1}$ s$^{-1}$. The G(MV$^{2+}$) was determined to be 1.6.

The transient absorption band of MV$^+$, formed in a pulse radiolysis of a N$_2$-saturated aqueous solution of MV$^{2+}$ (5 $\times$ 10$^{-3}$ mol dm$^{-3}$, $\lambda$ = 395 nm) was observed to decay faster in the presence of low concentrations of NIPA (1–4) $\times$ 10$^{-4}$ mol dm$^{-3}$).

### Table 2. Kinetic parameters of the transient species formed upon a reaction of hydroxy alkyl radicals with NIPA.

| Hydroxy alkyl radical | $E^o$ (V) | $\Delta$O.D. at 285 nm | $\Delta$O.D. at 410 nm | G(MV$^+$) |
|-----------------------|-----------|------------------------|------------------------|-----------|
| (CH$_3$)$_2$COH        | –1.05     | 0.0218                 | 0.0156                 | 3.8       |
| CH$_3$CHOH             | –0.95     | 0.0204                 | 0.0063                 | 3.2       |
| CH$_2$OH               | –0.73     | 0.0131                 | 0.0040                 | 2.8       |
| CH$_2$(CH$_3$)$_2$COH  | +0.15     | 0.0080                 | 0.0033                 | 0.8       |
showing electron-transfer between NIPA and MV⁺, and the existence of the following equilibrium (Reaction 8):

\[
\text{MV}^{2+} + \text{NIPA} \rightleftharpoons \text{MV}^{+} + \text{NIPA}^-. \tag{8}
\]

The lower yield of MV⁺, upon a reaction of NIPA⁻ with MV²⁺, may be due to the existence of the above equilibrium. These studies suggest that the reduction potential of the NIPA⁻/NIPA couple is close to that of the MV⁺/MV²⁺ couple \((E^\circ = -0.45 \, \text{V})\). The redox nature of the transient species formed upon the reaction of hydroxy alkyl radicals \([	ext{CH}_2\text{OH}, \text{CH}_2\text{CHOH}, (\text{CH}_3)_2\text{COH}, \text{CH}_3(\text{CH}_2)_2\text{COH}]\) with NIPA was also studied by monitoring the formation of MV⁺. These studies were carried out in N₂O-saturated solutions of alcohols \((1 \, \text{mol dm}^{-3})\) containing \(1 \times 10^{-2} \, \text{mol dm}^{-3}\) NIPA and \(1 \times 10^{-4} \, \text{mol dm}^{-3}\) MV²⁺. Under these conditions, the direct reaction of OH and hydroxy alkyl radicals with MV²⁺ would be negligible. The one-electron reduced species of NIPA would only react with MV²⁺ to form MV⁺. As expected, the bimolecular rate constant for the reaction of one-electron reduced species of NIPA, generated by different of hydroxy alkyl radicals, was nearly the same \((2 \pm 0.5) \times 10^9 \, \text{dm}^3 \, \text{mol}^{-1} \, \text{s}^{-1}\). However, the yield of MV⁺ decreased with a decrease in the reduction potential value of hydroxy alkyl radicals (Table 2). These studies also suggest that the reduction potential value of the NIPA⁻/NIPA couple is low. Although the nature of the transient species formed upon a reaction of the isopropyl ketyl radical with NIPA at pH = 1 is different, it was equally efficient in reacting with MV²⁺, and produced a comparable yield of MV⁺.

**Effect of the solute concentration, dose rate and matrix viscosity on the decay of transient species:** The decay of the transient species (λ = 420 nm), formed upon a reaction of the 'OH radical with NIPA, was studied as a function of the NIPA concentration \((10^{-1}–10^{-4} \, \text{mol dm}^{-3})\) and dose rate \((12–120 \, \text{Gy per pulse})\). At a low dose rate \((30 \, \text{Gy per pulse})\), for low monomer concentrations \((10^{-2}–10^{-4} \, \text{mol dm}^{-3})\), the decay followed first-order kinetics, whereas at a high concentration \((10^{-1} \, \text{mol dm}^{-3})\), the decay showed an appreciable contribution of second-order kinetics. Under these conditions, monomer radicals were produced close to each other, and the recombination reaction may have competed with the propagation reaction. The contribution of second-order kinetics was also appreciable at a higher dose rate, because a high concentration of radicals produced would favor the recombination reaction over propagation.

γ-radiolysis of an aqueous solution of NIPA results in the formation of monomer radicals, which propagate to form a linear polymer and a cross-linked hydrogel. The linear polymer and cross-linked hydrogel are the main products formed at low and high concentrations of NIPA, respectively. Upon γ-radiolysis of an aqueous solution of NIPA, the matrix viscosity increased due to the formation of the linear polymer and hydrogel. The decay of transient species formed upon the reaction of 'OH radicals with NIPA was studied as a function of the matrix viscosity. An aqueous solution of NIPA (4 wt%, N₂O-saturated) was irradiated for different radiation doses (dose rate = 8 kGy/h) varying from 1.3 to 9 kGy. The viscosity of the solution was expected to be different in samples irradiated with different γ-doses. These samples were then subjected to pulse radiolysis, and the decay of the transient species was monitored as a function of the γ-dose. A controlled sample (before γ-radiolysis) showed first-order kinetics with \(k = 1 \times 10^3 \, \text{s}^{-1}\). The decay became slow for samples irradiated with a γ-dose. The decay was \(4 \times 10^2 \, \text{s}^{-1}\) and \(8 \times 10^1 \, \text{s}^{-1}\) for samples given 3.3 and 8 kGy of the γ-dose, respectively. The restricted motion of the radical in the viscous matrix may lower its reactivity.

**Studies with a polymer of NIPA:** The gamma radiolysis of a 4 wt% aqueous solution of NIPA was found to give a very good yield of polymer after irradiating with a 8 kGy dose (dose rate = 8 kGy/h). An aqueous solution of polymer of NIPA \((10.25 \, \text{mg/ml})\) was observed to be a temperature-sensitive material. The lower critical solution temperature of the polymer was determined if the \(K\) and \(\alpha\) values were known. The \(K\) and \(\alpha\) values for NIPA were taken as being equal to \(4 \times 10^{-4}\) and 0.64 respectively, which are reported for polyacrylamide in water at 25°C. The molecular weight of the polymer was determined by measuring the time taken for the flow of a polymer solution of different concentrations through a constant volume in the Ubbelohde viscometer. By plotting \(\eta_0/C\) and \(\ln \eta/C\) versus \(C\) (Fig. 7) and using the Mark-Houwink relationship (Equation 1), the molecular weight of the polymer could be determined if the \(K\) and \(\alpha\) values were known. The \(K\) and \(\alpha\) values for NIPA were taken as being equal to \(4 \times 10^{-4}\) and 0.64 respectively, which are reported for polyacrylamide in water at 25°C.
The difference in the $K$ and $\alpha$ values for poly(NIPA) would change the molecular weight of poly(NIPA) accordingly.

Studies with a cross-linked NIPA hydrogel: 10 wt % aqueous solution of NIPA was $\gamma$-irradiated (dose rate = 0.48 kGy/h) for different periods of times, under conditions such that only one of the radiolytic species (OH, $H$, $e_{aq}$, tert-butyl alcohol radical) would react with NIPA. The gel % was observed to increase with the $\gamma$-dose (Fig. 8), but the yields did not follow the G values of the primary radiolytic species of water radiolysis. The tert-butyl alcohol radicals, formed by the scavenging of OH radicals, are normally considered to be inert, but the % of gel was comparable to the % of gel obtained upon a reaction with OH radicals. This may explain the high yield of gel formed upon a reaction with $e_{aq}$ and $H$ atoms, because under these conditions tert-butyl alcohol was present in the system. These studies suggest that all of the radiolytic species of water radiolysis and also tert-butyl alcohol radicals are equally efficient in initiating the polymerization of NIPA and forming a crosslinked polymer.

The swelling ratio of NIPA hydrogel was determined in aqueous solutions having different pH values. It is clear from Fig. 9 that the swelling ratio remained the same in the pH range of 3–10. Both at lower and higher pH values, an appreciable decrease in the swelling ratio was observed. These results might be exploited to use the swelling ratio of NIPA as a pH indicator.

CONCLUSIONS

The rate constant for the reaction of $e_{aq}$ ($1 \times 10^{10}$ dm$^3$ mol$^{-1}$ s$^{-1}$) is higher than that for the reaction of $H$ ($4 \times 10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$) and OH radicals ($6 \times 10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$) with NIPA. These rate constants represent the initiation rates for the polymerization of NIPA with these transient species, indicating that ionic polymerization is faster than polymerization initiated by free radicals. The rate constant for the reaction of a specific one-electron reductant (COO$^-$) is also high, thus supporting the fact that ionic polymerization is faster. The propagation rate constant ($7 \times 10^5$ s$^{-1}$) for polymerization initiated with $e_{aq}$ is also high compared to the propagation rate with $H$ and $OH$ radicals. Although the initiation and propagation rate constants for the reaction of $H/\text{OH}/e_{aq}$ with NIPA are different (high for $e_{aq}$), the yield of the hydrogel formed upon $\gamma$-radiolysis was comparable in each case. The % hydrogel formed increased with the $\gamma$-dose, and reached a saturation value of ~90% at a $\gamma$-dose of 0.22 kGy. Under identical conditions of the $\gamma$-dose, dose rate and monomer concentration, the total concentration of radicals initiating polymerization is expected to be the same, and thus the yield of polymer formed would also be observed to be identical. Even tert-butyl alcohol radicals, which are normally considered to be inert, were observed to be equally efficient in initiating polymerization. The difference in the swelling ratio of NIPA hydrogel at very
low and high pH values may be useful when using NIPA hydrogel as a pH-sensitive probe. The yield and nature of the polymer depend on the total \(\gamma\)-dose, dose rate and monomer concentration, but independent of the nature of the initiating radicals.

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