

Photodegradation of Poly(vinyl alcohol) Under UV and Pulsed-Laser Irradiation in Aqueous Solution

S. P. Vijayalakshmi, Giridhar Madras

Department of Chemical Engineering, Indian Institute of Science, Bangalore 560012, India

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ABSTRACT: The photodegradation of poly(vinyl alcohol) (PVA) in aqueous solution was investigated under UV exposure and pulsed-laser irradiation. The degradation under UV exposure was studied at different pH values and with the addition of potassium chloride and potassium dichromate. The pulsed-laser degradation of PVA was investigated with a Nd : YAG laser, operating at a wavelength of 266 nm with about 6-ns pulses. The pulsed-laser degradation was studied at different polymer concentrations and light intensities. Samples were analyzed by gel permeation chromatography. The degradation rate coefficients were determined by

the application of a continuous distribution model. The photodegradation rates under UV exposure were highest at extremes of pH and were greatly enhanced by the addition of potassium chloride and potassium dichromate. The pulsed-laser degradation of the polymer decreased with increasing polymer concentration, although a threshold light intensity was required to initiate the degradation process. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 958–966, 2006

Key words: degradation; photochemistry; recycling; water-soluble polymers

INTRODUCTION

Poly(vinyl alcohol) (PVA) is a commercially important polymer with many applications. It is mainly used in sizing agents that confer resistance to oils and greases upon paper and textiles to make films resistant to attack by solvents or oxygen. It is used as a component of adhesives, emulsifiers, and suspending and thickening agents. In the pharmaceutical industry, PVA is used as an ophthalmic lubricant and a viscosity-enhancing agent.¹

The degradation of PVA has been examined by various methods. Pyrolysis, the most common technique used to study degradation, has been used to investigate the degradation of PVA,^{2,3} and this degradation proceeds by random chain scission. The chemical oxidation of PVA by KMnO_4 resulted in the formation of poly(vinyl ketone) as the final product.⁴ Alkaline solutions of PVA caused gel formation, whereas alkaline hydrogen peroxide solutions caused complete dissolution of PVA in 10 min at 95°C.⁵ Oxidative photodegradation by the Fenton reaction showed that stoichiometric amounts of iron and hydrogen peroxide, with respect to PVA units, were needed for effective degradation.⁶ The heterogeneous photocatalytic degradation of PVA was investigated in an aqueous system with suspended TiO_2 particles.⁷

The concentration of PVA decreased to 55% within an hour, whereas the addition of H_2O_2 enabled complete mineralization. The degradation was pH-dependent, and the formation of $\text{C}=\text{O}$ and $\text{C}=\text{C}$ was detected by IR spectroscopy. The mechanism of PVA degradation under UV exposure has been elucidated.⁸

The earliest studies on laser flash photolysis, irradiation by high-energy electrons and γ rays, was initiated by Schnabel and coworkers.^{9–15} The kinetics of poly(phenyl vinyl ketone) degradation in solution was studied with 347.1-nm light pulses, and the first-order decay constant was found to be $1 \times 10^7 \text{ s}^{-1}$.⁹ The degradation of poly(methyl methacrylate) (PMMA) in solution by a 2- μs pulse of 15-MeV electrons was investigated by the observation of the changes in light scattering intensity (LSI).¹⁰ Two types of intermediates, one with a fast LSI decay mode and the other with slow LSI decay, were found to be the cause of main-chain scission. The presence of oxygen and $\text{C}_2\text{H}_5\text{OH}$ enhanced the degradation of PMMA. A similar study on poly(methyl vinyl ketone) showed that changes in LSI corresponded to a main-chain scission process and a subsequent crosslinking process.¹¹ The former process was found to be due to disentanglement, whereas the latter was ascribed to a chemical reaction due to the combination of macroradicals. Photolysis with 265-nm, 15-ns light pulses and irradiation with UV light of wavelength greater than 260 nm resulted only in main-chain degradation.¹¹ The light-scattering method was also used to monitor the degradation of polystyrene and poly(α -methyl styrene).^{12,13} Although the degradation of polystyrene

Correspondence to: G. Madras (giridhar@chemeng.iisc.ernet.in).

was found to increase in the presence of oxygen, a retarding effect was found for the degradation of the latter. In both cases, the polymer radicals ($P \cdot$'s) were produced by attack due to solvent radicals. In the presence of oxygen, $PO_2 \cdot$ radicals were produced. For poly(α -methyl styrene), the main degradation occurred by direct scission of the lateral $P \cdot$ with a lifetime of 2.9 ms rather than the scission of the $PO_2 \cdot$ oxyl radical. The cleavage in polystyrene occurred via polyoxyl radical, and thus, no degradation was observed in the absence of oxygen. The rate constant for the decay of $P \cdot$ in the absence of oxygen was $2.4 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ and in the presence of oxygen was $(5 \pm 1) \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$. Radiolysis of poly(dimethyl itaconate) resulted in main-chain degradation, which was suppressed by increasing oxygen and ethyl mercaptan concentrations.¹⁴ Indirect and direct radiation effects contributed to degradation in the radiolysis of poly(2,2,2-trichloroethyl methacrylate) in a dichloromethane solution.¹⁵ Degradation was observed in both the presence and absence of oxygen. In oxygen-saturated solutions, a second-order reaction relating to the recombination of $PO_2 \cdot$ radicals was found to be the rate-determining step.

Degradation of PVA was also conducted by the irradiation of aqueous solutions of PVA by γ rays at a dose rate of 66 Gy/min.¹⁶ The degradation was dependent on initial PVA concentration, the pH of the solution, and the addition of H_2O_2 . New absorption peaks were found for the formation of carbonyl groups. Similar result was obtained when irradiation by Co^{60} γ rays was performed on PVA films.¹⁷ The viscosity of a 0.1% PVA solution was also found to decrease on irradiation with X-rays (140 kV) and γ rays from a Co^{60} source at a dose rate of 1000 r/min in the presence of oxygen.¹⁸ There have been a few studies on PVA under irradiation both in solution and solid state. In aqueous solutions, degradation occurred in the presence of oxygen, and crosslinking was observed in the absence of oxygen when irradiated with ^{60}Co γ -ray source. The degradation proceeded via the formation of peroxy radicals by the reaction of $P \cdot$ with oxygen.^{19,20} A pulse radiolysis study on PVA by light generated by Ar-He laser demonstrated that the relation between changes in LSI and absorbed dose is nearly linear (at low doses). It was also proved that only a part of hydroxyl radicals react with the polymer macroradical.²¹ The effect of polymer concentration (in deoxygenated aqueous solutions) on crosslinking during γ irradiation was investigated.²² The G value, described as the radiation yield of crosslinking per energy absorption, was found to increase initially with concentration and gradually attain a maximum value. However, in a water-swollen PVA film (concentration $> 300 \text{ g/dm}^3$), degradation occurred. This was attributed to the lesser mobility

and diffusion of polymer chains, which retarded their ability to crosslink and disproportionate.

Apart from degradation in solution, the pulsed-laser technique has been used to study the photoetching, ablation, and deposition of polymer thin films onto surfaces.²³⁻²⁶ The theoretical model for the process of ablation considers it to be a nonstationary thermodestruction process that follows an Arrhenius equation, where degradation occurs for every laser pulse.²⁷ Studies on PVA films have shown that destruction occurred through the development of thermochemical instability on continuous irradiation.²⁸ The film of PVA treated with $ZnCl_2$ showed a reduction in crystallinity when irradiated with a γ -ray source. New bands were also observed corresponding to ketone groups.²⁹

The objective of this study was to investigate the degradation of PVA under UV exposure and by a pulsed laser. The effect of pH, KCl, and $K_2Cr_2O_7$ on the degradation of PVA in aqueous solution under UV exposure was investigated. The pulsed-laser degradation of PVA in aqueous solution was studied in the presence of oxygen. The effect of polymer concentration and laser intensity on degradation was also examined. A model based on continuous distribution kinetics was developed to determine the degradation rate coefficients for photodegradation.

EXPERIMENTAL

Materials

PVA was obtained from Sigma Aldrich (Milwaukee, WI). Double-distilled deionized water was used as the solvent for making the polymer solutions. The other reagents, potassium chloride and potassium dichromate (99% pure), used for photodegradation were obtained from S. D. Fine Chemicals (Mumbai, India). The pH of the solutions was adjusted with nitric acid and sodium hydroxide to get the required value.

Pulsed-laser experiments

The experimental setup is shown schematically in Figure 1(a). The fourth harmonic (266 nm) of a Nd : YAG laser (DCR 3G, Spectra Physics, Tucson, AZ), running at a 10-Hz repetition rate, was used as the light source. The pulse width of the laser at 266 nm was about 6 ns and had a Gaussian profile. The fourth harmonic was separated from the fundamental (1064 nm) and second (532 nm) harmonics with a Pellin Broca (PB) prism. The separated 266-nm light was then steered by a right-angle quartz prism and allowed to pass through the sample, which was kept in a 1.5-in. (38.1-mm) diameter cylindrical quartz cell (QC). To study the degradation in the absence and in the presence of oxygen, the quartz tube was closed with an air-tight

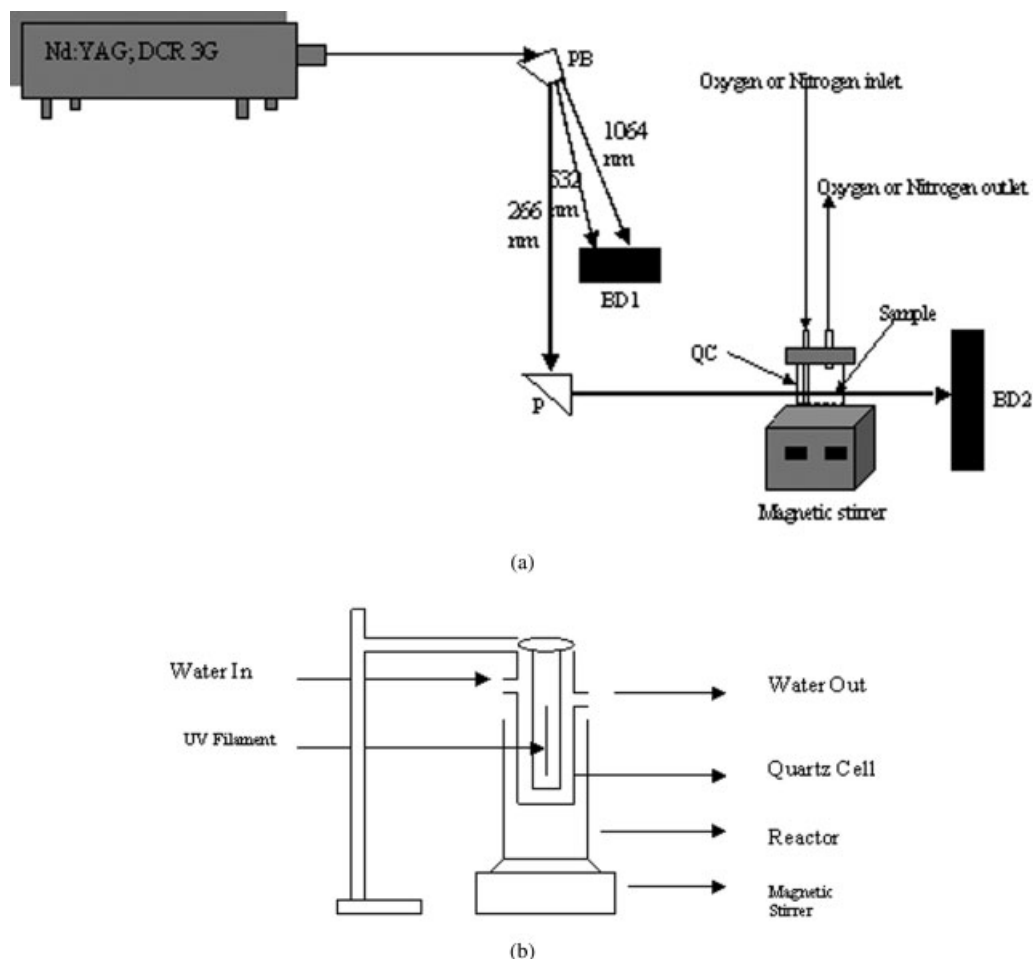


Figure 1 (a) Experimental setup, where BD is the beam dump and P is the right-angle quartz prism. (b) Schematic of the reactor used for the photocatalytic experiments under UV exposure.

brass screw cap (fitted with an O ring) with inlet and outlet for purging gas. The inlet was connected to an oxygen or nitrogen cylinder with a proper regulator, and the outlet was kept open. To ensure proper mixing of the solution during irradiation, a magnetic pellet was used as the stirrer. The intensity of incident radiation was measured with a laser power meter (OPHIR, 30A-P—Cal-BNC, S. R. No-4267, Wilmington, MA). The kinetics of degradation were investigated at a fixed polymer concentration at different time intervals with the power beam of the laser. The effect of varying the concentration of the polymer solution and the laser light intensity on the degradation process was examined. The change in molecular weight was followed by gel permeation chromatography (GPC). All the polymer solutions were made with double-distilled deionized water.

Photodegradation experiments

The photochemical reactor used in this study was like an annular reactor and had two parts (inner and outer). The

inner reactor consisted of a jacketed quartz tube of the following dimensions: i.d. = 3.4 cm, o.d. = 4 cm, and length = 21 cm. This held a 125-W high-pressure mercury vapor lamp (Philips, Bangalore, India). This was placed in a Pyrex glass outer reactor with an inner diameter of 5.7 cm and a height of 16 cm. Figure 1(b) is the schematic diagram of the reactor. The ballast and capacitor were connected in series with the lamp to avoid the fluctuations in the input supply. The solution was taken in the outer reactor and stirred uniformly with a magnetic stirrer during the course of reaction. The excess heating due to dissipative loss of the UV energy was constantly removed with water circulated through the annulus of the jacketed quartz tube. Further details on the operation of the reactor and the range of energy emission were given elsewhere.³⁰ The light source was concentrically placed inside the QC and predominantly emitted the wavelength 365 nm, corresponding to the energy of 3.4 eV, and the photon flux was 5.8×10^{-6} mol of photons/s. The preweighed amounts of catalyst were added to the solution and maintained in suspension with magnetic stirring in the reactor.

UV spectral analysis

The UV spectrum of the polymers before and after photodegradation was obtained with a spectrophotometer (PerkinElmer Lambda-35, Boston, MA). The wavelength ranged scanned was 500 to 200 nm. No absorbance was observed beyond 500 nm.

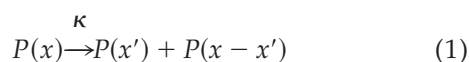
GPC analysis

The samples were taken at regular intervals and analyzed by GPC³¹ with double-distilled deionized water as eluent at a flow rate of 0.5 mL/min. The columns used were Ultrahydrogel linear columns (Waters, Milford, MA) measuring 7.8 × 300 mm maintained at 50°C. The refractive index was monitored continuously with a differential refractometer (model 401, Waters). About 800 μL of sample was injected into the system to obtain a chromatogram and converted to molecular weight with poly(ethylene oxide) (PEO) calibration standards, which are usually used as standards for water-soluble polymers.

Several experiments were repeated, and the error in experiments in the determination of the degradation rate coefficients was around 3%.

Theoretical model

Continuous distribution kinetics were used to follow the degradation kinetics and to determine the degradation rate coefficient. The polymer [P(x)], considered to be a mixture of homologous molecules with molecular weight x , underwent binary fragmentation to polymers of molecular weight x' and $x - x'$



The distribution function is defined such that $p(x,t) dx$ defines the molar concentration of the polymer in the interval $(x, x + dx)$. The governing population balance equation that describes the fragmentation of the polymer is³¹

$$\frac{\partial p(x,t)}{\partial t} = -\kappa p(x,t) + 2 \int_x^\infty \kappa p(x') \Omega(x,x') dx' \quad (2)$$

where $\Omega(x, x')$ is the stoichiometric kernel, which describes the probability of formation of polymer of size x' from breakage of polymer of size x ($x > x'$). The rate (κ) usually depends on molecular weight of the reacting polymers.

The photodegradation of PVA occurred by random chain scission, and $\Omega(x, x')$ is written as $1/x'$. The photodegradation rate was assumed to vary linearly

with chain length,³¹ and thus, $\kappa = kx$, where k is the molecular-weight-independent photodegradation rate coefficient.

When the moment operation, $p^{(n)}(t) = \int_0^\infty x^n p(x,t) dx$, is applied after the substitution of $\Omega(x, x') = 1/x'$ and $\kappa = kx$, to eq. (2), it yields³¹ and the variation of the n -th moment is given by

$$\frac{dp^{(n)}}{dt} = -\frac{(n-1)}{(n+1)} kp^{(n+1)}(t) \quad (3)$$

Equation (3) is solved with the initial condition $p^{(0)}(t = 0) = p_0^{(0)}$. The number-average molecular weight (M_n) is defined as the ratio of the first moment to the zeroth moment [$p^{(1)}/p^{(0)}$]. Thus, M_n with time is³¹

$$\frac{M_{n0}}{M_n} - 1 = kM_{n0}t \quad (4)$$

where the dependence of the ratio of the molecular weight with time, t , and the initial molecular weight is M_{n0} .

RESULTS AND DISCUSSION

Photodegradation of PVA

The photodegradation of PVA was investigated with TiO₂ (Degussa P-25), and nano-TiO₂ (CSN—TiO₂), synthesized by combustion method. Although these catalysts significantly enhanced the degradation³¹ of PEO and polyacrylamide, they had no effect on the photodegradation rate of PVA. This may appear to be in contradiction with a previous study⁷ that reported enhanced photodegradation with TiO₂. However, that study investigated the degradation from an initial PVA concentration of 30 mg/L and did not report on the reduction of molecular weight. Therefore, the photodegradation of PVA was investigated at different operating conditions.

Because the photodegradation of PVA occurs by random chain scission, eq. (4) gives the variation of M_n with reaction time. Figure 2(a) shows this plot for the photodegradation of PVA at various pH values. Degradation was highest in acidic and alkaline pH values, and M_n decreased by 90 and 85% at pH values of 2 and 11, respectively, within 40 min of irradiation. The rate coefficients for the photodegradation of PVA [k ($\times 10^{-6}$) mol g⁻¹ min⁻¹] obtained from linear regression were 1.6, 0.55, 0.35, 0.94, and 3.3 at pH values of 2, 4, 7, 9, and 11, respectively. The rate of photodegradation at pH 11 was nearly an order of magnitude higher than that obtained at the natural pH of the polymer solution. This was attributed to the dominance of chemical effects in aqueous media, wherein the pro-

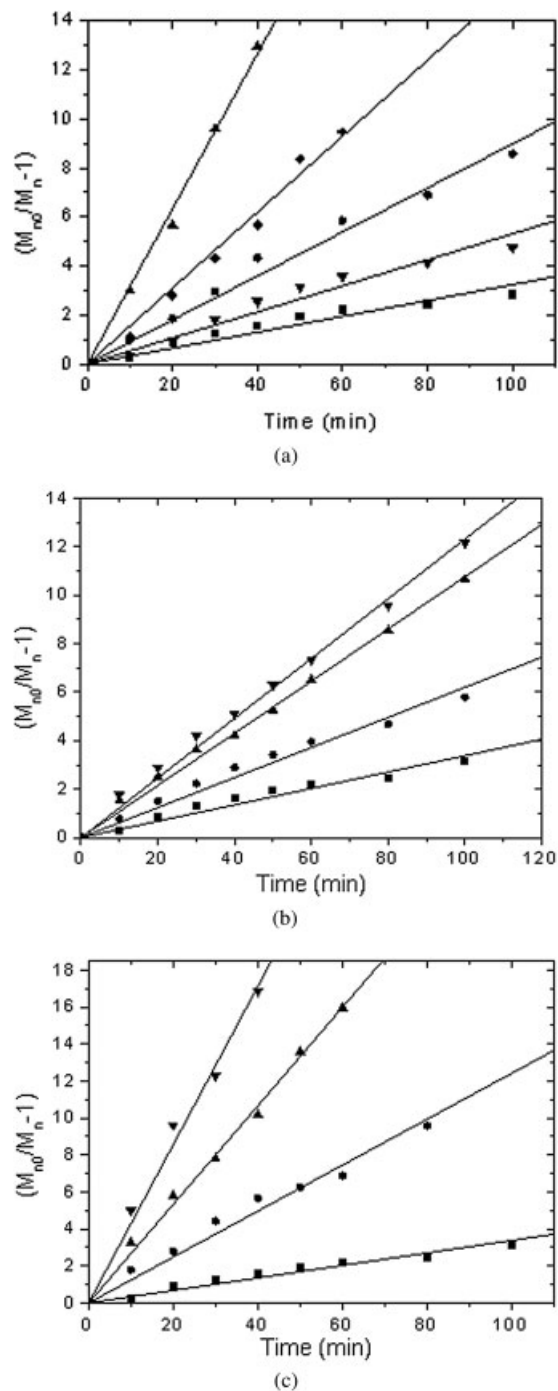


Figure 2 Variation of $(M_w/M_n) - 1$ with reaction time for the photodegradation of PVA under UV exposure at a constant polymer concentration of 2 g/L at various (a) pH values [(■) 7 (natural pH), (▼) 4, (●) 9, (◆) 2, and (▲) 11], (b) concentrations of KCl [(■) without KCl, (●) 1 g/L KCl, (▲) 2 g/L KCl, and (▼) 3 g/L KCl], and (c) concentrations of potassium dichromate [(■) without $K_2Cr_2O_7$, (●) 0.2 g/L $K_2Cr_2O_7$, (▲) 0.6 g/L $K_2Cr_2O_7$, and (▼) 1 g/L $K_2Cr_2O_7$].

duction of $OH \cdot$ radicals, which were mainly responsible for degradation, was higher at acidic and alkaline pH values than at neutral pH values. This was responsible for hydrogen abstraction from the polymer chain.

The direct removal of the OH group from polymer to give the $P \cdot$ is not a favorable reaction, and $P \cdot$ was formed due to hydrogen abstraction by the $OH \cdot$ radical, which was produced by the decomposition of H_2O_2 . The increased degradation rates at extremes of pH were similar to that of γ -ray irradiation of PVA¹⁶ and in the TiO_2 -initiated degradation of PVA in aqueous solution.¹³

The effect of different concentrations of potassium chloride was also studied at the natural pH of the solution. Figure 2(b) shows that the addition of KCl increased the photodegradation of PVA. The values of k ($\times 10^{-6} \text{ mol g}^{-1} \text{ min}^{-1}$) were 0.35, 0.64, 1.12, and 1.29 in the absence of KCl and in the presence of 1, 2, and 3 g/L KCl, respectively. This indicated that the rate coefficient was nearly four times in the presence of 3 g/L KCl compared to that obtained in the absence of KCl.

The addition of complex-forming salts such as potassium dichromate on the photodegradation of PVA was also examined. The presence of even small amounts of potassium dichromate greatly enhanced the rate of degradation of PVA [Fig. 2(c)]. Complete degradation was achieved within 40 min at a dichromate concentration of 1 g/L. The rate coefficients for the degradation [k ($\times 10^{-6}$) $\text{mol g}^{-1} \text{ min}^{-1}$] were 0.35, 1.30, 2.78, and 4.47 in the absence of $K_2Cr_2O_7$ and in the presence of 0.2, 0.6, and 1 g/L $K_2Cr_2O_7$, respectively. This indicated that the rate coefficient obtained with 0.2 g/L $K_2Cr_2O_7$ was nearly equal to that obtained in the presence of 3 g/L KCl, which was four times that obtained in the absence of these salts.

The mechanism of PVA photodegradation in aqueous solution is hypothesized to proceed by hydrogen abstraction at an α or β position followed by rapid chain rupture and oxidation of C—OH to CO, which results in the formation of ketones and carboxylic acids.⁸ However, no low-molecular-weight products, such as oxalic or acetic acid or aldehyde or ketone, could be detected by HPLC during the photochemically enhanced Fenton reaction.⁶ This was probably because total mineralization of PVA was achieved with H_2O_2 , which resulted in CO_2 and H_2O . In our experiments, new peaks were observed, which indicated the formation of carbonyl bonds. Figure 3 shows the absorption spectra for undegraded and degraded PVA at different experimental conditions. The spectra at pH values of 2 and 11 [Fig. 3(a,b)] showed the appearance of new peaks between 200 and 300 nm for the degraded polymer. This indicated the formation of carbonyl groups that absorbed around 280 nm. The peaks around 220 nm were due to the presence of $-C=C-C=O$ unsaturation in the backbone. Similar peaks were obtained for the polymer sample degraded with KCl [Fig. 3(c)]. With the addition of dichromate to PVA solution, a PVA-dichromate complex was formed. This complex absorbed at 258 and 350 nm.

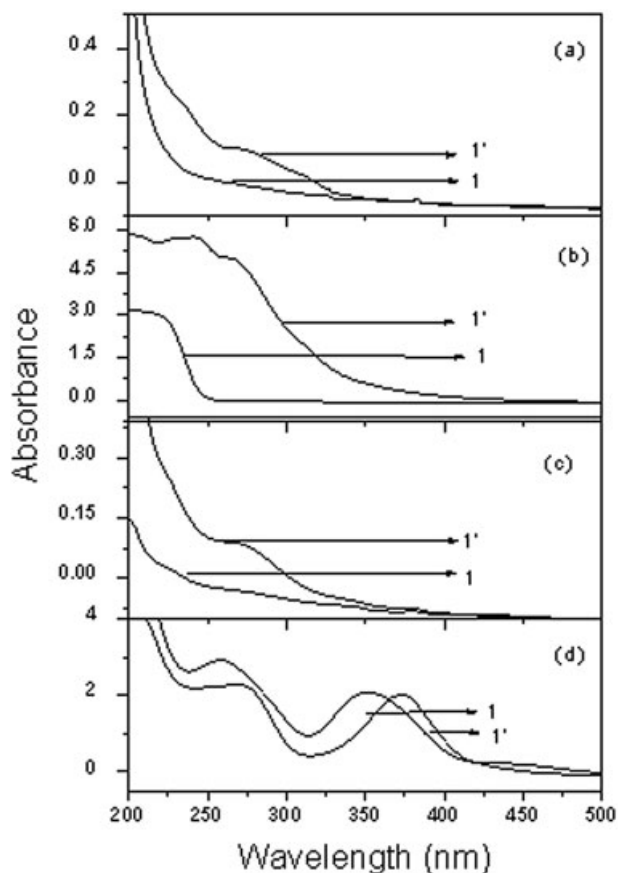


Figure 3 UV absorption spectra for undegraded and degraded polymers at different experimental conditions at (b) pH 11, (c) at pH 2, and (d) with KCl (1 g/L) with $K_2Cr_2O_7$ (0.2 g/L). 1 and 1' correspond to undegraded and degraded PVA solutions.

The small peak at 450 nm was due to absorbance by free dichromate ions [Fig. 3(d)]. On irradiation and subsequent degradation, the peaks corresponding to the complex shifted to 270 and 373 nm, and the peak at 450 nm disappeared. In the dichromate–PVA complex, the shift in absorbance after degradation could have also been due to new end groups and byproducts that were formed after degradation that complexed differently with dichromate. However, the pH of the solution and the color of the solution did not change before or after degradation in the presence of dichromate and KCl (pH \approx 6–7, yellow solution with dichromate and a colorless solution with KCl). If complete mineralization had occurred, a significant drop in pH, to make the solution more acidic, would have been observed.

The mechanism of degradation of PVA in the presence of the salts, KCl and dichromate, is hypothesized as follows. The addition of salt to the polymeric solution changed the conformation of the polymer in solution.³² The addition of salt to water disrupted the tetrahedral orientation of water molecules, which af-

ected the hydrogen bonding.^{33,34} Thus, the phenomenon of salting out disrupted the hydrogen bonding between PVA and water molecules, which led to competition for the water of hydration between PVA and the salt. The PVA molecules were, thus, more closely packed and exhibited more solubility in the water-rich phase than in the salt rich phase. This effect was dependent more on the anion than the cation, with multivalent ions causing more disruption than monovalent ions. However, the mechanism for the degradation of PVA in the presence of these salts was not established. This was the first study that reported the enhancement of degradation in the presence of KCl and dichromate, and further investigations are required to establish the mechanisms.

Pulsed-laser degradation of PVA

The degradation experiments were carried out both in the presence and absence of oxygen (by purging oxygen and nitrogen) and in atmospheric conditions. The polymer degraded only in the presence of oxygen and in atmospheric (contains both oxygen and nitrogen) conditions. In fact, all the polymers crosslinked to a higher molecular weight polymer in an inert atmosphere of nitrogen (which was not studied in detail here). The oxygen effect manifested in three different modes during the main-chain degradation.³⁵ It acted as a promoter, inhibitor, or fixing agent for the main-chain breakage. For PVA, oxygen promoted the degradation process by preventing crosslinking. However, nearly the same amount of degradation was observed when the study was carried out in atmospheric conditions and in saturated conditions where oxygen was purged continuously. This indicated that although oxygen was required for degradation to occur, there were saturation conditions above which no further degradation was seen with increasing oxygen concentration. In aqueous solutions, hydrogen abstraction from a polymer is by attack of $OH\cdot$ radicals, and the number of $P\cdot$'s formed by this indirect method exceeds the number of radicals formed by the direct scission of covalent bonds in polymer on irradiation.³⁶ On the basis of experimental observations, we perceived that the degradation proceeded by the following sequential reactions:

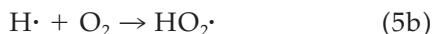
Solvent excitation



Solvent dissociation



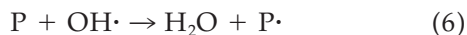
Addition of the hydrogen radical to oxygen



Production of hydrogen peroxide



Hydrogen abstraction from the polymer

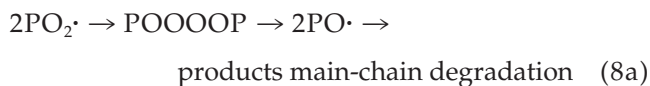


$\text{P}\cdot$ could be (1) $\text{—CH}\cdot\text{—CH(OH)—CH}_2\text{—}$, (2) $\text{—CH—C}\cdot\text{(OH)—CH}_2\text{—}$, or (3) $\text{—CH}_2\text{—CH(OH)—CH}\cdot\text{—}$, but it was found that the α -hydroperoxy radical (2) was formed in larger amounts.¹⁹

Reaction of $\text{P}\cdot$ with oxygen



Products of the main-chain degradation



Termination reaction



The first step of polymer degradation was the abstraction of hydrogen from the polymer backbone by the solvent generated $\text{OH}\cdot$ [eq. (6)]. The H—OH bond dissociation energy of H_2O was 5.118 ± 0.01 eV ($\cong 242$ nm),³⁰ which indicated that one-photon excitation of a water molecule at 266 nm (absorption coefficient = 0.01 cm^{-1}) could not lead to the breakage of the H—OH bond. However, consecutive two-photon absorption could provide the sufficient energy and lead to the breakage of the H—OH bond. The hydroxyl radicals formed from the solvent had a high propensity for hydrogen abstraction from the polymer, which resulted in the formation of $\text{P}\cdot$. $\text{P}\cdot$ then added to oxygen to form the active species [eq. (7)]. We inferred that $\text{PO}_2\cdot$ was the active species involved in main-chain degradation from the fact that no degradation occurred in the absence of oxygen. Because no increase in the rate was observed when atmospheric conditions were replaced by saturated oxygen conditions, we concluded that all of the $\text{P}\cdot$'s were scav-

enged above a certain concentration of oxygen. The peroxy radical underwent a variety of reactions that led to the introduction of new functional groups, such as —OH , —CHO , —HCHO , and CO , and unsaturation in the end products.^{37–39} It also underwent intramolecular rearrangement by internal hydrogen transfer before scission took place.¹² Reactions (8a) and (8b) represent the main-chain scission that resulted in a reduction in molecular weight. Although $\text{P}\cdot$'s were formed in the absence of oxygen, too, the only pathway they could follow was termination by any one of the reactions from eq. (9) to eq. (9c). This did not result in chain scission, and hence, no degradation was observed.

On the basis of eq. (4), a linear plot should be obtained when $(M_{n0}/M_n - 1)$ is plotted against reaction time. k was obtained from the slope of the regressed line [Fig. 4(a)] and was 6.5×10^{-7} $\text{mol g}^{-1} \text{min}^{-1}$ for the pulsed-laser degradation of PVA. Pulsed-laser degradation is a very rapid process, and M_n decreased by about 77% for a 45-min irradiation. The effect of polymer concentration on the degradation rate is shown in Figure 4(b), which indicates that the rate decreased with increasing polymer concentration. The degradation of the polymers was higher in a less concentrated solution than in a more concentrated solution because the mobility of polymer chains was higher in a less viscous solution. The concentration effect was also enough evidence to show that the polymer did not directly absorb the incident light and degraded by breakage of covalent bonds. Because if this were so, the degradation rate would have increased with polymer concentration due to increased absorption by polymer chains. The average number of radical sites per polymer chain was higher in a less concentrated solution.⁴⁰ This led to a greater amount of degradation in a less concentrated solution. Consequently, the probability of intramolecular reactions occurring was also high compared to intermolecular reactions in dilute conditions.

Another parameter that influenced the degradation was the intensity of photons striking the polymer solution. When the intensity was below a certain threshold, no degradation occurred. This intensity was found to be 8 mJ/cm^2 for the degradation of PVA. The threshold effect of laser intensity was due to the two-photon absorption of water molecules at a particular intensity, which produced the $\text{OH}\cdot$ radicals and started the polymer degradation process. A similar threshold effect was observed for the ablation of PMMA films by a laser pulse of 248 nm.¹² This indicated that no radicals that were responsible for initiating degradation were formed below the threshold value. Above this threshold, degradation increased with intensity and gradually attained a saturation value, above which no further increase in degradation was observed with intensity [Fig. 4(c)]. The line in the

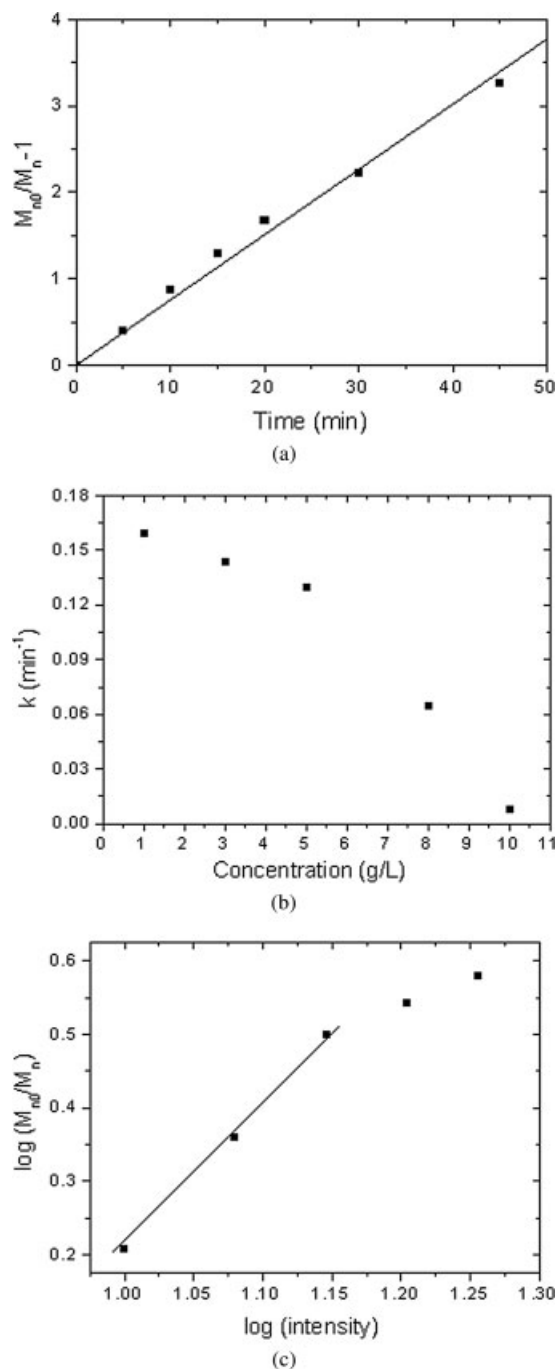


Figure 4 Variation of (a) $(M_{n0}/M_n) - 1$ with reaction time for the pulsed-laser degradation of PVA at a constant polymer concentration of 5 g/L and an irradiation intensity of 10 mJ/cm^2 , (b) rate coefficient with concentration of the polymer solution for the pulsed-laser degradation of PVA at an irradiation intensity of 10 mJ/cm^2 , and (c) M_{n0}/M_n with laser intensity for the pulsed-laser degradation of PVA, PEO, and polyacrylamide at a constant polymer concentration of 5 g/L with an irradiation time of 15 min. The line is drawn with a fixed slope of 2.

figure was drawn with the first three points with a fixed slope of 2. This indicated that at lower intensities, there was the absorbance of two consecutive

266-nm photons from the same laser pulse, which led to the breakage of the H—OH bond and thereby produced $\text{OH}\cdot$, which initiated the degradation process. The initial increase in degradation at a constant polymer concentration was due to the increase in the number of $\text{OH}\cdot$ radicals formed, which was responsible for the increase in sites by hydrogen abstraction. At higher intensities, saturation was observed, which implied that there was no change in the number of radicals that initiated the degradation process. Experiments were also performed at irradiation wavelengths of 235 and 350 nm at intensities of 2 and 15 mJ/cm^2 , respectively. However, no degradation was observed because the intensity of the laser was below the threshold value for the two-photon absorption of water molecules. Because of experimental limitations, higher intensities could not be examined at these wavelengths. The results of this study clearly indicate that the photodegradation of PVA can be carried out with UV exposure and with a pulsed laser. Although the mechanism of the degradation was not clear, the findings and the effect of different parameters on degradation are interesting.

CONCLUSIONS

The photodegradation of PVA was investigated at different pH values and with the addition of potassium chloride and potassium dichromate. The degradation was very effective at acidic and alkaline pH values. The addition of KCl and dichromate enhanced the reaction rate significantly. The rate coefficient obtained with 3 g/L KCl was nearly equal to that obtained in the presence of 0.2 g/L $\text{K}_2\text{Cr}_2\text{O}_7$, which was four times than that obtained in the absence of these compounds.

The pulsed-laser degradation of PVA was examined with a Nd:YAG laser operating at 266 nm. Oxygen was essential for degradation. The degradation proceeded via the formation of peroxy radical. The rate decreased with increasing concentration of the polymer solution. An increase in intensity increased the pulsed-laser rate initially, but the rate gradually attained saturation at higher intensities.

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