

Effects of the pH, Concentration, and Solvents on the Ultrasonic Degradation of Poly(vinyl alcohol)

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ABSTRACT: The ultrasonic degradation of poly(vinyl alcohol) was investigated at different pHs of the solvent, in different water/solvent binary mixtures, and at different polymer concentrations. The samples were analyzed with gel permeation chromatography. The degradation rate coefficients were determined with a continuous distribution model. A higher degradation rate was obtained at pH ex-

trêmes, in better solvents, and at lower polymer concentrations. The results are explained and discussed. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 4888–4892, 2006

Key words: degradation; water-soluble polymers; molecular weight distributions; ultrasound

INTRODUCTION

The disintegration of macromolecules subjected to ultrasound is primarily due to the action of cavitation bubbles. The earliest study of ultrasonic effects concerned natural polymers such as gelatin, starch, and guar gum.^{1,2} The irreversible and permanent reduction of the viscosity of polymer solutions was first observed in solutions of polystyrene and polyacrylates.^{3,4} Since then, research has been conducted relating the factors concerned with ultrasound, polymers, and solvents. There are two major characteristics of ultrasonic polymer degradation. One is the presence of a limiting molecular weight (M_{lim}), and the other is the nonrandom mode of breakage.^{5–7} The major advantages of ultrasonic degradation are that there is breakage of only the most susceptible chemical bond and that no chemical changes occur in the molecule. The effects of temperature and solvents have been correlated to the cushioning effect produced upon the bubble collapse. A higher temperature causes more solvent vapor to enter the bubble, thereby reducing the forces during collapse.^{7–10} Solvents with high volatility also decrease the rate of degradation because of the aforementioned effect.^{11–13} However, Basedow et al.¹⁴ studied the degradation of poly(ethylene oxide) in water/methanol and dextran in water/deuterium oxide systems with similar enthalpy of the vaporization of the solvent. They found that the rate of degradation was higher in the better solvent [deuterium

oxide for dextran and water for poly(ethylene oxide)] and that the rate decreased with the addition of the poor solvent. Studies were also conducted to determine the influence of the solvent density on the degradation of the polymer, and within experimental error, no influence of density on degradation was found.^{15,16} The concentration effect shows that there is an optimum polymer concentration for the ultrasonic degradation of carboxymethylcellulose.¹⁷ However, the highest degradation was found at the lowest polymer concentration for dextran¹⁸ and for other polymers.^{19,20} This indicates that several parameters influence the ultrasonic degradation of polymers.

However, to the best of our knowledge, the effects of the pH, solvent, and polymer conformation have not been investigated for the ultrasonic degradation of poly(vinyl alcohol) (PVA). In this study, we investigated the ultrasonic degradation of PVA at different pHs and polymer concentrations and in different binary solvent mixtures. A model based on continuous distribution kinetics was developed to determine the degradation rate coefficients. We have found that the conformation of the polymer in solution is the most important parameter in the degradation of PVA.

EXPERIMENTAL

Materials

PVA was obtained from Sigma–Aldrich (Milwaukee, WI). Double-distilled deionized water was used as the solvent for making polymer solutions. Acetone, methanol, and acetonitrile were obtained from Merck, Inc. (Mumbai, India), and were high-performance-liquid-chromatography-grade.

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Experiments

A polymer solution (40 mL) with a desired concentration was degraded in a horn-type ultrasonic processor (Vibronics, India; the design/geometry of the ultrasonic horn is available on the website of the manufacturer). The processor delivered the sound energy to the polymer solution through a horn tip with a flat, radiating, circular surface 1" (2.54 cm) in diameter. The transformer or velocity horn amplified the small vibrations. It was attached to a pair of lead zirconate titanate transducer elements. The applied intensity and frequency of the sound generated were 36 W/cm² and 25 kHz, respectively. This was the maximum intensity that could be generated in our experimental setup. The temperature of the polymer solution was maintained within $\pm 1^\circ\text{C}$ with a thermostated ice-water bath.

The ultrasonic degradation of PVA was investigated at 30°C at a fixed polymer concentration of 2 g/L in different binary solvent mixtures, water being kept as one of the solvents and acetone, methanol, or acetonitrile being added to water in appropriate amounts so that the vapor pressures of the mixtures were nearly the same.

The effect of pH on the degradation of PVA was studied by the variation of the pH from 2 to 12 at a fixed polymer concentration of 2 g/L. The pH of the polymer solution was adjusted with nitric acid and sodium hydroxide solutions. The pH was measured at various time intervals with a pH meter (Eutech Instruments, Singapore; resolution = 0.1 pH) by the immersion of the electrode 2 cm into the solution. The pH of the solution was measured before, during, and after irradiation by ultrasound, and it did not change with time. Several experiments were repeated, and the error in the experiments in the determination of the degradation rate coefficient was around 3%.

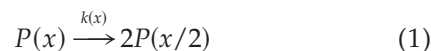
The samples were taken at regular intervals and analyzed with a gel permeation chromatograph²¹ with double-distilled deionized water as the eluent at a flow rate of 0.5 mL/min. The columns were Ultrahydrogel linear columns (Waters; Milford, MA) measuring 7.8 mm \times 300 mm and maintained at 50°C. The refractive index was monitored continuously with a differential refractometer (model 401, Waters). About 800 μL of the sample was injected into the system to obtain a chromatogram; this was converted to the molecular weight with poly(ethylene oxide) calibration standards, which are usually used as the standards for water-soluble polymers.

The continuous distribution model used to determine the degradation rate coefficient required M_{lim} for the degradation of the polymer. Several experiments were conducted for 10 h; no detectable change in the

molecular weight was noticed after 6 h, and this weight was used as M_{lim} .

THEORETICAL MODEL

Continuous distribution kinetics was employed to follow the degradation kinetics and determine the degradation rate coefficient. For polymer $P(x)$, which is considered to be a mixture of homologous molecules of weight x , the ultrasonic midpoint degradation can be represented as follows:^{10,22,23}



The population balance equation for midpoint scission is given by¹⁰

$$\frac{\delta p(x,t)}{\delta t} = -k(x)p(x,t) + 2 \int_x^\infty k(x')p(x',t)\delta(x-x'/2)dx' \quad (2)$$

The degradation is assumed to be first-order with the polymer concentration, $p(x,t)$, and the degradation rate, $k(x)$, is assumed to be of the form $k(x) = k(x - M_{\text{lim}})$. Applying a moment operation to the previous equation yields

$$\frac{dp^{(n)}}{dt} = kp^{(n+1)}(2^{1-n} - 1) - kp^{(n)}M_{\text{lim}}(2^{1-n} - 1) \quad (3)$$

The moments, $p^{(n)}(t) = \int_0^\infty x^n p(x,t)dx$, are obtained from the experimental molecular weight distribution (MWD). A representative MWD is shown in Figure 1. The number-average molecular weight (M_n) is obtained from the ratio of the first moment to the zero moment, $p^{(1)}/p^{(0)}$. Solving eq. (3) with the initial condition $p^{(0)}(t=0) = p_0^{(0)}$ yields^{10,22,23}

$$\ln \left[\frac{(M_{n0}^{-1} - M_{\text{lim}}^{-1})}{(M_n^{-1} - M_{\text{lim}}^{-1})} \right] = X_{Mn} = kM_{\text{lim}}t \quad (4)$$

A more detailed derivation of these equations has been provided in previous publications.^{10,21,22,23} The experimental data (especially at low reaction times) do not follow the linear behavior envisaged by the theory [eq. (4)]. This could be attributed to the assumption that the chain scission occurs only at the midpoint. A more detailed model that takes into account that the cleavage of the main chain occurs with a distribution around the midpoint of the chain²⁴ satisfactorily models the deviation of the experimental data points from

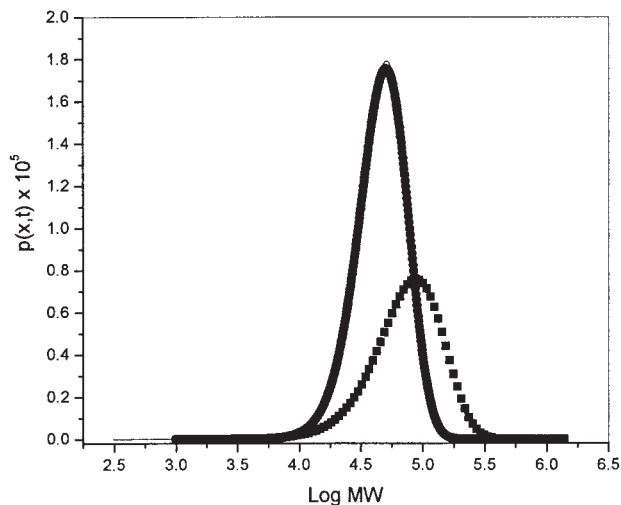


Figure 1 Representative MWD for the ultrasonic degradation of PVA: (■) initial distribution and (●) distribution after degradation for 90 min. The solid line is the prediction by the model.

TABLE I
Rate Coefficients for the Ultrasonic Degradation of PVA Under Different Conditions

Condition	Rate coefficient ($\times 10^{-7}$ mol $\text{g}^{-1} \text{min}^{-1}$)
Effect of the polymer concentration	
2 g/L	1.94
3.5 g/L	1.44
5 g/L	1.11
10 g/L	0.88
Effect of pH	
pH 2	4.23
pH 4	3.9
pH 7	1.94
pH 9	2.3
pH 12	5.17
Effect of the solvent	
Water (vapor pressure = 7.3 kPa)	1.94
Water/acetone (vapor pressure = 7.6 kPa)	0.96
Water/methanol (vapor pressure = 7.7 kPa)	0.70
Water/acetonitrile (vapor pressure = 7.2 kPa)	1.26

the linearity. However, the value of the rate coefficient does not significantly change with this assumption.

RESULTS AND DISCUSSION

The ultrasonic degradation of PVA was performed at different pHs, in different binary solvent mixtures, and at different polymer concentrations. Figure 2 shows the effect of the polymer MW concentration on the

degradation. Other investigators²⁵ have obtained similar results for the degradation of PVA. The rate coefficients, determined from the linearly regressed line of X_{Mn} with time [as suggested by eq. (4)], are shown in Table I. This indicates that the rate of polymer degradation decreases with an increase in the polymer concentration, with the rate of degradation obtained at a concentration of 2 g/L more than twice than that obtained at a concentration of 10 g/L. This observa-

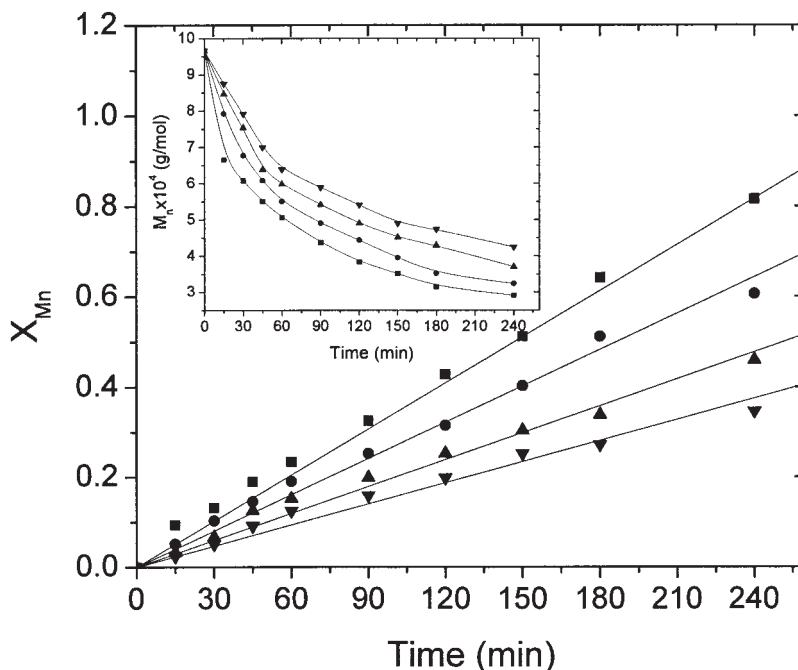


Figure 2 Variation of X_{Mn} with time at different polymer concentrations: (■) 2, (●) 3.5, (▲) 5, and (▼) 10 g/L. The inset shows the variation of M_n with time.

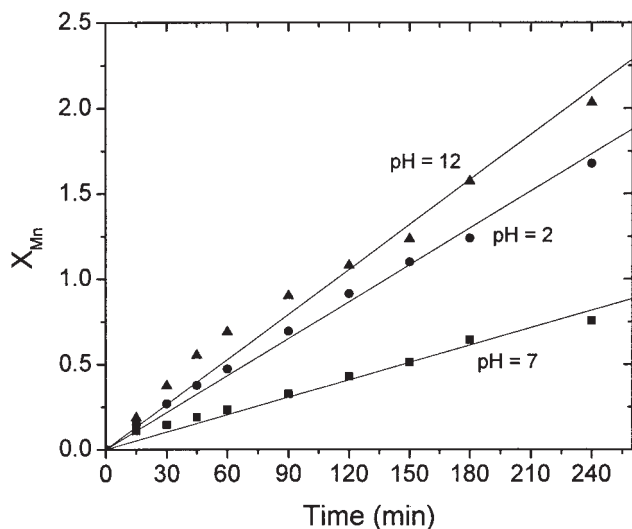


Figure 3 Variation of X_{Mn} with time at different pHs at a fixed initial polymer concentration of 2 g/L.

tion cannot be attributed to the effect of viscosity. The viscosity of the polymer solution increases with increasing polymer concentration, but the ultrasonic degradation rate decreases with increasing polymer concentration. However, when the viscosity of the polymer solution increases, the degradation rate^{12,13} increases. Therefore, the reduction of the degradation rate of the polymer with increasing polymer concentration may be attributed to the overlapping of polymer chains at higher concentrations, which reduces the efficiency of cavitation in a viscous solution.

The ultrasonic degradation of polymers is influenced by the solvent quality, that is, the polymer-solvent interaction and the polymer conformation in the particular solvent. In this work, the influence of different solvents and aqueous solvents at different pHs on the ultrasonic degradation of PVA is discussed. The effect of the pH on the degradation of PVA was studied at pHs 2, 4, 7, 9, and 12 (Fig. 3). Higher degradation was obtained at pH extremes (i.e., pHs 12 and 2), and the lowest degradation was seen at the natural pH of the polymer solution (pH 7). This can be attributed to different chemical effects that are predominant in aqueous media during irradiation by ultrasound. Water favors the formation of cavitation bubbles. Electrical charges may arise when bubbles form, and water helps in the electronic breakdown of bubbles. In the presence of oxygen, water decomposes to OH, HO₂, and H radicals, which combine to form peroxide. The radicals that form can also participate in various oxidation reactions of the polymer macroradicals, thereby affecting the rate of degradation. The decomposition of water is initiated by the ejection of an electron from the water molecule due to the action of ionizing radiation followed by a series of secondary reactions, as discussed in detail previously.²⁶ This ef-

fect was also seen in the degradation of poly(methyl methacrylic acid) when it was degraded with ultrasound at 250 kilocycles/s.²⁷ At very high and very low pHs, the production of OH and H radicals increases, and this makes chemical effects dominant in the degradation of PVA. In fact, the intensity of cavitation, which is enhanced when radicals are formed from solvents, has been detected during the decomposition of organic halogen derivatives irradiated in aqueous media.²⁶ The rate coefficients for the degradation of PVA at various pHs are shown in Table I. Alkaline aqueous PVA solutions have the highest degradation rate under ultrasound irradiation. The ultrasonic degradation of PVA was also investigated in different binary solvent mixtures. The vapor pressure of the PVA solutions in only water and in other binary mixtures was approximately kept the same to determine whether the vapor pressure was the dominant influence in the degradation. There are studies showing that the degradation rate decreases with an increase in the vapor pressure because of a cushioning effect on the cavitation bubbles.^{7,10,12,13,21} Thus, it becomes interesting to observe the variation of the degradation rate coefficient in mixtures of approximately the same vapor pressure. Thus, the vapor pressures in water and water/acetone, water/methanol, and water/acetonitrile mixtures were 7.3, 7.6, 7.7, and 7.2 kPa, respectively. However, the rate coefficients, determined from the linearly regressed line of X_{Mn} with time (Fig. 4), were 1.94, 0.96, 0.70, and 1.26 $\times 10^{-7}$ mol g⁻¹ min⁻¹, respectively (as shown in Table I). This indicates that even though the vapor pressures differ by less than 10%, the degradation rate coefficients change by nearly 170%. This can probably be explained by the polymer conformation in various solvents. It is generally known that degradation is higher in a good solvent in which the polymer is in an extended conformation.²⁸ The polymer-solvent interaction is thus significant in controlling the degradation process. The solvation of the polymer is better in good solvents, resulting in an extended, open-coil structure. This extended conformation of polymer chains is the reason for obtaining the highest degradation rate for PVA in water. Thus, the addition of nonsolvents such as methanol and acetone in small amounts causes the collapse of the polymer chains, resulting in the coiled conformation and thereby reducing the degradation rate. Moreover, the M_{lim} value attained in water is lowest in comparison with those in other water/solvent mixtures. A higher degradation of dextran and poly(ethylene glycol) was observed by Basedow et al.¹⁴ in better solvents. Hence, it can be concluded that the conformation of the polymer in solution contributes significantly to the degradation rate and, in fact, plays a more dominant role than vapor pressure for the degradation of PVA. To further test this hypothesis, experiments were conducted at a fixed polymer con-

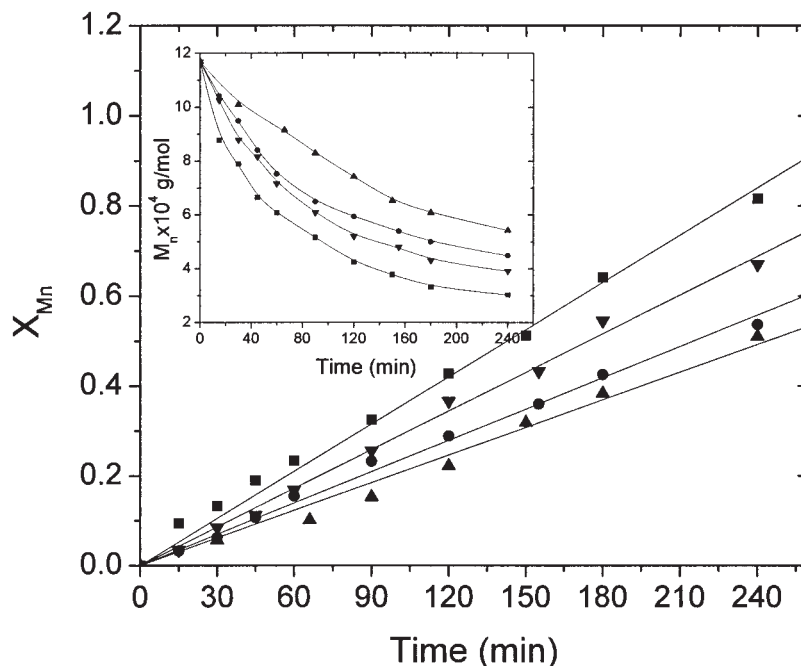


Figure 4 Variation of X_{Mn} with time in different water/solvent mixtures at a fixed initial polymer concentration of 2 g/L: (■) water, (●) water/acetone mixture, (▲) water/methanol mixture, and (▼) water/acetonitrile mixture. The inset shows the variation of M_n with time.

centration (2 g/L) in water at various temperatures (15–50°C). Although the vapor pressure of water, determined from the Antoine equation,²⁹ varied from 1.7 kPa at 15°C to 12.3 kPa at 50°C, no appreciable change in the degradation rate was observed. This also indicates that the conformation of the polymer plays a more critical role than the vapor pressure in the degradation of PVA.

CONCLUSIONS

The ultrasonic degradation of PVA at different concentrations and pHs and in different binary solvent mixtures was investigated. The results showed that the degradation rate was highest when the polymer concentration was lowest. A higher rate was also obtained at pHs 2 and 12 in comparison with that at the natural pH (7) of the polymer solution. The degradation in binary solvent mixtures was dependent on the polymer conformation in solution and was independent of the vapor pressure.

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