

Effect of pH, Concentration and Solvents on the Ultrasonic Degradation of Polyvinyl Alcohol

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Abstract

The ultrasonic degradation of polyvinyl alcohol was investigated at different pH of solvent, in different water/solvent binary mixtures and at different polymer concentrations. Samples were analyzed by gel permeation chromatography. The degradation rate coefficients were determined by applying a continuous distribution model. Higher degradation rate was obtained at extremes of pH, in better solvents and at lower polymer concentration. The results obtained have been explained and discussed.

Keywords: Ultrasound; Degradation; pH, binary mixtures, conformation, concentration

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Introduction

The disintegration of macromolecules when subjected to ultrasound is primarily due to the action of cavitation bubbles. The earliest study of ultrasonic effects was noted in natural polymers like gelatin, starch and guar gum [1-2]. The irreversible and permanent reduction in 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, polymer and solvent. It is well known that there are two major characteristics of ultrasonic polymer degradation. One is the presence of a limiting molecular weight and the other is the non-random mode of breakage [5-7]. The major advantage of ultrasonic degradation is that there is breakage of only the most susceptible chemical bond and no chemical changes occur in the molecule. The effect of temperature and solvent has been correlated to the cushioning effect produced on the bubble collapse. 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 due to above-mentioned 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 under condition of similar enthalpy of vaporization of solvent. They found that the rate of degradation was higher in the better solvent viz deuterium oxide for dextran and water for poly(ethylene oxide) and the rate decreased with addition of the poor solvent. Studies were also conducted to determine the influence of solvent density on degradation of polymer and it was found that within experimental error, no influence of density on degradation was found [15, 16]. The concentration effect showed that there is an optimum in polymer concentration for the

ultrasonic degradation of carboxymethyl cellulose [17]. However, the highest degradation was found at the lowest polymer concentration for dextran [18] and for other polymers [19,20]. This indicates several parameters influence the ultrasonic degradation of polymers.

However, to the best of our knowledge, the effect of pH, solvent, conformation of polymer has not been investigated for the ultrasonic degradation of polyvinyl alcohol (PVA). In the present article, we have investigated the ultrasonic degradation of PVA at different pH, polymer concentration and in binary mixtures of solvents. A model based on continuous distribution kinetics has been developed to determine the degradation rate coefficients. It is shown that the conformation of the polymer in solution is the most important parameter in the degradation of PVA.

2. Materials and methods

2.1 Materials

Polyvinyl alcohol was obtained from Sigma Aldrich. Double distilled deionized water was used as solvent for making polymer solutions. Acetone, methanol and acetonitrile were obtained from Merck Inc. and were of HPLC grade.

2.2 Experiments

40 ml of the polymer solution 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 web site of the manufacturer. The processor delivers the sound energy to the polymer solution through a horn tip with a flat radiating circular surface of 1" (2.54 cm) in diameter. The transformer or velocity horn amplifies the small vibrations. It is attached to a pair of lead Zirconate titanate transducer elements. The applied

intensity and frequency of the sound generated was 36 W cm^{-2} and 25 kHz, respectively. This is the maximum intensity possible to generate in our experimental setup. The temperature of the polymer solution was maintained within $\pm 1 \text{ }^\circ\text{C}$ using a thermostated ice water bath.

The ultrasonic degradation of PVA was investigated at $30 \text{ }^\circ\text{C}$ at a fixed polymer concentration of 2 g/L in different binary mixtures of solvents, water being kept as one of the solvents and acetone, methanol and acetonitrile added to water in appropriate amounts such that the vapor pressures of the mixtures are nearly the same.

The effect of pH on degradation of PVA was studied by varying the pH from 2-12 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 of 0.1 pH) by immersing the electrode 2 cm into the solution. The pH of the solution was measured before, during and after irradiation by ultrasound and it was found that it did not change with time. Several experiments were repeated and the error in experiments in the determination of the degradation rate coefficient was around 3%.

The samples were taken at regular intervals and analyzed by gel permeation chromatograph [21] (GPC) with double distilled deionized water as eluent at a flow rate of 0.5 ml/min. The columns used were Ultrahydrogel linear column (Waters, USA) measuring 7.8 mm x 300 mm maintained at 50°C . The refractive index was monitored continuously with a Differential Refractometer (Waters, Model 401). About 800 μl of sample was injected into the system to obtain a chromatogram and converted to

molecular weight by using polyethylene oxide calibration standards, which is usually used as the standard for water-soluble polymers.

The continuous distribution model to determine the degradation rate coefficient requires the limiting molecular weight for the degradation of the polymer. Several experiments were conducted for 10 hours and no detectable change in the molecular weight was noticed after 6 hours and was used as the limiting molecular weight, M_{lim} .

3. Theoretical model

Continuous distribution kinetics was employed to follow the degradation kinetics and determine the degradation rate coefficient. For a 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 by [10]

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

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 $k(x) = k(x-M_{lim})$, where the M_{lim} represents the limiting molecular weight. Applying moment operation to the above equation yields

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

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 zeroth moment, $p^{(1)}/p^{(0)}$. Solving equation (3) with initial condition, $p^{(0)}(t=0) = p_0^{(0)}$ yields [10,22,23],

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

A more detailed derivation of the above equations is provided in previous publications [10, 21, 22,23]. It should be noted that 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 chain [24] satisfactorily models the deviation of the experimental data points from the linearity. However, the value of the rate coefficient does not significantly change by this assumption.

4. Results and discussion

The ultrasonic degradation of polyvinyl alcohol was done at different pH, in different binary mixtures of solvent and at different polymer concentrations. Figure 2 shows the effect of polymer concentration on the degradation. Other investigators [25] have obtained similar results for the degradation of PVA. The rate coefficients ($k \times 10^{-7} \text{ mol g}^{-1} \text{ min}^{-1}$), determined from the linearly regressed line of X_{Mn} with time (as suggested by Eq 4), are shown in Table 1. This indicates that the rate of polymer degradation decreases with increase in 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 observation 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 decrease of the degradation rate of the polymer with increasing polymer concentration may be attributed to the overlap of polymer chains at higher concentrations thereby reducing the efficiency of cavitation in a viscous solution.

The ultrasonic degradation of polymers is influenced by the solvent quality i.e., 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 pH on the ultrasonic degradation of PVA is discussed. The effect of pH on degradation of PVA was studied at the pH values of 2, 4, 7, 9 and 12 (Figure 3). Higher degradation was obtained at extremes of pH i.e at pH 12 and 2 and the lowest degradation was seen at the natural pH of the polymer solution i.e at pH 7. It 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 electronic breakdown of bubbles. In the presence of oxygen, water decomposes to OH, HO₂ and H radicals, which combine to form peroxide. The radicals formed 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 effect was also seen in the degradation of poly(methyl methacrylic acid) when degraded with ultrasound at 250 kilocycles/sec [27]. At very high and very low pH, the production of OH and H radicals increases thereby making chemical effects dominant in the degradation of PVA. In fact, the intensity of cavitation, which is enhanced when radicals

are formed from solvents, was detected during decomposition of organic halogen derivatives when irradiated in aqueous media [26]. The rate coefficients for degradation of PVA at various pH are shown in Table 1. It can be seen that alkaline aqueous PVA solutions have the highest degradation rate under ultrasound irradiation. The ultrasonic degradation of PVA was also investigated in different binary mixtures of solvents. The vapor pressure of PVA solution in only water and in other binary mixtures was approximately kept the same in order to verify if vapor pressure was the dominant influence in the degradation. There are studies showing that degradation rate decreases with increase in vapor pressure due to cushioning effect on the cavitation bubbles [7, 10, 12, 13, 21]. Thus it becomes interesting to observe the variation of degradation rate coefficient in mixtures of approximately same vapor pressure. And thus the vapor pressures in water, water/acetone, water/methanol and water/acetonitrile mixtures were 7.3, 7.6, 7.7, 7.2 kPa, respectively. However, the rate coefficients ($k \times 10^{-7} \text{ mol g}^{-1} \text{ min}^{-1}$), determined from the linearly regressed line of X_{Mn} with time (Figure 4), are 1.94, 0.96, 0.70 and 1.26, respectively (as shown in Table 1). This indicates that even though vapor pressures differ by less than 10%, the degradation rate coefficients change by nearly 170%. This can probably be explained based on polymer conformation in various solvents. It is generally known that degradation is higher in a good solvent where the polymer is in extended conformation [28]. The polymer-solvent interaction is thus significant in controlling the degradation process. Solvation of polymer is better in "good solvents" resulting in 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 non-solvents like methanol and acetone in small amounts causes

collapse of the polymer chains, resulting in coiled conformation, thereby reducing the degradation rate. It was also seen that the limiting molecular weight attained in water is the lowest when compared to that in other water-solvent mixtures. A higher degradation of dextran and polyethylene glycol was observed by Basedow et al. [14] in better solvents. Hence it can be concluded that conformation of 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. In order to further test this hypothesis, experiments were conducted at a fixed polymer concentration (2 g/L) in water at various temperatures (15-50 °C). Though the vapor pressure of water, determined from the Antoine equation [29], varies 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 conformation of the polymer plays a more critical role than the vapor pressure in the degradation of PVA.

4. Conclusions

The ultrasonic degradation of PVA at different concentrations, pH and in different binary mixtures of solvents was investigated. The results show that degradation rate is highest when polymer concentration is lowest. Higher rate was also obtained at pH 2 and 12 compared to the natural pH 7 of the polymer solution. The degradation in binary mixtures of solvents was dependent on the polymer conformation in solution and was independent of the vapor pressure.

References

1. Szalay AZ, *Phy. Chem. A*, 1933; 164: 234.
2. Gyorgi AS, *Nature*, 1933; 131: 278.
3. Schmid G, Rommel OZ, *Elektrochem.*, 1939; 45: 659.
4. Schmid G, *Phys. Chem.*, 1940; 186: 113.
5. Mostafa MA, *J. Polym. Sci.*, 1958; 28: 499.
6. Jellinek HH, *J. Polym. Sci.*, 1959; 37: 485.
7. Price GJ, Smith PF, *Polymer*, 1993; 34: 4111.
8. Schmid G, Beuttenmuller E, *Elektrochem.*, 1944; 50: 209.
9. Thomas BB, Alexander WJ, *J. Polym. Sci.*, 1957; 25: 285.
10. Chattopadhyay S, Madras G, *J. Appl. Polym. Sci.*, 2003; 88: 2818.
11. Basedow AM, Ebert KH, *Makromol Chem.*, 1975; 176: 745.
12. Madras G, Karmore V, *Poly. Intl.*, 2001; 50: 683.
13. Madras G, Chattopadhyay S, *Polym. Degrad. Stability*, 2001; 71: 273.
14. Basedow AM, Ebert KH, Fosshag E, *Makromol Chem.*, 1978; 179: 2565.
15. Henglein A, Gutierrez M, *J. Phys. Chem.*, 1988; 92: 3705.
16. Schmid G, Beuttenmuller E, *Elektrochem.*, 1943; 49: 325.
17. Gronroos A, Pirkonen P, Ruppert O, *Ultrasonics Sonochemistry*, 2004; 11: 9.
18. Lorimer JP, Mason TC, Cuthbert TC, Brookfield EA, *Ultrasonics Sonochemistry*, 1995; 2: 55.
19. Malhotra SL, *J. Macromol. Sci. Chem.*, 1982; A17: 601.
20. Gooberman G, Lamb J, *J. Polym. Sci.*, 1960; 47: 229.
21. Vijayalakshmi SP, Madras G, *Polym. Degrad. Stability*, 2004; 84: 341.

22. Chakraborty J, Sarkar J, Kumar R, Madras G, *Polym. Degrad. Stability*, 2004; 85: 555.
23. Madras G, McCoy BJ. *AIChE. J.*, 2001; 47: 2341.
24. Sivalingam G, Agarwal N, Madras G. *AIChE. J.*, 2004; 50: 4835.
25. Taghizadeh MT, Mehrdad A, *Ultrasonics Sonochem.*, 2003; 10: 309.
26. Basedow AM, Ebert KH, *Adv. Polym. Sci.*, 1977; 22: 83.
27. Alexander P, Fox M, *J. Polym. Sci.*, 1954; 12: 533.
28. Price GJ. In: Mason TJ, editor. *Advances in Sonochemistry*. vol. 1. Cambridge: Jai Press. 1990: 231.
29. Perry RH, Chilton CH, editors. *Chemical Engineers Handbook*, New York: McGraw-Hill, 1973.

TABLE 1. Rate coefficients for the ultrasonic degradation of PVA at different conditions.

Condition	Rate coefficient, $k \times 10^{-7}, \text{mol g}^{-1} \text{min}^{-1}$
Effect of 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 solvents	
Water (VP = 7.3 kPa)	1.94
Water/acetone (VP = 7.6 kPa)	0.96
Water/methanol (VP = 7.7 kPa)	0.70
Water/acetonitrile (VP = 7.2 kPa)	1.26

Figure captions

Figure 1. Representative MWD for the ultrasonic degradation of PVA.

Legend ■ initial distribution ● after degradation for 90 minutes. The solid line is the prediction by the model.

Figure 2 Variation of X_{Mn} with time at different polymer concentrations.

Legend ■ 2 g/L ● 3.5 g/L ▲ 5 g/L ▼ 10 g/L

Inset: Variation of number-average molecular weight with time.

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

Figure 4 Variation of X_{Mn} with time in different water/solvent mixtures at a fixed initial polymer concentration of 2 g/L.

Legend ■ water ● water/acetone mixture ▲ water/methanol mixture L

▼ water/acetonitrile mixture

Inset: Variation of number-average molecular weight with time.

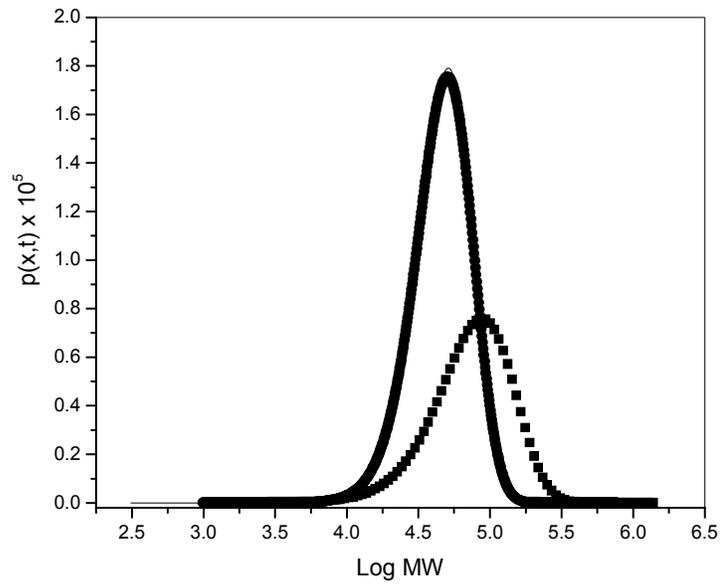


Figure 1

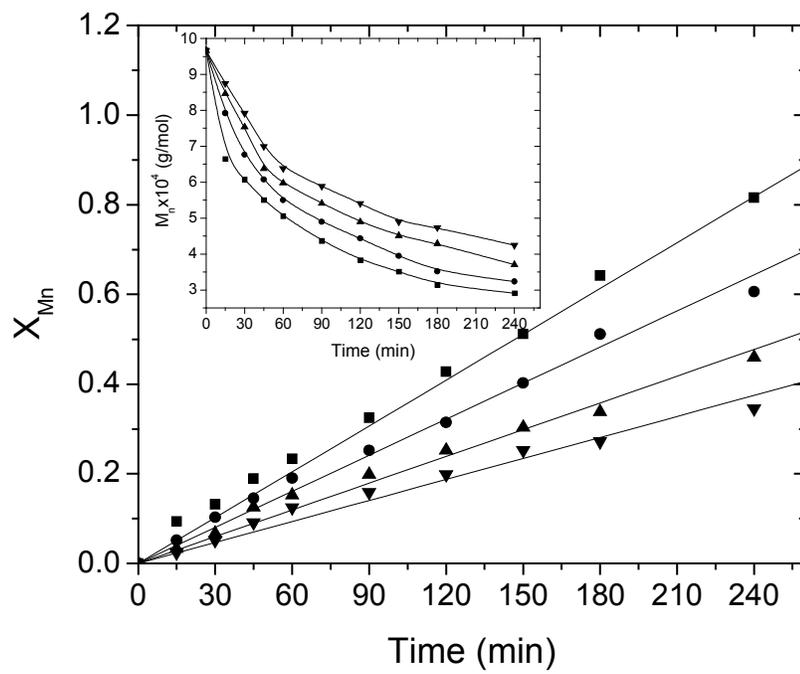


Figure 2

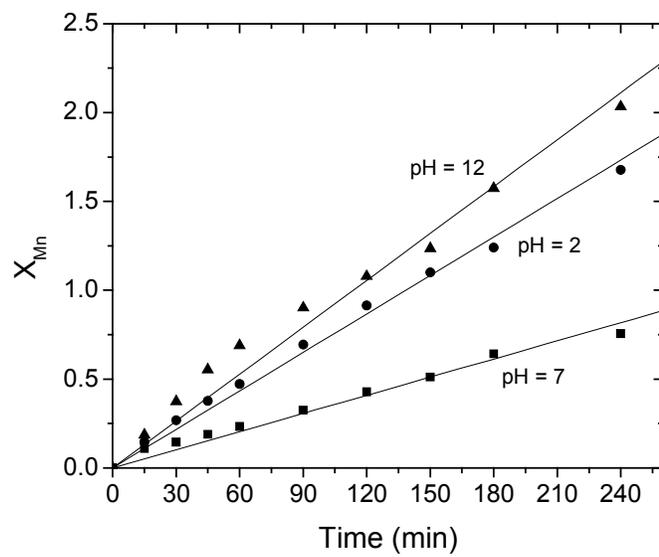


Figure 3

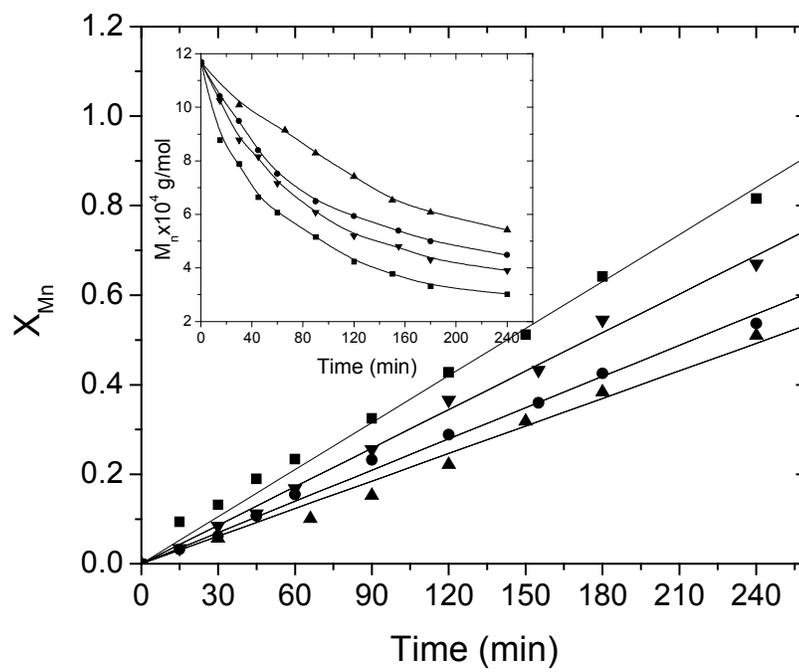


Figure 4