

Original Research Article

Ultrasonic degradation of polyvinyl pyrrolidone (PVP): effect of power of ultrasound, Temperature and Concentration

ABSTRACT

In this study, the effect of power of ultrasound, temperature and concentration of polyvinyl pyrrolidone (PVP) solution on the rate of ultrasonic degradation were investigated, and a kinetic model based on viscometry data was used to calculate the rate constants in different conditions. In order to investigation of effect of ultrasonic power on the degradation of PVP, the power of ultrasound was changed in the range of 30-150W and observed that the viscosity of the PVP solution was decreased with an increase in the power of ultrasound, but the extent of the degradation in a constant power was found to decrease with an increase in concentration or temperature. The ultrasonic degradation of PVP solutions was carried out at 5, 25, 45 and 65 °C to investigate the effect of the temperature on the rate of degradation. The calculated rate constants indicated that the degradation rate of the PVP solutions decreased as the temperature increased. The average molecular weight of ultrasonicated PVP was determined by measurements of relative viscosity of samples.

Keywords: Polyvinyl pyrrolidone (PVP); ultrasonic degradation; viscosity; rate constant

1. INTRODUCTION

The ultrasonic polymer degradation has several unique characteristics that make it interesting both from practical and theoretical viewpoints [1]. High-intensity ultrasonic treatment can be applied to degrade polymers and to facilitate emulsifying and cleaning processes in homogenous liquid phase [2]. The degradation of several polymers such as polystyrene [3], polyvinyl acetate [4], polypropylene [5], poly(methylmethacrylate) [6], dextran [7], hydroxy propyl cellulose [8], carboxymethyl cellulose [9], polyacrylamide [10] and poly(ϵ -caprolactone) [11] has been investigated. This work has been summarized in a review paper by Price [12]. Ultrasonic irradiation induces the production of cavitation bubbles in the liquid through which it is transmitted. These microbubbles grow during the subsequent compression–rarefaction cycles until they reach a critical size. Further compression leads to the collapse of the bubbles, with the concomitant release of heat and production of chemically active species during the last phase of the bubble collapse [13]. Indeed, energy concentrated in the bubbles is sufficient to break strong chemical bonds [14]. Cavitation produces vibrational wave energy, shear stresses at the cavitation interphase, and local high pressure and temperature. These are the major factors causing the degradation of polymers [15]. Application of high-intensity ultrasound to dispersions of macromolecules can lead to depolymerization because of the intense mechanical and chemical effects associated with

cavitation [16]. Cavitation thermolysis may produce hydroxyl radicals and hydrogen atoms that can be followed by formation of hydrogen peroxide [17]. Some cavities exist only for one cycle of the sound field and collapse violently (transient cavities), while other are long-lived and oscillate around some equilibrium size (stable cavities) [18]. These transient reactive species can subsequently react with carbohydrates. In addition, hydrolysis and cleavage due to the strong mechanical forces has been reported for a variety of polymers [19].

A variety of different theoretical models have been proposed to attempt to explain the way in which the factors such as frequency, intensity, solvent, temperature, nature of dissolved gas, external pressure and the molecular mass distribution influence the rate and final molecular mass of degraded species [20]. Three models are proposed to account for this chemical change based on cavitation induced by ultrasound [21]. In the first model, the degradation is interpreted in terms of the high temperature and pressure generated during bubble collapse. The Jellinek model attributes chain scission to the increased frictional force generated on cavitation collapse. In the final model, Doulah [22] suggests that the shock-wave energy released on bubble collapse gives rise to a series of eddies which interact with the macromolecules in solution. The factors influencing ultrasonic degradation rate and final molecular weight of degraded species have also been studied and explained carefully based on these models [23, 24]. The following conclusions were obtained:

(1) In general, ultrasound with greater intensity or lower frequency leads to both faster degradation and a lower limiting molecular weight.

(2) Different from majority of chemical processes, the ultrasonic degradation of polymer solutions is inhibited by an increase of temperature. Moreover, the effect of temperature is greater than the variation due to the ultrasonic intensity and frequency.

(3) In a certain range, the ultrasonic degradation rate increases with the reduction of solution concentration.

(4) A solvent with higher volatility promotes cavitation and consequently can accelerate the ultrasonic degradation of polymer solutions.

In this study nine different concentration of poly (vinyl-pyrrolidone) (PVP) are examined. PVP is a biocompatible material and has wide applications as biomaterials. The objective was to introduce a simple kinetic model for the evaluation of degradation rate of polymers via viscometry. This was performed by the correlation of viscosity measurements at different sonication times to average molecular weight (M_v) and number average molecular weight (M_n). Finally, these quantities are correlated with the molar concentration with a meaningful expression.

2. MATERIAL AND METHODS

2.1. MATERIALS

Polyvinyl pyrrolidone (PVP) with weight-average molecular weight 1300000 kDa was purchased from Across Co. Ltd. Molecular weight was 756000 kDa, which was determined by viscometer. All other chemicals were of laboratory reagent grade and were purchased from Merck. All solutions were prepared using distilled and deionized water.

77 2.2. METHODS

78 2.2.1. PVP solution preparation

79 PVP solutions containing 5, 10, 15, 20, 25, 30, 35, 40 and 45g/L PVP were prepared. The
80 solutions were stirred overnight to ensure complete solubilisation of the PVP molecules, and
81 then filtered to remove any impurities and 100 ml samples were immediately sonicated.

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83 2.2.2. Experimental setup and procedure

84 Reactions were carried out in a cylindrical 100ml Pyrex glass vessel. An ultrasound
85 generator (Dr. Hielscher Ultrasonic Processor UP200 H) operating at a fix frequency of 24
86 kHz and a variable power output up to 150W nominal value, in aqueous media was used for
87 sonication experiments. A titanium-made H3 sonotrode ($\phi=3\text{mm}$) immersed in liquid from the
88 open to the atmosphere top of the vessel was used to deliver the ultrasound energy in the
89 reaction mixture. The vessel was fed with a 100ml PVP solution and the reaction
90 temperature in the case of sonolysis processes for the study of effect of concentration and
91 power of ultrasound was kept constant at $25\pm1^\circ\text{C}$ through the use of cooling water
92 circulating through the double-walled compartment, thus acting as cooling jacket. The
93 reaction vessel was covered with a dark cloth to avoid unwanted photochemical reactions
94 induced by natural light.

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96 2.3. VISCOSITY MEASUREMENTS

97 The intrinsic viscosities of the original PVP and its degraded solutions at 25°C were
98 measured using the capillary viscometer (Setavic Kinematic viscometer). Efflux times were
99 measured for PVP solutions (t_s) and the solvent (t_0). Measurement of efflux times were
100 repeated two times and average efflux time was then converted to the ratio of t_s/t_0 , which is
101 proportional to relative viscosity, η_r , of PVP solution.

$$102 \quad \eta_r = \frac{t}{t_0}, \eta_{sp} = \eta_r - 1 \quad (1, 2)$$

103 The intrinsic viscosity $[\eta]$ values can be related to the specific viscosity, η_{sp} , and relative
104 viscosity, η_r , by the Huggins and Kramer equations [25]. The conditions used in this work
105 ($\alpha = 0.55$ and $k = 6.67 \times 10^{-5} \text{ L/g}$) were adopted on the basis of previous findings in the
106 literature [26].

107

108 2.4. KINETIC MODEL

109 The rate of degradation is defined as the number of scission that occurs in 1 L in unit time
110 and we must keep in mind that a scission in a chain yields two pieces. Thus, the rate
111 equation of the degradation is as follows [27]:

$$R = \frac{dM}{dt} = kM^n \quad (3)$$

Where, M, is the total molar concentration of the polymer, k, is the rate constant and, n, is the order of reaction with respect to the total molar concentration of the polymer. From the experimental data, it is clear that the degradation rate decreases with increasing solution concentration, so “n” is negative. Harkal et al. was found that the order of ultrasonic degradation reaction for poly (vinyl alcohol) obtained from this kinetic model is -1[28].

It is noted that solution concentration (g/L) is constant and the total molar concentration (mol/L) increases during the degradation of polymer. The solution of differential Eq. (3) is:

$$M^{1-n} - M_0^{1-n} = (1-n)kt \quad (4)$$

Where M₀ is the initial total molar concentration of polymer. The total molar concentration is related to the number average molecular weight through [29]:

$$M = \frac{C}{M_n} \quad (5)$$

Moreover, viscosity average molecular weight, M_v, is related to the number average molecular weight, M_n, through [30].

$$M_v = \left[(1+\alpha) \Gamma(1+\alpha) \right]^{\frac{1}{\alpha}} M_n \quad (6)$$

Where, $\Gamma(1+\alpha) = \int_0^\infty e^{-t} t^\alpha dt$, M_v is related to the intrinsic viscosity, [η], through Marck-Houwink equation:

$$M_v = \left(\frac{[\eta]}{K} \right)^{\frac{1}{\alpha}} \quad (7)$$

Where α and k are the Mark–Houwink constants.

Finally, [η] can be related to the specific viscosity, η_{sp}, and relative viscosity, η_r, by Huggins and Kramer equations:

$$\frac{\eta_{sp}}{C} = [\eta] + K'[\eta]^2 C \quad (8)$$

$$\frac{Ln\eta_r}{C} = [\eta] + (K' - 0.5)[\eta]^2 C \quad (9)$$

From Eq. (8) and (9), intrinsic viscosity is:

$$[\eta] = \frac{\sqrt{2(\eta_{sp} - L\eta_r)}}{C} \quad (10)$$

Substitution of Eq. (10) in (7) and Eq. (7) in (6) yields

$$M_n = \left[\frac{\sqrt{2(\eta_{sp} - L\eta_r)}}{(1+\alpha)\Gamma(1+\alpha)KC} \right]^{1/\alpha} \quad (11)$$

Finally, the substitution Eq. (11) in (5) yields:

$$M = \left[\frac{(1+\alpha)\Gamma(1+\alpha)KC^{1+\alpha}}{\sqrt{2}} \right]^{1/\alpha} \Delta\eta \quad (12)$$

In addition, substitution Eq. (12) in (4) yields:

$$\Delta\eta^{1-n} - \Delta\eta_0^{1-n} = (1-n) \left[\frac{\sqrt{2}}{(1+\alpha)\Gamma(1+\alpha)KC^{1+\alpha}} \right]^{(1-n)/\alpha} kt \quad (13)$$

Or

$$\Delta\eta^{1-n} - \Delta\eta_0^{1-n} = k't \quad (14)$$

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3. RESULTS AND DISCUSSION

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3.1. DETERMINATION OF REACTION ORDER OF DEGRADATION OF PVP

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At the level of interatomic distances within the macromolecules, there is still some debate regarding the place where the bond breakage occurs. By analogy with the chemical degradation, it is expected to take place at the weakest links in the polymer backbone, but some works [31, 32] suggested that it mainly occurs at the midpoint of the polymer chains and the existence of a final limiting molecular weight is predicted; below which ultrasounds have no more effect. In general, polymer mechanochemistry induced by an acoustic field is a non-random process; for example, the scission of polymer chains in solution occurs at a preferential position near the midpoint [33]. Moore et al. approved this idea by an isotope labeling experiment on ultrasonic degradation of linear PEG. They demonstrated that when a single weak azo link was positioned at the center of a linear PEG chain, mechanically-induced cleavage was localized almost exclusively to the single weak site [34].

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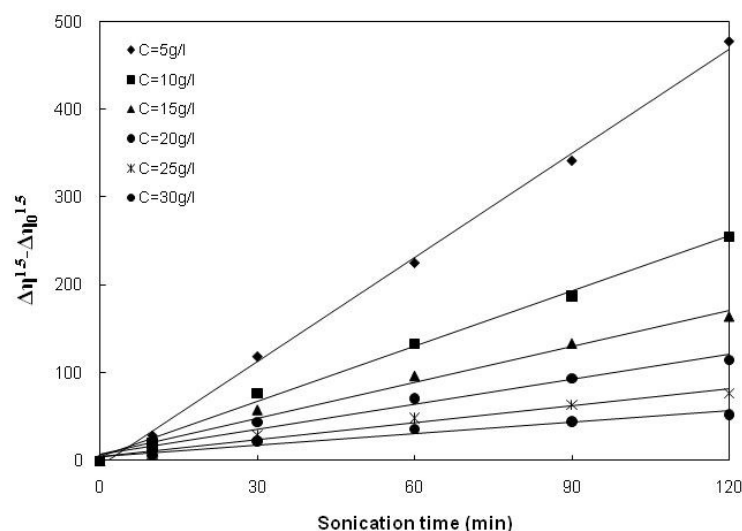
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Several studies propose a random chain breakage but still consider that some bonds are more resistant, in relation to the decrease in the scission rate constant as lower values of degree of polymerization are reached [35]. Due to the polydisperse nature of most polymers, an accurate analysis of the degradation kinetics is almost impossible without information about the location of chain scission and the dependence of rate coefficients on the molecular weight of the polymer. Two simplified models, based on different assumptions of the location

of chain scission, have been proposed to quantitatively describe the degradation process of polymers [36]. Although, a number of different rate models have been proposed for the degradation of polymers [37, 38], but in this study a simple model was employed via viscometry, Using Eq. (12). A negative order for the dependence of the reaction rate on total molar concentration of PVP solution within the degradation process was suggested. In the initial sonication times, for different concentration of polymer we calculate total molar concentration of polymer. The results are depicted in Fig. 1.



174

175 **Fig. 1. The plot of $\Delta\eta^{1.5}-\Delta\eta_0^{1.5}$ versus the sonication time for different concentration of**
 176 **PVP solution at 25°C.**
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178 Previous studies were proved that with an increase in concentration, the rate constant, k ,
 179 was decreased obviously [39, 40]. These observations are explained in terms of viscosity
 180 changes for different polymer concentrations. At higher concentrations, the solution viscosity
 181 increases. An increase in viscosity raises the cavitation threshold. This increased threshold
 182 makes it more difficult for cavitation bubbles to form. More importantly, the velocity gradients
 183 around collapsing bubbles become smaller, and the elongation of the polymer backbone is
 184 reduced [41]. The slopes of plots give the initial rate of degradation using Eq.20, the plot of
 185 $\ln R$ versus $\ln[M]$ are linear and it is shown in Fig. 2.

186 The slope of curve is -0.5, which suggest the order of reactions with respect to total molar
 187 concentration of polymer. From substitution of the value of “ n ” in Eq.14, we obtain the
 188 following:

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$$\Delta\eta^{1.5} - \Delta\eta_0^{1.5} = k't \quad (15)$$

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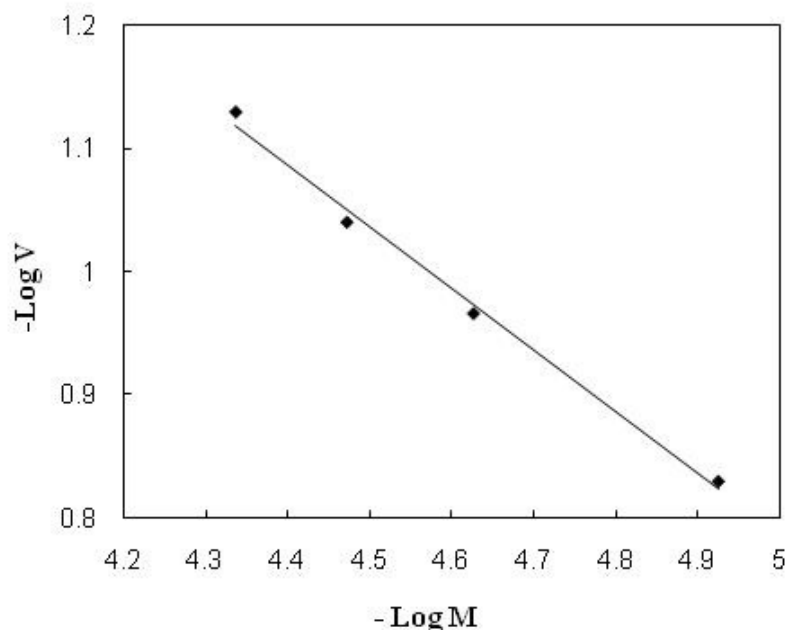


Fig. 2. The plot of $\ln V$ versus $\ln M$ for degraded PVP at 25°C.

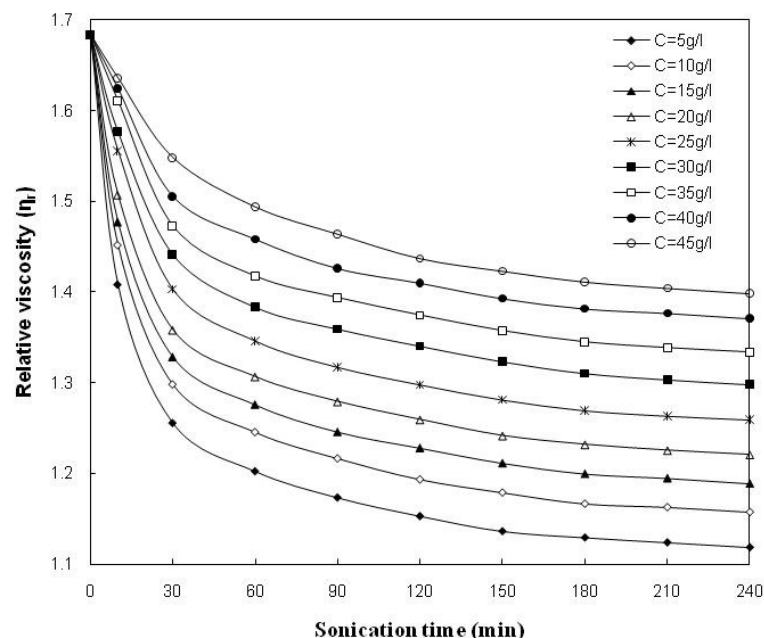
3.2. Effect of concentration on the rate of PVP degradation

The data of limited viscosities (relative and intrinsic) listed in Table 1 show that the viscosity increases with increasing of concentration of polymer, at the end of 240 min.

Table 1. Limiting relative viscosity, η_r , and limiting viscosity-average molecular weight, M_v , of PVP samples degraded by ultrasonic irradiation in various concentrations and 25°C at the end of 240min.

C (g/L)	Limiting η_r	Limiting M_v (kDa)
5	1.119	40679
10	1.157	66514
15	1.189	90855
20	1.221	119042
25	1.260	156552
30	1.298	197143
35	1.334	238453
40	1.371	283806
45	1.399	319741

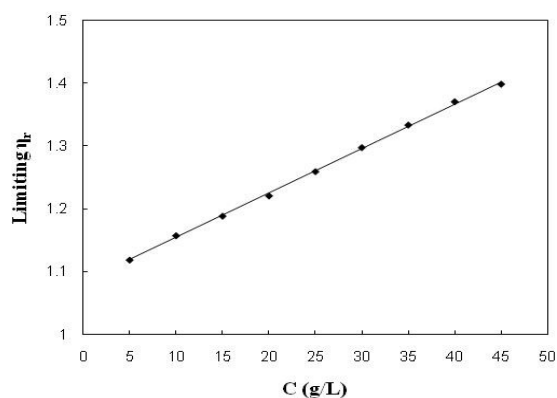
Sonication was carried out for nine different PVP concentrations at 25 °C. The relationship between η_r and sonication time are presented in Fig. 3.



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205 **Fig. 3. The relationship between η_r and sonication time for different PVP**
 206 **concentrations at 25°C and fixed power of ultrasonic irradiation (150W).**
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208 Based on these findings, it is clear that η_0 decreases with sonication time and tends to have
 209 a constant value. It can be deduced that there is a limiting molecular weight that below which
 210 chain scission does not occur. Under the same conditions, the decrease in η_r of the sample
 211 with a high polymer concentration is lower than of the sample with a low polymer
 212 concentration. The relationship between the limiting value of η_r and solution concentration is
 213 presented in Fig. 4.



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215 **Fig. 4. The relationship between the limiting value of η_r and solutions concentration.**
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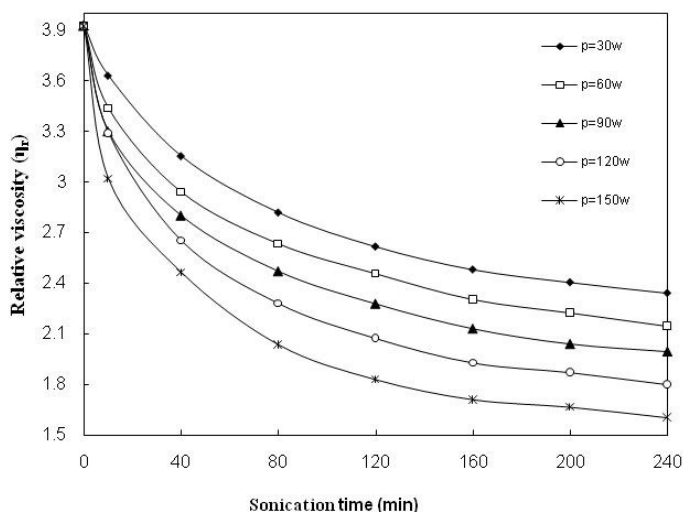
217 These results indicate that the extent of degradation is more pronounced in more dilute
 218 solutions. This might be due to the fact that the probability of chemical bond scission caused

219 by efficient shearing in the polymer chain is greater in dilute solution. These findings are
220 consistent with the results of other investigators [42].

221

222 3.3. Effect of power of ultrasound on the rate of PVP degradation

223 Fig. 5 shows the effect of increasing changing ultrasound power on relative viscosity (η_r) of
224 PVP solution as a function of the sonication time at 15g/L initial PVP concentration under air.
225 As seen, η_r decreases with increasing the nominal applied power from 30 to 150W.



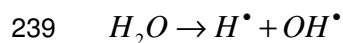
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227 **Fig. 5. The relationship between η_r and sonication time in for different power of**
228 **ultrasound at 25°C and 15g/L.**

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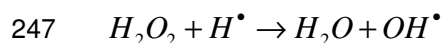
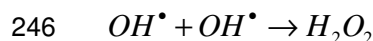
230 In aqueous solutions, the main pyrolytic reaction is the dissociation of water. This thermal
231 dissociation leads to the production of highly reactive radicals ($\text{OH}^\bullet$, $\text{H}^\bullet$) inside the bubbles
232 [43].

233 In aqueous phase sonolysis, there are three potential sites for sonochemical activity,
234 namely: (i) the gaseous region of the cavitation bubble where volatile and hydrophobic
235 species are easily degraded through pyrolytic reactions as well as reactions involving the
236 participation of hydroxyl radicals with the latter being formed through water sonolysis. The
237 heat from the cavity implosion decomposes water into extremely reactive hydrogen atoms
238 ($\text{H}^\bullet$) and hydroxyl radicals ($\text{OH}^\bullet$) [44].

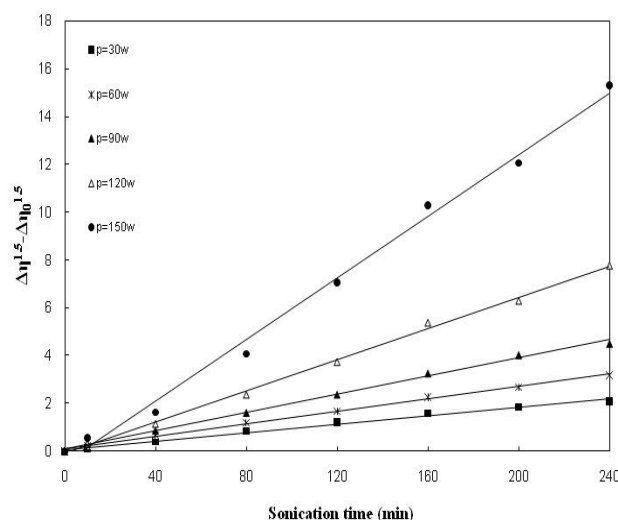


240 (ii) the bubble–liquid interface where hydroxyl radicals are localized and, therefore, radical
241 reactions predominate although pyrolytic reactions may also, to a lesser extent, occur and
242 (iii) the liquid bulk where secondary sonochemical activity may take place mainly due to free
243 radicals that have escaped from the interface and migrated to the liquid bulk. It should be

pointed out that hydroxyl radicals could recombine yielding hydrogen peroxide, which may in turn react with hydrogen to regenerate hydroxyl radicals:



Given that PVP is a non-volatile and soluble polymer, hydroxyl radical-mediated reactions occurring primarily in the liquid bulks as well as at the bubble interface are likely to be the dominant degradation pathway. A polymer molecule near the vicinity of a collapsing bubble is pulled toward the cavity of the bubble, and the solvodynamic shear elongates the polymer backbone, leading to scission [45]. Ulanski et al. have been study the effect of power of ultrasound on degradation of carbohydrates and found that the mechanism of ultrasonic was complex and could be mainly ascribe to radical random scissions, accompanied too some extend with mechanical breakage caused by hydrodynamic and shear forces [46]. The plots of $\Delta\eta^{1.5}-\Delta\eta_0^{1.5}$ versus sonication time for different powers of ultrasound are presented in Fig. 6.



258

259 **Fig. 6. The plot of $\Delta\eta^{1.5}-\Delta\eta_0^{1.5}$ versus the sonication time for different power of**
 260 **ultrasound at 25°C and 15g/L.**
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262 The apparent degradation rate constant, k' , defined in Eq. 14, can be estimated from the
 263 slopes of the plots of this Figure. Based on these results, degradation rate constants, k , were
 264 calculated that are shown in Table 2. It can be seen that at the same concentration (15g/L),
 265 the extent of degradation increases with an increase in applied ultrasound power. In
 266 quantitative terms, in 240min of irradiation time the extent of degradation at 150W is seven
 267 times higher as compared to degradation at 30W.

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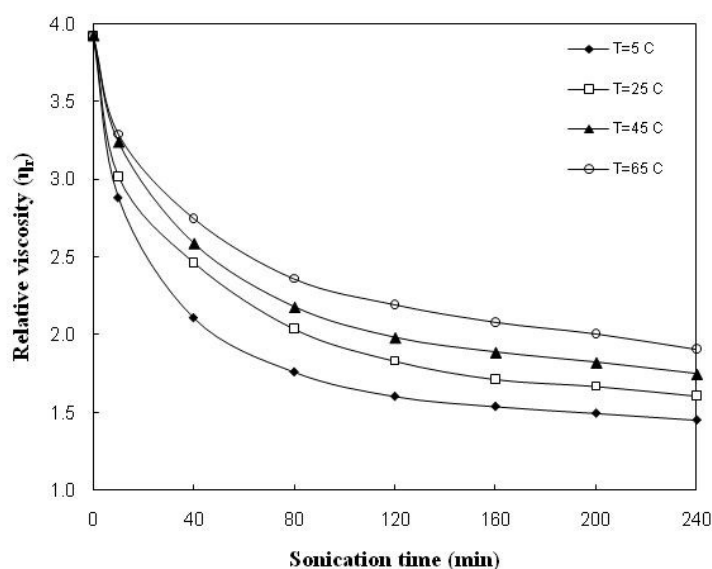
270 **Table 2. The effect of power of ultrasound on the degradation rate constants at 15g/L**
 271 **concentration of PVP and 25°C.**

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P (W)	30	60	90	120	150
$K \times 10^9 (\text{MOL}^{-1.5} \cdot \text{L}^{-1.5} \cdot \text{MIN}^{-1})$	2.12	3.11	4.54	7.75	15.27

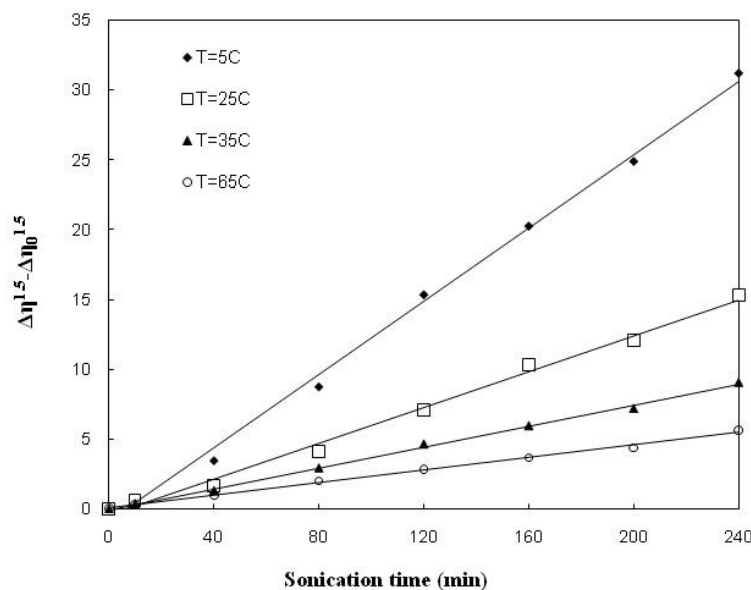
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 276 **3.4. Effect of temperature on the rate of PVP degradation**

277 Majority of chemical reactions are accelerated by an increase of temperature. However,
 278 opposite effect is often seen for the chemical reaction induced by ultrasound. Indeed, the
 279 negative 'temperature coefficient' has been cited as proof that a solution process is
 280 mechanical in origin. Ultrasonic degradation of polymer solution often gives faster rate at
 281 lower temperature [47]. Fig. 7 shows relative viscosity-sonication time curves during the
 282 ultrasonic degradation of PVP at an initial concentration of 15g/L and various temperatures,



283
 284 **Fig. 7. The relationship between η_r and sonication time in for different temperatures at**
 285 **150W and 15g/L.**

286 And plots of the $\Delta\eta^{1.5} - \Delta\eta_0^{1.5}$ versus sonication time are presented in Fig. 8,



287

288 **Fig. 8. The plot of $\Delta\eta^{1.5}-\Delta\eta_0^{1.5}$ versus the sonication time for different temperatures at**
 289 **150W and 15g/L.**

290 While values of degradation rate constants are summarized in Table 3.

291 **Table 3. The effect of temperature on the degradation rate constants at 15g/L**
 292 **concentration of PVP and fixed power of ultrasonic irradiation (150W).**

TEMPERATURE (°C)	5	25	45	65
$K \times 10^9 (\text{MOL}^{1.5} \cdot \text{L}^{-1.5} \cdot \text{MIN}^{-1})$	31.22	15.27	8.92	5.42

293

294 Our results indicated that the extent of degradation is more pronounced at low temperatures.
 295 This might be because, with increasing temperature, v_p of the solvent increases, and so the
 296 vapor enters the cavitation bubbles during their growth. This causes a reduction in collapsing
 297 shock because of a cushioning effect; therefore, the extent of degradation is reduced [48].

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300 **4. CONCLUSIONS**

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302 It has been demonstrated on PVP, that treatment with a variety of output ultrasound powers
 303 in aqueous solution is an efficient procedure for reduction of molecular weight of PVP. Under
 304 sonolysis conditions, degradation is caused by OH radicals and mechanochemical effects.
 305 The effect of concentration of polymer and different reaction temperature, the results of
 306 ultrasonic degradation of PVP in solution indicated that the degradation rate reduced with
 307 increasing solution concentration and temperature. This study confirms the general
 308 assumption that the shear forces generated by the rapid motion of the solvent following
 309 cavitation collapse are responsible for the breakage of the chemical bonds within the

polymer. The effect of polymer concentration can be interpreted in terms of the increase in viscosity with concentration, causing the molecules to become less mobile in solution and the velocity gradients around the collapsing bubbles to, therefore, become smaller.

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