

Original Research Article

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

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ABSTRACT

The ultrasonic degradation of polyvinyl pyrrolidone (PVP) was carried out in a range of different concentration of polymer solution to investigate on the changes of molecular weights. Also the ultrasonic degradation at different temperatures and power of ultrasound (30-150W) was investigated. Most of the effects involved in controlling molecular weight can be attributed to the large shear gradients and shock waves generated around collapsing cavitation bubbles. 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. The degradation rate of this polymer was followed by a kinetic model based on viscosity measurements. Rate constants of ultrasonic degradation were calculated, and the results showed their dependence on polymer concentration.

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 ($M_w=1300000$ kDa) was purchased from Across Co. Ltd. Molecular weight was ($M_v=756000$ kDa), which was

79 determined by viscometer. All other chemicals were of laboratory reagent grade and were
80 purchased from Merck. All solutions were prepared using distilled and deionized water.

81

82 2.2. METHODS

83 2.2.1. PVP solution preparation

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

87

88 2.2.2. Experimental setup and procedure

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

100

101 2.3. VISCOSITY MEASUREMENTS

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

$$107 \quad \eta_r = \frac{t}{t_0} \quad (1)$$

$$108 \quad \eta_{sp} = \eta_r - 1 \quad (2)$$

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

113

114 2.4. KINETIC MODEL

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

$$118 \quad R = \frac{dM}{dt} = kM^n \quad (3)$$

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

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

$$126 \quad M^{1-n} - M_0^{1-n} = (1-n)kt \quad (4)$$

127 Where M_0 is the initial total molar concentration of polymer. The total molar concentration is
 128 related to the number average molecular weight through [29]:

$$129 \quad M = \frac{C}{M_n} \quad (5)$$

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

$$132 \quad M_v = \left[(1+\alpha) \Gamma(1+\alpha) \right]^{\frac{1}{\alpha}} M_n \quad (6)$$

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

$$135 \quad M_v = \left(\frac{[\eta]}{K} \right)^{\frac{1}{\alpha}} \quad (7)$$

136 Where α and k are the Mark–Houwink constants.

137 Finally, $[\eta]$ can be related to the specific viscosity, η_{sp} , and relative viscosity, η_r , by Huggins
 138 and Kramer equations:

$$139 \quad \frac{\eta_{sp}}{C} = [\eta] + K'[\eta]^2 C \quad (8)$$

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

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

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

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

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

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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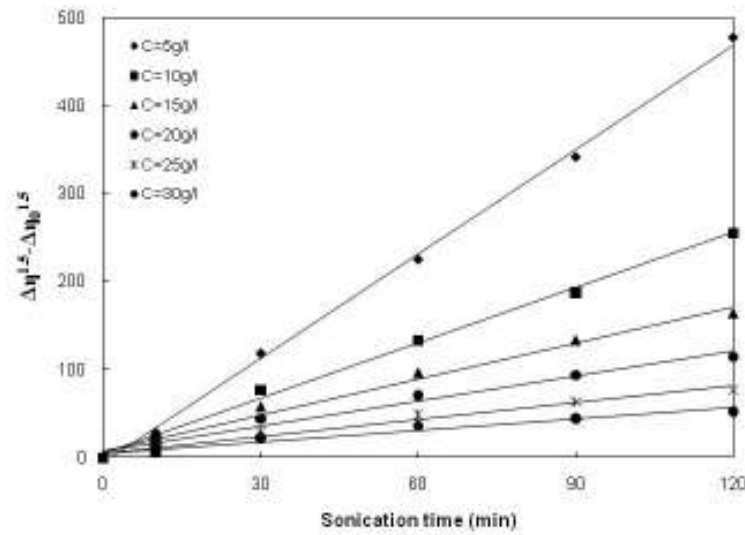
153 3. RESULTS AND DISCUSSION

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155 3.1. DETERMINATION OF REACTION ORDER OF DEGRADATION OF PVP

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

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. The data of these three concentrations overlapping by the data resulted from concentration of 30g/L. Therefore, the results of these temperatures were not reported.



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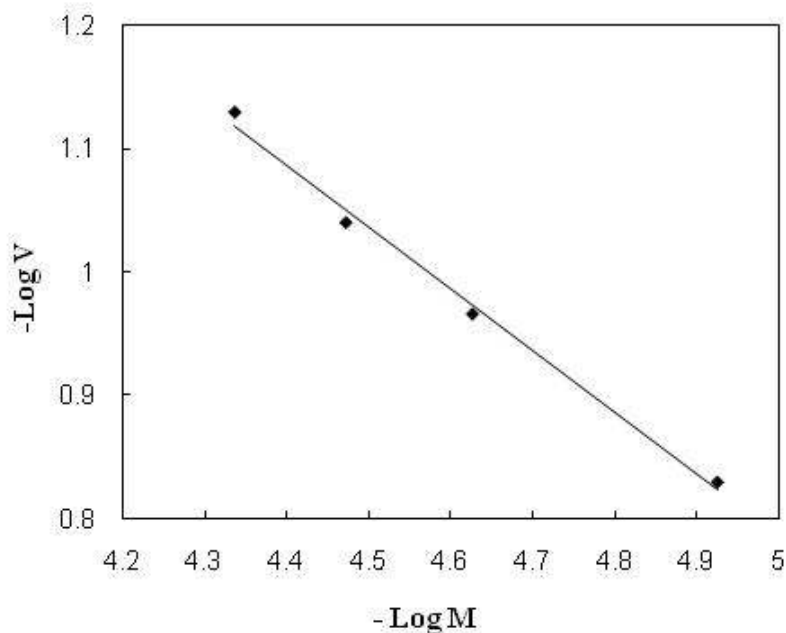
183 **Fig. 1. The plot of $\Delta\eta^{1.5}-\Delta\eta_0^{1.5}$ versus the sonication time for different concentration of**
 184 **PVP solution at 25°C.**
 185

186 Previous studies were proved that with an increase in concentration, the rate constant, k ,
 187 was decreased obviously [39, 40]. These observations are explained in terms of viscosity
 188 changes for different polymer concentrations. At higher concentrations, the solution viscosity
 189 increases. An increase in viscosity raises the cavitation threshold. This increased threshold
 190 makes it more difficult for cavitation bubbles to form. More importantly, the velocity gradients
 191 around collapsing bubbles become smaller, and the elongation of the polymer backbone is
 192 reduced [41]. The slopes of plots give the initial rate of degradation using Eq.14, the plot of
 193 $\log V$ versus $\log[M]$ are linear and it is shown in Fig. 2.

194 The slope of curve is -0.5, which suggest the order of reactions with respect to total molar
 195 concentration of polymer. From substitution of the value of "n" in Eq.14, we obtain the
 196 following:

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

198



199

200 **Fig. 2. The plot of logV versus logM for degraded PVP at 25°C.**

201

202 3.2. Effect of concentration on the rate of PVP degradation

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

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

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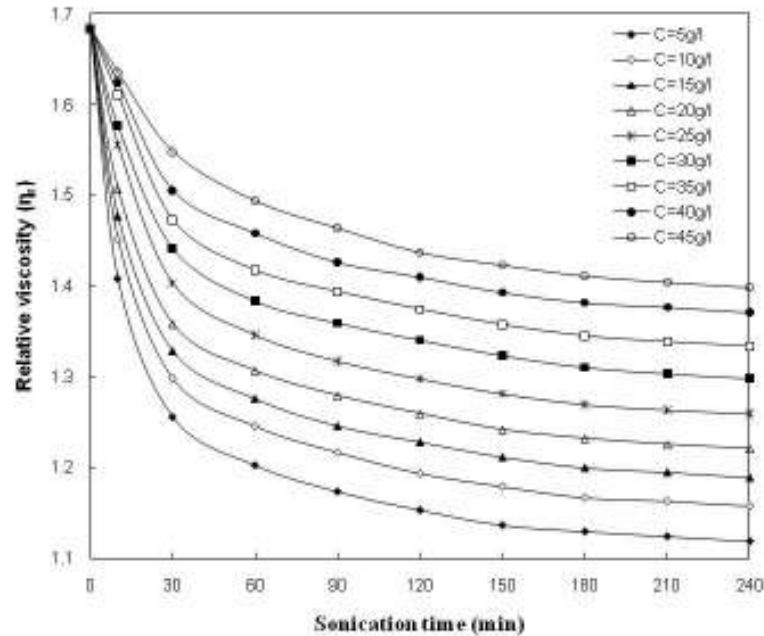
C (g/L)	Limiting η_r	Limiting M_v (kDa)
5	1.119	40679
10	1.157	66514
15	1.189	90855
20	1.221	119042
25	1.260	156552
30	1.298	197143
35	1.334	238453
40	1.371	283806

209

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211

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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Fig. 3. The relationship between η_r and sonication time for different PVP concentrations at 25°C and fixed power of ultrasonic irradiation (150W).

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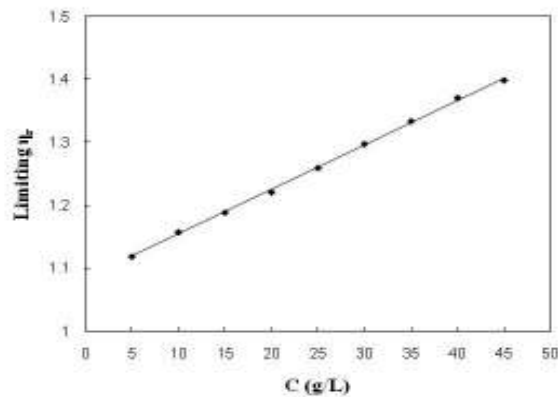
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Based on these findings, it is clear that η_0 decreases with sonication time and tends to have a constant value. It can be deduced that there is a limiting molecular weight that below which chain scission does not occur. Under the same conditions, the decrease in η_r of the sample with a high polymer concentration is lower than of the sample with a low polymer concentration. The relationship between the limiting value of η_r and solution concentration is presented in Fig. 4.



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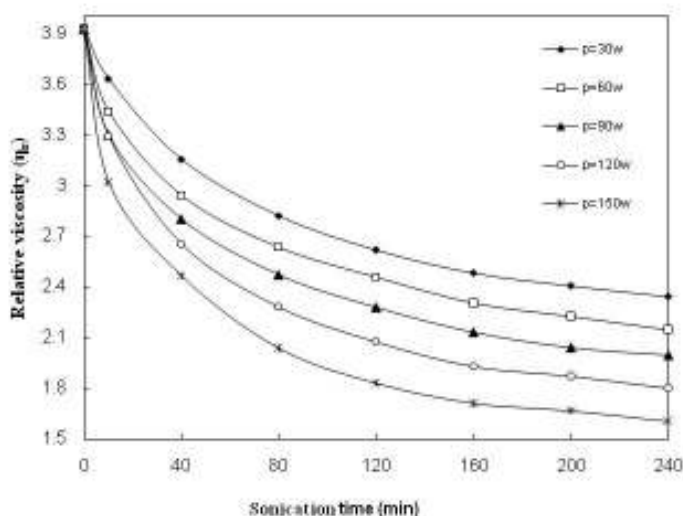
223 **Fig. 4. The relationship between the limiting value of η_r and solutions concentration.**
 224

225 These results indicate that the extent of degradation is more pronounced in more dilute
 226 solutions. This might be due to the fact that the probability of chemical bond scission caused
 227 by efficient shearing in the polymer chain is greater in dilute solution. These findings are
 228 consistent with the results of other investigators [42].

229

230 3.3. Effect of power of ultrasound on the rate of PVP degradation

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



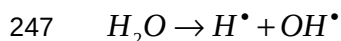
234

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

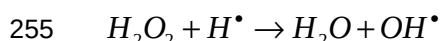
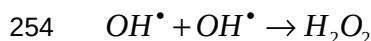
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238 In aqueous solutions, the main pyrolytic reaction is the dissociation of water. This thermal
 239 dissociation leads to the production of highly reactive radicals ($\text{OH}^\bullet$, $\text{H}^\bullet$) inside the bubbles
 240 [43].

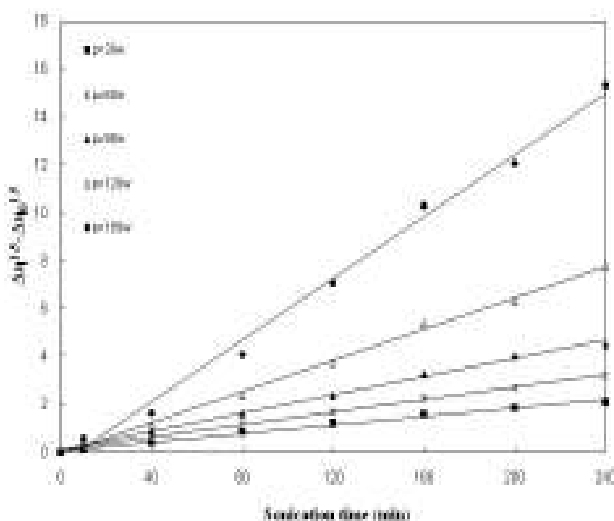
241 In aqueous phase sonolysis, there are three potential sites for sonochemical activity,
 242 namely: (i) the gaseous region of the cavitation bubble where volatile and hydrophobic
 243 species are easily degraded through pyrolytic reactions as well as reactions involving the
 244 participation of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



(ii) the bubble–liquid interface where hydroxyl radicals are localized and, therefore, radical reactions predominate although pyrolytic reactions may also, to a lesser extent, occur and (iii) the liquid bulk where secondary sonochemical activity may take place mainly due to free 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.



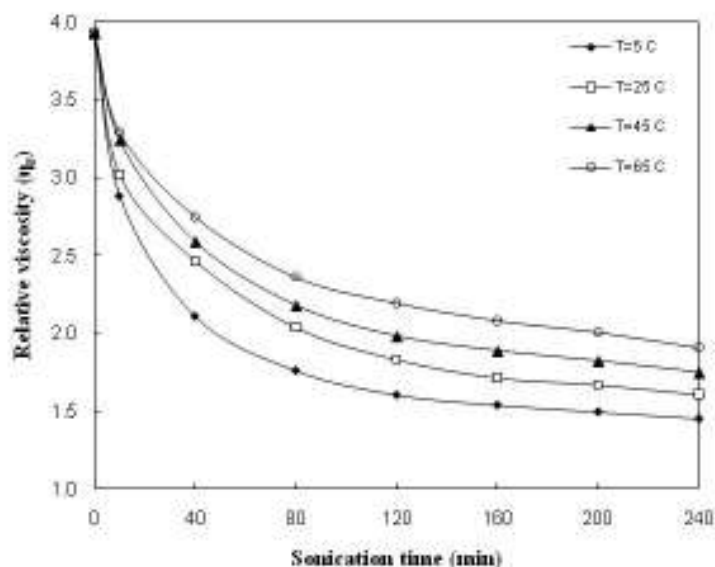
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267 **Fig. 6. The plot of $\Delta\eta^{1.5}-\Delta\eta_0^{1.5}$ versus the sonication time for different power of**
 268 **ultrasound at 25°C and 15g/L.**
 269

270 The apparent degradation rate constant, k' , defined in Eq. 14, can be estimated from the
 271 slopes of the plots of this Figure. It can be seen that at the same concentration (15g/L), the
 272 extent of degradation increases with an increase in applied ultrasound power. In quantitative
 273 terms, in 240min of irradiation time the extent of degradation at 150W is seven times higher
 274 as compared to degradation at 30W.

275 3.4. Effect of temperature on the rate of PVP degradation

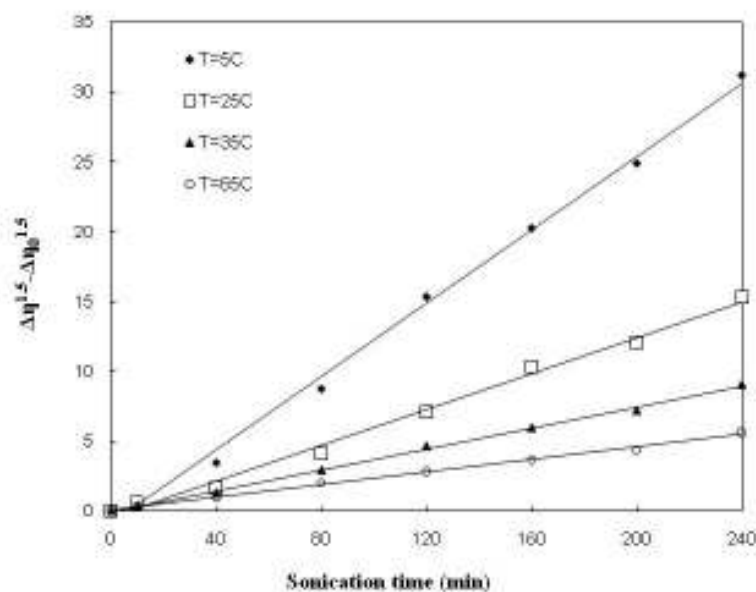
Majority of chemical reactions are accelerated by an increase of temperature. However, opposite effect is often seen for the chemical reaction induced by ultrasound. Indeed, the negative 'temperature coefficient' has been cited as proof that a solution process is mechanical in origin. Ultrasonic degradation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



282

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

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



286

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

289 Results indicated that the extent of degradation is more pronounced at low temperatures.
 290 This might be because, with increasing temperature, v_p of the solvent increases, and so the
 291 vapor enters the cavitation bubbles during their growth. This causes a reduction in collapsing
 292 shock because of a cushioning effect; therefore, the extent of degradation is reduced [48].
 293

294 4. CONCLUSIONS

295

296 It was found that the ultrasonic degradation of PVP solution increased with increasing
 297 temperature and with decreasing concentration. The results of ultrasonic degradation
 298 behavior of polyvinyl pyrrolidone (PVP) solution were studied under various conditions, such
 299 as power of sonication, reaction temperature and solution concentration, by kinematics
 300 viscometry. It was found that the ultrasonic degradation of PVP solution increased with
 301 increasing temperature and with decreasing concentration. It was found that, the ultrasonic
 302 degradation is an efficient procedure for reduction of molecular weight of PVP. The
 303 degradation rate reduced with increasing solution concentration and temperature. The effect
 304 of concentration of polymer and different reaction temperature, the results of ultrasonic
 305 degradation of PVP in solution indicated that the degradation rate reduced with increasing
 306 solution concentration and temperature. The most extensive degradation took place when
 307 using an ultrasonic input power of 150W. The possible explanation for the degradation is the
 308 shear forces created by ultrasonic waves. As the power of the wave increases, the shear
 309 forces will be complemented by the increased cavitational effects.
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