

# Degradation kinetics of poly (vinyl-pyrrolidone) under ultrasonic irradiation

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**Abstract** Ultrasonicaton has proved to be a highly advantageous method for depolymerizing macromolecules because it reduces their molecular weight simply by splitting the most susceptible chemical bond without causing any changes in the chemical nature of the polymer. Solution of poly (vinyl-pyrrolidone) in chloroform with different concentrations and different molecular weights at a fined temperature were subjected to ultrasonic degradation. This study confirms the general assumption that the shear forces generated by the rapid motion of the solvent following cavitation collapse are responsible for the breakage of the chemical bonds within the polymer. A method of viscometry was used to study the degradation behavior and kinetic model was developed to estimate the degradation rate constant. The results were indicated that the polymers with height molecular mass degraded faster than the polymers laving low molecular mass thus the rate of ultrasonic degradation increased with increasing molecular weight. It was found that rate constant decreases as the concentration increases. The calculated rate constants correlated in terms of inverse concentration and relative viscosity of PVP solutions. This behavior in the rate of degradation was interpreted in terms of viscosity and concentration of polymer solution. 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 and it causes a reduction in the cavitation efficiency thus, the rate of degradation will be decreased. The experimental results

show that the viscosity of polymers decreased with ultrasonic irradiation time and approached a limiting value, below which no further degradation took place.

**Keywords** Ultrasound · Degradation · Poly (vinyl-pyrrolidone) · Viscosity · Initial molecular weight · Rate constant

## Introduction

Various methods like application of heat, light, chemical reagents, and ultrasonic radiation can cause polymer degradation [1]. Application of ultrasonic energy for polymer degradation date back to the 1930s when natural polymers were subjected to sonication, which resulted in a reduction of viscosity [2]. Ultrasonic power and ultrasonic time are factors influencing the mechanical properties of nano composites [3, 4]. Ultrasonication has subsequently provided to be a highly advantageous method for depolymering macromolecules because it reduces their molecular weight simply by splitting the most susceptible chemical bond without causing any changes in the chemical nature of the polymer. The work has been summarized in a review paper by Price [5]. The ultrasonic degradation of polymers is of great interest [6] and [7] and the degradation of several polymers such as polystyrene [8], polyvinyl acetate [1], polypropylene [9], polybutadiene [9], poly(methylmethacrylate) [10], dextran [11], hydroxy propyl cellulose [12], carboxymethyl cellulose [13], polyacrylamide [14] and poly ( $\epsilon$ -caprolactone) [15] has been investigated.

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

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distribution influence the rate and final molecular mass of degraded species [8, 16, 17].

Three models are proposed to account for this chemical change based on cavitation induced by ultrasound [18].

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 [19] 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 [8, 20, 21]. 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.

The exact mechanism by which degradation occurs is still open to discussion, It is generally agreed that the hydrodynamic forces have the primary importance. Hydrodynamic forces may originate as a result of increased frictional forces between the ultrasonically accelerated faster moving solvent molecules and the larger, less mobile, macromolecules, Hydrodynamic forces may also be due to the high pressure associated with the collapse of cavitation bubbles [2, 22].

The sonochemical cleavage of polymer chains in solution leads to the formation of macroradicals, and a copolymer can be formed by recombination of different macroradicals if there are more than two kinds of polymer in solution [23, 24]. The macroradicals also initiate polymerization of monomers in solution [25].

The effect of concentration on ultrasonic degradation has also been under investigations. It has been found that the extent of degradation decreases with an increase in solution concentration or that there is an optimum polymer concentration for degradation [13, 26–28]. In general, the increase of polymer concentration increases the viscosity of the solution, and thus the decrease in degradation has been interpreted in terms of the increased viscosity.

The effect of molecular weight on the thermal degradation kinetics has been investigated and a non-linear dependence of

the degradation rate on molecular weight was observed depending on the change in the molecular weight and the initial molecular weight [29, 30]. Thus, it is apparent that a determination of the effect of initial molecular weight on the degradation rate is essential to a molecular understanding of the chain scission mechanism [31]. The influence of molecular weight on the rate of ultrasonic degradation is not clear. For example, a direct proportionality between the rate of ultrasonic degradation and the molecular weight,  $x$ , was established for the degradation of dextran [32]. However, a quadratic dependence,  $k=k_d x^2$ , was established for the ultrasonic degradation of synthetic polymers like polystyrene [33–35]. Experimental data [31] showed that the degradation rate depends non-linearly on molecular weight.

In this study three different molecular weight of poly (vinyl-pyrrolidone) are examined. PVP is a biocompatible material and has wide applications as biomaterials.

The effect of solution concentration on the ultrasonic degradation of PVP has been investigated.

The objective of this study was to present new experimental data for the ultrasonic degradation of polymer with different molecular weights and introduces 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 the average molecular weight ( $M_v$ ) and the number average molecular weight ( $M_n$ ). The variation of the rate coefficients with concentration is attributed to the change in the viscosity. Finally, these quantities are correlated with the molar concentration of polymer, resulting in a kinetically meaningful expression.

## Experiments

### Materials

Poly (vinyl-pyrrolidone) samples (PVP) of different average molecular weights (58,000, 360,000 and 1,300,000) were obtained from Fluka without purification. Chloroform from Merck as a solvent.

### Apparatus and procedure

#### *Ultrasonic degradation*

Solutions of 5, 10, 20  $\text{glit}^{-1}$  of polymer in chloroform were prepared.

For the degradation, 50  $\text{cm}^3$  polymer solution was placed in a jacket flask, and its temperature was controlled to  $25 \pm 0.1^\circ\text{C}$  by circulating thermostated water (Grant model RC 1400 G England) through the Jacket and sonicated for a long time. An ultrasonic generator (Dr. Hielscher UP 200 H ultrasonic processor) with an H3 sonotrode ( $\varphi=3$  mm) was

used in this experiment. The frequency of the ultrasound was 24 KHz, and output was set at 100 w.

*Viscosity measurements*

Periodically, samples of the sonicated solution were removed and their viscosities were measured using a viscometer (setavic kinematics viscometer, England) thermostated at 25°C. In order to compare viscosity changes readily during the sonication, after removing samples (5, 10 and 20 glit<sup>-1</sup>) they were diluted to 5 glit<sup>-1</sup> next, their viscosities were determined using flow times measured in viscometer. Relative and Specific viscosities were calculated according to

$$\eta_r = \frac{t}{t_0}, \eta_{sp} = \eta_r - 1 \tag{1}$$

Where t and t<sub>0</sub> are the flow times for the given polymer solution and the solvent respectively. The values of Mark-Houwink constants [36] were α=0.64 and k=1.94×10<sup>-5</sup> litg<sup>-1</sup>, Experiments were repeated twice to check the reproducibility of the obtained data for the variation of concentration against time for all the sets and it has been observed that experimental errors were within the standard accuracy (i.e. within ±5%)

**Kinetic model**

The rate of degradation is defined as the number of scission that occur in 1 l in unit time and we must keep in mind that a scission in a chain yields two pieces. Thus, the rate equation of the degradation is as follows [26]:

$$R = \frac{dM}{dt} = kM^n \tag{2}$$

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. It is noted that solution concentration (glit<sup>-1</sup>) is constant and the total molar concentration (mol lit<sup>-1</sup>) increases during the degradation of polymer.

The solution of differential Eq. (2) is

$$M^{1-n} - M_0^{1-n} = (1 - n)kt \tag{3}$$

Where M<sub>0</sub> is the initial total molar concentration of polymer. The total molar concentration is related to the number average molecular weight through [37]:

$$M = \frac{C}{M_n} \tag{4}$$

Also viscosity average molecular weight, M<sub>v</sub>, is related to the number average molecular weight, M<sub>n</sub>, through [38]:

$$M_v = [(1 + \alpha)\Gamma(1 + \alpha)]^{\frac{1}{\alpha}} M_n \tag{5}$$

where  $\Gamma(1 + \alpha) = \int_0^\infty e^{-t} t^\alpha dt$ , M<sub>v</sub> is related to the intrinsic viscosity, [η], through Mark- Houwink equation:

$$M_v = \left(\frac{[\eta]}{K}\right)^{\frac{1}{\alpha}} \tag{6}$$

where α and K are the Mark- Houwink constants.

Finally, [η] can be related to the specific viscosity, η<sub>sp</sub>, and relative viscosity, η<sub>r</sub>, by Huggins and Kramer equations [39]:

$$\frac{\eta_{sp}}{C} = [\eta] + k_h[\eta]^2 C \tag{7}$$

$$\frac{\ln \eta_r}{C} = [\eta] + (k_h - 0.5)[\eta]^2 C \tag{8}$$

From Eqs. (7) and (8), intrinsic viscosity is

$$[\eta] = \frac{[2(\eta_{sp} - \ln \eta_r)]^{0.5}}{C} \tag{9}$$

Substitution of Eq. (9) in (6) and Eq. (6) in (5) yields

$$M_n = \left(\frac{[2(\eta_{sp} - \ln \eta_r)]^{\frac{1}{2}}}{CK[(1 + \alpha)\Gamma(1 + \alpha)]}\right)^{\frac{1}{\alpha}} \tag{10}$$

Finally, the substitution Eq. (10) in (4)

$$M = \left(\frac{C^{\alpha+1}K[(1 + \alpha)\Gamma(1 + \alpha)]}{\sqrt{2}}\right)^{\frac{1}{\alpha}} \Delta\eta \tag{11}$$

where  $\Delta\eta = \left(\frac{1}{\eta_{sp} - \ln \eta_r}\right)^{\frac{1}{2\alpha}}$

Substitution Eq. (11) in (3) yields

$$\Delta\eta^{1-n} - \Delta\eta_0^{1-n} = (1 - n)\left(\frac{\sqrt{2}}{C^{\alpha+1}K[(1 + \alpha)\Gamma(1 + \alpha)]}\right)^{\frac{1-n}{\alpha}} kt \tag{12}$$

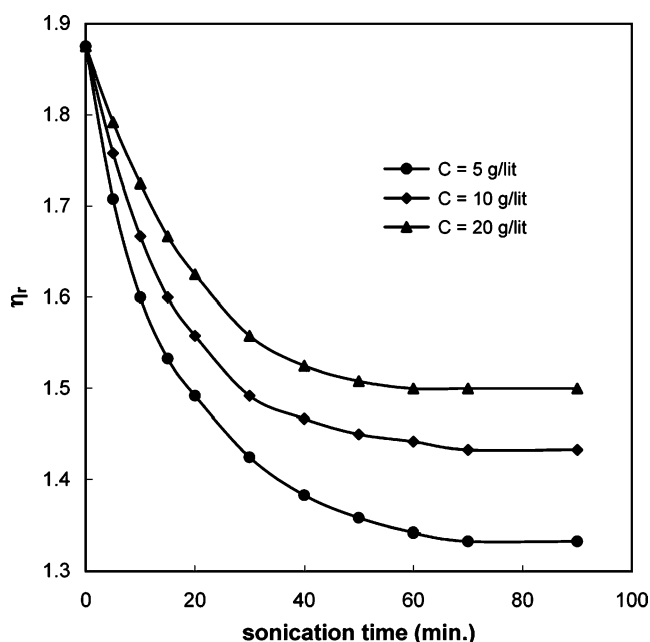
or

$$\Delta\eta^{1-n} - \Delta\eta_0^{1-n} = k't \tag{13}$$

**Results and discussion**

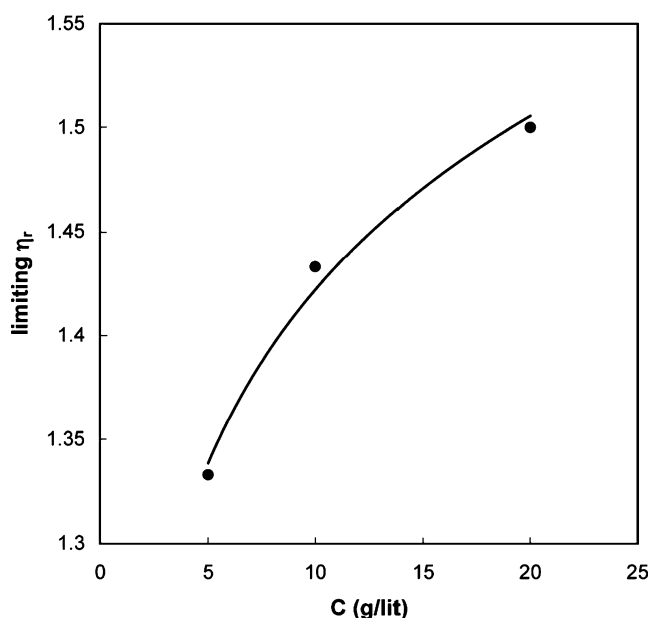
Effect of concentration on the rate of degradation

The effect of polymer concentration on degradation was studied using PVP (360,000). Sonication was carried out for three different PVP concentrations at 25 °C. The relationship between η<sub>r</sub> and sonication time are presented in Fig. 1. Based

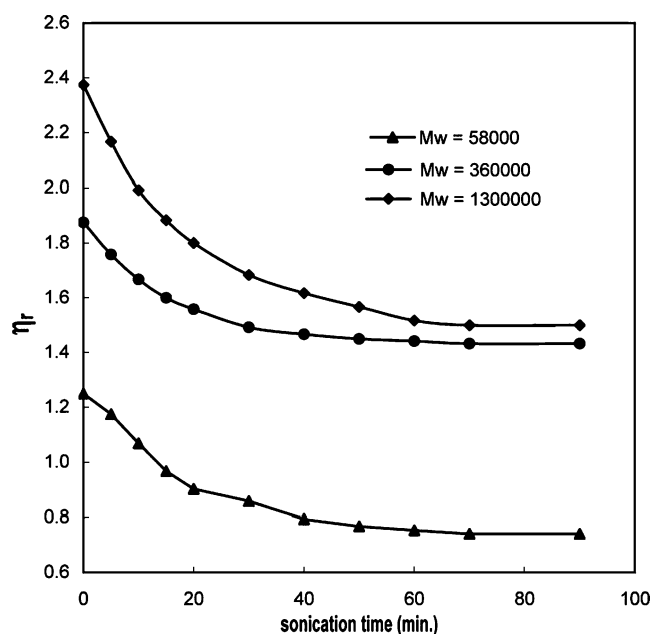


**Fig. 1** The relationship between  $\eta_r$  and sonication time for different concentration of PVP solutions with  $M=360,000 \text{ g/l}$  at  $25^\circ\text{C}$

on these findings, it is clear that  $\eta_r$  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  $\eta_r$  of the sample with a high polymer concentration is lower than of the sample with a low polymer concentration. This is in agreement with previous studies [40, 41]. At high concentration, entanglements influence the

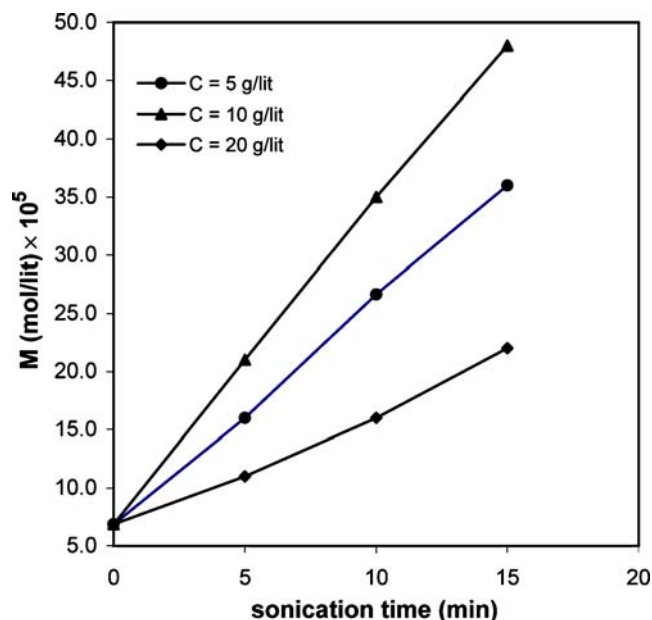


**Fig. 2** The relationship between the limiting value of  $\eta_r$  and solution concentration of PVP solutions with  $M=360,000 \text{ g/l}$  at  $25^\circ\text{C}$



**Fig. 3** Variation of viscosity of PVP samples as a function of ultrasonic irradiation time for a  $10 \text{ g/lit}^{-1}$  solution of poly (vinyl-pyrrolidone) in chloroform at  $25^\circ\text{C}$  (Frequency 24 kHz, intensity 100 W)

energy transfer processes between solvent and polymer and appears to reduce the probability of degradation accruing. It has been pointed out previously [40, 41] That an increase in the viscosity of the solution will increase the energy required for cavitations to occur. Therefore, the remainder of the study was carried out at on 5 g/l solution of PVP so as to avoid possible complications arising from entanglement effects on the viscoelastic response of the polymer solutions.



**Fig. 4** Variation of total molar concentration with sonication time for different concentration of PVP solutions with  $M=58,000 \text{ g/l}$  at  $25^\circ\text{C}$

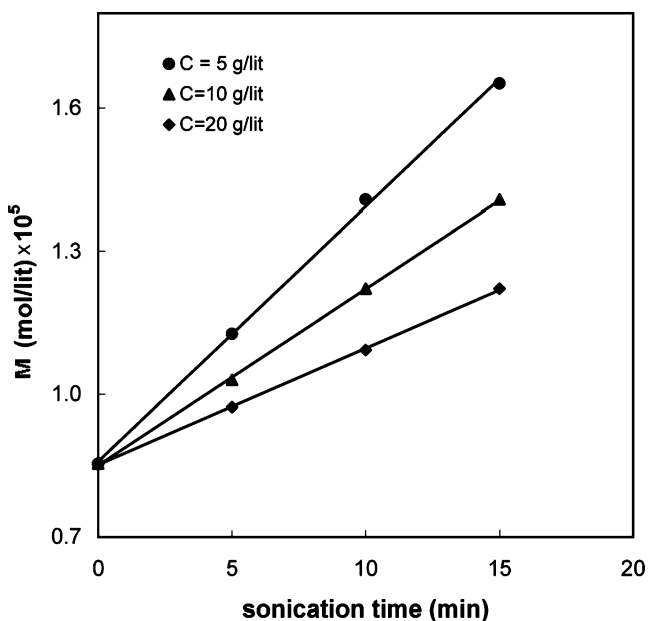


Fig. 5 Variation of total molar concentration with sonication time for different concentration of PVP solutions with  $M=360,000 \text{ g mol}^{-1}$  at  $25^\circ\text{C}$

The relationship between the limiting value of  $\eta_r$  and solution concentration is presented in Fig. 2. These results indicate that the extent of degradation is more pronounced in more dilute solutions. This might be due to the fact that the probability of chemical bond scission caused by efficient shearing in the polymer chain is greater in dilute solution. These findings are consistent with the results of other investigators [42]

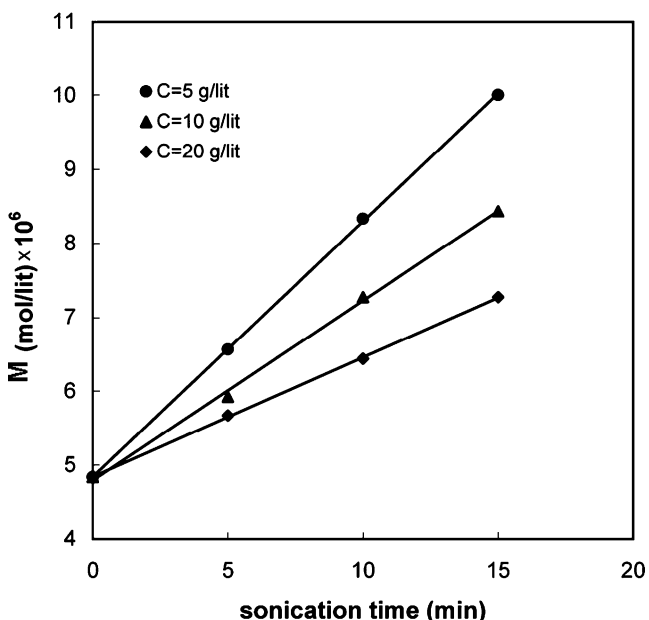


Fig. 6 Variation of total molar concentration with sonication time for different concentration of PVP solutions with  $M=1,300,000 \text{ g mol}^{-1}$  at  $25^\circ\text{C}$

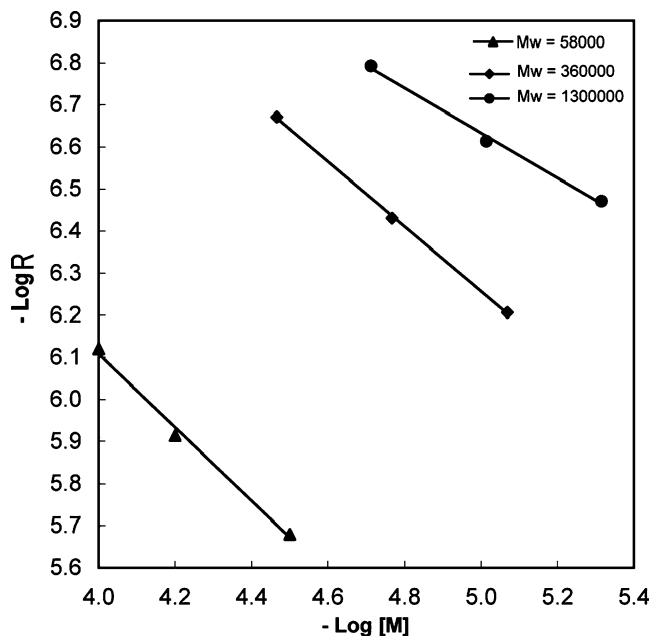


Fig. 7 The plot of  $\ln R$  versus  $\ln [M]$  for various initial molecular weights of PVP at  $25^\circ\text{C}$

#### Effect of the initial molecular weight of polymer

The effect of initial molecular weight of polymer on the degradation rate was studied for an initial concentration of  $10 \text{ g lit}^{-1}$ . The viscosity decreased significantly for these polymers having large molecular weight (Fig. 3). The viscosity decrease was minor with the polymers having

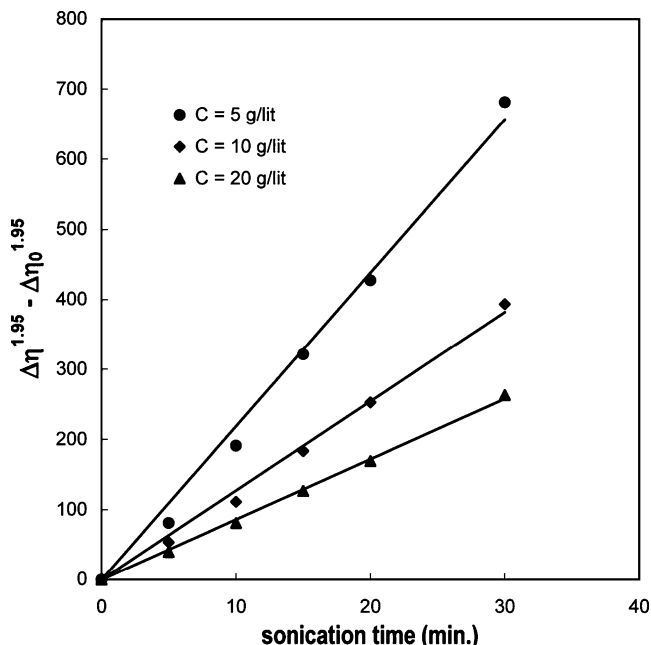
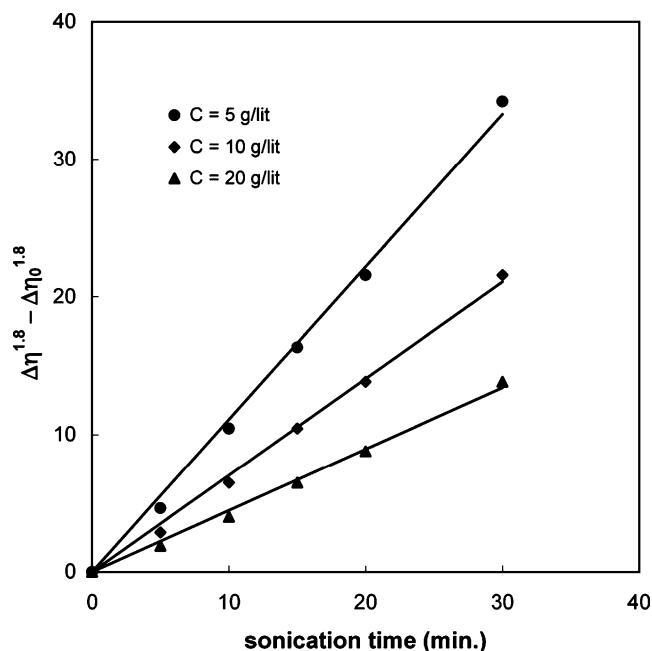


Fig. 8 The plot of  $\Delta\eta^{1.95} - \Delta\eta_0^{1.95}$  versus the sonication time for different concentration of PVP solutions with  $M=58,000 \text{ g mol}^{-1}$  at  $25^\circ\text{C}$



**Fig. 9** The plot of  $\Delta\eta^{1.8} - \Delta\eta_0^{1.8}$  versus the sonication time for different concentration of PVP solutions with  $M=360,000 \text{ g mol}^{-1}$  at  $25^\circ\text{C}$

small molecular weight. Thus, the extent of ultrasonic depolymerization decreased with decreasing molecular weight of the polymer. The studies showed also that the degradation of molecules continued only to a certain limiting molecular weight. This is in agreement with the results obtained in earlier studies [22]. The limiting viscosity was also dependent on the molecular weight of polymer.

Below the limit, the polymer chain was so short that it followed ultrasonic vibration flexibly and cleavage at the center of the molecule did not take place anymore. From Fig. 3, it was found that the viscosity decreased more and faster with the polymers having higher molecular weight.

According to this examination the extent of ultrasonic depolymerization decreased with decreasing molecular weight of the polymer, this observation strengthens the claim that ultrasonic degradation, unlike chemical or thermal decomposition, is a non-random process with cleavage taking place roughly at the center of the molecule and with larger molecules degrading the fastest.

#### Determination of reaction order of degradation of PVP

A number of different rate models have been proposed for the degradation of polymers [43, 44], but in this study a simple model was employed via viscometry. Using Eq. (11), in the initial sonication times, from data of Fig. 1 for different concentration of polymer we calculate total molar concentration of polymer ( $M$ ). The results are depicted in Figs. 4, 5 and 6. The slopes of plots give the initial rate of

degradation using Eq. (2), the plots of  $\ln R$  vs.  $\ln [M]$  are linear and they are shown in Fig. 7. the slopes of the curves are  $-0.95$  for PVP with  $M=58,000$  and  $-0.8$  for PVP with  $M=360,000$  and  $-0.5$  for PVP with  $M=1,300,000$ , which suggest the orders of reactions with respect to total molar concentration of polymer.

The substitution of the value of  $n$  in Eq. (13), we obtain the following:

For PVP with  $M=58,000$

$$\Delta\eta^{1.95} - \Delta\eta_0^{1.95} = k't \quad (14)$$

For PVP with  $M=360,000$

$$\Delta\eta^{1.8} - \Delta\eta_0^{1.8} = k't \quad (15)$$

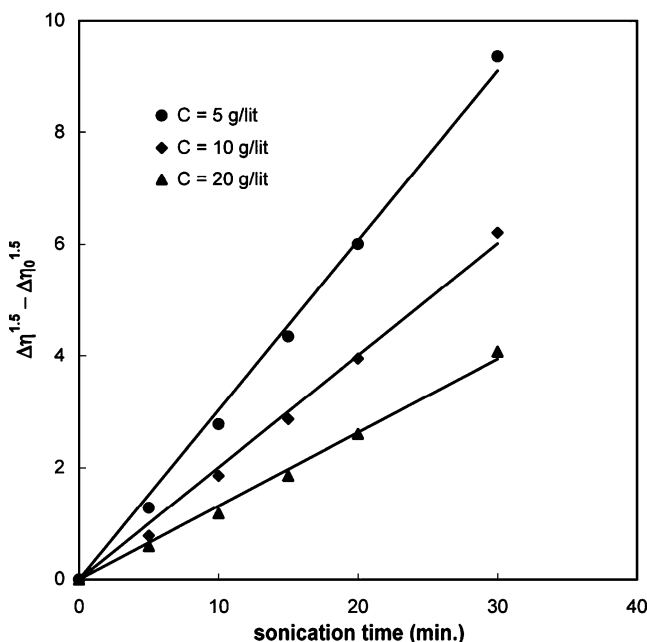
And for PVP with  $M=1,300,000$

$$\Delta\eta^{1.5} - \Delta\eta_0^{1.5} = k't \quad (16)$$

Estimation of rate constant ( $k$ )

The plots of  $\Delta\eta^{1-n} - \Delta\eta_0^{1-n}$  versus sonication time for different PVP concentrations and molecular weights are presented in Figs. 8, 9 and 10). The apparent degradation rate constants,  $k'$ , defined in Eq. (13), can be estimated from the slopes of the plots in Figs. 8, 9 and 10). Based on these, degradation rate constants,  $k$ , were calculated. The experimental values are shown in Table 1.

It can be seen from Figs. 8, 9 and 10) that at the same concentration for different molecular weights, the extent of



**Fig. 10** The plot of  $\Delta\eta^{1.5} - \Delta\eta_0^{1.5}$  versus the sonication time for different concentration of PVP solutions with  $M=1,300,000 \text{ g mol}^{-1}$  at  $25^\circ\text{C}$



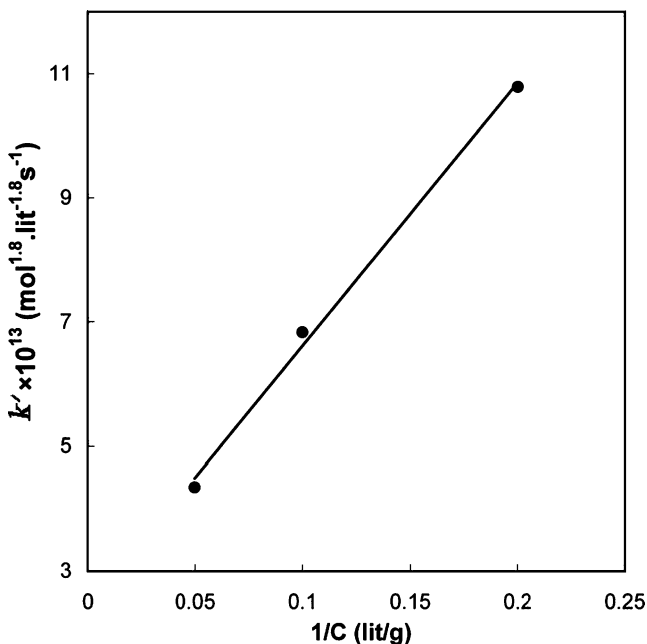
**Table 1** The effects of concentration of PVP and molecular weight on the apparent degradation rate constants at 25°C

Concentration of PVP aqueous solution (g lit <sup>-1</sup> )	M <sub>w</sub> =58,000 go <sup>-1</sup>	M <sub>w</sub> =360,000 go <sup>-1</sup>	M <sub>w</sub> =1,300,000 go <sup>-1</sup>
	$k' \times 10^{13}$ (mol <sup>1.95</sup> lit <sup>-1.95</sup> s <sup>-1</sup> )	$k' \times 10^{12}$ (mol <sup>1.8</sup> lit <sup>-1.8</sup> s <sup>-1</sup> )	$k' \times 10^{12}$ (mol <sup>1.5</sup> lit <sup>-1.5</sup> s <sup>-1</sup> )
5	12.48	1.079	16.360
10	9.25	0.684	10.770
20	6.10	0.435	7.065

degradation decreases with an increase in molecular weight. In quantitative terms, in 30 min of irradiation time the extent of degradation at M=58,000 is 18 times higher as compared to degradation at M=360,000 and extent of degradation at M=360,000 is 4 times higher as compared to degradation at M=1,300,000. It can be also seen from Figs. 8, 9 and 10, the extent of degradation decreases with an increase in solution concentration.

In quantitative terms, in 30 min of irradiation time the extent of degradation at 5 glit<sup>-1</sup> concentration is 2.4 times higher as compared to degradation at 20 glit<sup>-1</sup> concentration. Thus observed effect of concentration are quite similar to those reported in literature for different chemical constituents [45, 46].

The calculated values of  $k'$  indicate that the rate of degradation decreases with increasing concentration, and increase with increasing molecular weight of polymer. The rate constants,  $k'$ , are correlated in terms of reverse solution concentration (Fig. 11). These data indicate that, the rate constant of ultrasonic degradation increases with increasing inverse solution concentration.

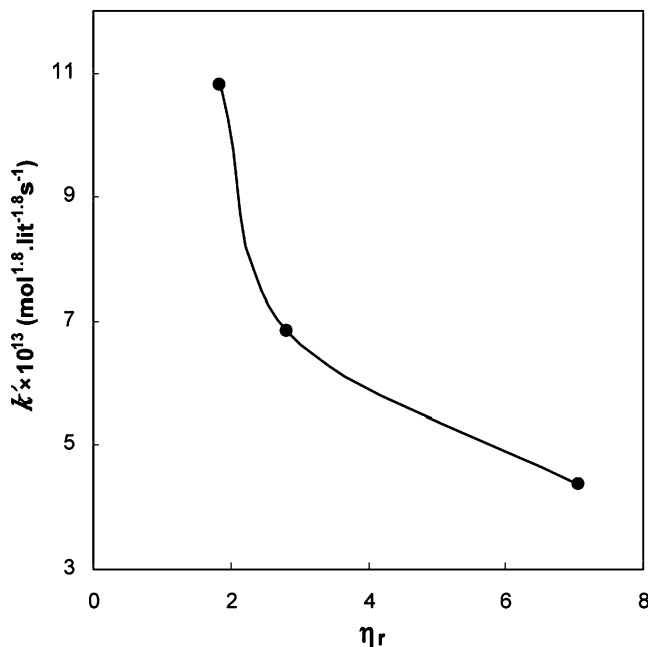


**Fig. 11** The relationship between the calculated rate constants and reverse concentration of PVP solutions with M=360,000 go<sup>-1</sup> at 25°C

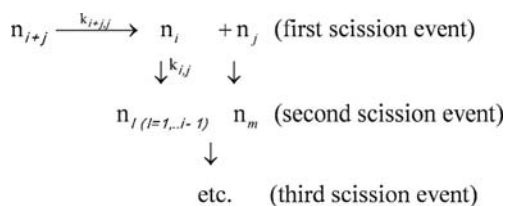
The interpretation of this observation is that, there is less overlap between polymer chains at low concentration. Therefore, they are more susceptible to the hydrodynamic forces generated around cavitation bubbles. The relationship between the calculated rate constants and relative viscosities of PVP aqueous solutions is presented in Fig. 12. It can be seen that, with decreasing rate constant, their viscosities increase and it reduces the shear gradients around the collapsing bubbles; therefore, degradation rate decreases too. The results of Table 1 clearly reveal the greater rate constant of degradation PVP relative to the molecular weight. The rate constant of degradation increases with increasing molecular weight of polymer. The probability of cleavage of the polymers with short chains is less than the polymers with long chains; therefore, in an extent of degradation, the numbers of cleavage long chains is more than the short chains [47].

#### Proposed Mechanism

The number of broken bonds increases with the duration of sonication. Different kinetics expressions have been derived



**Fig. 12** The relationship between the calculated rate constant and relative viscosities of PVP solutions with M=360,000 go<sup>-1</sup> at 25°C



**Scheme 1** The degradation scheme for single scission kinetics

in the past with the purpose characterizing the reaction in terms of a rate constant. The degradation occurs randomly, each intact polymer chain present has the same probability of being broke in a given time interval. Chain scission should therefore follow a first-order reaction kinetics. Essentially, the process of degradation could be described by a series of parallel and consecutive reactions. A polymer chain,  $n_i$ , of degree of polymerization  $i$  has  $(i-1)$  bonds linking monmeric units, which may be split during the reaction. The rate constant for cleavage of the  $j$ th bond is designated by  $k_{ij}$ .

Independently from the degradation mechanism, the fate of the polymer chain at a given time could be described by the degradation scheme shown (Scheme 1).

Information on the bond scission probability along the chain is essential for the knowledge of the stress distribution, and hence indirectly on the molecular conformation prior to bond rupture. The localization of the bond scission position remains one of the most difficult task in polymer degradation studies. A few studies suggested that ultrasonic degradation was non-random with a significant propensity for midchain fracture [52]. The non-linear molecular weight scale, however, is misleading since the distribution is distorted towards the high molecular fractions. Good agreement between the simulated and experimental data are observed only for  $M_0 < 10^5$ . The quality of the fit degrades rapidly with increasing molecular weight. For  $M$  in the  $10^6$  molecular weight range, the degradation scheme (Scheme 1) valid for single scission kinetics must be modified to include the possibility for multiple scission. Multiple scission is modeled as a succession of single-scission events. The formation of fragments with  $\bar{M} \cong M_0/4$  can be formally described by the competitive reactions (a) and (b) in Scheme 2, whereas those with  $\bar{M} \cong M_0/8$  require an additional step (c). The relative importance of each process depends on the initial polymer molecular weight. Any fragment, once formed, can be further

degraded according to the same kinetics, which we have denoted as Scheme 2. According to the proposed degradation model, chains can only be broken in multiples of  $2^n$  fragments (2, 4, 8, etc.) [48, 49].

Effect of molecular weight and concentration on limiting viscosity

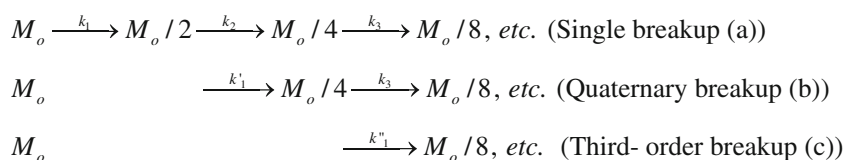
Changes in the viscosity were monitored as a function of the irradiation time. Figure 13 for all the solution where irradiation occurs, the effect of the ultrasonic irradiation process is to produce a convergence of the final solution viscosity values. One basic effect of the ultrasonic degradation is shown in Fig. 13, in which the symbols illustrate the variation in molecular weight for PVP. Clearly, the molecular weight of PVP strongly depends on the time of ultrasonic irradiation. In the first 60 min of irradiation, PVP undergo great degradation, causing a significant decrease of molecular weight. After that, the molecular weight tends to a limiting value, below which no further degradation take place. It is evident that the viscosity of polymer decreases with the decrease of molecular weight, indicating the shorter relaxation time of macromolecules. The viscosity decrease was minor with the polymers having small molecular mass. Thus, the extent of ultrasonic depolymerization decreased with decreasing molecular mass of the polymer.

The studies showed also that the degradation of molecules continued only to a certain limiting molecular mass. Below the limit, the polymer chain was so short that it followed ultrasonic vibration flexibly and cleavage at the centre of the molecule did not take place anymore. Figure 13 show that the viscosity decreased more and faster with the polymers having higher molecular mass. It was found, that at the applied experimental conditions, the values of limiting viscosities were reached after about 90 min of ultrasonic treatment.

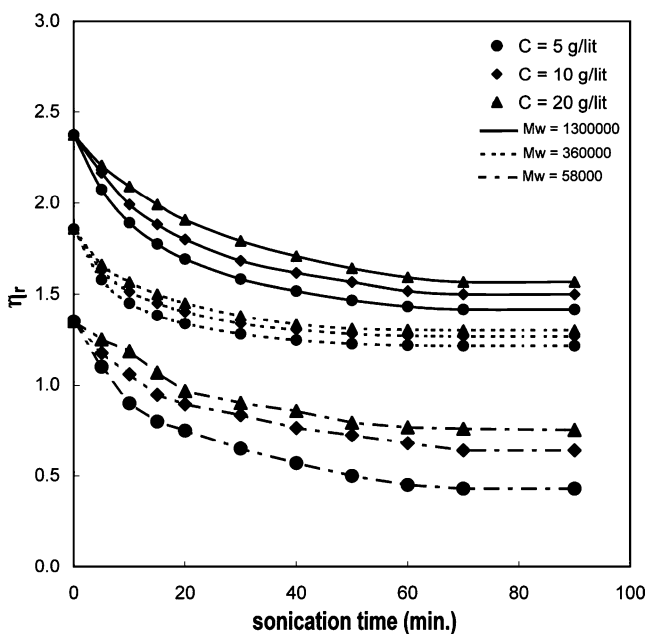
It was found from this Figure that as the concentration of the polymer in the solution is increased so the rate of degradation decreased. At high concentrations, entanglements influence the energy transfer processes between solvent and polymer and appears to reduce the probability of degradation occurring.

It has been pointed out previously [40, 50, 51] that an increase in the viscosity of the solution will increase the energy required for cavitation to occur. Therefore, the

**Scheme 2** The degradation scheme for multiple scission kinetics







**Fig. 13** Effect of molecular weight and Concentration on limiting viscosity

remainder of the study was carried out at on 5 g/lit solution of PVP so as to avoid possible complications arising from entanglement effects on the viscoelastic response of the polymer solution. It is clear that the ultrasonic degradation process is faster at lower concentration than at higher concentrations.

The sonolytic degradation was dependent on the molecular mass and on the concentration of the polymer. The polymer with high molecular mass or high polymer concentration degraded faster than the polymers having low molecular mass or low polymer concentration.

Figure 13 shows the effect of molecular weight on the limiting viscosity of PVP solution when it is subjected to ultrasonic degradation. Figure 13 shows that the limiting viscosities for 1,300,000 and 360,000  $\text{g}\cdot\text{ol}^{-1}$  of polymer at 5, 10, 15  $\text{g}\cdot\text{lit}^{-1}$  concentration is nearly equal but for 58,000  $\text{g}\cdot\text{ol}^{-1}$  of polymer the limiting viscosities have been varied.

## Conclusions

The aim of this research was to study the effect of concentration and different initial molecular weights of polymer on the ultrasonic degradation of PVP in solution at 25°C. The experimental results indicated that the degradation rate reduced with increasing solution concentration and increased with increasing of molecular weight of polymer.

Relative viscosity decreases on sonication time and inclines to a limiting value, below which no further

degradation occurs. The limiting value is dependent of the initial molecular weight for PVP. A simple kinetic model using viscosity data was used for studying kinetics of degradation. Based on the experimental data on the ultrasonic degradation of PVP in different molecular weights, we have determined the degradation rate coefficient. The degradation rate coefficient decreased with increasing concentration and increased with increasing the molecular weight of polymer. This is in agreement with earlier studies [22]. This model interpreted the experimental findings in an optimal way and thus, viscosity is a practical approach for monitoring the degradation of polymers in a solution.

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