

# Ultrasonic Degradation of Polyvinyl Pyrrolidone in Mixed Water/Acetone

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**ABSTRACT:** The ultrasonic degradation of polyvinyl pyrrolidone solutions was carried out in mixtures water and acetone at 25°C to investigate the effect of solvent composition and solution concentration on the rate of degradation. The obtained limiting molecular weights indicate that the extent of degradation was decreased by increasing acetone volume fraction and solution concentration. The obtained limiting molecular weights were correlated in terms of concentration and acetone volume fraction. The calculated rate constants indicate that the rate of degradation was decreased by increasing acetone volume fraction and solution concentration. The calculated rate constants were correlated in terms of concentration, acetone volume fraction and molecular weight of polymer. This degradation behav-

ior was interpreted in terms of vapor pressure of mixtures water and acetone, viscosity and concentration of polymer solutions. Vapor pressure of mixtures water and acetone were increased by increasing acetone volume fraction, and so the vapor easily entered the cavitation bubbles during their growth. This caused a reduction in collapsing shock because of a cushioning effect; therefore, the rate of degradation decreased. As the solution concentration increased, the viscosity increased and caused a reduction in the cavitation efficiency, and so the rate of degradation is decreased. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 3701–3708, 2011

**Key words:** modeling; ultrasonic degradation; polyvinyl pyrrolidone; kinetic

## INTRODUCTION

The degradation of polymers can occur because of heat, light, chemical reagents or ultrasonic radiation.<sup>1</sup> The ultrasonic degradation process has several unique features that distinguish it from thermal or photochemical degradation, such as a nonrandom nature and molecular weight dependence.<sup>2</sup> The scission of polymer chains in a solution occurs preferentially near the middle of the chain.<sup>3,4</sup> Ultrasonication has subsequently proved to be a highly advantageous method for degrading macromolecules because it reduces their molecular weight simply by splitting the most susceptible chemical bond in the center of the chain without causing any changes in the chemical nature of the polymer.<sup>5</sup> The main effects of sonication are due to cavitation.<sup>3</sup> Formation, growth, and rapid collapse of microscopic bubbles generate high temperatures and pressures during bubble collapse in the region of several thousands Kelvin and several hundred atmospheres, depending on the system.<sup>6</sup> These extreme conditions are primarily responsible for sonochemical reaction. In a dilute solution, the role of the generated heat is

probably of minor importance for polymer degradation. Accordingly since the hot regions are highly localized and should be quenched in less than 1  $\mu$ s, the polymer molecules do not have time to diffuse and to reach these spots in such a short interval.<sup>6</sup> The motion of the wall of imploding bubble causes the movement of the solvent molecules around the bubbles. These movements set up large shear fields that are primarily responsible for the degradation of polymer.<sup>3,7,8</sup> The effects of solvent composition on the ultrasonic degradation of polymer are investigated by many researchers.<sup>9–11</sup> Taghizadeh et al. are investigated the effect of molecular weight on the ultrasonic degradation of PVP in water and chloroform.<sup>12,13</sup> Aarthi et al. are studied the degradation of PVP under ultrasonic, ultraviolet radiation, and combined ultrasonic and ultraviolet.<sup>14</sup> Akyuz et al. are studied the ultrasonic degradation of PVP in mixtures of water/methanol.<sup>15</sup> In this study, the effect of solvent composition and solution concentration on the ultrasonic degradation of PVP are investigated in aqueous solution of acetone.

## KINETIC MODEL

The rate of degradation is defined as the number of moles of scissions that occur in 1 L at time and we must keep in mind that a scission in chain yields two pieces. Thus the effective rate of the degradation is as follow<sup>16</sup>

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$$R = \frac{dM}{dt} = kM^\alpha \quad (1)$$

where  $M$  is the total molar concentration of polymer,  $k$  is the apparent rate constant, and  $\alpha$  is the order of reaction with respect to total molar concentration of polymer. In ultrasonic degradation apparent rate constant is dependent the molecular weight of polymer. The apparent rate constant of degradation is related to  $M_n$  through<sup>17</sup>

$$k = k'(M_n - M_{lim})^\beta \quad (2)$$

where  $k'$ ,  $M_{lim}$ , and  $\beta$  are the rate constant, the limiting number average molecular weight and a constant which is dependent of condition experience respectively.

The total molar concentration is related to the number average molecular weight,  $M_n$ , through

$$M = \frac{C}{M_n} \quad (3)$$

Thus the rate equation of the degradation is as follow:

$$R' = -\frac{dM_n}{dt} = kC^{\alpha-1}M_n^{2-\alpha} \quad (4)$$

Substitution of eq. (2) in eq. (4) yields the rate equation of the degradation as follow:

$$R' = -\frac{dM_n}{dt} = k'C^{\alpha-1}M_n^{2-\alpha}(M_n - M_{lim})^\beta \quad (5)$$

$$\int_{M_{n0}}^{M_n} \frac{-dM_n}{k'C^{\alpha-1}M_n^{2-\alpha}(M_n - M_{lim})^\beta} = \int_0^t dt \quad (6)$$

where  $M_{n0}$  is the initial molecular weight. Solution the above integral is given by<sup>18</sup>

$$\frac{M_n^{(\alpha-1)}(M_n - M_{lim})^{-\beta}(1 - M_n/M_{lim})^\beta {}_2F_1(\alpha - 1, \beta, \alpha, M_n/M_{lim})}{k'C^{\alpha-1}(\alpha - 1)} - \frac{M_{n0}^{(\alpha-1)}(M_{n0} - M_{lim})^{-\beta}(1 - M_{n0}/M_{lim})^\beta {}_2F_1(\alpha - 1, \beta, \alpha, M_{n0}/M_{lim})}{k'C^{\alpha-1}(\alpha - 1)} = t \quad (7)$$

where  ${}_2F_1$  is Hypergeometric function which is given by<sup>19</sup>

$${}_2F_1(a, b, c, x) = \sum_{n=0}^{\infty} \frac{(a+n-1)!(b+n-1)!(c-1)!x^n}{(c+n-1)!(a-1)!(b-1)!(c)_n n!} \quad (8)$$

## EXPERIMENTAL

### Materials

Polyvinyl pyrrolidone, PVP, with mass average molecular weight,  $M_w$ , of 130,000 (Acros Organics) was used without further purification. Acetone which supplied by Merck was used without further purification. Distilled water was used for preparation of solutions.

### Apparatus and procedure

PVP solutions (5, 10, and 15 g L<sup>-1</sup>) were prepared gravimetrically by an analytical balance (Sartorius CP224 S) with a precision of  $\pm 1 \times 10^{-4}$ g. Ultrasonic degradation was performed in six aqueous solutions with different acetone volume fractions ( $\phi_a = 0, 0.1, 0.2, 0.3, 0.4,$  and  $0.5$ ) at 25°C. For the degradation, 80

cm<sup>3</sup> polymer solutions was placed in the jacket flask, and its temperature was controlled within  $\pm 0.5^\circ\text{C}$  by circulating thermostated water and sonication has been continued for a time which viscosity of solution tends to have a constant value. An ultrasonic generator (Dr. Hielscher UP400 S ultrasonic processor) with an H3 sonotrode with diameter 3 mm was used in this experiment. The frequency of the ultrasound was 24 kHz and output was set at 350 W.

Periodically, samples of the sonicated solution were removed and their viscosities were measured using a jacketed Ubbelohde viscometer the temperature of which was kept at  $25 \pm 0.1^\circ\text{C}$  with a temperature controller (Eyela, UA-10, Tokyo Rikakiai Co.). For the ready comparison of viscosity changes during sonication, after the removal of the samples (10 and 15 g L<sup>-1</sup>), they were diluted to 5 g L<sup>-1</sup>. Next, their viscosities were measured. The flow times for the solutions used in this work were never less than 230 s. The relative viscosity,  $\eta_r$ , and specific viscosity,  $\eta_{sp}$ , were calculated as follows:

$$\eta_r = \frac{t}{t_0}, \quad \eta_{sp} = \eta_r - 1 \quad (9)$$

where  $t$  and  $t_0$  are the flow time for the given polymer solution and the solvent respectively.

The intrinsic viscosity,  $[\eta]$ , is related to the relative viscosity and specific viscosity through<sup>20</sup>

$$[\eta] = \frac{(2(\eta_{sp} - \ln \eta_r))^{0.5}}{C} \quad (10)$$

On the other hand the viscosity average molecular weight,  $M_v$ , is related to the intrinsic viscosity through the Mark-Houwink equation<sup>21</sup>

$$M_v = \left(\frac{[\eta]}{K}\right)^{1/a} \quad (11)$$

where  $a$  and  $K$  are the Mark-Houwink constants. Also number average molecular weight is related to the viscosity average molecular weight through<sup>21</sup>

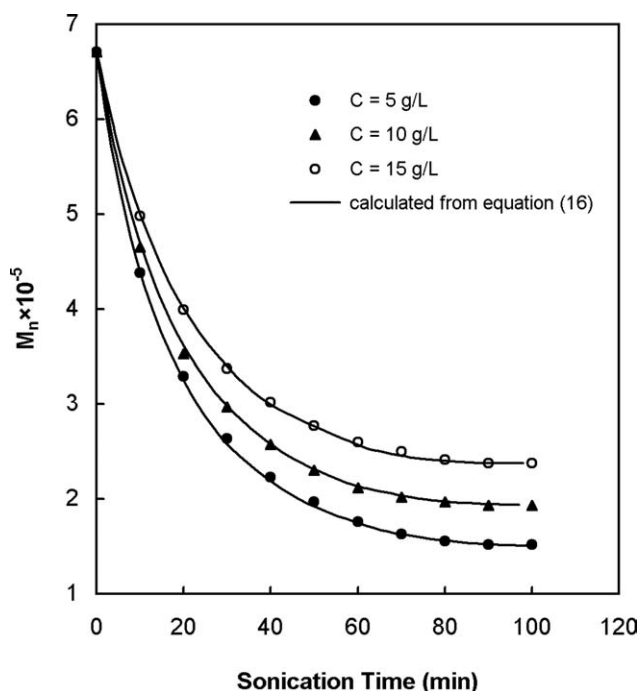
$$M_n = [(1+a)\Gamma(1+a)]^{-1/a} M_v \quad (12)$$

where  $\Gamma(1+a) = \int_0^\infty e^{-t} t^a dt$ .

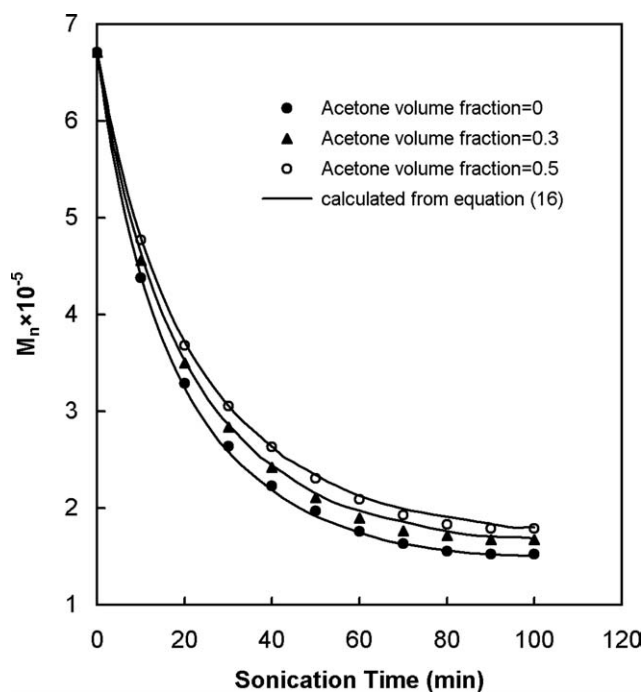
Substitution of eq. (9) in (11) and eq. (11) in (12) yields

$$M_n = \left(\frac{(2(\eta_{sp} - \ln \eta_r))^{0.5}}{(1+a)\Gamma(1+a)KC}\right)^{1/a} \quad (13)$$

In this work ( $a = 0.55$ ) and ( $K = (6.76, 6.48, 6.37, 6.41, 6.23, \text{ and } 6.00) \times 10^{-5} \text{ L g}^{-1}$ ) were adopted on the basis of standard molecular weights for PVP in



**Figure 1** Relationship between  $M_n$  and sonication time in water with different polymer concentration at 25°C.

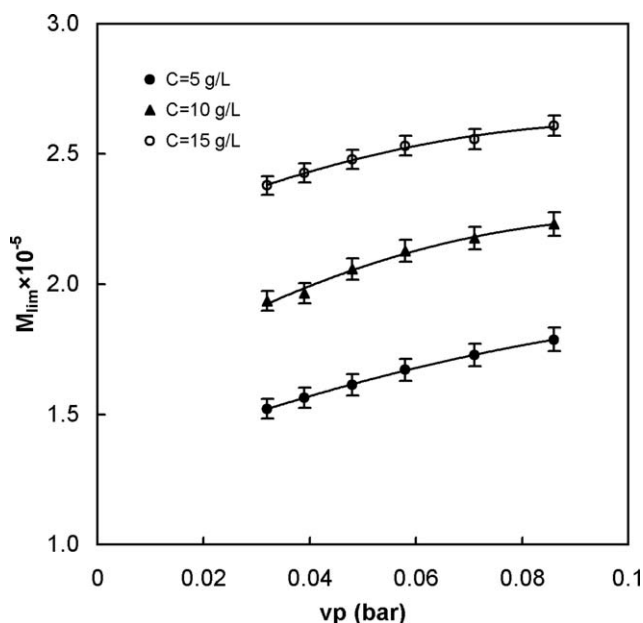


**Figure 2** Relationship between  $M_n$  and sonication time in different acetone volume fractions with  $[PVP] = 5 \text{ g L}^{-1}$  at 25°C.

mixed water/acetone solvent with acetone volume fractions  $\phi_a = 0, 0.1, 0.2, 0.3, 0.4,$  and  $0.5$ , respectively. The time evolution of number average molecular weight was evaluated by eq. (13).

## RESULTS AND DISCUSSION

Sonication was carried out for three different PVP concentrations in six mixed water/acetone solvent with different acetone volume fractions ( $\phi_a = 0, 0.1, 0.2, 0.3, 0.4,$  and  $0.5$ ) at 25°C. The relationships between  $M_n$  and sonication time are presented in Figures 1 and 2. For clarity of diagram, the plots of  $M_n$  versus sonication time alone for acetone volume fractions ( $\phi_a = 0, 0.3,$  and  $0.5$ ) are presented in Figure 2. From these findings, it is clear that  $M_n$  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  $M_n$  of the sample with a high polymer concentration is lower than that of the sample with a low polymer concentration. 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.<sup>5</sup> The obtained results indicate that the extent of degradation



**Figure 3** Relationship between  $M_{lim}$  and vapor pressure of mixed solvents at 25°C.

were decreased by increasing acetone volume fractions. This might be because of, with increasing acetone volume fractions, vapor pressure of the solvent increases, (vapor pressure acetone is greater than its water, therefore, vapor pressure of the mixture solvent are increased by increasing acetone volume fraction) and so the vapor easily enters the cavitation bubbles during their growth. This causes a reduction in collapsing shock because of a cushioning effect; therefore, the extent of degradation is reduced.<sup>22</sup> The relationships between limiting molecular weight and vapor pressure of mixed solvents,  $v_p$ , are presented in Figure 3. However the Raoult equation has been used to estimate  $v_p$  of the mixtures of water and acetone and the Vagner equation has been used to estimate  $v_p$  of water and acetone.<sup>23</sup>

From the time-evolution of  $M_n$ , the rate of degradation evaluated and the calculated rates fit to the eq. (5) and the value of parameters  $\alpha$  and  $\beta$  in eq. (5) were obtained 1 and 0.6, respectively, the obtained order reaction is consistent with the results of Giz et al.<sup>15</sup> and Madras et al.<sup>14</sup> Nevertheless Taghizadeh

et al.<sup>13</sup> reported various order of reaction for various molecular weights. The authors believed that the order of reaction can not be dependent to the molecular weight. By considering the value of parameters  $\alpha$  and  $\beta$ , the eq. (5) as follows:

$$R' = -\frac{dM_n}{dt} = k'M_n(M_n - M_{lim})^{0.6} \quad (14)$$

$$\int_{M_{n0}}^{M_n} \frac{-dM_n}{k'M_n(M_n - M_{lim})^{0.6}} = \int_0^t dt \quad (15)$$

$$M_{nt}^{-0.6} {}_2F_1(0.6, 0.6, 1.6, M_{lim}/M_{nt}) - M_{n0}^{-0.6} {}_2F_1(0.6, 0.6, 1.6, M_{lim}/M_{n0}) = 0.6k't \quad (16)$$

Then the experimental molecular weights fit to the eq. (16) to obtain the rate constant,  $k'$ . The obtained rate constants,  $k'$ , and correlation coefficients,  $r$ , are listed in Table I. The correlation coefficient is defined as

$$r^2 = \frac{(\sum (x_i - \bar{x})(y_i - \bar{y}))^2}{\sum (x_i - \bar{x})^2 \sum (y_i - \bar{y})^2} \quad (17)$$

where  $x$  and  $y$  are denote time and left hand side of the eq. (16), respectively.

This model is compared with Schmid, El'tsefon-Berlin, Tang-Liu, Madras, Malhotra, Ovenall, and Giz models. Schmid proposed an equation relating the rate of scission to the molecular weight. The integral form of Schmid's model is<sup>2,24</sup>.

$$M_{lim}(M_0^{-1} - M_t^{-1}) + \ln\left(\frac{M_{lim}^{-1} - M_0^{-1}}{M_{lim}^{-1} - M_t^{-1}}\right) = k_s\left(\frac{M_{lim}^2}{Cm_0^2}\right)t \quad (18)$$

A plot of the left hand side of the equation versus time yields a straight line. The rate constant is calculated from its slope. Here the polymer concentration,  $C$ , is written explicitly to give the dependence of scission rate on concentration. The obtained rate constants of this model,  $k_s$ , and correlation coefficients,  $r$ , are listed in Table II.

**TABLE I**  
The Rate Constant of Ultrasonic Degradation of Polyvinyl Pyrrolidone in Various Conditions

$\varphi_a$	$k' \times 10^5$			$r^2$		
	$C = 5 \text{ g L}^{-1}$	$C = 10 \text{ g L}^{-1}$	$C = 15 \text{ g L}^{-1}$	$C = 5 \text{ g L}^{-1}$	$C = 10 \text{ g L}^{-1}$	$C = 15 \text{ g L}^{-1}$
0	1.900	1.662	1.368	0.996	0.999	0.999
0.1	1.805	1.623	1.366	0.999	0.999	1.000
0.2	1.795	1.587	1.333	0.999	0.998	0.999
0.3	1.775	1.524	1.289	0.996	0.997	0.996
0.4	1.620	1.450	1.249	0.990	0.992	0.997
0.5	1.606	1.411	1.237	0.993	0.995	0.996

**TABLE II**  
The Rate Constant of Ultrasonic Degradation of Polyvinyl Pyrrolidone in Various Conditions on the Bases Schmid Model

$\varphi_a$	$k_S \times 10^8$			$r^2$		
	$C = 5 \text{ g L}^{-1}$	$C = 10 \text{ g L}^{-1}$	$C = 15 \text{ g L}^{-1}$	$C = 5 \text{ g L}^{-1}$	$C = 10 \text{ g L}^{-1}$	$C = 15 \text{ g L}^{-1}$
0	6.236	9.099	9.094	0.74	0.823	0.834
0.1	5.363	8.861	9.300	0.779	0.787	0.819
0.2	5.326	8.616	8.956	0.786	0.780	0.800
0.3	5.293	7.974	8.537	0.780	0.760	0.760
0.4	4.371	7.273	7.918	0.720	0.724	0.780
0.5	4.280	6.739	7.833	0.749	0.757	0.781

Malhotra proposed that the time dependence of the molecular weight is given by<sup>25,26</sup>

$$M_t^{-1} - M_0^{-1} = k_M t \quad (19)$$

A plot of the left hand side of the equation versus time yields a straight line which its slope is rate constant. The lack of a limiting molecular weight is failure of this model. The rate constants of this model,  $k_M$ , and correlation coefficients,  $r$ , are listed in Table III.

Tang and Liu are proposed a kinetic equation<sup>27</sup>

$$(M_t - M_{\text{lim}})^{-1} - (M_0 - M_{\text{lim}})^{-1} = k_T t \quad (20)$$

The degradation rate constant,  $k_T$ , can be found as the slope of the line from a plot of the left hand side of the equation versus time. The efficiency of this model was poor for our data. Therefore the rate constants of this model is not reported.

El'tsefon and Berlin have suggested that<sup>4,28</sup>

$$M_t^{-2} - M_0^{-2} = \beta k_E t \quad (21)$$

where  $\beta$  is a constant accounting for the polydispersity of the polymer so that the rate constant can be found as the slope of the left hand side of the equation versus time. This model also lacks a limit molecular weight. By considering  $\beta = 1$ , the rate constants of this model,  $k_E$ , and correlation coefficients,  $r$ , are listed in Table IV.

A model proposed by Ovenall and coworkers as an approximate description of the degradation process gives the time dependence of the molecular weight during sonication by<sup>4,29</sup>

$$\ln \left( \frac{M_{\text{lim}}^{-1} - M_0^{-1}}{M_{\text{lim}}^{-1} - M_t^{-1}} \right) = k_O \left( \frac{M_{\text{lim}}}{C m_0} \right) t \quad (22)$$

so that a plot of the left hand side of the equation versus time produces a linear relationship, the slope of which yields the rate constant. Here the polymer concentration is written explicitly to give the dependence of scission rate on concentration. The rate constants of this model,  $k_O$ , and correlation coefficients,  $r$ , are listed in Table V.

Madras and coworkers have proposed a model that takes the continuous distribution kinetics into account.<sup>10,15</sup> The time dependence of the average molecular weight in this model is same as in the Ovenall model.

$$\ln \left( \frac{M_{\text{lim}}^{-1} - M_0^{-1}}{M_{\text{lim}}^{-1} - M_t^{-1}} \right) = k_{Ma} M_{\text{lim}} t \quad (23)$$

The rate constants of this model,  $k_{Ma}$ , and correlation coefficients are listed in Table VI.

Giz and coworkers are suggested that the average molecular weight evolution could be approximated as<sup>14</sup>

**TABLE III**  
The Rate Constant of Ultrasonic Degradation of Polyvinyl Pyrrolidone in Various Conditions on the Bases Malhotra Model

$\varphi_a$	$k_M \times 10^8$			$r^2$		
	$C = 5 \text{ g L}^{-1}$	$C = 10 \text{ g L}^{-1}$	$C = 15 \text{ g L}^{-1}$	$C = 5 \text{ g L}^{-1}$	$C = 10 \text{ g L}^{-1}$	$C = 15 \text{ g L}^{-1}$
0	6.760	5.152	3.809	0.980	0.943	0.925
0.1	6.447	4.985	3.709	0.977	0.958	0.934
0.2	6.268	4.704	3.576	0.974	0.958	0.936
0.3	6.026	4.452	3.422	0.977	0.961	0.945
0.4	5.529	4.224	3.326	0.987	0.971	0.956
0.5	5.355	4.075	3.233	0.985	0.969	0.956



**TABLE IV**  
The Rate Constant of Ultrasonic Degradation of Polyvinyl Pyrrolidone in Various Conditions on the Bases El'tsefon Model

$\varphi_a$	$k_E \times 10^{13}$			$r^2$		
	$C = 5 \text{ g L}^{-1}$	$C = 10 \text{ g L}^{-1}$	$C = 15 \text{ g L}^{-1}$	$C = 5 \text{ g L}^{-1}$	$C = 10 \text{ g L}^{-1}$	$C = 15 \text{ g L}^{-1}$
0	4.825	3.141	2.007	0.986	0.990	0.986
0.1	4.473	2.998	1.935	0.989	0.992	0.988
0.2	4.276	2.749	1.837	0.989	0.991	0.989
0.3	4.029	2.534	1.728	0.985	0.993	0.993
0.4	3.538	2.350	1.663	0.987	0.996	0.995
0.5	3.367	2.230	1.598	0.987	0.995	0.995

**TABLE V**  
The Rate Constant of Ultrasonic Degradation of Polyvinyl Pyrrolidone in Various Conditions on the Bases Ovenall Model

$\varphi_a$	$k_O \times 10^4$			$r^2$		
	$C = 5 \text{ g L}^{-1}$	$C = 10 \text{ g L}^{-1}$	$C = 15 \text{ g L}^{-1}$	$C = 5 \text{ g L}^{-1}$	$C = 10 \text{ g L}^{-1}$	$C = 15 \text{ g L}^{-1}$
0	1.230	2.157	2.584	0.857	0.910	0.913
0.1	1.114	2.122	2.652	0.890	0.880	0.898
0.2	1.122	2.119	2.596	0.893	0.870	0.882
0.3	1.132	2.022	2.516	0.882	0.854	0.848
0.4	0.988	1.895	2.377	0.841	0.824	0.865
0.5	0.986	1.806	2.379	0.859	0.852	0.864

**TABLE VI**  
The Rate Constant of Ultrasonic Degradation of Polyvinyl Pyrrolidone in Various Conditions on the Bases Madras Model

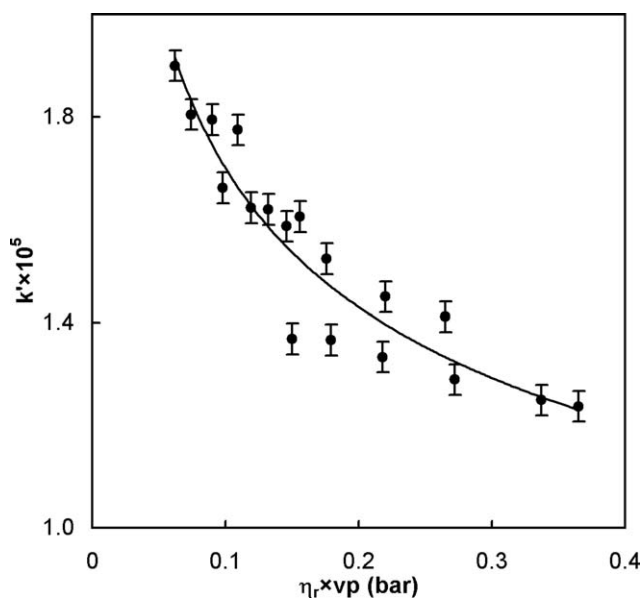
$\varphi_a$	$k_{Ma} \times 10^7$			$r^2$		
	$C = 5 \text{ g L}^{-1}$	$C = 10 \text{ g L}^{-1}$	$C = 15 \text{ g L}^{-1}$	$C = 5 \text{ g L}^{-1}$	$C = 10 \text{ g L}^{-1}$	$C = 15 \text{ g L}^{-1}$
0	2.217	1.944	1.552	0.857	0.910	0.913
0.1	2.007	1.912	1.593	0.890	0.880	0.898
0.2	2.022	1.909	1.559	0.893	0.870	0.882
0.3	2.039	1.822	1.511	0.882	0.854	0.848
0.4	1.780	1.707	1.428	0.841	0.824	0.865
0.5	1.777	1.627	1.429	0.859	0.852	0.864

**TABLE VII**  
The Rate Constant of Ultrasonic Degradation of Polyvinyl Pyrrolidone in Various Conditions on the Bases Giz Model

$\varphi_a$	$k_G \times 10^{-1}$			$r^2$		
	$C = 5 \text{ g L}^{-1}$	$C = 10 \text{ g L}^{-1}$	$C = 15 \text{ g L}^{-1}$	$C = 5 \text{ g L}^{-1}$	$C = 10 \text{ g L}^{-1}$	$C = 15 \text{ g L}^{-1}$
0	2.162	2.158	2.012	0.992	0.994	0.994
0.1	2.088	2.132	2.039	0.990	0.997	0.997
0.2	2.108	2.144	2.020	0.992	0.997	0.996
0.3	2.125	2.104	1.982	0.996	0.996	0.990
0.4	1.990	2.033	1.929	0.990	0.990	0.993
0.5	2.005	2.004	1.937	0.995	0.994	0.993

**TABLE VIII**  
The Mean Correlation Coefficient,  $\bar{r}^2$  of the Used Models

Model	Mehrdad	Schmid	Malhotra	Tang	El'tsefon	Ovenall	Madras	Giz
$\bar{r}^2$	0.997	0.776	0.961	0.536	0.990	0.871	0.871	0.994



**Figure 4** Relationship between  $k'$  and the product of  $\eta_r$  and  $v_p$  at 25°C.

$$\ln\left(\frac{M_{\text{lim}} - M_0}{M_{\text{lim}} - M_t}\right) = (k_G t)^\beta \quad (24)$$

where  $\beta$  is a measure of the heterogeneity of the process and left as a fit parameter. This model is fitted to experimental data and the best value of  $\beta$  is found to be 1/3. The rate constants of this model,  $k_G$ , and correlation coefficients,  $r$ , are listed in Table VII. For comparison efficiency of the used models, the mean correlation coefficient of these models are listed in Table VIII.

The obtained values of  $k'$  indicate that the rates of degradation were decreased by increasing polymer concentrations and acetone volume fractions. The viscosities of polymer solutions were increased by increasing solution concentration which reduce the shear gradients around the collapsing bubbles; therefore, the degradation rate decreases too. The eq. (14) is reveals that the rate constant should be independent from the polymer concentration; nevertheless the results of Table I indicate that the rate constant is dependent to the polymer concentration. This behavior might be attributed to the viscosity of solutions. In other word the rate constant is independent from the polymer concentration but is not independent from the viscosity of polymer solutions.

The vapor pressure of mixtures of water and acetone were increased by increasing acetone volume fractions; therefore, the vapor easily enters the cavitation bubbles during their growth and causes a reduction in collapsing shock because of a cushioning effect. Consequently, the rate of degradation is reduced. Vapor pressure of solvents were changed

by variation of solvent composition also viscosity of polymer solutions were changed by variation concentration, therefore the rate constant of ultrasonic degradation were correlated in terms of the product of  $\eta_r$  and  $v_p$  in Figure 4. The other reason for decreasing rate constant by increasing acetone volume fractions is related to the conformation of polymer chains. The mixtures of water and acetone were performed poorer solvent for PVP by increasing acetone volume fractions; therefore, the chains of PVP shrinks and the end-to-end distance of polymer chains become smaller; therefore, strain rate were reduced and the degradation rate decreases too.

## CONCLUSIONS

The ultrasonic degradation of PVP solutions was carried with concentration 5, 10, and 15 g L<sup>-1</sup> in mixed water/acetone at 25°C. The obtained limiting values of molecular weight indicated that the extent of degradation was decreased by increasing of solution concentration and acetone volume fraction. The order reaction with respect to molar concentration of polymer was 1. The rate of the degradation of the polymer decreased as the acetone volume fraction and solution concentration increased. The rate of the degradation and the limiting values of molecular weight of the polymer correlated in terms of the viscosity of polymer solution and vapor pressure of solvent.

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