# Ultrasonic Degradation of Poly(acrylic acid)

**Neelesh Bharti Shukla, Nagu Darabonia, Giridhar Madras**

*Department of Chemical Engineering, Indian Institute of Science, Bangalore, India 560012*

**ABSTRACT:** The ultrasonic degradation of poly(acrylic acid), a water-soluble polymer, was studied in the presence of persulfates at different temperatures in binary solvent mixtures of methanol and water. The degraded samples were analyzed by gel permeation chromatography for the time evolution of the molecular weight distributions. A continuous distribution kinetics model based on midpoint chain scission was developed, and the degradation rate coefficients were determined. The decline in the rate of degradation of poly(acrylic acid) with increasing temperature and with an increment in the methanol content in the binary solvent mixture of methanol and water was attributed to the increased vapor pressure of the solutions. The experimental data showed an augmentation of the degradation rate of the polymer with increasing oxidizing agent (persulfate) concentrations. Different concentrations of three persulfates—potassium persulfate, ammonium persulfate, and sodium persulfate—were used. It was found that the ratio of the polymer degradation rate coefficient to the dissociation rate constant of the persulfate was constant. This implies that the ultrasonic degradation rate of poly(acrylic acid) can be determined *a priori* in the presence of any initiator. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 991–997, 2009

**Key words:** degradation; gel permeation chromatography (GPC); kinetics (polym.); mass distribution; water-soluble polymers

## INTRODUCTION

The ultrasonic degradation of polymers is interesting because of its distinctive characteristics. The ultrasonic degradation of polymers in solutions, unlike other chemical and thermal degradation processes, is a nonrandom process in which the polymer molecule undergoes scission preferentially at the midpoint of the chain.[1] Only the most susceptible chemical bond breaks during degradation, and no chemical changes take place. The ultrasonic degradation depends on the molecular weight, with higher molecular weight species degrading faster than lower molecular weight species.[2] Furthermore, there exists a limiting molecular weight ($x_l$) for a polymer below which degradation by ultrasound does not occur.

The ultrasound waves do not directly interact with polymer molecules during the degradation process. The degradation results from cavitation, which is the growth and rapid collapse of microbubbles that are formed when ultrasound waves of sufficient intensity propagate through the solution. Intense shear fields are generated during the collapse of the microbubbles, and the segment of polymer chains near the collapsing cavity moves faster than those farther away from the collapsing cavity. This relative motion of the polymer segments and solvent molecules gives rise to shear stresses on the polymer chain leading to the scission of the polymer chain.[3]

The effects of various parameters such as the polymer concentration, solvents,[2] initial molecular weight,[4] temperature,[4] dissolved gases,[5] and ultrasound intensity[6] on the degradation of numerous polymers have been investigated and summarized in a review.[3]

Poly(acrylic acid) (PAA) is an innocuous water-soluble polymer. PAA and its derivatives find applications in biomedicine as sensor heads for the photochemical detection of the pH and $CO_2$ content of water solutions,[7] in drug delivery applications,[8] and as cleaning agents.[9] Despite the large number of studies on the ultrasonic degradation of polymers, only two studies have investigated the effects of oxidizers on the ultrasonic degradation of poly(vinyl acetate)[10] and poly(*n*-alkyl acrylate)s.[11]

To best of our knowledge, this is the first study investigating the effect of persulfate oxidizing agents on the ultrasonic degradation of PAA. Ultrasonic degradation at various temperatures and in solutions of different binary solvent mixtures of methanol and water was examined. A radical mechanism based on Rice–Herzfeld kinetics[12] is proposed, and a new theoretical model based on continuous distribution kinetics is developed to account for the effect of

*Correspondence to:* G. Madras (giridhar@chemeng.iisc.ernet.in).

persulfates on the ultrasonic degradation of PAA. It is shown that the degradation rate of PAA in the presence of persulfates increases with an increasing concentration of persulfates.

## EXPERIMENTAL

### Materials

PAA with a viscosity-average molecular weight of 450,000 was purchased from Sigma–Aldrich (St. Louis, MO). The number-average molecular weight ($M_n$) and polydispersity index, as determined by gel permeation chromatography (GPC) analysis, were 340,000 and 2.6, respectively. Potassium persulfate (KPS), ammonium persulfate (APS), and sodium persulfate (SPS) were procured from SD Fine-Chem, Ltd. (Mumbai, India), Spectrochem Pvt., Ltd. (Mumbai, India), and Rolex Laboratory Reagents (India), respectively. Methanol was obtained from SD Fine-Chem. Sodium nitrate was obtained from Merck (India). All chemicals were used without further purification. Milli-Q water was used for all the experiments.

### Degradation experiments

All the ultrasonic degradation experiments were carried out with 60 mL of a 1 g/L PAA solution in a 100-mL glass beaker. This beaker was placed in a horn-type ultrasonic processor (Vibronics, Mumbai, India) with the horn dipped in the solution at the same level for all experiments. The samples were irradiated at a frequency of 25 kHz with an intensity of 36 W/cm$^2$. PAA solutions in water were maintained at 25, 40, 50, and 60°C ($\pm1$°C) with a thermostated water bath to study the effect of temperature on the degradation. Various compositions of the methanol/water mixtures (100/0, 70/30, 50/50, 30/70, and 0/100 v/v) at 25°C were used to observe the effect of vapor pressure on the degradation. The effect of the oxidizing agents—KPS, APS, and SPS—at concentrations of 1, 3, and 5 g/L was also examined.

### GPC analysis

Samples (0.5 mL) were taken at various reaction times and quenched in an ice–water bath before being analyzed by GPC to determine the molecular weight distributions. A solution of $0.1N$ NaNO$_3$ in double-distilled water was used as the eluent. The eluent was pumped at a flow rate of 1 mL/min with a Waters (Milford, MA) 515 high-performance liquid chromatography isocratic pump. The column was a Waters ultrahydrogel linear GPC column (7.8 mm $\times$ 300 mm). The column temperature was maintained
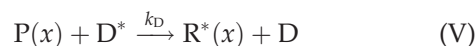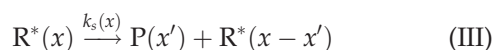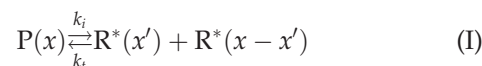
at 50°C with a column heater. A 200-μL aliquot of each sample was injected into a Rheodyne 7725i injector. The refractive index was measured continuously with a Waters 401 differential refractometer. Molecular weights of the samples were determined with poly (ethylene oxide) calibration standards.

The model required the determination of $x_l$. Several experiments were conducted for 8 h. There was no reduction in the molecular weight of PAA beyond 6 h. This molecular weight ($M_n$ = 20,000) was taken as $x_l$, and it was independent of the temperature or solvent.

Several experiments were repeated in triplicate, and the error in the determination of the molecular weight was less than 1%, whereas the error in the rate coefficient was less than 3%.

## THEORETICAL MODEL

A theoretical model based on continuous distribution kinetics satisfactorily describes the ultrasound degradation of the polymer, involving a free-radical mechanism based on Rice–Herzfeld kinetics.[12] The proposed radical mechanism for the degradation of the polymer can be given as follows:

$$P(x) \underset{k_t}{\overset{k_i}{\rightleftharpoons}} R^*(x') + R^*(x - x') \qquad (I)$$

$$P(x) \underset{k_H}{\overset{k_h}{\rightleftharpoons}} R^*(x) \qquad (II)$$

$$R^*(x) \overset{k_s(x)}{\longrightarrow} P(x') + R^*(x - x') \qquad (III)$$

$$D_2 \overset{k_d}{\longrightarrow} 2D^* \qquad (IV)$$

$$P(x) + D^* \overset{k_D}{\longrightarrow} R^*(x) + D \qquad (V)$$

Reaction (I) represents the initiation and termination steps in which polymer P(x) of molecular weight $x$ breaks into two radicals of molecular weights $x'$ and $x - x'$; the initiation and termination rate coefficients are denoted $k_i$ and $k_t$, respectively. The reversible intermolecular hydrogen abstraction is represented by reaction (II). As polymer P(x) and radical R*(x) differ only by a hydrogen atom, their molecular weights are assumed to be identical. Reaction (III) depicts the depropagation reaction with the depropagation reaction rate constant $k_s(x)$. In reaction (IV), the persulfate molecule, denoted D$_2$, decomposes to give initiator radical D*. D* reacts with the polymer to form a polymer radical in reaction (V), and the rate coefficient for this reaction is $k_D$.

Continuous distribution kinetics considers molecular weight $x$ as a continuous variable. The time-dependent molecular weight distributions of the polymer and polymer radical are given by $p(x,t)$ and $r(x,t)$, respectively, where $p(x,t)dx$ denotes the molar concentration of the polymer in the interval $[x,x + dx]$. The population balance equations[12] for polymer P($x$), polymer radical R*($x$), initiator $D_2$, and initiator radical D* can be written as follows:

$$\frac{\partial p(x,t)}{\partial t} = -k_h p(x,t) + k_H r(x,t) - k_D p(x,t)D^*(t)$$
$$- k_s(x)r(x,t) + \int_x^\infty k_s(x')\Omega(x,x')r(x',t)dx \quad (1)$$

$$\frac{\partial r(x,t)}{\partial t} = k_h p(x,t) - k_H r(x,t) + k_D p(x,t)D^*(t)$$
$$- k_s(x)r(x,t) + \int_x^\infty k_s(x')\Omega(x,x')r(x',t)dx \quad (2)$$

$$\frac{dD^*(t)}{dt} = 2k_d D_2(t) - \int_0^\infty k_D D^*(t)p(x',t)dx' \quad (3)$$

$$\frac{dD_2(t)}{dt} = k_d D_2(t) \quad (4)$$

where $\Omega(x,x')$ represents the symmetric stoichiometric kernel representing a reaction in which a molecule of molecular weight $x$ breaks into two progenies of molecular weights $x'$ and $x - x'$. The stoichiometric kernel for scission occurring at mid-chain, as in ultrasonic degradation, is given by the Dirac delta function:[13] $\Omega(x,x') = \delta(x - x'/2)$.

The initial conditions for eqs. (1)–(4) are $p(x,t = 0) = p_0(x)$, $r(x,t = 0) = 0$, and $D_2(t = 0) = D_{20}$ (where $D_{20}$ is the initial initiator concentration). Reaction (I) is necessary for the complete mechanism, but its effect on the overall reaction is negligible and can be neglected according to the long-chain reaction approximation.[14,15] The rate coefficients for hydrogen abstraction, $k_h$ and $k_H$, are assumed to be independent of the molecular weight.[11] $k_s(x)$ is assumed to be a linear function of $x$: $k_s(x) = \kappa_s(x - x_l)$. This relationship ensures that the rate coefficient becomes zero when the molecular weight reaches $x_l$, and no further degradation takes place.

Applying the moment operation $f^n(t) = \int_0^\infty x^n f(x,t)dx$ to eqs. (1–3), we obtain the following:

$$\frac{dp^{(n)}(t)}{dt} = -k_h p^{(n)}(t) + k_H r^{(n)}(t) - k_D D^*(t)p^{(n)}(t)$$
$$+ \frac{\kappa_S}{2^n}[r^{(n+1)}(t) - x_l r^{(n)}(t)] \quad (5)$$

$$\frac{dr^{(n)}(t)}{dt} = k_h p^{(n)}(t) - k_H r^{(n)}(t) + k_D D^*(t)p^{(n)}(t)$$
$$- \kappa_s[r^{(n+1)}(t) - x_l r^{(n)}(t)] + \frac{\kappa_S}{2^n}[r^{(n+1)}(t) - x_l r^{(n)}(t)] \quad (6)$$

$$\frac{dD^*(t)}{dt} = 2k_d D_2(t) - k_D D^*(t)p^{(0)}(t) \quad (7)$$

The zero and first moments, $p^{(0)}(t)$ and $p^{(1)}(t)$, represent the molar and mass concentrations, respectively. The initial conditions for the moments are $p^{(0)}(t = 0) = p_0^{(0)}$, $r^{(0)}(t = 0) = 0$, and $D_2(t = 0) = D_{20}$. For $n = 0$, eqs. (5) and (6) become

$$\frac{dp^{(0)}(t)}{dt} = -k_h p^{(0)}(t) + k_H r^{(0)}(t) - k_D D^*(t)$$
$$+ \kappa_s[r^{(1)}(t) - x_l p^{(0)}(t)] \quad (8)$$

$$\frac{dr^{(0)}(t)}{dt} = k_h p^{(0)}(t) + k_H r^{(0)} + k_D D^*(t)p^{(0)} \quad (9)$$

If we apply the quasi-steady-state assumption, the rate of change of polymer radicals can be neglected because their concentration is extremely small.[12] Thus, $\frac{dr^{(0)}(t)}{dt} = 0$, which gives

$$r^{(0)} = \frac{k_h + k_D D^*(t)}{k_H} \quad (10)$$

Equation (4) with the initial condition $D_2(t = 0) = D_{20}$ yields $D_2(t) = D_{20}\exp[-k_d t]$. Substituting this in eq. (7) gives

$$\frac{dD*(t)}{dt} = 2k_d D_{20}\exp(-k_d t) - k_D D^*(t)p^{(0)} \quad (11)$$

Because the second term in eq. (11) is very small, it can be neglected, and the equation can be solved with the initial condition $D^*(t = 0) = 0$ to obtain the following:

$$D^*(t) = 2D_{20}[1 - \exp(-k_d t)] \quad (12)$$

Equations (8) and (10) are solved to obtain

$$\frac{dp^{(0)}(t)}{dt} = \kappa_s[r^{(1)}(t) - x_l p^{(0)}(t)] \quad (13)$$

Because $\frac{dr^{(1)}(t)}{dt} = 0$,

$$r^{(1)}(t) = \frac{[k_h + k_D D^*(t)]}{[k_H - \frac{\kappa_s x_l}{2}]}p^{(1)}(t) - \frac{\kappa_s}{2[k_H - \frac{\kappa_s x_l}{2}]}r^{(2)}(t) \quad (14)$$

As $r^{(2)}(t)$ is assumed to be small and the second term is neglected in the expression for $r^{(1)}(t)$, eq. (14) reduces to

$$r^{(1)}(t) = \frac{[k_h + k_D D^*(t)]}{k_H[1 - \frac{\kappa_s x_l}{2k_H}]}p^{(1)}(t) \quad (15)$$

As $t \rightarrow \infty$, $M_n \rightarrow x_l$, and this implies $\frac{\kappa_s x_l}{2k_H} \ll 1$; the simplified expression for $r^{(1)}(t)$ is

$$r^{(1)}(t) = \frac{[k_h + k_D D^*(t)]}{k_H} p^{(1)}(t) \quad (16)$$

Using $r^{(1)}(t)$ and $D^*(t)$ in eq. (13) yields

$$\frac{dp^{(0)}(t)}{dt} = [k_1 + 2k_2 D_{20}(1 - \exp(-k_d t))][p^{(1)}(t) - x_l p^{(0)}(t)] \quad (17)$$

where $k_1 = \frac{\kappa_s k_h}{k_H}$ and $k_2 = \frac{\kappa_s k_D}{k_H}$. Equation (17) can be solved with the initial condition $p^{(0)}(t = 0) = p_0^{(0)}$ to give

$$p^{(0)}(t) = \frac{p^{(1)}(t)}{x_l} + \left[ -\frac{p^{(1)}(t)}{x_l} + p_0^{(0)} \right]$$
$$\times \exp\left[ -\left\{ k_1 x_l t + \frac{2x_l D_{20} k_2}{k_d}(-1 + k_d t + \exp(-k_d t)) \right\} \right] \quad (18)$$

Equation (18) can be rewritten as

$$\ln Y = k_1 x_l t + \frac{2x_l D_{20} k_2}{k_d}[-1 + k_d t + \exp(-k_d t)] \quad (19)$$

$$Y = \frac{\left( \frac{1}{x_l} - \frac{1}{M_{n0}} \right)}{\left( \frac{1}{x_l} - \frac{1}{M_n} \right)} \quad (20)$$

where $M_n \left( = \frac{p_0^{(1)}}{p^{(0)}} \right)$ and $M_{n0}$ represent the number-average molecular weights at time $t$ and time $t = 0$, respectively, and $k_d$ is the initiator decomposition rate coefficient. In the absence of a persulfate initiator, $D_{20} = 0$, and eq. (19) reduces to

$$\ln Y = k_1 x_l t \quad (21)$$

## RESULTS AND DISCUSSION

Equation (19) gives the relationship between $M_n$ and the sonication time in terms of $M_{n0}$, $x_l$, $D_{20}$, and $k_d$. This equation gives the effect of the initiator concentration on the ultrasonic degradation of PAA. Equation (19) reduces to eq. (21) for cases in which the initiator has not been used, that is, $D_{20} = 0$.

To study the effect of temperature on the ultrasonic degradation of PAA with time, PAA was degraded in water at 25, 40, 50, and 60°C. The experimental data were plotted as the variation of $M_n$ with time [Fig. 1(a)] and as $\ln Y$ with the sonication time [Fig. 1(b)]. In both figures, the lines represent the model prediction. In all cases modeled in this study, the regression coefficient is higher than 0.95. However, in some figures, the plot of $\ln Y$ with the sonication time is not linear at long times. This is because at long reaction times, $M_n$ approaches $x_l$, the
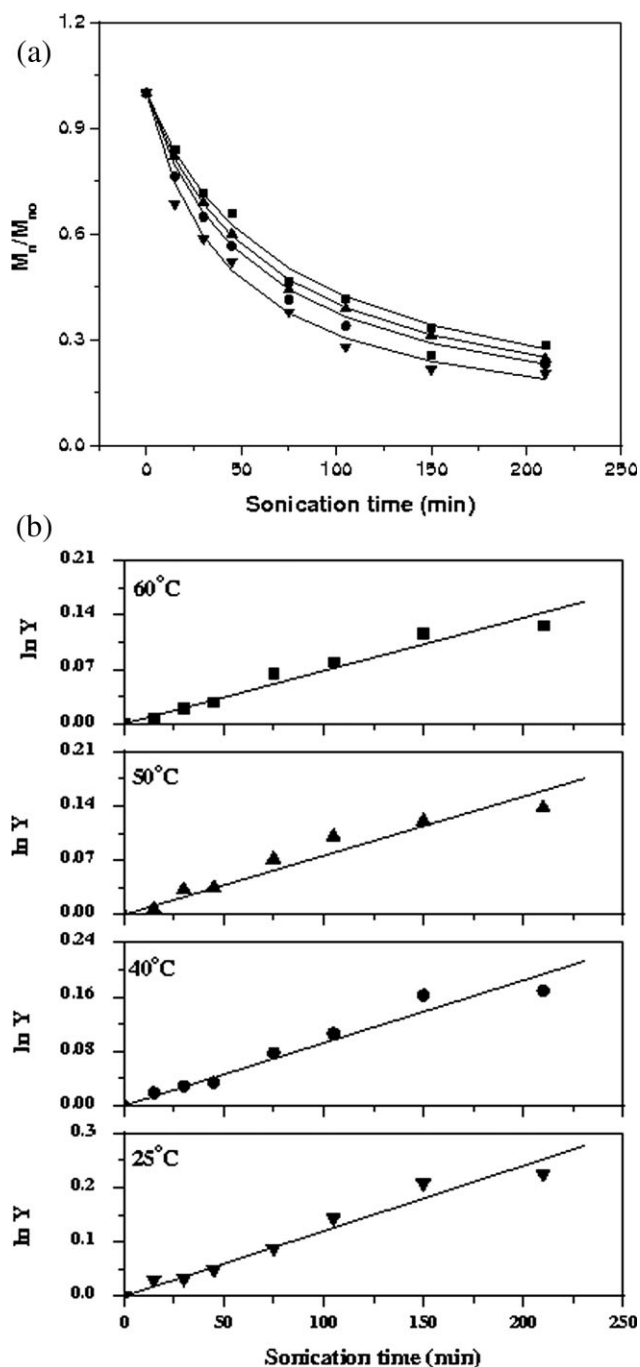
**Figure 1** Variation of (a) $M_n/M_{n0}$ and (b) $\ln Y$ with the sonication time for PAA in water at (▼) 25, (●) 40, (▲) 50, and (■) 60°C. The lines represent the model prediction.

denominator of eq. (20) approaches zero, and the expression approaches infinity. The variation of $\ln Y$ with time is nearly linear, as suggested by eq. (21). The degradation rate coefficient ($k_1$) was obtained by the division of the slope of the regressed line with $x_l = 20,000$. The values of $k_1$ thus obtained are 6.00, 4.60, 3.80, and 3.40 $\times 10^8$ mol g$^{-1}$ min$^{-1}$ for 25, 40, 50, and 60°C, respectively.

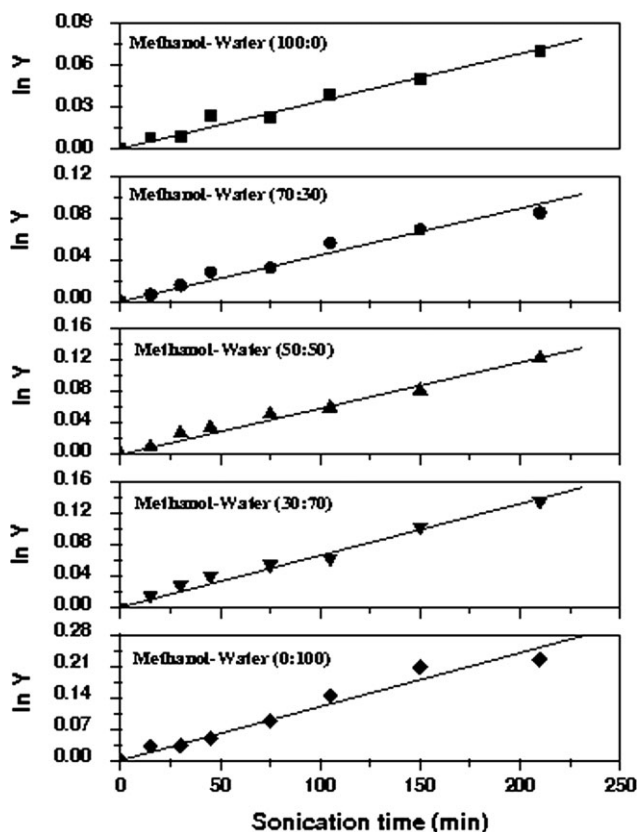The effects of different compositions of methanol/ water binary mixtures as solvents on the ultrasonic

**Figure 2** Variation of ln $Y$ with the sonication time for PAA at 25°C in binary mixtures of methanol and water (vol/vol): (■) 100/0, (●) 70/30, (▲) 50/50, (▼) 30/70, and (◆) 0/100.

tion zone and the effect of the vapor pressure. The former accelerates the degradation rate, whereas the latter slows the degradation rate. The relative magnitude of these opposing factors ultimately dictates how the degradation rate varies with the temperature. However, the effect of vapor pressure dominates at temperatures[16] above 25°C, and the degradation rate decreases with increasing temperature, as observed in this study. The observed reduction in the degradation rate coefficients with increasing temperature is in accordance with that observed for the degradation of polyacrylamide,[17] poly(ethylene oxide)[17] poly(vinyl chloride),[18] poly (vinyl acetate),[18] and poly(n-butyl acrylate).[11]

The increase in the degradation rate with the increase in the water content of the binary water/methanol mixture can be attributed to the change in the vapor pressure of the solution. These observations are in agreement with the ultrasonic degradation of poly(ethylene oxide) in methanol/water and acetonitrile/water binary mixtures in which the degradation rate coefficients decreased with a reduction in the vapor pressure of the binary mixture solvents.[4] The ultrasonic degradation of poly(n-butyl methacrylate),[11] poly(vinyl acetate),[19] and poly (methyl methacrylate)[20] has been investigated in several solvents, and it was determined that as the vapor pressure of the solvent increased, the degradation rate coefficients decreased. The vapor pressures for methanol/water binary mixtures at 25°C and for water at various temperatures were obtained from the literature.[21,22] The variation of the degradation rate coefficients with the vapor pressure is shown in
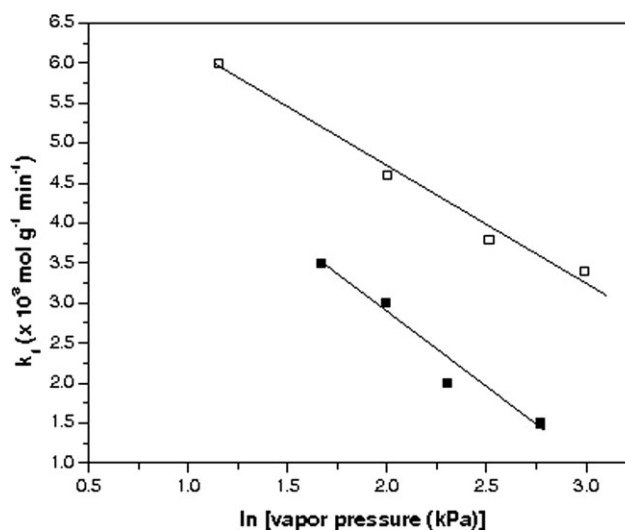
degradation of PAA were investigated. Figure 2 shows the effects of different methanol/water binary mixtures on $k_1$. The values of $k_1$ obtained from Figure 2 for methanol/water (100/0, 70/30, 50/50, 30/70, and 0/100 v/v) at 25°C are 1.70, 2.23, 2.94, 3.30, and 6.00 $\times 10^8$ mol g$^{-1}$ min$^{-1}$.

Two conclusions can be drawn from these effects. Increasing the temperature leads to lower degradation rates. Similarly, increasing the methanol content in the binary methanol/water mixture leads to lower degradation rates. The cavitation in a liquid system is affected by the surface tension, vapor pressure, and viscosity. An increase in the temperature results in the reduction of the cavitation threshold, as it leads to a decrease in the surface tension and viscosity of the solvent. This lowering of the cavitation threshold leads to ease of cavity formation, making higher temperatures favorable for degradation. However, as the vapor pressure increases with temperature, the cushioning effect of increased vapor pressure at a higher temperature leads to a reduction of the cavitation intensity and hence in the degradation rate. The effect of temperature is influenced by two distinct factors, the size of the active cavita-



**Figure 3** Variation of $k_1$ with the vapor pressure. The solid symbols in the figure refer to the variation of the rate coefficients with the vapor pressure at different methanol/water compositions, whereas the open symbols refer to the variation of the rate coefficients with the vapor pressure at different temperatures.
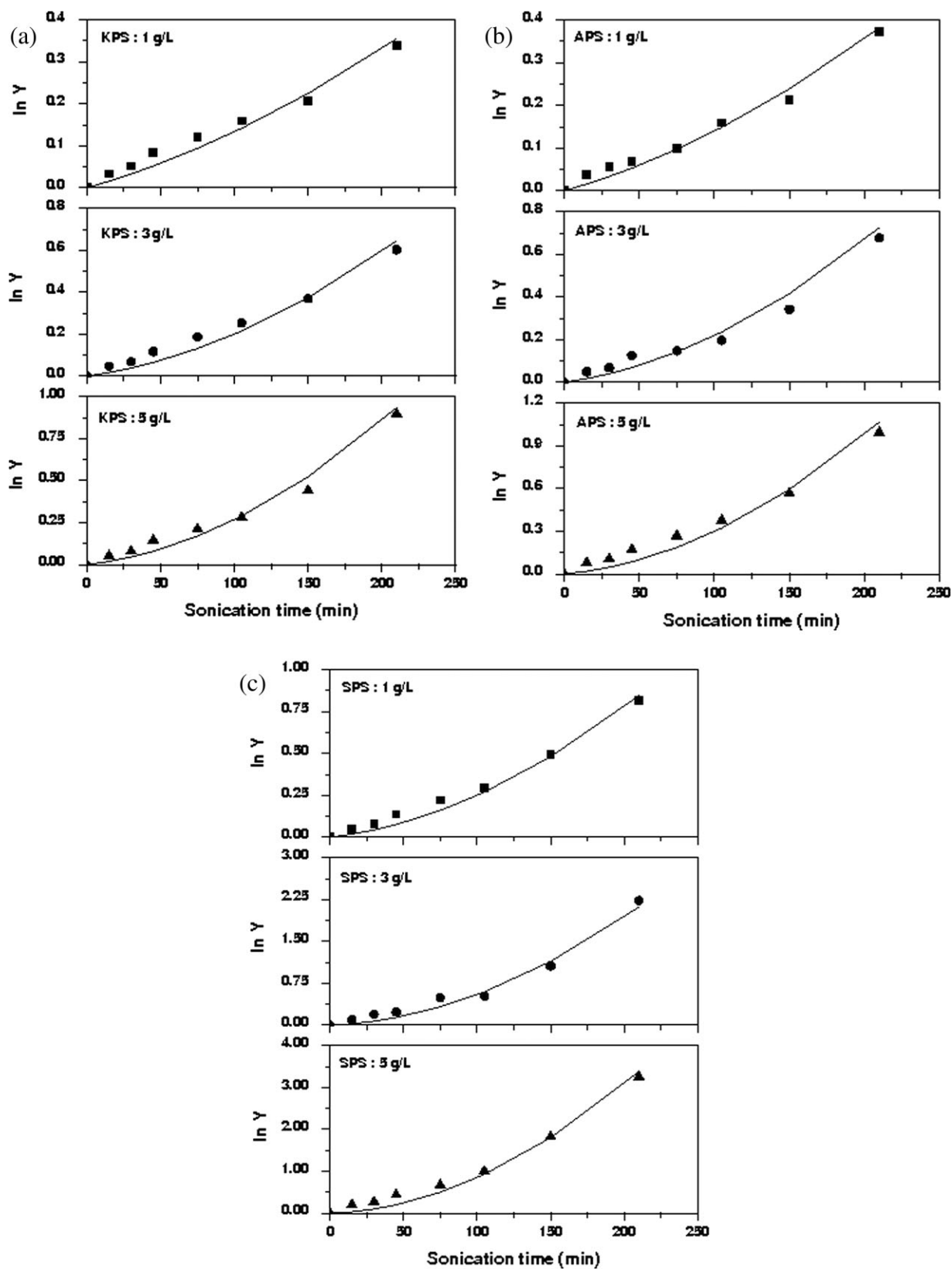
**Figure 4** Variation of ln $Y$ with the sonication time (min) for PAA in water at 25°C with (a) KPS concentrations of (■) 1, (●) 3, and (▲) 5 g/L, (b) APS concentrations of (■) 1, (●) 3, and (▲) 5 g/L, and (c) SPS concentrations of (■) 1, (●) 3, and (▲) 5 g/L.

Figure 3. The variations with the temperature and solvent are both linear, but they do not follow the same linearity because other properties such as the viscosity and surface tension also play a role in determining the rate coefficients.

Our next study examined the effects of oxidizers (persulfates) on the degradation rate. The model equation [eq. (20)] indicates that the value of the decomposition rate constant of the persulfates needs to be known. Price and Clifton[23] investigated the sonochemical decomposition of KPS, and the first-order decomposition rate constant ($k_d$) at 25°C was $5.1 \times 10^{-4}$ min$^{-1}$. Schneider et al.[24] studied the decomposition of APS, compared their results with the decomposition of KPS investigated by Santos et al.,[25] and found that the rate coefficients for decomposition were similar for APS and KPS. Henton et al.[26] examined the decomposition of SPS and found that the decomposition rate was approximately twice that of KPS reported by Kolthoff and Miller.[27] From these studies, the $k_d$ values for KPS, APS, and SPS were determined to be $5.1 \times 10^{-4}$, $5.1 \times 10^{-4}$, and $1.02 \times 10^{-3}$ min$^{-1}$, respectively.

Figure 4(a–c) shows the effects of different concentrations of KPS, APS, and SPS on the ultrasonic degradation of PAA in water at 25°C. The values of the degradation rate coefficient of PAA in the presence of persulfate ($k_2$) were determined from the parametric fit of the model [eq. (19)] with experimental data. $k_2$ was predicted to be $9.0 \times 10^{-5}$, $9.0 \times 10^{-5}$, and $1.8 \times 10^{-4}$ L min g$^{-1}$ for KPS, APS and SPS, respectively. This implies that the polymer degraded more in the presence of the initiator with the higher $k_d$ value. It was determined that the value of $k_2/k_d$ was 0.176 L min$^2$ g$^{-1}$ in all cases, and the degradation of PAA was enhanced by an increase in the concentration of the initiator. This effect can be attributed to the formation of polymer radial R*($x$) in reaction (V) of the proposed mechanism, which further breaks into P($x'$) and R*($x - x'$) in the depropagation step. This is in contrast to previous studies[10,11] in which the effect of the initiator reduces the degradation rate of the polymer. From this study, it can be concluded that the effect of the initiator (oxidizer/persulfate) on the ultrasonic degradation rate of the polymer depends on the particular system. However, interestingly, the value of $k_2/k_d$ is invariant with the persulfate used.

## CONCLUSIONS

The ultrasonic degradation of PAA has been investigated in the presence of different oxidizing agents (KPS, APS, and SPS) at 25°C, at different temperatures, and in various methanol/water binary solvent mixtures. Continuous distribution kinetics has been applied to model the experimental data and determine the rate coefficients. The rate of degradation of PAA decreased with an increase in the temperature and with an increase in the vapor pressure of the methanol/water binary solvent mixtures. The degradation of PAA increased with the increasing concentration of the oxidizing agents in all cases. The highest degradation rate was observed with SPS, which had the highest degradation rate constant of the persulfates, whereas the degradation rate was the same for KPS and SPS, which had very similar degradation rate constants. The ratio of the degradation rate of the polymer to the degradation rate of the persulfate was constant, and this indicates that the degradation rate of the polymer can be determined *a priori* when the dissociation rate of the persulfate is known.

## References

1. Price, G. J.; Smith, P. F. Polym Int 1991, 24, 159.
2. Price, G. J.; Smith, P. F. Eur Polym J 1993, 29, 419.
3. Price, G. J. In Advances in Sonochemistry; Mason, T. J., Ed.; Jai: Cambridge, United Kingdom, 1990; Vol. 1, p 231.
4. Vijayalakshmi, S. P.; Madras, G. Polym Degrad Stab 2005, 90, 116.
5. Price, G. J.; Smith, P. F. Polymer 1990, 34, 4111.
6. Basedow, A. M.; Ebert, K. H. Adv Polym Sci 1977, 22, 83.
7. Pokhrel, M. R.; Bossmann, S. H. J Phys Chem B 2000, 104, 2215.
8. Yang, S.; Fu, Y.; Jeong, S. H.; Park, K. J. Pharm Pharmacol 2001, 56, 429.
9. Carretti, E.; Dei, L.; Baglioni, P. Prog Colloid Surf Sci 2004, 123, 280.
10. Madras, G.; Chattopadyay, S. Polym Degrad Stab 2001, 73, 33.
11. Mahalik, J. P.; Madras, G. Ind Eng Chem Res 2005, 44, 6572.
12. Kodera, Y.; McCoy, B. J. AIChE J 1997, 43, 3205.
13. McCoy, B. J. AIChE J 1993, 39, 1827.
14. Gavalas, G. R. Chem Eng Sci 1996, 21, 133.
15. Nigam, A.; Fake, D. M.; Klein, M. T. AIChE J 1994, 40, 908.
16. Raman, V.; Abbas, A. Ultrason Sonochem 2008, 15, 55.
17. Vijayalakshmi, S. P.; Madras, G. Polym Degrad Stab 2004, 84, 341.
18. Chattopadhyay, S.; Madras, G. J Appl Polym Sci 2003, 88, 2818.
19. Chattopadhyay, S.; Madras, G. Polym Degrad Stab 2001, 71, 273.
20. Madras, G.; Karmore, V. Polym Int 2001, 50, 683.
21. Gmehling, J.; Onken, U.; Arit, W. Vapor Liquid Equilibrium Data Collection; DECHEMA Chemistry Data Series; DECHEMA: Frankfurt, Germany, 1977; Vol. 1, Part 1.
22. Kurihara, K.; Minoura, T.; Takeda, K.; Kojima, K. J Chem Eng Data 1995, 40, 679.
23. Price, G. J.; Clifton, A. Polymer 1996, 37, 3971.
24. Schneider, M.; Graillat, C.; Boutti, S.; McKenna, T. F. Polym Bull 2001, 47, 269.
25. Santos, A. M.; Vindevoghel, P. H.; Graillat, C.; Guyot, A.; Guillot, J. J Polym Sci Part A: Polym Chem 1996, 34, 1271.
26. Henton, D. E.; Powell, C.; Reim, R. E. J Appl Polym Sci 1997, 64, 591.
27. Kolthoff, I. M.; Miller, I. K. J Am Chem Soc 1951, 73, 3055.