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## Kinetics of sonodegradation of poly(acrylic acid co acrylamide) hydrogels by viscometry

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### ABSTRACT

In this work ultrasonic degradation of one commercially important hydrogel based on acrylic acid and acrylamide was carried out in aqueous solution at room temperature (25°C). Also, the effect of power and pulse on the rate of degradation was investigated. A method of viscometry was used to study the degradation behavior of the hydrogel and a first order kinetic equation was employed to calculate the degradation rate constants. The experimental results indicated that the rate of ultrasonic degradation increased with increasing ultrasonic power and pulse. The degradation proceeds by mechanical forces and also involves radical scission mechanism.

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### KEYWORDS

Sonication;  
Degradation;  
Hydrogel;  
Viscosity;  
Kinetics.

### INTRODUCTION

For certain applications, polymers with lower molecular mass have advantages over the high molecular mass candidates due to their improved diffusion into biological tissues. Shortening of the macromolecular chains can be achieved by various methods such as thermal, photo and catalytic degradation<sup>[1-3]</sup>. The methods like UV<sup>[4-8]</sup>, gamma radiation<sup>[8,9]</sup>, microwave<sup>[9,10]</sup> are also important. Polymers can be degraded thermally by pyrolysis, But the process consumes much energy. Ultrasound, photo and chemical methods require less energy for polymer degradation. Further, interaction between them and the polymeric systems can help find the degradation pathways or mechanisms<sup>[3-5,11-13]</sup>. Many Scientists have investigated the ultrasound

degradation of polymers. The effects of various parameters like ultrasound pulse and intensity, frequency, temperature, vapor pressure, volume, solvent, dissolved gases, molecular weight and polymer concentration on the ultrasonic degradation of polymers have been investigated<sup>[2,5,7-9,11-23]</sup>.

One of the unique feature of ultrasonic degradation is the fact that, in contrast to all chemical and thermal decomposition reactions, the ultrasound depolymerization is a non-random process which produces fragmentation at the mid-point of the chain. The existence of certain and limiting molecular weight, below which ultrasonic degradation does not take place, has the additional effect in which the initial molecular weight distribution is broad and then becomes narrow during degradation<sup>[13-15,21-25]</sup>. For any polymer degradation pro-

## Microreview

cess to become acceptable to industry, it is important to be able to specify the sonication conditions to produce a particular relative molecular mass distribution.

Acrylic acid (AA) and acrylamide (AAM) are two water-soluble important monomers in industry that the research work on their polymers and gels and some another hydrogels in solution mainly focused on following categories:

- Synthesis and gelation, without ultrasound<sup>[3,26-33]</sup> and in the presence of ultrasound<sup>[33-36]</sup>
- Degradation, without ultrasound<sup>[4,37,38]</sup> and in the presence of ultrasound<sup>[5,7,8,12,17,24]</sup>
- Swelling and degradation, without ultrasound<sup>[39-41]</sup> and in the presence of ultrasound<sup>[6]</sup>

The hydrogels based on acrylic acid and acrylamide are important commercial polymeric gels. Although their sonochemical polymerization has been reported<sup>[33-35]</sup>, but ultrasonic degradation have not been investigated. The purpose of this study is to present new experimental data for the ultrasonic degradation of these hydrogels in water. The effectiveness of the ultrasonic process has been evaluated by measuring the changes in viscosity. It is shown that the rate of ultrasonic degradation of the hydrogels follows a first order dependency of the viscosity with irradiation time. The effects of other parameters such as concentration, external pressure, temperature, volume and solvent will be carried out in the next work.

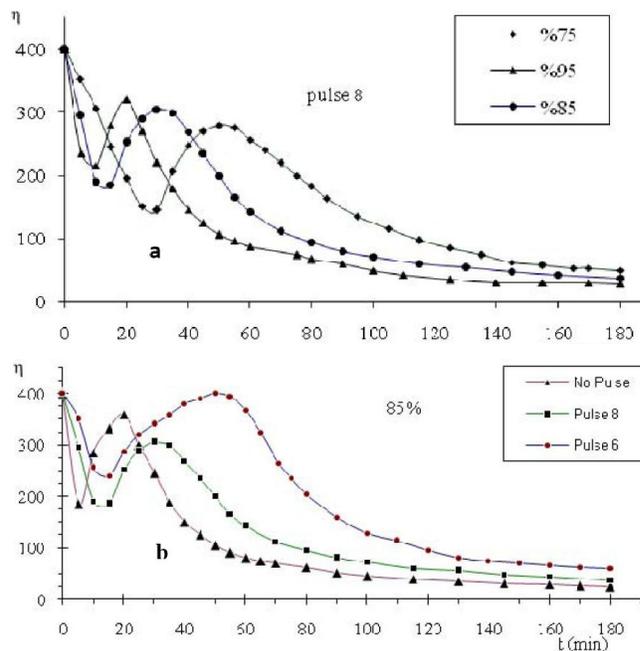
## RESULTS AND DISCUSSION

### Effect of ultrasonic waves on the viscosity

The ultrasonic degradation is a fluid mechanical process, thus viscosity of the solvent plays an important role in determining the degradation rate. It was not observed any appreciable degradation under pulse 5 and power 70%. Figure 1 shows the changes in viscosity  $\eta_r$  which have been observed by sonicating of the hydrogel solution after gelatinization. In order to study the effects of ultrasonic irradiation time on the degradation of hydrogel, viscosities at the various cycles and powers were also measured. Some data are shown in Figure 1.

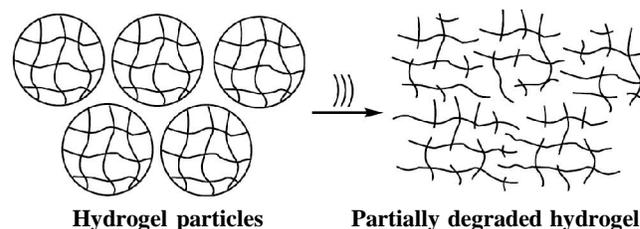
It is clear that  $\eta_r$  greatly decreases at the beginning, then increases with the irradiation time, and finally decreases toward a limited and constant value, which is

sometimes the characteristic of mechanochemical degradation of the polymers in aqueous solutions. The increase in viscosity after the initial decrease was not adequately explained in literature. We propose the following reason for this observation.



**Figure 1 : Viscosity variations with irradiation time in different powers in pulse 8 (a) and in different pulses in power 85% (b).**

As shown in Figure 2, it seems that partial degradation of the hydrogel increases the contact surface of the hydrogel particles and the chain of polymer can interpenetrated to each other more intensely.



**Figure 2 : A diagrammatic description of gelatinization and partially degradation of hydrogel by ultrasound**

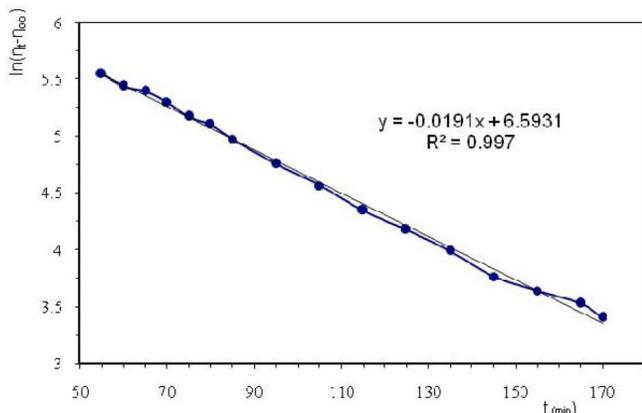
It can be deduced that there is a limiting molecular weight that below which chain scission does not occur. The viscosity limit of the hydrogel solution was about 38 in 25°C. Below the limit, the polymer chain was so short that cleavage at the center of the molecule did not take place anymore<sup>[21-23]</sup>. At the end of the ultrasonic treatment, the viscosity is near to that of water (about 10 mPa s).

### Ultrasonic degradation kinetics (reaction order and rate constants)

Ultrasonic irradiations to hydrogel aqueous solutions lead to the first-order reaction (for reduction part, after climax) as shown in Figure 3. The rate constants were deducted from the slopes of curves issued from equation 2<sup>[13,16]</sup>.

$$\ln\left(\frac{\eta_t - \eta_{oo}}{\eta_o - \eta_{oo}}\right) = -kt \quad (2)$$

where  $k$  is the rate constant,  $\eta_o$  the initial hydrogel viscosity (400 mPa s),  $\eta_t$  its value at later times and  $\eta_s$  the final hydrogel viscosity. Rate constants of sonodegradation listed in TABLE 1, ranged from 0.762 h<sup>-1</sup> (power 75% and pulse 6) to 1.806 h<sup>-1</sup> (power 95% and no pulse). The average experimental error was about 3% according to the standard deviations of the slopes.



**Figure 3 :** The plot of  $\ln(\eta_t - \eta_s)$  versus sonication time for hydrogel degradation (power 75% and pulse 8).

**TABLE 1 :** The relationships between the calculated rate constant  $k$  (h<sup>-1</sup>) with power and pulse of ultrasound

	Power 75%	Power 85%	Power 95%
No pulse	1.234	1.476	1.806
Pulse 8	1.046	1.134	1.230
Pulse 6	0.762	1.068	1.108

### Effect of power on the rate of degradation

The effect of ultrasound intensity on the ultrasonic degradation of the hydrogel was investigated. The data listed in Figure 1a shows that the increment of the ultrasonic intensity reduces intrinsic viscosity of the hydrogel more rapidly, indicating that the extent of degradation of hydrogel increases with the increment of ultrasonic intensity. The rate of changes in viscosity becomes faster with increasing the power of ultrasonic radiation.

TABLE 1 show that the degradation rate coefficient of the hydrogel increases with increasing in ultrasound intensity, as reported for other polymers<sup>[24,33]</sup>. The relationship between the degradation rate coefficient and intensity is linear as observed in Figure 3 and in the other studies. This is because an increase in intensity leads to formation of further number of the cavitation bubbles. Above the cavitation threshold, the bubble reaches the maximum radius, and the radius is proportional to the square root of intensity<sup>[43,44]</sup>. The larger cavitation bubbles collapse and produce high shear forces, so the gel degrades faster at higher intensities.

### Effect of the pulse on the rate of degradation

The data listed in TABLE 1 and Figure 1b show that the extent of degradation of the hydrogel increases with the rise of ultrasonic pulse. With increasing the ultrasonic pulse, the rate of changes in viscosity becomes faster (similar behavior was observed for the increasing in ultrasonic power as mentioned in previous section).

Pulse 5 means in any 1 second, 0.5 sec irradiate and 0.5 sec keep silent, no pulse is related to full irradiation and so on. Pulse makes irradiation time be different from degradation reaction time. On the other hand, when the pulse is different, the irradiation time is different, even if the reaction time is the same. Pulse allows the reaction mixture to cool down.

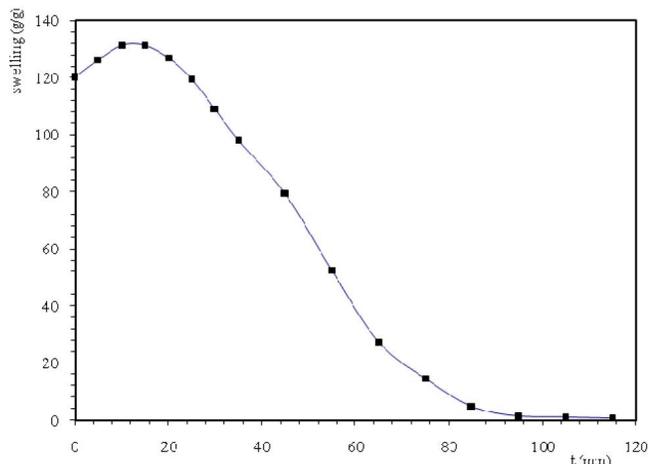
### Swelling properties

The swelling capacity was investigated as a function of ultrasonic exposure time. Swelling of a sample (intensity 85% and pulse 8) was measured at mentioned time intervals and the results are shown in Figure 4. According to this figure, the absorbency is increased by passing the time from 0 up to 15 min and, then, it decreases considerably with a further increase in the time of ultrasonic exposure. The maximum absorbency (130 g/g) is obtained in 15 min, where viscosity was minimum (figure 1). Similar variations was observed in degradation behavior of dextran hydrogels composed of positively and negatively charged microspheres<sup>[38]</sup>.

The initial increase in swelling capacity can be attributed to the degradation of some crosslinkers which lead to a hydrogel network with low density of cross linking (figure 2). As a result swelling capacity increases. The swelling decrease after the maximum can be attributed to the ultrasonic degradation of the hydrogel net-

## Microreview

work. At first, methylene bisacrylamide can be attacked by a nucleophile such as water under ultrasonic conditions. Then, reduction of the polymer molar mass is done with further irradiation. Finally, swelling decreases toward a limited and constant value. Almost all of the degraded samples passed through the tea bag and swelling becomes zero.



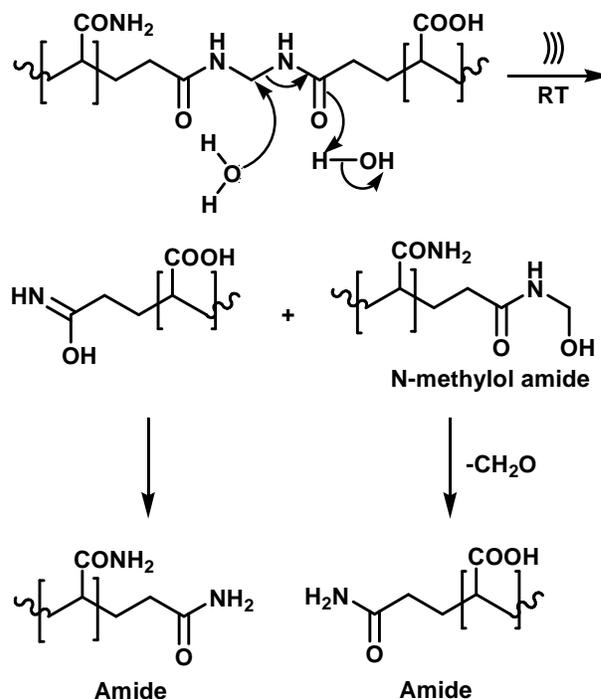
**Figure 4 :** Swelling of the hydrogel as a function of ultrasonic exposure time (intensity 85% and pulse 8)

### Degradation reaction and mechanism

To find the hydrogel degradation mechanism, chemical structure of the gel and crosslinker (MBAAm) is considered. It was reported that methylenebisacrylamide was hydrolytically unstable<sup>[45]</sup>. In this molecule, two electronegative atoms are bonded to a carbon atom. The methylene group has a relatively positive charge. So under normal conditions it can be attacked easily by a nucleophile such as water molecule. The reaction is catalyzed and progressed more easily by ultrasonic radiation.

Methylenebisacrylamide in the midpoints and other point of the polymer chains are considered as the positions of initial and the next chain scission, respectively. This process shows approximately a wide molecular weight distribution under ultrasonic irradiation. When molecular weight of the polymer decreases to a limiting value, the stress induced by the deformation of chain is not enough to break down chemical bond, and mechanical degradation stops. The shear forces generated by the rapid motion of the solvent are responsible for the breakage of the chemical bonds within the polymer<sup>[46]</sup>. In the case of diluted aqueous solutions of the hydrogel, hydroxyl and hydrogen radicals are able to

abstract hydrogen atoms from the gel structure. Thus, macroradicals are formed. Subsequent reactions of macroradicals can be: chain scission, hydrogen transfer, inter- and intramolecular recombination and finally disproportionation of macroradicals<sup>[13,16,33,35]</sup>. The effect of chain scission can be followed by a reduction in the molecular weight of the polymer. Accordingly, ultrasonic degradation of hydrogel can be represented by the following mechanism (figure 5).



**Figure 5 :** Schematic representation of ultrasonic degradation of the crosslinked hydrogel

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