Ultrasonic Degradation of Solutions of Poly(vinyl acetate) in Tetrahydrofuran

Mohammad Taghi Taghizadeh, Abbas Mehrdad

Physical Chemistry Department, Chemistry Faculty, Tabriz University, Tabriz, Iran

ABSTRACT: The ultrasonic degradation of poly(vinyl acetate) (PVAc) solutions was carried out in tetrahydrofuran (THF) at 20, 25, 30, and 35°C to investigate the effects of the temperature and solution concentration on the rate of degradation. The degradation kinetics were studied with viscometry. The calculated rate constants indicated that the degradation rate of the PVAc solutions decreased as the temperature and solution concentration increased. The calculated rate constants were correlated in terms of the concentration, temperature, vapor pressure of THF, and relative viscosity of the PVAc solutions. This degradation behavior was interpreted in terms of the vapor pressure of THF and the viscosity and concentration of the polymer solutions. With increasing temperature, the vapor pressure of the solvent increased, and so the vapor entered the cavitation bubbles during their growth. This caused a reduction in the 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 decreased. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 96: 2373–2376, 2005

Key words: degradation; kinetics (polym.); modeling; viscosity

INTRODUCTION

The degradation of polymers can occur because of heat, light, chemical reagents, or ultrasonic radiation.[1] Ultrasound has been used for the degradation of a wide range of polymers.[2,3] The ultrasonic degradation process has several unique features that distinguish it from thermal or photochemical degradation, such as its nonrandom nature and molecular weight dependence.[4] The scission of a polymer chain in a solution occurs preferentially near the middle of the chain.[5–7] Ultrasonication has been 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.[8] The passage of a longitudinal sound wave through a liquid causes cavitation.[6] The formation, growth, and rapid collapse of microscopic bubbles generate high temperatures and pressures during bubble collapse in the region of several thousand Kelvins and several hundred atmospheres, according to the system.[9] These extreme conditions are primarily responsible for sonochemical reactions. In a dilute solution, the role of the generated heat is probably of minor importance for polymer degradation. Accordingly, because the hot regions are highly localized and should be quenched in less than 1 μs, the polymer molecules do not have time to diffuse and to reach these spots in such a short interval.[9] The motion of the wall of an 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.[6,10,11] The effect of the temperature on the ultrasonic degradation of hyaluronic acid[11] and polybutadiene[12] has been investigated: with increasing temperature, the rate of degradation decreases. The effects of the solvent and stabilizer on the ultrasonic degradation of poly(vinyl acetate) (PVAc) have been investigated also; with increasing vapor pressure (v_p) of the solvent, the rate of degradation decreases.[1,3,13] In a previous work,[14] we studied the ultrasonic degradation of PVAc in dioxane. In the continuation of our research on the ultrasonic degradation of PVAc, we report here the results of the ultrasonic degradation of PVAc in tetrahydrofuran (THF).

In this study, we examined the effects of the temperature and solution concentration on the degradation rate of PVAc in THF. The degradation kinetics were studied via viscometry.[15] This was performed by the correlation of viscosity measurements at different sonication times to the viscosity-average molecular weight (M_v) and number-average molecular weight (M_n). Finally, these quantities were correlated with the molar concentration with a meaningful expression.

Correspondence to: A. Mehrdad (a.mehrdad@tabrizu.ac.ir).

KINETIC MODEL

The rate of degradation is defined as the number of moles of scissions that occur in 1 L at a 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:[15]

$$\frac{dM}{dt} = kM^n \tag{1}$$

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 M. From the experimental data, it is clear that the degradation rate decreases as the solution concentration increases; therefore, n is negative. The solution concentration ($C = $ g L^{-1}) is constant, and the total molar concentration (mol L^{-1}) increases during the degradation of the polymer.

The solution of the differential equation [eq. (1)] is

$$M^{1-n} - M_0^{1-n} = (1-n)kt \tag{2}$$

where M_0 is the initial total molar concentration of the polymer.

By the correlation of the viscosity measurements at different sonication times to M_v and M_n, the molar concentration can be determined as follows:[15]

$$M = \left(\frac{(1+\alpha)\Gamma(1+\alpha)KC^{\alpha+1}}{\sqrt{2}} \right)^{1/\alpha} \Delta\eta \tag{3}$$

where $\Delta\eta$ is equal to $(1/\eta_{sp} - \ln\eta_r))^{1/(2\alpha)}$, $\Gamma(1+\alpha)$ is equal to $\int_0^\infty e^{-t}t^\alpha dt$, and α and K are the Mark–Houwink constants.

The substitution of eq. (3) into eq. (2) yields

$$\Delta\eta^{1-n} - \Delta\eta_0^{1-n} = (1-n)$$
$$\times \left(\frac{\sqrt{2}}{(1+\alpha)\Gamma(1+\alpha)KC^{\alpha+1}} \right)^{(1-n)/\alpha} kt \tag{4}$$

or

$$\Delta\eta^{1-n} - \Delta\eta_0^{1-n} = k't \tag{5}$$

where k' is the apparent degradation rate constant.

EXPERIMENTAL

Materials

PVAc, with an average molecular weight of 140,000 (Aldrich), and THF (Merck) were used without further purification.

Apparatus and procedure

PVAc solutions (10, 20, 30, and 40 g L^{-1}) were prepared gravimetrically with an analytical balance (321-34553, Shimadzu Co., Kyoto, Japan) with a precision of $\pm 1 \times 10^{-4}$ g. Ultrasonic degradation was performed at four different temperatures (20, 25, 30, and 35°C). For the degradation, a 50-cm^3 polymer solution was placed in the jacket flask, and its temperature was controlled within ± 0.5°C by the circulation of thermostated water and sonication for a long time. An ultrasonic generator (UP200 H ultrasonic processor, Dr. Hielscher) with an H3 sonotrode (diameter $= 3$ mm) was used in this experiment. The frequency of the ultrasound was 24 kHz, and the output was set at 150 W.

Periodically, samples of the sonicated solution were removed, and their viscosities were measured with a jacketed Ubbelohde viscometer, the temperature of which was kept at 25 $\pm$ 0.1°C with a temperature controller (Eyela UA-10, Tokyo Rikakiai Co., Tokyo, Japan). For the ready comparison of viscosity changes during sonication, after the removal of the samples (20, 30, and 40 g L^{-1}), they were diluted to 10 g L^{-1}. Next, their viscosities were measured. η_r and η_{sp} were calculated as follows:

$$\eta_r = \frac{t}{t_0}, \quad \eta_{sp} = \eta_r - 1 \tag{6}$$

where t and t_0 are the flow times for the given polymer solution and the solvent, respectively. The flow times for the solutions used in this work were never less than 100 s. The conditions used in this work ($\alpha = 0.7$ and $K = 1.6 \times 10^{-5}$ L g^{-1}) were adopted on the basis of previous findings in the literature.[16]
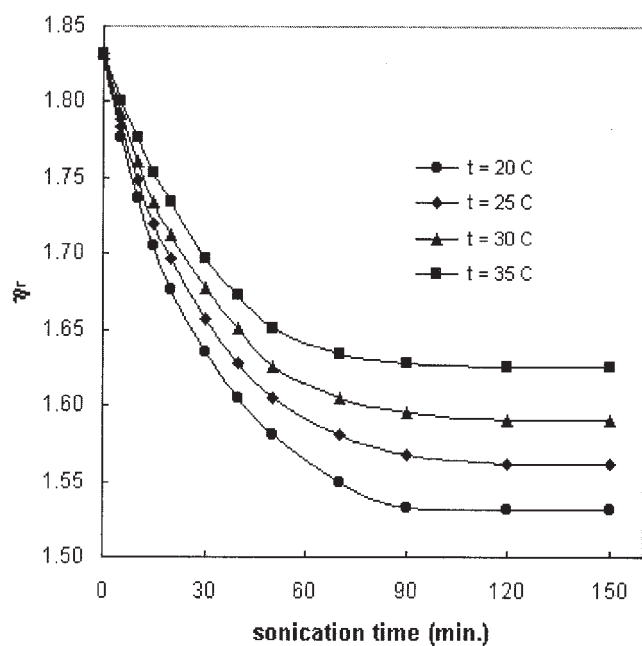
RESULTS AND DISCUSSION

Sonication was carried out for four different PVAc concentrations at 20, 25, 30, and 35°C. The relationships between η_r and the sonication time are presented in Figures 1 and 2. From these findings, it is clear that η_r decreases with the sonication time and tends to have a constant value. It can be deduced that there is a limiting molecular weight below which chain scission does not occur. Under the same conditions, the decrease in η_r of a sample with a high polymer concentration is lower than that of a sample with a low polymer concentration. These results indicate that the extent of degradation is more pronounced under 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 solutions. These findings are consistent with the results of other investigators.[8] Our results indicate that the extent of degradation is more pronounced at low temperatures. This might be be-
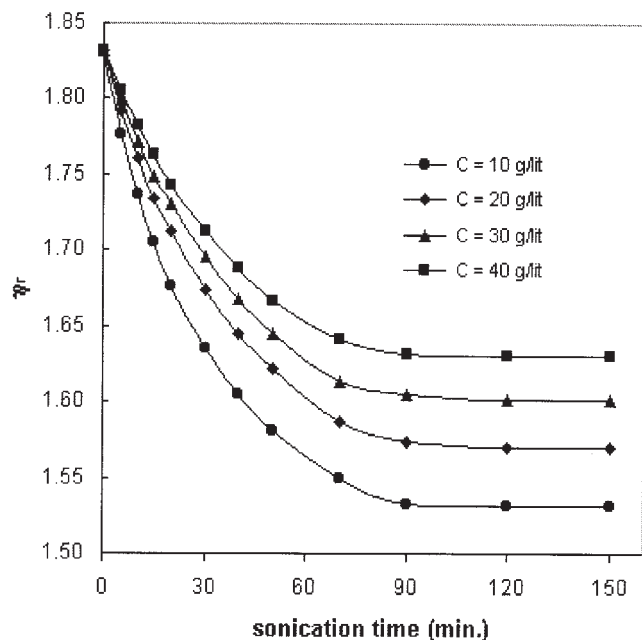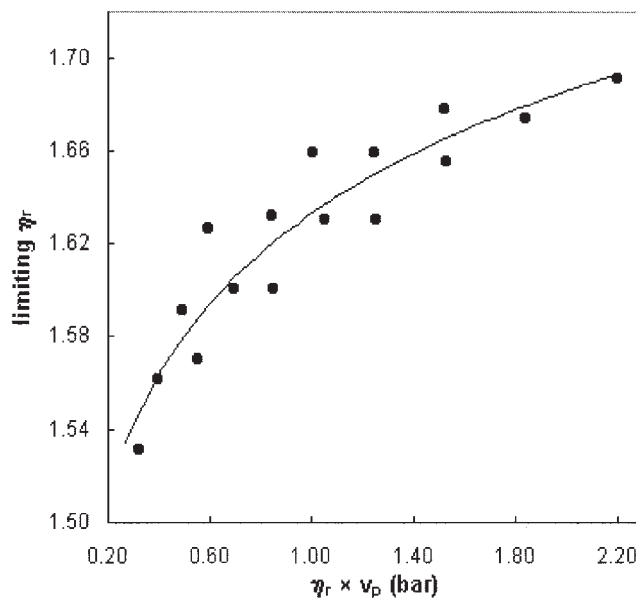
Figure 1 Relationship between η_r and the sonication time at different concentrations at 20°C.

Figure 3 Relationship between the limiting value of η_r and the product of η_r and v_p.

cause, with increasing temperature, v_p of the solvent increases, and so the vapor enters the cavitation bubbles during their growth. This causes a reduction in the collapsing shock because of a cushioning effect; therefore, the extent of degradation is reduced. With increasing temperature, two solution factors, the viscosity and v_p of the solvent, change. The first factor decreases with increasing temperature, and this accel-

erates the rate of degradation. The second factor increases with increasing temperature, and this reduces the rate of degradation. The limiting values of η_r are correlated in terms of the product of η_r and v_p (Fig. 3). Our data indicate that effect of v_p is dominant. The Antoine equation has been used in estimating v_p of THF.[17]

A number of different rate models have been proposed for the degradation of polymers,[3,9] but in this study a simple model has been employed via viscom-

Figure 2 Relationship between η_r and the sonication time at different temperatures with [PVAc] = 10 g/L.
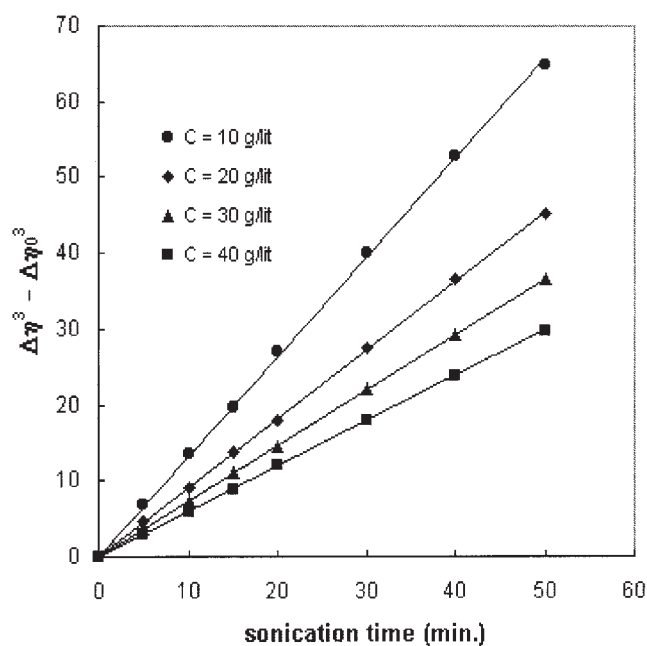
Figure 4 $\Delta\eta^3 - \Delta\eta_0^3$ versus the sonication time at different concentrations at 20°C.
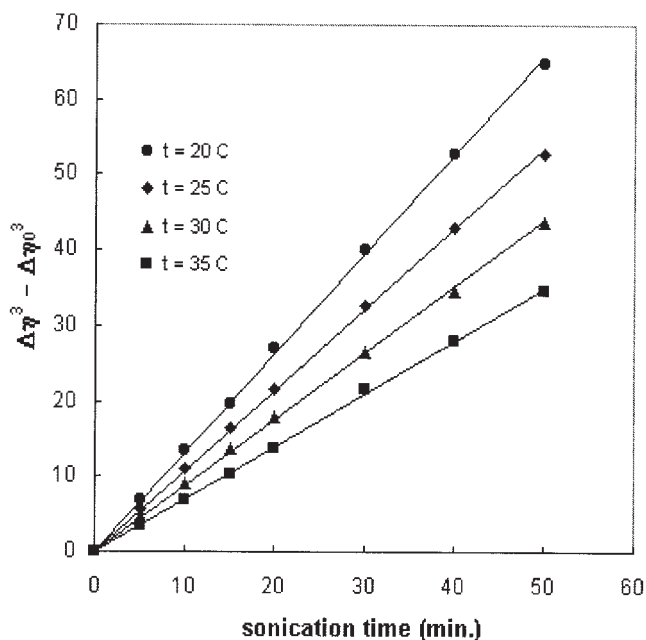
etry.[15] Our data are consistent with eq. (5). By setting the reaction order, with respect to the molar concentration, to -2, we obtain the following:

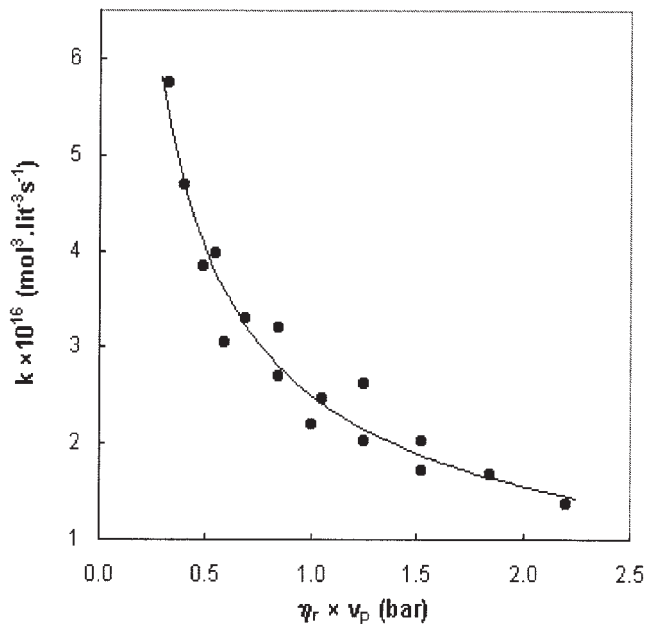$$\Delta \eta^3 - \Delta \eta_0^3 = k't \qquad (7)$$

Plots of $\Delta \eta^3 - \Delta \eta_0^3$ versus the sonication time at different temperatures for different PVAc concentrations are presented in Figures 4 and 5. The apparent degradation rate constant defined in eq. (7) can be estimated from the slopes of the plots in these figures. On this basis, k has been calculated. The calculated values of k indicate that the rate of degradation decreases with increasing concentration and temperature. With increasing solution concentration, the viscosities increase and reduce the shear gradients around the collapsing bubbles; therefore, the degradation rate decreases too. With increasing temperature, v_p of the solvent increases; therefore, the vapor enters the cavitation bubbles during their growth and causes a reduction in the collapsing shock because of a cushioning effect. Consequently, the rate of degradation is reduced. Using the usual Arrhenius treatment produces a linear relation, albeit with a negative apparent activation energy. Clearly, this bears no relation to the bond breakage process. This may occur because the process of ultrasonic degradation is mechanical in origin. The calculated values of k are correlated in terms of the product of η_r and v_p in Figure 6. Our data indicate that the effect of v_p on the degradation rate is dominant.

CONCLUSIONS

The ultrasonic degradation of PVAc solutions was carried in THF at 20, 25, 30, and 35°C. The rate and

Figure 6 Relationship between the calculated values of k and the product of η_r and v_p.

extent of the degradation of the polymer decreased as the temperature and solution concentration increased. A simple kinetic model with viscosity data was used to study the kinetics of degradation. Our data indicate that the effect of v_p in ultrasonic degradation is dominant in comparison with the effect of viscosity.

Figure 5 $\Delta \eta^3 - \Delta \eta_0^3$ versus the sonication time at different temperatures with [PVAc] = 10 g/L.

References

1. Madras, G.; Chattopadhyay, S. Polym Degrad Stab 2001, 73, 33.
2. Portenlanger, G.; Heusinger, H. Ultrason Sonochem 1997, 4, 127.
3. Madras, G.; Chattopadhyay, S. Polym Degrad Stab 2001, 71, 273.
4. Price, G. J.; Smith, P. F. Polym Int 1991, 24, 159.
5. Koda, S.; Mori, H.; Matsumoto, K.; Nomura, H. Polymer 1994, 35, 30.
6. Price, G. J.; Smith, P. F. Polymer 1993, 34, 4111.
7. Price, G. J.; Smith, P. F. Eur Polym J 1993, 29, 419.
8. Gronroos, A.; Pirkonen, P.; Heikkinen, J.; Ihalainen, J.; Mursunen, H.; Sekki, H. Ultrason Sonochem 2001, 8, 259.
9. Nguyen, T. Q.; Kausch, H. H. Adv Polym Sci 1992, 100, 73.
10. Kanwal, F.; Liggat, J. J.; Pethrick, R. A. Polym Degrad Stab 2000, 68, 445.
11. Miyazaki, T.; Yomota, C.; Okada, S. Polym Degrad Stab 2001, 74, 77.
12. Xu, X. Macromol Symp 1997, 118, 189.
13. Madras, G.; Kumar, S.; Chattopadhyay, S. Polym Degrad Stab 2000, 69, 73.
14. Taghizadeh, M. T.; Mehrdad, A. J Polym Sci Part B: Polym Phys 2004, 42, 445.
15. Taghizadeh, M. T.; Mehrdad, A. Ultrason Sonochem 2003, 10, 309.
16. Brandrup, J.; Immergut, E. H. Polymer Handbook, 2nd ed.; Wiley-Interscience: New York, 1975.
17. Reid, R. C.; Prausnitz, J. M.; Poling, B. E. The Properties of Gases and Liquids, 4th ed.; McGraw-Hill: New York, 1986.