A Proposed Mechanism for the Degradation of Addition Polymers in Cavitating Ultrasonic Fields

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Synopsis

A mechanism for the degradation of polymer molecules in ultrasonic cavitation has been proposed which takes into account the energy released by imploding cavitation bubbles in the form of hydrodynamic waves. Relationships for degradation rate constant and limiting chain length linking with the cavitation energy have been derived and are compared with published results on 1% solutions of polystyrene in benzene. These results show satisfactory agreements with the theory presented when the cavitation wave energy is taken proportional to the energy supplied to the ultrasound generating transducer.

INTRODUCTION

It is well known that degradation of long-chain polymers occurs when their solutions are irradiated with ultrasounds. Schmid and coworkers[1-6] carried out extensive studies on the degradation of a number of polymers. Later, several publications[7-16] appeared on the theoretical and experimental works done in this field. An excellent review of these works has been given by Jellinek.[17] More recent reviews on the subject have been published by Grassie[18] and Elpiner.[19]

From these publications it appears that the main emphasis has been on kinetic studies and much less has been directed to the mechanism of degradation in ultrasonic fields. Gooberman[15] has proposed a mechanism in which it is assumed that solvent molecules are compressed within a stationary polymer molecule by the pressure created by a cavitation shock wave, and when this pressure falls the solvent molecules expands generating friction forces between them and the polymer molecule to cause scission of the polymer molecule. The basic concept of this mechanism is not, however, different from that of the two theories advanced by Schmid to explain the effect of ultrasounds on polymers in solutions.

In his first theory Schmid[1] considered that polymer molecules are rigidly held in solutions, and the flow of solvent molecules induced by ultrasounds would generate friction forces across polymer molecules to break a C—C bond. In the second theory the polymer molecules are assumed to move with solvent molecules. In this situation the friction forces between the solute and solvent molecules are shown to be much smaller in magnitude than in the first case.

These theories, however, do not consider the influence of molecular configurations and motions on the friction forces. Since each segment of a macromolecule performs vibrations and rotations, Mark[20] pointed out that a part of the friction forces considered in Schmid's theories would be absorbed by a molecule with no contribution toward degradation.

Besides, intramolecular rotations cavitation is also not considered in Schmid's

theories. Experimental evidence suggests that degradation of macromolecules in ultrasonic fields is due to cavitation effects.[10,11,21] Cavitation in ultrasonic fields implies nucleation, growth, and subsequent collapse of bubbles or cavities, resulting in violent shock waves. Ultrasonic irradiation of polymer solutions usually leads to cavitation when the acoustic energy input exceeds a threshold level.

The degradation of polymer molecules in cavitation fields occurs by the action of hydrodynamic forces[11] of cavitation rather than by the associated thermal and chemical effects. At high frequencies (2000 kHz) cavitation bubbles, depending on the nature of media, may perform pulsations only, without going to a collapse phase. Such bubble motions could generate shear stresses owing to velocity gradients near a bubble surface, causing depolymerization of macromolecules. Polymer degradation to a certain extent observed by Mostafa[22] at the frequency of 2000 kHz may be attributed to bubble motions.

Since the polymer degradation in ultrasonic fields occurs by the action of hydrodynamic forces which owe their origin to cavitation, it is desirable to understand the mode of actions of these forces on polymer molecules. An insight into the subject could be obtained from the studies on drop breakage in flow fields. Hinze[23] has noted that the breakage of drops in flow fields occurs by a dynamic force developed by the flows existing across a drop. Obviously this force depends on the nature of flows. In shear flows the force is developed by the velocity gradients when there is a distribution of velocity over a space engulfing the drop. In turbulent flows the force is created by the fluctuating velocities of eddies constituting the flow field.

Jellinek and White[24] reported that the degradation theory on the basis of friction forces arising from velocity gradients of solvent flows relative to polymer molecules was found inadequate to explain their results. Cavitation forces, apart from generating shear stresses that could cause the degradation of polymers in solutions, release a large quantity of energy as mechanical energy in the form of elastic waves. Noltingk and Neppiras[25] predicted this energy to be of the order of 10^6 atm. Many disruptive effects such as solid disruption, erosion,[26] and disintegration of microorganisms[27] are attributed to this energy of cavitation. It is believed that this energy is also capable of polymer degradation. But no adequate theory for the degradation of macromolecules by cavitation shock wave energy has yet been developed. The object here is to propose a mechanism for the degradation of polymer on the basis of a flow model of ultrasonic fields in which shock waves are generated by imploding cavitation bubbles.

DESCRIPTION OF MECHANISM

The collapsing bubbles in cavitating ultrasonic fields are viewed as power transformers by which acoustic energy is converted into hydrodynamic energy owing to the release of elastic waves. The elastic waves in the field disintegrate into small sets of eddies owing to interaction with each other and with the field medium. In the same way the larger eddies break up into smaller eddies until they reach a size which could be damped by the viscosity of the medium. At a constant power input into the field the elastic waves would work as a continuous source of eddies so that over the period of polymer degradation the sonic field contains eddies of various sizes and intensities.

To ensure the release of elastic waves continuously, there should exist in the field a large stock of bubbles. Nyborg and Hughes,[28] in a motion picture study of bubbles in cavitation at 20 kHz, observed that visible bubbles were continuously being formed and disappearing, leading to an apparently constant number of bubbles in the field at any time.

The elastic waves of cavitation are also the source of the energy content of the eddies. The first set of eddies formed from the elastic waves will inherit their energy from the waves. During the eddy dispersion process, the larger eddies will transmit their energy to the smaller eddies formed from them, and finally the energy of the smallest eddies will be dissipated in the medium through viscosity as heat.

The length scale η of the eddies through which viscous dissipation of energy becomes dominant can be obtained by a dimensional analysis.[29] As this scale is a function of viscosity and energy dissipation rate only, dimensional considerations yield

$$\eta = (\nu^3/\epsilon)^{1/4} \tag{1}$$

where ν is the kinematic viscosity of the liquid medium, in cm^2/sec, and ϵ is the energy dissipation rate, in ergs/(g sec). The velocity of the eddies much smaller than η is given by

$$\bar{u}^2(r) = C\frac{\epsilon}{\nu} r^2 \tag{2}$$

where C is a constant for which a value in the order of unity is admissible, r is the distance, in cm, separating two points in the medium. For eddies much larger than η, the velocity is[30]

$$\bar{u}^2(r) = C_1[(\epsilon r)^{2/3}] \tag{3}$$

in which C_1 is a constant.

Consider a macromolecule suspended in a cavitation field containing eddies as previously described. The molecule in this field will experience motions of various amplitudes and intensities due to eddy motion. The eddies with scales larger than a polymer molecule will simply carry it from place to place, while eddies smaller than the molecule will impart motions of varying intensities. Owing to these eddy motions it is expected that a dynamic force will be set up across the length of a molecule, and when this force exceeds the bond strength the molecule will degrade.

The dynamic force ΔP exerted by eddy motions across a suspended particle has been given by Shinnar and Church.[30] In line with their theory, the dynamic force acting against a macromolecule can be expressed by

$$\Delta P = k_f \frac{\rho}{2} \bar{u}^2(X) \tag{4}$$

where k_f is the drag coefficient of flow around the molecule; ρ is the density of the medium; and $\bar{u}^2(X)$ is the velocity of an eddy with scale equal to the length X of a molecule which is considered to be in the form of a random coil made up of many segments. ΔP in eq. (4) can be written in terms of energy dissipation if $\bar{u}^2(X)$ is substituted by the expression taken either from eqs. (2) or (3). The velocity in eq. (3) is for an eddy size which is very large compared with the

dissipative scale η. For a macromolecule, this eddy size is too large to cause effective eddy motions for the degradation. Therefore, substituting eddy velocity from eq. (2), which gives the velocity for smaller eddies, into eq. (4) gives

$$\Delta P = k_f \frac{\rho \epsilon}{2\nu} X^2 \tag{5}$$

If a molecule is to be degraded by the eddy velocities, ΔP in eq. (5) must exceed the bond strength of that molecule. But for a stable molecule there exists a force balance

$$k_f \frac{\rho \epsilon}{2} X_m^2 = f_0 \tag{6}$$

where X_m is the largest stable length and f_0 represents the weakest strength in a molecule. Equation (6) can be rearranged to give

$$X_m = \left(\frac{2\nu f_0}{k_f \rho \epsilon}\right)^{1/2} \tag{7}$$

The extent of degradation corresponding to X_m can be determined if a size distribution of molecules is known. Assuming the size distribution N_x can be represented by the expression developed by Flory,[31]

$$N_x = (1 - p)p^{X-1} \tag{8}$$

the cumulative fraction of X-mers with sizes less than or equal to X_m is

$$F_N(X_m) = \int_0^{X_m} N_x \, dX = \frac{1-p}{p \log p} (p^{X_m} - 1) \tag{9}$$

where p is the probability factor which is independent of chain length X. Let $(1 - p)/(p \log p) = -C_2$; then

$$F_N(X_m) = C_2(1 - p^{X_m}) \tag{10}$$

The total number of molecules, N_{x0}, at the beginning of degradation is given by

$$N_{x0} = \int_0^\infty N_x \, dX = -\frac{1-p}{p \log p} = C_2$$

Therefore, the fraction that was degraded equals $C_2 - F_N(X_m)$, and from eq. (10) it leads to

$$C_2 - F_N(X_m) = C_2 p^{X_m} \tag{11}$$

Although eq. (11) can be used to obtain the fractional degradation corresponding to a given limiting chain length X_m, an expression in terms of cavitation energy is rather useful. The expression that satisfies end conditions and the relationship between ϵ and X_m is found to be

$$F_N(\epsilon) = 1 - \exp(-k_1 \epsilon^{1/2}) \tag{12}$$

where k_1 is a constant that includes bond strength and the parameters appearing in eq. (7).

Taking the degradation rate equation as

$$N_{xt} = N_{x0} \exp(-Kt) \tag{13}$$

which is found to be valid to represent the change in the number of molecules occurring by degradation only, the extent of degradation $F_N(t)$ at a time t is

$$F_N(t) = 1 - \exp(-Kt) \tag{14}$$

where K is the rate constant. In eq. (13), N_{xt} and N_{x0} represent the number of molecules at $t = t$ and $t = 0$, respectively. Comparison of eqs. (12) with (14) shows that

$$K = C_3 \epsilon^{1/2} \tag{15}$$

where C_3 is a constant of proportionality.

EVALUATION OF CAVITATION ENERGY ϵ

As stated previously, ϵ is the energy that is dissipated through smaller eddies by viscous dissipation. The origin of this energy is, however, in the shock waves of cavitation from where it is transferred through eddy propagation to the smaller eddies. A part of shock wave energy also goes to form free radicals, sonoluminescence, and noise. Therefore, ϵ should represent the energy released by bubble collapse minus the part that is spent in the creation of free radicals, sonoluminescence, and noise.

In the earlier stage of the cavitation process, acoustic energy goes to the formation and growth of cavitation bubbles. When the bubbles collapse, the energy stored in them is released in the medium mainly as shock wave energy. Sirotyuk[32] has reported that the energy required for the formation of cavitation is proportional to the power input measured as square of the voltage applied to the ultrasound generating transducer. If the part of cavitation energy which is spent in producing sonoluminescence, free radicals, and noise is negligible compared with eddy energy, then

$$\epsilon = C_4(P - P_0) \tag{16}$$

where P is the power input into the system with cavitation, P_0 is the threshold power at which energy conversion to ϵ is zero, and C_4 is a constant.

Substituting ϵ in eq. (15) leads to

$$K = C_5[(P - P_0)^{1/2}] \tag{17}$$

in which C_5 includes the constants appearing in eqs. (15) and (16). Equation (7) after substituting ϵ from eq. (16) gives

$$X_m = C_6 \left(\frac{2\nu f_0}{k_f \rho}\right)^{1/2} (P - P_0)^{-1/2} \tag{18}$$

where C_6 is a constant. From eqs. (17) and (18) it can be shown that

$$K = C_7 X_m^{-1} \tag{19}$$

where C_7 is a proportionality constant.

To compare this work with published experimental results, Mostafa's[9] studies on polystyrene were found to be useful. In his work Mostafa irradiated 25-cm^3 batches of 1% solution of polystyrene in benzene by an ultrasonic generator with a frequency of 0.75 mc/sec for 35 hr. The degradation rate constant and the limiting chain length were determined at four sonic intensities. The ultrasound

was generated by a quartz crystal which was energized by an oscillator. The energy output by the crystal was measured by a radiation balance in the form of acoustic intensities, and these values were found to vary directly with the square of the anode voltage of the oscillator within the range of operations. Since the square of the voltage is a measure of power, the energy input by the crystal into the degradation processs is proportional to the square of the anode voltage. If the energy dissipation rate through cavitation is proportional to the power inputs in the process, then from eq. (17)

$$K = C_8(V^2 - V_0^2)^{1/2} \qquad (20)$$

where C_8 is a constant, and V and V_0 are the anode voltage during cavitation and at threshold, respectively. The limiting chain length X_m from eq. (18) is

$$X_m = C_9[(V^2 - V_0{}^2)^{-1/2}] \qquad (21)$$

where C_9 is a constant for a particular degradation system. The degradation rate constant in Mostafa's work was determined from the equation

$$F_N(t) = 1 - \exp[-K_M(X - 1)t] \qquad (22)$$

in which K_M is the rate constant. Comparing this equation with eq. (14) gives

$$K = K_M(X - 1) \qquad (23)$$

To evaluate the rate constant K from eq. (23), a mean value of the chain length X between the initial and limiting values is required. A geometric mean between weight-average chain lengths at $t = 0$ and $t = 10$ hr at which the limiting chain length is assumed to reach has been used.

The power input in a cavitation field increases with the increase in acoustic intensity. It is therefore sufficient to demonstrate for the lowest intensity used in Mostafa's studies that the hydrodynamic force developed is strong enough to break a C—C bond in polystyrene molecules. The lowest intensity was 4.89 W/cm^2, and the corresponding power input into a solution of 25 cm^3 with density 0.89 g/cm^3 was 70 W. The threshold power P_0 was estimated to be 60 W. On the basis of a conservative estimate of 10% energy conversion into hydrodynamic form,

$$\epsilon = \frac{10 \times 0.10}{25 \times 0.89} = 0.045 \text{ W/g}$$

The dynamic force ΔP across a polysyrene molecule can be estimated from eq. (5) if the drag coefficient k_f is known. The drag coefficient can be expressed as[33]

$$k_f = 6\pi d_{eq}{}^2/Re \qquad (24)$$

where Re is the Reynolds number defined by

$$Re = \rho d_{eq} v/\mu \qquad (25)$$

d_{eq} is the diameter of the sphere equivalent to the coil presented by a polymer molecule in dilute solutions with respect to viscosity increase. For a polystyrene molecule of molecular weight 10^6 and viscosity number $\eta = 290$ cm^3/g, the equivalent diameter[34] d_{eq} is 715 Å. The velocity v in the Reynolds number represents the relative velocity between the molecule and the solvent. The

relative velocity of a molecule free to move in solutions is due its macro-Brownian motion; and in the absence of any external force, the average velocity of such motion is in the range[20] of 0.5 to 1.0 μm/sec. Taking for benzene $\rho = 0.89$ g/cm^3 and $\mu = 0.0062$ g/(cm sec), and for the polystyrene molecule $v = 1 \times 10^{-4}$ cm/sec, Re is 1.026×10^{-7}. Therefore, k_f from eq. (24) is 9.39×10^{-3} cm^2.

For a polystyrene molecule of initial chain length $X = 1.5 \times 10^{-4}$ cm, the dynamic force ΔP from eq. (5) becomes

$$\Delta P = 9.39 \times 10^{-3} \frac{0.89 \times 0.045 \times 10^7 (1.5 \times 10^{-4})^2}{2 \times 0.00697} = 6.069 \times 10^{-3} \text{ dyne}$$

which, being approximately 10 times larger than the C—C bond strength of 5.64×10^{-4} dyne, satisfies the condition for degradation that ΔP must be greater than the weakest link in a molecule. However, all the eddies in a cavitation field do not produce ΔP of the same magnitude. As stated previously, eddies larger than a molecule simply carry it away from place to place without exerting any breakup force, while only equal and smaller eddies develop a dynamic force that could cause bond scission.

The cavitation field is assumed to contain eddies of various sizes. As the dynamic force ΔP is proportional to the square of an eddy length, the breakup force decreases as the eddy size becomes smaller and smaller. At a certain eddy size, the breakup force would balance the C—C bond strength of a molecule, leading to the formation of a molecule stable against a given cavitation intensity. The existence of a limiting chain length in cavitation fields has been confirmed experimentally.

The size of a macromolecule in dilute solutions is randomly altered owing to micro-Brownian motions. Compared with a thermodynamically "poor" solvent, a molecule in a "good" solvent is relatively extended, and thus the cavitation force in such solvents should be more effective. In general, the period of eddy action on a molecule must be shorter than the time required by a molecule to alter its configurations if the dynamic force is to be effective in bond scission. The time for a configuration change is in the order of 10^{-3} sec.[20] The period of an eddy defined by the equation

$$\tau = l/u \qquad\qquad (26)$$

where τ is the period of the eddy having length l and velocity u, is determined with the help of eq. (2) to give

$$\tau = (\nu/\epsilon)^{1/2} = \left(\frac{0.00697}{0.045 \times 10^7}\right)^{1/2} = 1.24 \times 10^{-4} \text{ sec}$$

a value which is shorter than the time required for a molecule to change its configuration.

To compare the other results with the theory, the values of K and X_m have been plotted versus $(V^2 - V_0^2)^{1/2}$ in Figure 1 where the results fit linear relations satisfying eqs. (20) and (21) of the theory. For a further check, K is plotted versus X_m in Figure 2, which also gives a linear relation in accordance with eq. (19). For the comparison of the results, V_0 has been estimated from the work done by
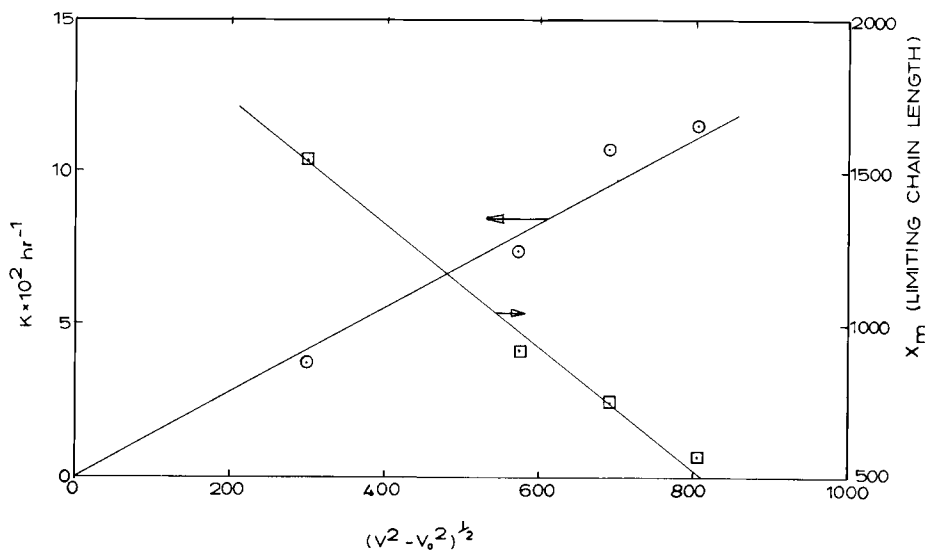
Fig. 1. Effect of cavitation energy on rate constant and limiting chain length.
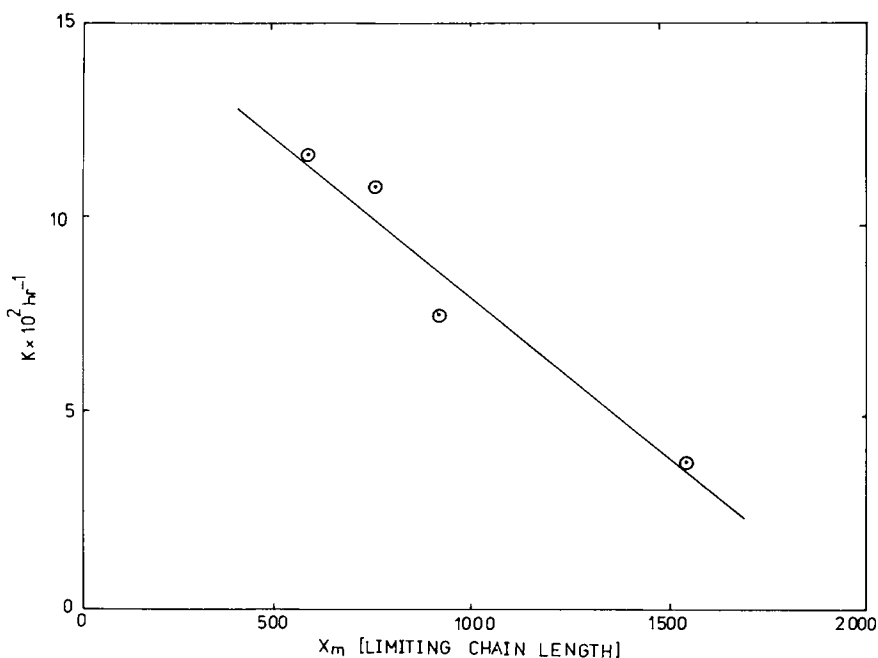

Fig. 2. Relationship between rate constant and limiting chain length.

Mostafa to be 400 V at which the disintegration of polymer molecules by the cavitation is assumed negligible.

The mechanism proposed for the degradation of macromolecules in ultrasonic cavitation shows many points of agreement with the experimental results of polystyrene in benzene, suggesting that it can be generally applicable.

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