

Mechanics of Ultrasonic Degradation of Linear High Polymer and Ultrasonic Cavitation

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INTRODUCTION

When the irradiation of intensive ultrasonics into a polymer solution is continued, the viscosity of the solution first decreases rapidly, then gradually, and at last it reaches a constant value. For example, the result of Akiya, Nomoto, and Okui¹ is shown in Figure 1. According to the experiments of Sata et al.² and Schmid et al.,³ the molecular weight distribution becomes very sharp in the last step. This fact that a monodisperse solution can be obtained easily is a noteworthy characteristic of the ultrasonic degradation.

The final value of the degree of polymerization g is not or only slightly dependent on the initial degree of polymerization, the concentration and volume of solution, and the shape of the vessel, it is dependent primarily on temperature and the kind of solvent. It seems most important to us that the g values in Figure 1 practically coincide with each other, irrespective of the ultrasonic intensity applied. From this fact, we know that the force of degradation on a polymer molecule is very insensitive to ultrasonic intensities J .

On the other hand, Prudhomme and Grabar⁴ and Weissler⁵ verified experimentally that ultrasonic degradation is ascribed to the mechanical reaction of ultrasonic cavitation. Therefore the result of Figure 1 shows that the cavitation force or cavitation intensity does not increase so much with increasing ultrasonic intensity. Both intensities should be distinguished from each other. We can utilize the g value as a measure of cavitation intensity.

As was proved previously^{6,7} from reaction kinetics, the reaction rate B is a function of the degree of polymerization and ultrasonic intensity J .

Therefore two characteristic constants of chemical reaction (g and B) can be used respectively as measures of physical intensities. Speaking geometrically about the meaning of g and B in Figure 1, g is an asymptotic

value of the ordinate at $t = \infty$ and B corresponds to slope of the curve at $t = 0$.

Sata and Okuyama discussed previously⁶ the mechanism of ultrasonic degradation. Later, Okuyama and Hirose⁸ expressed mathematically the proposed mechanism with special consideration of g . The present paper deals with essentially the same material as the previous discussion.⁸

The phenomenon of cavitation has received considerable attention from throughout the field of engineering, but the cavitation intensity can not yet be measured accurately by any physical technique, and so the mechanical theory of cavitation has little conclusive basis. Therefore one of the present aims is to contribute to the mechanical theory of cavitation with the help of g values obtained from chemical substances.

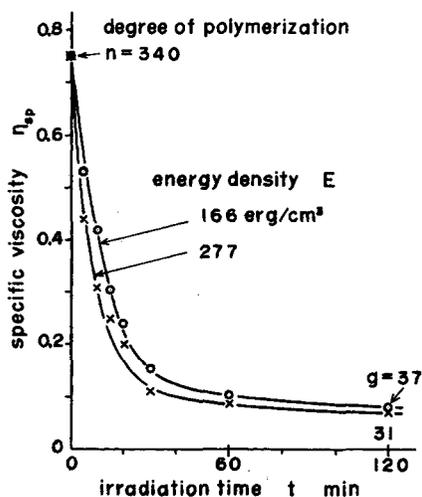


Fig. 1. Effect of ultrasonic intensity on the degradation of methylcellulose. —OCH₃ content: 22%; solvent: water; concentration: 0.2%; 470 keycycles/sec.

We will here describe briefly ultrasonic cavitation. During continuous ultrasound irradiation of medium intensity, bubbles are formed which become larger and larger from the following causes. (1) Bubbles coalesce with each other. (2) During expansion of the bubble, dissolved air molecules are sucked out from liquid to bubble, while during the contraction phase those air molecules do not always dissolve back into the liquid, owing to the extremely rapid speed of collapse and to the decrease of bubble surface. Then during one cycle of vibration causes air molecules accumulate little by little in the bubble, and the bubble increases gradually in size. This is Harvey's rectified diffusion.⁹

Once the bubble has grown to some extent (say, to a radius of 10^{-2} cm.) the quantity of air in the bubble before and after each cycle should become the same. This type of vibration we call stationary cavitation.¹⁰

On intensive ultrasonic irradiation, a very small bubble (say, of radius

10^{-5} cm.) in liquid vibrates violently before reaching stationary cavitation. This vibration we call nascent cavitation.^{11,12}

2. Mechanism of Ultrasonic Degradation

Both the magnitude v and the direction of velocity in cavitating liquid depend on both time t and distance r from the cavitating bubble. The velocity of solvent molecules increases with decreasing distance from bubble. The maximum velocity gradient $\partial v/\partial r$ is found at the bubble surface during contraction of the bubble.

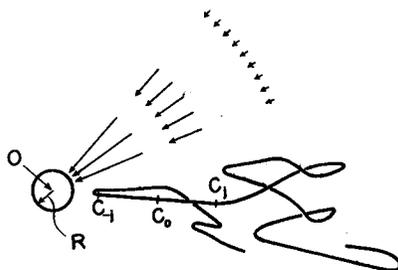


Fig. 2. During the contracting step of bubble-vibration, a polymer molecule is torn off at atom C_0 , the middle atom of partial chain j .

Since, during contraction of a vibrating bubble, solvent molecules stream toward the bubble, so a polymer molecule in the solvent streams also with them. As Figure 2 shows, j repeating units in the polymer molecule (partial chain j) stream along a straight line through the center of bubble, and are subject to the tension as follows.

The carbon atom C_0 at the center of gravity of the partial chain j should stream in the same motion as its neighboring solvent molecule. That is to say, there occurs no shear between atom C_0 and its neighboring solvent molecule. In the straight part of a polymer there occurs inevitably the slipping (shear) between C atoms and their neighboring solvent molecules with the velocities vanishing at C_0 and increasing toward both ends C_j or C_{-j} . Accordingly, the friction forces, caused by the slipping, also increase toward both ends. Since the tension acting on each C—C bond is the sum of these frictional forces, the maximum tension should occur at C_0 , in spite of its frictionless condition. The longer the effective length j , the larger is the tension.

If the tensile force is greater than the ultimate strength of the C—C bond, the bond is broken; in this case $j_1 > g$. If it is smaller than the bond strength, the bond is not broken; then $j_2 < g$.

The tension F_j , which is a function of j , increases the interatomic distance between C_0 and C_1 , i.e., it performs work on C_0 . If the work surpasses the dissociation energy D between the carbon-carbon atoms which is independent of j , then the C—C bond cannot completely absorb the work,

and so the bond is broken. Here, g is the degree of polymerization j on the condition that the work approaches D .

During long-term irradiation, all polymer molecules impartially receive frequent blows of cavitation, and at last, they are torn off to the degrees of polymerization from g to $2g$ -mers. Thus we obtain practically a mono-disperse solution. This was explained previously⁶ in another way.

3. Motion of Partial Chain j

As time origin, we take the moment when a part of polymer chain begins to be stretched into a straight line. The distance of atom C_0 from the center of bubble, O is designated as r_0 . Under the assumption that the motion of solvent is not disturbed by the presence of polymer molecules, the velocity of solvent at time t and at the distance r from the bubble center O is expressed as $v(r, t)$ in Eulerian expression. The velocity of C_0 at zero time $t = 0$ should be just the same as that of its neighboring solvent molecule:

$$v_p[C_0, 0] = v(r_0, 0) \equiv v_0, \quad (1)$$

and the acceleration of C_0 is

$$\alpha_p[C_0, 0] = \left(v \frac{\partial v}{\partial r} + \frac{\partial v}{\partial t} \right)_{r=r_0, t=0} = v_0 \left(\frac{\partial v}{\partial r} \right)_0 + \left(\frac{\partial v}{\partial t} \right)_0 \quad (2)$$

where the subscript zero means the value at $r = r_0$ and $t = 0$. Since the time necessary to tear off a C—C bond by cavitation is very short, the acceleration could be treated as constant through this mechanical action. Thus, at time $t = t$, the position, velocity, and acceleration of C_0 can be written respectively,

$$r[C_0, t] = r_0 + v_0 t \quad (3)$$

$$v_p[C_0, t] = v_0 + v_0 t \left(\frac{\partial v}{\partial r} \right)_0 + t \left(\frac{\partial v}{\partial t} \right)_0 \quad (4)$$

$$\alpha_p[C_0, t] = v_0 \left(\frac{\partial v}{\partial r} \right)_0 + \left(\frac{\partial v}{\partial t} \right)_0 \quad (5)$$

Next, we will consider the motion of atom C_x , which is atom x apart from C_0 at $t = 0$.

$$r[C_x, t] = r_0 + v_0 t + x + q \quad (6)$$

$$v_p[C_x, t] = v_0 + v_0 t \left(\frac{\partial v}{\partial r} \right)_0 + t \left(\frac{\partial v}{\partial t} \right)_0 + \frac{\partial q}{\partial t} \quad (7)$$

$$\alpha_p[C_x, t] = v_0 \left(\frac{\partial v}{\partial r} \right)_0 + \left(\frac{\partial v}{\partial t} \right)_0 + \frac{\partial^2 q}{\partial t^2} \quad (8)$$

where $q(x, t)$ is the displacement of C_x with respect to C_0 .

On the other hand, the motion of the solvent molecules in contact with C_x at time t is

$$v_s[C_x, t] = v(r[C_x, t], t) = v_0 + (v_0 t + x + q) \left(\frac{\partial v}{\partial r} \right)_0 + t \left(\frac{\partial v}{\partial t} \right)_0 \quad (9)$$

$$\alpha_s[C_x, t] = \left(t \frac{\partial v}{\partial r} \right) + \left(\frac{\partial v}{\partial t} \right)_{r=r[C_x, t], t=t} = v_0 \left(\frac{\partial v}{\partial r} \right)_0 + \left(\frac{\partial v}{\partial t} \right)_0 \quad (10)$$

In order to establish the equation of motion of the infinitesimal part dx at C_x , we will consider the forces acting on it.

Since hydraulic pressures on both sides of part dx are equal to those on the adjacent solvent molecules, the pressure difference between both sides can be calculated from the acceleration $\alpha_s[C_x, t]$ caused in the adjacent solvent.

Then

$$\text{pressure difference} = m_s dx \left\{ v_0 \left(\frac{\partial v}{\partial r} \right)_0 + \left(\frac{\partial v}{\partial t} \right)_0 \right\} \quad (11)$$

where $m_s = \rho A$, ρ being the density of solvent and A the cross-sectional area of chain.

From the velocity difference (i.e., shear velocity) between C_x and its neighboring solvent molecule a frictional force is generated which is assumed to be proportional to this shear velocity:

$$\begin{aligned} \text{Frictional force} &= \zeta dx \{ v_s[C_x, t] - v_p[C_x, t] \} \\ &= \zeta dx \left\{ (x + q) \left(\frac{\partial v}{\partial r} \right)_0 - \frac{\partial q}{\partial t} \right\} \end{aligned} \quad (12)$$

where ζ is the microscopic friction coefficient between a polymer molecule and its neighbors, namely the frictional force per unit length of polymer molecule and per unit shear velocity.

Since the acceleration of C_x in its solvent drugs with it the adjacent solvent molecules, there is an apparent increase in mass. The force from acceleration difference (i.e., shear acceleration) is assumed to be proportional to this difference.

$$\begin{aligned} \text{Force from shear acceleration} &= \Delta m_p dx \{ \alpha_s[C_x, t] - \alpha_p[C_x, t] \} \\ &= \Delta m_p (\partial^2 q / \partial t^2) dx \end{aligned} \quad (13)$$

where Δm_p is the apparent increase of linear density m_p of polymer.

The difference between the interatomic forces at bond $C_x - C_{x+1}$ and bond $C_{x-1} - C_x$ bond is

$$-dF = -(\partial F / \partial x) dx \quad (14)$$

The force of inertia of C_x is then given by

$$\text{Inertia force} = -m_p dx \alpha_p[C_x, t] \quad (15)$$

As the inertia force, eq. (15), is balanced against the sum of the various forces defined in eqs. (11), (12), (13), and (14), the equation of motion is

$$(m_p + \Delta m_p) \frac{\partial^2 q}{\partial t^2} = (m_s - m_p) \left\{ v_0 \left(\frac{\partial v}{\partial r} \right)_0 + \left(\frac{\partial v}{\partial t} \right)_0 \right\} + \zeta \left\{ (x + q) \left(\frac{\partial v}{\partial r} \right)_0 - \frac{\partial q}{\partial t} \right\} - \frac{\partial F}{\partial x} \quad (16)$$

Now putting $m_p = m_s$ and for an apparent linear density of polymer m_p' given by

$$m_p' = m_p + \Delta m_p$$

we get for motion of partial chain j eq. (17):

$$m_p' \frac{\partial^2 q}{\partial t^2} = \zeta \left\{ (x + q) \left(\frac{\partial v}{\partial r} \right)_0 - \frac{\partial q}{\partial t} \right\} - \frac{\partial F}{\partial x} \quad (17)$$

4. Estimation of the g Value

When the maximum tension, which acts on the middle atom C_0 of a partial chain, exceeds the critical value F_k , the interatomic distance between C_0 and C_1 (or C_{-1}) increases to infinity, that is to say, the bond to C_0 is torn off. But the tensions on the other C atoms never exceed F_k . Therefore in comparison with the stretch of the C_0 bond, the stretch of the other bonds in the partial chain is negligibly small. At the moment when a polymer molecule is torn off, no bond of the partial chain j stretches significantly except the C_0 bond. Thus, all the bonds other than the C_0 bond can be considered rigid; accordingly two quantities q ($= l - l_0$, where l_0 is the interatomic distance at zero slippage) and dx ($= l_0$) are common to these C atoms. Therefore integrating eq. (17) with respect to x from zero to jl_0 , we get

$$m_p' j l_0 \frac{d^2 l}{dt^2} = \zeta \left\{ \left[\frac{j^2 l_0^2}{2} + j l_0 (l - l_0) \right] \left(\frac{\partial v}{\partial r} \right)_0 - j l_0 \frac{dl}{dt} \right\} - F[C_j, t] + F[C_0, t] \quad (18)$$

Equation (18) can be simplified as follows. Firstly, $l - l_0 \ll (1/2)j l_0$. Secondly, because $(1/2)j l_0 (\partial v / \partial r)_0 - dl/dt$ is the velocity difference between the middle point $x = (1/2)j l_0$ of the right-hand half of the partial chain j and its adjacent molecule, $(1/2)j l_0 (\partial v / \partial r)_0 \gg dl/dt$. Thirdly, there is no tension acting on the free end C_j of the partial chain; then $F[C_j, t] = 0$. Therefore eq. (18) becomes

$$m_p' j l_0 \frac{d^2 l}{dt^2} = j^2 Z - \frac{\partial}{\partial l} U(l) \quad (19)$$

where

$$Z = 1/2 l_0^2 \zeta (\partial v / \partial r)_0 \quad (20)$$

is independent of j , and $U(l) = -\int F dl$ is the interatomic potential energy.

Multiplying both sides of eq. (19) by dl/dt and integrating with respect to t from zero to t under the initial conditions: $l = l_0$ and $dl/dt = 0$ at $t = 0$, we obtain

$$\frac{1}{2}m'_p j l_0 (dl/dt)^2 = j^2 Z(l - l_0) - [D + U(l)] \quad (21)$$

where the dissociation energy D is given by $D = -U(l_0)$.

The left-hand side of eq. (21) does not become negative. If there is no l value which makes the right-hand side equal to zero, the value of l increases infinitely, i.e., polymer is torn off. If the right-hand side of eq. (21) becomes negative at any value of l (which is larger than l_0 , of course), the polymer can not be stretched up to this l value. In short, the polymer molecule can be broken only under the following condition:

$$j^2 Z(l - l_0) - D > U(l) \quad (22)$$

Figure 3 shows the right-hand side of eq. (22) as curve U and the left-hand side as the straight line which passes through the minimum point E of curve U and has a slope of $j^2 Z$. According to eq. (22), if this straight

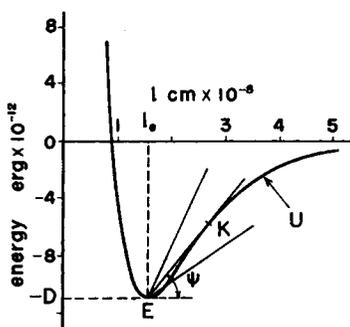


Fig. 3. The relation between potential energy U and the work done by frictional force.

line lies above the U curve, the polymer molecule is broken; if this line crosses the U curve, the polymer molecule is not broken. Therefore, the condition of eq. (22) can be modified to

$$j^2 Z > \tan \psi = F_k = - \left(\frac{\partial v}{\partial l} \right)_k, \quad (23)$$

where $\tan \psi$ is the slope of the tangent to the U curve and passing through its minimum point E . In short, the cavitation can tear off a chain longer than $(F_k/Z)^{1/2}$,

$$j > (F_k/Z)^{1/2} \quad (24)$$

The polymer molecule is torn off shortest when and where Z becomes maximum. Therefore we get from eq. (24),

$$g = (F_k/Z_{\max})^{1/2} \quad (25)$$

where

$$Z_{\max} = 1/2 l_0^2 \zeta (\partial v / \partial r)_{\max}. \quad (26)$$

In order to express $(\partial v / \partial r)_{\max}$ by the surface velocity $(-\dot{R})$ of the rapidly contracting bubble of radius R , we use the condition of continuity in the noncompressible fluid:

$$r^2 v = R^2 \dot{R} \quad (27)$$

Then,

$$(\partial v / \partial r)_{\max} = (-2R^2 \dot{R} / r^3)_{\max} = 2(-\dot{R} / R)_{\max} \quad (28)$$

where $(-\dot{R} / R)_{\max}$ is the maximum of the shear velocity, not of the velocity gradient. The equations available to the estimation of g -value are eqs. (25), (26), and (28).

As F_k in eq. (25) is $(\partial U / \partial l)_k$, its value can be calculated from the Morse function

$$U(l) = D [\exp\{-2\kappa(l-l_0)\} - 2 \exp\{-\kappa(l-l_0)\}], \quad (29)$$

where $2 \kappa^2 D$ is the curvature at the bottom of curve U , and $D = 11 \times 10^{-12}$ erg, $\kappa = 1.025 \times 10^8$ cm., $l_0 = 1.55 \times 10^{-8}$ cm.

Then,

$$F_k = 4.6 \times 10^{-4} \text{ dyne} \quad (30)$$

At last we obtain g from eqs. (25), (26), (28), and (30):

$$g = 1.4 \times 10^6 [\zeta(-\dot{R} / R)_{\max}]^{-1/2} \quad (31)$$

Now in order to estimate ζ , we use Debye's formula¹³ of intrinsic viscosity

$$[\eta] = \left(\frac{1}{36}\right) \left(\frac{a\zeta}{m\eta}\right) \left(\frac{1+c_0}{1-c_0}\right) n a^2 \quad (32)$$

where η is the viscosity coefficient of the solvent, m is the mass of a repeating unit, c_0 denotes the cosine of the bond angle, a is the distance between neighboring repeating units, and n is the degree of polymerization. Then taking $\eta = 0.01$ poise, $[\eta] = 100$ cm.³/g., $m = 1.7 \times 10^{-22}$ g., $c_1 = 1/3$, $a = 2 l_0 = 2 \times 1.55 \times 10^{-8}$ cm., and $n = 10^4$, we obtain $\zeta = 0.01$ (dyne/cm.)/(cm./sec.).

In case of the stationary cavitation, the value of $(-\dot{R} / R)_{\max}$ is $1-3 \times 10^6$ sec.⁻¹, from the results of our numerical calculation.¹⁰ Then from eq. (31) we obtain $g_{\text{stat}} = 0.8-1.2 \times 10^4$, which is too large in comparison with $g_{\text{exp}} = 250$, the experimental g value of polystyrene in toluene. Therefore the stationary cavitation proves not to contribute to ultrasonic degradation.

There is at present no satisfactory mechanical theory on the nascent cavitation. According to G \ddot{u} th's theory,¹⁴ if the voluminal change of gas in bubble is assumed to be adiabatic, the maximum velocity of bubble contraction is

$$(-\dot{R})_{\max} = \left(\frac{2p_A}{3\rho}\right)^{1/2} \left(\frac{\gamma - 1}{\gamma} \frac{p_A + \bar{p}_0}{p_A}\right)^{\gamma/[2(\gamma-1)]} \left(\frac{p_A}{P}\right)^{1/[2(\gamma-1)]} \quad (33)$$

and the bubble radius at this moment is given by

$$R_w = R_{\max} \left(\frac{\gamma}{\gamma - 1} \frac{P}{p_A + \bar{p}_0}\right)^{1/[3(\gamma-1)]} \quad (34)$$

where R_{\max} is the maximum radius of the vibrating bubble, P is the gas pressure inside the bubble at R_{\max} , p_A is the atmospheric pressure, \bar{p}_0 is the effective pressure of ultrasonic waves, and γ the ratio of two specific heats of air in bubble. According to the present authors,^{12,15} R_{\max} is expressed by

$$R_{\max} = \frac{3.2}{\omega} \left(\frac{\bar{p}_0}{\bar{p}_0 + p_A}\right)^{1/2} \left(\frac{\bar{p}_0 - p_A}{\rho}\right)^{1/2} \quad (35)$$

where ω is the circular frequency of ultrasonic waves. If the maximum shear velocity in eq. (31) is approximated by

$$(-\dot{R}/R)_{\max} = (-\dot{R})_{\max}/R_w, \quad (36)$$

this value can be estimated as $1.8 \times 10^{10} \text{ sec}^{-1}$ by the use of eqs. (33)–(35), where $p_A = 10^6$ (c.g.s. unit), $\bar{p}_0 = 4 \times 10^6$, $\omega = \pi \times 10^6$, $\rho = 1$, $\gamma = 1.4$, and $P = 0.01 \times 10^6$ (which is the saturated vapor pressure of water). From $(-\dot{R}/R)_{\max} = 1.8 \times 10^{10}$ and $\zeta = 0.01$, the g value in case of nascent cavitation can be estimated as $g_{\text{nas}} = 100$ by eq. (31). This value for g_{nas} ($= 100$) is nearer to the value for g_{exp} ($= 250$) than that for g_{stat} ($= 0.8\text{--}1.2 \times 10^4$). This shows clearly that the final value of the degree of polymerization is exclusively determined by the nascent cavitation.

Even if the bubble bursts before perfect collapse as photographed by Willard,¹⁶ or further even if the cause of ultrasonic degradation is not in nascent cavitation but in the shock wave, the present theory is still adaptable in a similar manner.^{11,17}

5. Further Discussions

The present theory explains further the experimental facts that cavitation intensity is insensitive to ultrasonic intensity and that ultrasonic degradation occurs even in solutions of infinite dilution.

a. Cavitation Intensity Insensitive to Ultrasonic Intensity. We will show theoretically from the data of Figure 1 that g values are almost same, irrespective of different J values. The ultrasonic intensity J , the energy flow [erg/(cm.²-sec.) = 10^{-7} watt/cm.²] passing in unit time through a unit section perpendicular to the direction of sound is in the following relation to the mean density of energy E (erg/cm.³) = radiation pressure S (dyne/cm.²):

$$J = Ec = p_0^2/2\rho c \quad (37)$$

where c is the ultrasonic velocity ($=1500 \times 10^2$ cm./sec.), ρ is the mean density of medium ($=1$ g./cm.³), and p_0 is ultrasonic pressure amplitude.

Numerical values of m , c_0 , a , and n used in the previous section are very different from those of methylcellulose, but the value of ζ for polystyrene in toluene will be used also, as that for the water-methylcellulose, system probably does not differ appreciably in order. The results of the numerical calculations are summarized in Table I. Because of the roughness of the approximation, the absolute values of g_{calc} , 133 and 117, do not agree with those of g_{exp} , 37 and 31. But the relative value g_2/g_1 agrees well between theoretical ($133/117 = 1.1$) and experimental ($37/31 = 1.2$). Therefore it has been shown theoretically that the g value, and consequently cavitation intensity, is very insensitive to ultrasonic intensity.

TABLE I
Relation between p_0 Values and g Values

	Case 1		Case 2
S , g. wt./1.8 cm. ²	1		3
E , erg/cm. ³	166		277
p_0 , dyne/cm. ²	2.73×10^6		3.53×10^6
R_{max} , cm.	1.26×10^{-3}		1.56×10^{-3}
$(-\dot{R})_{\text{max}}$, cm./sec.	2.84×10^5		4.05×10^5
R_w/R_{max}	0.0204		0.0174
$(-\dot{R}/R_{\text{max}})$	1.1×10^{10}		1.5×10^{10}
g_{calc}	133		117
$g_{\text{calc}2}/g_{\text{calc}1}$		1.1	
g_{exp}	37		31
$g_{\text{exp}2}/g_{\text{exp}1}$		1.2	

When contracting velocity of bubble increases over a certain limit, the liquid layer near the bubble has some rigidity;^{11,17} as a result of this, the cavitation intensity is even more insensitive to ultrasonic intensity than the results of the calculations above mentioned.

b. Ultrasonic Degradation occurs even in Solutions of Infinite Dilution. This was indicated previously⁶ by one of the authors based on the viewpoint that the cause of ultrasonic degradation exists in the frictional force between polymer molecule and its adjacent solvent molecule, not in the collision between polymer molecules. Later on, this was ascertained experimentally by Thomas and Alexander,¹⁸ and further became clearer by mathematical expression of ultrasonic degradation in our paper.

The authors wish to express their thanks to Prof. N. Sata for his interest and encouragement in the course of the work.

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Synopsis

A mechanism for ultrasonic degradation is proposed as follows. At the contracting step of a violently vibrating bubble in liquid, j structural units of a polymer molecule (partial chain j) take a linearly extended configuration owing to the suction force of bubble, which occurs as a result of slipping and friction between solvent molecules and the extended part of polymer. This partial chain is subject to a tensile force arising from the friction which is maximum at the middle carbon bond of the partial chain. If it is greater than the critical tensile strength of a carbon-carbon bond, the bond at the middle is unable to absorb the work done by it, so the bond is torn off, i.e., the polymer degrades. Under such considerations a formula for the final value of the degree of polymerization after infinite irradiation is deduced, from which the following results are obtained. (1) Cavitation which can degrade polymer molecules effectively is not stationary but nascent. (2) The cavitation intensity is very insensitive to ultrasonic intensity. Moreover, from the proposed mechanism, several experimental facts can be explained: practically monodisperse solution is obtained after long-term irradiation; and ultrasonic degradation occurs even in solutions of infinite dilution.

R sum 

On propose le m canisme suivant de d gradation par ultrasons. Dans l' tape de contraction d'une bulle vibrant violement dans un liquide, des unit s structurales j d'une cha ne partielle j d'une mol cule de polym re prennent une configuration lin airement  tendue   cause de la force de succion de la bulle, qui se produit par glissement et friction entre des mol cules de solvant et la partie  tendue du polym re. Cette cha ne partielle subit la force de tension d coulant de la friction qui est maximum au lieu du carbone occupant le milieu de la cha ne partielle. Si elle est plus grande que la r sistance critique   la tension d'un lien carbone-carbone, le lieu du milieu est incapable d'absorber le travail effectu ; de cette fa on le lien est cass , c. .d. que le polym re est d grad . Etant donn  ces consid rations, on d duit une formule pour la valeur finale du degr  de polym risation apr s irradiation infinie, d'o  l'on obtient les r sultats suivants: (1) la cavitation qui peut effectivement d grader des mol cules de polym re n'est pas "stationnaire" mais "naissante," (2) l'intensit  de cavitation est fort insensible   l'intensit  ultrasonique. De plus,   partir du m canisme propos , on peut expliquer plusieurs faits exp rimentaux: une solution pratiquement monodispers e est obtenue apr s de longues heures d'irradiation, et la d gradation ultrasonique a lieu m me dans une solution de dilution infinie.

Zusammenfassung

Für den Ultraschallabbau wird folgender Mechanismus vorgeschlagen. Bei der Kontraktionsphase einer heftig vibrierenden Blase in einer Flüssigkeit nehmen j Struktureinheiten eines Polymermoleküls (Partialkette j) durch die Saugkraft der Blase eine lineare gestreckte Konfiguration ein, was unter Gleitung und Reibung zwischen den Lösungsmittelmolekülen und dem gedehnten Polymerteil verläuft. Diese Partialkette wird infolge der Reibung durch eine Zugkraft beansprucht, die an der mittleren Kohlenstoffbindung der Partialkette ein Maximum erreicht. Ist sie grösser als die kritische Zugfestigkeit einer Kohlenstoff-Kohlenstoff-Bindung, so kann die mittlere Bindung die erzeugte Arbeit nicht aufnehmen und die Bindung wird gesprengt, d.h. das Polymere wird abgebaut. Aus diesen Überlegungen wird eine Beziehung für den Endwert des Polymerisationsgrades nach unendlich langer Bestrahlung abgeleitet, aus der folgende Ergebnisse erhalten werden. (1) Zum Abbau von Polymermolekülen geeignete Kavitation ist nicht "stationär" sondern "naszierend." (2) Die Kavitationsintensität ist von der Ultraschallintensität weitgehend unabhängig. Weiters kann der vorgeschlagene Mechanismus einige experimentelle Tatsachen erklären: nach langstündiger Bestrahlung werden praktisch monodisperse Lösungen erhalten, und Ultraschallabbau findet auch in unendlich verdünnter Lösung statt.

Received November 2, 1961