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Tim Patraboy

POLYMERIZATION OF METHYL - METHACRYLATE
INITIATED BY INTENSE ULTRASOUND.

by

© Timothy J. Patraboy

A thesis submitted to the Faculty of
Graduate Studies in partial
fulfillment of the requirements for
the degree of

Master of Science

Department of Chemistry

Carleton University

Ottawa, Ontario

September, 1984

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ABSTRACT

Experiments with methyl methacrylate prove that polymerization can be initiated in a pure vinyl monomer using intense ultrasound. Variation of the polymerization rate with time, volume and intensity are explained by a simple reaction mechanism. The number average molecular weight of the polymer produced is about $400,000 \text{ g mol}^{-1}$; rate constants for the polymerization mechanism obtained from the molecular weight data agree well with literature values. Presence of the radical scavenger DPPH inhibits the polymerization. The temperature dependence of the DPPH reaction is explained well over a wide (-17 to 40°C) temperature range by relations based on reversible or irreversible adiabatic collapse of the cavitation bubble. Furthermore it is in agreement with sonochemical experiments, where composition rather than temperature was changed to vary the vapor pressure. Initiation rates calculated from polymerization rates and DPPH consumption rates are of the same order of magnitude, but show an unexplainable difference in temperature dependence. The nature and mechanism of formation of a coloured compound which appears at lower temperatures is also not properly explainable by these experiments.

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Chapter 1 INTRODUCTION

1.1 ULTRASOUND

1.1.1 ELEMENTARY PHYSICS OF ULTRASOUND

Ultrasound is the acoustic analogue of ultraviolet light. More precisely it is sound with a frequency higher than the upper frequency detection limit of human hearing (15kHz). Sound and ultrasound differ from electromagnetic radiation such as light, however, in that they are mechanical vibrations requiring a physical medium in which they propagate as waves. Ultrasonic waves are disturbances of the medium that change their position with time. A description of the motion of the particles disturbed by the wave is provided by the wave equation (in one dimension):

$$\frac{d^2S}{dx^2} = \frac{1}{C^2} \frac{d^2S}{dt^2} \quad [1.10]$$

where: $S(x,t)$ describes the displacement of any particle at a position x and a time t as the wave moves with a speed C in

the X direction. The speed of an ultrasonic wave in fluids depends on the density and compressibility of a medium. This relation is given by the equation:

$$C = \frac{1}{\beta_{ad}\rho} = \frac{\gamma}{\beta_{is}\rho} \quad [1.11]$$

where: ρ is the density, γ is the ratio of specific heats of the medium, and β is the adiabatic or isothermal bulk compressibility of the medium. If the wavelength and frequency of the ultrasound are denoted by λ and f respectively, then the speed C is given by:

$$C = f\lambda \quad [1.12]$$

The speed of ultrasound has a characteristic value for a particular frequency and a particular medium. Thus on passing from one medium to another the wavelength of an ultrasonic wave will change if its speed changes since the frequency is determined by the source of the ultrasonic vibrations.

Generally speaking the sources employed in the investigation of ultrasonic chemical processes produce waves

which cause a sinusoidal displacement of the medium with time given by:

$$S = S_0 \sin(2\pi ft) \quad [1.13]$$

where: S_0 is the displacement amplitude. It is assumed in [1.13] that $x=0$ at $t=0$, and that the source is a vibrating plane.

Acoustic vibrations propagating in a medium also create a pressure in addition to the mean pressure in the medium. This is referred to as the acoustic pressure. For a plane wave this acoustic pressure is given by:

$$P = P_0 \sin(2\pi ft) \quad [1.14]$$

Where P is the pressure at any given point at any instant and P_0 is the pressure amplitude given in turn by:

$$P_0 = 2\pi f S_0 \rho c \quad [1.15]$$

The term $2\pi f S_0 \sin(2\pi ft)$ is also defined as the vibrational velocity (u). Substituting for u into [1.14] and rearranging

slightly gives the expression:

$$\frac{P}{U} = \rho C \quad [1.16]$$

The quantity ρC is often referred to as the specific acoustic impedance of the medium. It represents the ratio of the acoustic pressure to the velocity of the vibrating particle. It must be noted, however, that the above mentioned relationships are strictly applicable only to unbounded media and exclude any absorption or scattering effects.

An ultrasonic wave propagating in a medium carries a certain amount of energy with it. The amount of energy carried by a wave through a unit area in a unit time defines the intensity of the sound (I). For a plane sine wave the acoustic intensity is given by :

$$I = \frac{P^2}{2\rho C} = \frac{1}{2} U^2 \rho C = \frac{1}{2} P U \quad [1.17]$$

The sound intensity level is sometimes expressed as a logarithmic quantity x measured in decibels. If sound of intensity I_1 is compared with that of intensity I_2 , then x is given by the following expression:

$$\alpha = 10 \log \left(\frac{I_1}{I_2} \right)$$

[1.18]

For reference measurements the intensity I_1 is generally taken as the threshold of audibility of the human ear (about $10^{-16} \text{ W cm}^{-2}$). A sound intensity of $10^{-2} \text{ W cm}^{-2}$ will produce significant pain. The average intensity of ultrasonic and sonic waves used for laboratory investigations in liquids is of the order of 10 W cm^{-2} .

1.1.2 THE GENERATION OF ULTRASOUND

The generation of sonic or ultrasonic waves is accomplished using a transducer. Transducers function by converting energy of one kind (usually electrical) into ultrasonic energy. Two types of transducers are commonly used in ultrasonic studies - piezoelectric and magnetostrictive transducers.

1.1.2.1 PIEZOELECTRIC TRANSDUCERS

As the name suggests, piezoelectric transducers depend on the piezoelectric effect for their function. This involves the generation of an electrical potential on the surfaces of certain crystals when they are subjected to pressure or mechanical stress. It was discovered in 1880 by the Curie

brothers. Materials that display the piezoelectric effect include: quartz, barium titanate and many ceramics. In 1881 Lippman found that application of an electrical potential to a piezoelectric material resulted in a mechanical deformation of the material - a reverse piezoelectric effect. The magnitude and sign of the generated potential in the case of the piezoelectric effect depend directly on the magnitude and sign of the applied stress. The same is true of the reverse effect.

A piezoelectric transducer generally consists of a thin plate of piezoelectric material with a thin metallic film evaporated onto its front and back faces which forms two electrodes. The front electrode (in contact with the liquid medium) is usually grounded to prevent shock. An oscillating electrical potential is then applied to the back electrode to produce the crystal vibrations which in turn produce the ultrasonic waves. A typical transducer design is shown in figure 1.1.

1.1.2.2 MAGNETOSTRICTIVE TRANSDUCERS

The other major type of transducer is the magnetostrictive transducer. The basis for its function is the discovery, by Joule that certain ferromagnetic materials such

Figure 1.1 A Typical Piezoelectric Transducer Design.

as iron and nickel respond to a magnetic field by changing their dimensions. Thus vibrations in the ferromagnetic material can be produced by subjecting it to an alternating magnetic field. This is easily accomplished by surrounding it with a coil and passing an alternating current through it.

The simplest form of magnetostrictive transducer is, as already mentioned, a ferromagnetic rod wound with a coil. Provisions must be made for cooling since eddy currents generate a considerable amount of heat. Eddy current effects can be reduced by forming the ferromagnetic material into thin laminations which are electrically insulated from one another. A typical transducer design is shown in figure 1.2.

Piezoelectric transducers are generally used to generate and detect ultrasound at all frequencies and intensities. Magnetostrictive transducers, on the other hand, are used more at lower frequencies (20 kHz - 60 MHz) and in industrial applications where higher power levels and durability are essential [1].

1.1.3 APPLICATIONS OF ULTRASOUND

Currently ultrasound enjoys widespread use in a vast number of applications. Although they are roughly separable

Figure 1.2 A Typical Magnetostrictive Transducer Design.

into applications requiring low and high power, there is no clear boundary between the two classes. It has been suggested that low intensity applications do not involve any change in the medium when the ultrasonic energy is transmitted through it [2]. Low intensity applications include: medical imaging, non-destructive testing, relaxation studies of molecular processes, and measurements of the elastic properties of various media. High intensity applications involve changes of the medium or its contents as a result of passing the ultrasound through it. Changes that may occur include: homogenization, atomization, chemical reactions, and physical erosion of surfaces. High power applications are generally used for industrial applications. Among high power industrial applications are: cleaning, plastic and metal welding, emulsification, drying and atomization. For a further discussion of the applications of ultrasound the reader is directed to reference [1].

1.2 CAVITATION

1.2.1 INTRODUCTION

Cavitation is a phenomenon associated with the ^{PASSAGE} introduction of high intensity ultrasound through a liquid. It is frequently accompanied by a variety of physical and

chemical effects. These may include: chemical reactions [3-8], sonoluminescence (the weak emission of light from a liquid undergoing cavitation) [9-20], and physical erosion. It is essentially a three step process involving the: formation, slow growth, and rapid, violent collapse of tiny bubbles in a liquid experiencing a transient tensile stress which exceeds its tensile strength. Underwater explosions, high speed flow through a narrow opening or jet, waterfalls, and rotating turbine blades are all examples of transient stresses causing cavitation.

The pressure variation in a liquid due to the passage of an ultrasonic wave can also cause cavitation. This will occur if the transient pressure reduction during the low pressure phase of the wave falls below the tensile strength of the liquid. Relatively slow cavity growth occurs during the low pressure phase of the wave. This is followed by a rapid collapse of the cavity during the subsequent compressive phase of the wave. In some cases, depending on: the initial cavity radius, acoustic pressure amplitude, and acoustic frequency, the cavity may not collapse completely in one acoustic period. Instead, it may oscillate non - linearly about an equilibrium radius for several acoustic periods.

1.2.2 BASIC DYNAMICS

The complexities which must be overcome in order to arrive at an adequate theoretical account of the motion of cavitation bubble in a liquid are enormous. They include effects from: surface tension, evaporation and condensation of vapor, viscosity, compressibility, diffusion, thermal conduction, variations of the hydrostatic and acoustic pressures, interactions with other cavities etc. It has been impossible, to date, to obtain a completely satisfactory theoretical description of cavitation dynamics that fully accounts for all of these factors. The achievement of any theoretical model for cavitation dynamics requires a multitude of simplifications and approximations. Even with these limitations any results are strictly applicable only to an isolated, spherical cavity. This situation never really exists, but it will be assumed for the purposes of this discussion.

1.2.2.1 GENERAL RELATIONS

Consider the case of an isolated, spherical cavitation bubble of radius R , where $R = R(t)$ and such that R is smaller than the wavelength of the ultrasound. The pressure P and velocity u in the liquid at a point r such that $r > R$ at any time t are related by the following relations:

$$\frac{\partial u}{\partial t} + u \left(\frac{\partial u}{\partial r} \right) = - \frac{1}{\rho} \left(\frac{\partial p}{\partial r} \right) \quad [1.19]$$

and

$$\frac{\partial \rho}{\partial t} + \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \rho u) = 0 \quad [1.20]$$

These relations are often referred to as the equations of motion and continuity respectively. They are obtained from the laws of conservation of momentum and mass. Introducing the velocity potential ϕ such that:

$$u = - \left(\frac{d\phi}{dr} \right) \quad [1.21]$$

and integrating equation [1.19] from r to ∞ the equation of motion becomes:

$$- \left(\frac{d\phi}{dt} \right) + \frac{u^2}{2} + \int_{P_\infty}^{P(r)} \frac{1}{\rho} dP = 0 \quad [1.22]$$

1.2.3 IDEAL INCOMPRESSIBLE LIQUID

The condition of incompressibility requires that:

$$\frac{\partial p}{\partial t} = \frac{\partial p}{\partial r} = 0. \quad [1.23]$$

If the velocity of the cavitation bubble wall is U , then the boundary conditions at the bubble surface are given by:

$$r = R \text{ and } u = U \quad [1.24]$$

After some transformations it can be shown [21] that the equation of motion becomes:

$$R \left(\frac{d^2 R}{dt^2} \right) + \frac{3}{2} \left(\frac{dR}{dt} \right)^2 = \frac{1}{\rho} [P(R) - P_\infty] \quad [1.25]$$

This describes the general motion of a cavitation bubble for a pressure P_∞ at infinity and $P(R)$ at the bubble surface. P_∞ and $P(R)$ depend on the pressure as a function of time and on the bubble contents respectively.

1.2.3.1 SIMPLEST CASE

The simplest case for which solutions of equation [1.25] can be obtained is that where the bubble contains a vacuum so that $P(R) = 0$ and the value of P_∞ is the hydrostatic pressure of the liquid P_H . Application of these conditions reduces equation [1.25] to the familiar Rayleigh

equation:

$$U^2 = \frac{2}{3} \frac{P_H}{\rho} \left(\frac{R_m^3}{R} - 1 \right) \quad [1.26]$$

This equation can be solved exactly by analytical methods. Upon integration, equation [1.26] yields the collapse time τ of an empty cavity as:

$$\tau = 0.915 R_m \left(\frac{\rho}{P_H} \right)^{1/2} \quad [1.27]$$

Where R_m is the maximum radius before collapse. For example, if: $R_m = 10 \mu\text{m}$, $\rho = 1000 \text{ kg m}^{-3}$, $P_H = 100 \text{ kPa}$ are used in equation [1.27], a value of $\tau = 10 \mu\text{s}$ results. Equation [1.27] places no restrictions on the values of R . Thus R can range from 0 to infinity. Unfortunately as R approaches a value of 0, the value of U approaches infinity which is impossible.

1.2.3.2 GAS FILLED CAVITY

The next simplest case is that of a cavity filled with a non condensable gas or vapor. Consider a cavity with radius R_0 filled with such a gas at a pressure P_{g0} . This pressure is related to the surface tension of the liquid σ and the external pressure P_H by the expression:

$$P_{go} = P_H + \frac{2\sigma}{R_o} \quad [1.28]$$

The variation of the gas pressure in the cavity as a function of the cavity radius is given by the expression:

$$P_g(R) = \left(P_H + \frac{2\sigma}{R_o} \right) \left(\frac{R_o}{R} \right)^{3b} \quad [1.29]$$

Where b is the polytropic index of the bubble contents ($b = 1$ for isothermal processes and $b = \gamma$ for an adiabatic one).

If the vapor pressure of the liquid is considered to be a constant P_v depending only the temperature of the bulk liquid, then the following boundary conditions must be met at the bubble surface:

$$\left(P_H + \frac{2\sigma}{R_o} \right) \left(\frac{R_o}{R} \right)^{3b} + P_v = P(R) + \frac{2\sigma}{R} \quad [1.30]$$

Rearranging this expression gives:

$$P(R) = \left(P_H + \frac{2\sigma}{R_0} \right) \left(\frac{R_0}{R} \right)^{3b} + P_V - \frac{2\sigma}{R} \quad [1.31]$$

If this bubble is then acted upon by a sinusoidal ultrasonic field of frequency f and amplitude P_0 , then:

$$P_\infty(t) = P_H - P_0 \sin(2\pi ft) \quad [1.32]$$

Substitution of equations [1.31] and [1.32] into equation [1.25] gives:

$$R \left(\frac{d^2 R}{dt^2} \right) + \frac{3}{2} \left(\frac{dR}{dt} \right)^2 + \frac{1}{\rho} \left(P_H - P_V - P_0 \sin(2\pi ft) + \frac{2\sigma}{R} - \left(P_H + \frac{2\sigma}{R_0} \right) \left(\frac{R_0}{R} \right)^{3b} \right) = 0 \quad [1.33]$$

This equation was first derived by Noltingk and Neppiras [22] for gas filled cavities under isothermal conditions where $b = 1$ and $P_V = 0$. It is not solvable mathematically, but numerical solutions using computers are possible. A typical plot of R versus t can be seen in figure 1.3. These plots show that the cavity radius grows to a maximum and then shows an increasingly rapid collapse. The inward motion of the cavity

Figure 1.3 Radius-Time Curve For A Cavitation Bubble Calculated From The Noltingk-Neppiras Equation.

$$P_0 = 4 \text{ atm}, f = 15 \text{ kHz}, R_0 = 16 \mu m$$

walls is repelled by the increasingly compressed gas within the cavity. This means that, unlike the Rayleigh equation, R cannot approach a value of 0. During the final stages of the collapse, however, the velocity achieved by the cavity walls exceeds the speed of sound. This renders the assumption of an incompressible liquid invalid. Consequently the Noltingk - Neppiras equation does not provide an accurate description of the cavity during the final stages of collapse.

1.2.4 ALLOWANCE FOR COMPRESSIBILITY

The problem of a supersonic collapse of the bubble wall can be overcome by considering the effect of the compressibility of the liquid. Generally speaking, these treatments involve numerical solutions of the equations of motion and continuity which have been modified to include terms for the liquid compressibility. The forms of these additional terms depend on a number of approximations and assumptions. A detailed description of the resulting relations is beyond the scope of this work. Interested readers can find a thorough description in references [21] and [39].

1.2.5 OTHER APPROACHES

A description of the dynamics of a cavitation bubble can be provided by numerical solutions of the above mentioned

equations of motion. Solutions have been obtained for a large number of variations and extensions of these basic equations [23-26] taking into account factors such as: heat transfer, phase transitions within the bubble, and other modes of energy dissipation.

Although practical, numerical solutions have the disadvantage that there is no easily discernible relationship between the various parameters and the dynamics of the cavitation bubble. Consequently a number of approximate analytical techniques have been developed [29-33]. These techniques involve some form of perturbation method and their derivation is quite involved, so an example will not be given here. Generally speaking, these techniques are useful in describing only small amplitude oscillations of a cavitation bubble. Nevertheless, they do provide information on the effects of the initial conditions on the subsequent oscillations of the bubble. Furthermore they also predict the experimentally established [34-38] relationship between the appearance of subharmonic signals and the onset of cavitation.

1.2.6 CAVITY TYPES

1.2.6.2 DEFINITIONS

The motion of a cavitation bubble in a sound field may be very complicated. Frequently it is convenient to define two classes of cavities based upon extremes of motional behavior. These are often referred to as "transient" and "stable" cavities. Flynn [39] has suggested the following definitions: (1) A transient cavity, after growing to some maximum radius, contracts, so that the initial motion approximates that described by the Rayleigh equation [1.26]. The inward speed of the bubble walls increases rapidly until it is arrested by the rapidly rising pressure within the cavity. (2) A stable cavity undergoes a series of nonlinear oscillations about its equilibrium radius.

1.2.6.1 STABLE VS. TRANSIENT CAVITIES

In the presence of an ultrasonic field, a cavitation nucleus can grow into either a stable or transient cavity depending on the frequency and pressure amplitude of the ultrasound. In order to determine which type of cavity will be formed the equation of motion (equation [1.19]) can be split into two acceleration functions [39] as shown below:

$$\frac{dU}{dt} = F_1 + F_2 \quad [1.34]$$

Where:

$$F_1 = -\frac{3}{2R} U^2 \quad [1.35]$$

and:

$$F_2 = \frac{1}{\rho R} \left[\left(P_H + \frac{2\sigma}{R_0} \right) \left(\frac{R_0}{R} \right)^{3b} + \quad [1.36]$$

$$P_V - \frac{2\sigma}{R} - \frac{2U}{R} \left(\frac{dR}{dt} \right) - P_H + P_0 \sin(2\pi ft) \right]$$

F_1 is referred to as the inertial function and represents the inward acceleration of the cavity walls during contraction. It is always an inward acceleration, decreasing in magnitude with increasing cavity radius until it vanishes at the maximum cavity radius.

F_2 is dependent only on the radius and pressure at the cavity interface. At the maximum radius R_m , it is a small inward acceleration, but as R decreases, F_2 rapidly becomes a large outward acceleration that ultimately stops the inward acceleration of the cavity walls. The transition in F_2 can be

ascribed to the cushioning action of the compressed cavity contents. At some radius R_x , F_2 will have a minimum.

Numerical solutions [39] show F_1 and F_2 to be curves of the form shown in figure 1.4. The intersection point of the acceleration functions depends on the value of R_m . Thus, a critical value of R_m , (R_c) exists such that F_1 will intersect F_2 at its minimum. The competition between F_1 and F_2 determines the cavity behavior on collapse. It can be shown [39] that a cavity will be transformed into a transient cavity if F_1 lies below F_2 at R_x (cf. curve 1 in figure 1.4). If on the other hand F_1 lies above F_2 at R_x , then the cavity will become a stable cavity (cf. curve 2 in figure 1.4).

Since F_1 and F_2 are derived from a non dissipative equation of motion for an incompressible liquid, the argument above can only provide a qualitative description of the conditions that transform a cavity into a stable or a transient cavity.

1.2.7 CAVITATION NUCLEI

Ultrasonic intensities sufficient to produce acoustic pressure amplitudes of the order of one atmosphere can cause

Figure 1.4 Acceleration Functions For Large Amplitude Motion Of Bubbles With Different Initial Radii.

cavitation in liquids. The tensile strengths of pure, gas free liquids, on the other hand, are of the order of hundreds of atmospheres [40]. Thus on first glance, it appears that ultrasonic cavitation should not occur in liquids. The presence of microscopic particles, undissolved gas microbubbles and other impurities is known to drastically reduce the tensile strength of a liquid. These impurities are often called cavitation nuclei. It is thought that they facilitate cavitation by providing weak spots in the structure of the liquid where cavitation can occur. Some support for this position is offered by the observation that cavitation occurs only with difficulty and only at higher intensities in freshly distilled, degassed liquids, where cavitation nuclei should not exist in large numbers. Yet in argon saturated liquids, where cavitation nuclei should be numerous, cavitation occurs at much lower acoustic intensities [41].

1.2.8 THEORIES OF CAVITATION AND ITS EFFECTS

A theoretical description of ultrasonic cavitation and its effects is very difficult to achieve owing to the profusion of complicating factors involved in the process. To date several theories and models have been advanced in an attempt to account for cavitation effects. They can be

broadly grouped into two major categories (although some models exist which are variations of these categories). These categories are: the electric discharge and thermal theories.

1.2.8.1 MICRO - ELECTRIC DISCHARGE THEORY

The micro - electric discharge theory of Frenkel [42] involves the formation of an initially lens shaped cavity. As this cavity forms, each side of the cavity becomes oppositely charged by a process akin to the piezoelectric effect. This creates, in effect, a microscopic parallel plate capacitor. The magnitude of the charge on each side of the cavity increases as the cavity continues to grow. This continues until the electric field within the cavity is so great that there is a discharge across the cavity. Such a discharge is accompanied by a flash of light, ionizations and chemical reactions. The basic process is shown schematically in figure 1.5.

1.2.8.2 THERMAL THEORY

The thermal or "Hot - Spot" theory was proposed by Noltingk and Neppiras [22] in 1950. In developing their model, Noltingk and Neppiras solved the equation of motion for a gas filled cavity after making some simplifying assumptions. The

Figure 1.5 Frenkel's Structure Of A Cavitation Bubble.

model assumes a spherical cavity filled with a non-condensable gas that undergoes a slow isothermal growth to some maximum radius R_m . This is followed by a rapid reversible adiabatic compression to some minimum radius R_{min} . For a completely adiabatic compression, the temperature within the cavity at the minimum radius is given by [22]:

$$T = T_0 \left(\frac{R_m}{R_{min}} \right)^{3(\gamma - 1)} \quad [1.37]$$

Where T_0 is the initial temperature of the cavity contents. Furthermore, according to Noltingk and Neppiras [22]:

$$T = T_0 \left(\frac{P}{3Q} \right)^{3(\gamma - 1)} \quad [1.38]$$

Where: P is the algebraic sum of the hydrostatic and acoustic pressures and Q is the pressure inside the cavity at its maximum radius.

Consider the case $T_0 = 300$ K, $P = 1$ atm, and $Q = .01$ atm. According to equation [1.38] this set of conditions produces a temperature of about 10,000 K within the cavity at its minimum radius. Temperatures of this magnitude

are certainly high enough to heat the cavity contents to incandescence. They would also generate reactive species which could initiate chemical reactions or produce luminescence by radiative deexcitations and recombinations.

In reality, the temperatures within the cavity would be lower than those predicted by equation [1.38]. Firstly the cavity contents would contain some liquid vapor which might alter the cavity dynamics [39] or absorb some energy for chemical reactions. Furthermore there would be a large temperature gradient between the cavity contents and the cavity surface, which would remain at T_0 . This would lead to heat loss from thermal conduction. Models have been proposed by Hsiao [9], and Young [43] that quantitatively account for the effect of thermal conductivity. Kruus [7] has suggested that the compression is closer to an irreversible adiabatic compression than the reversible adiabatic compression proposed by Noltingk and Neppiras [22].

1.2.8.3 SUPPORT FOR THE THERMAL THEORY

The bulk of recent experimental evidence suggests that the thermal theory is the most accurate model proposed to date for describing cavitation effects. Sonoluminescence studies [14,19,44,45] indicate that the "Micro - Electric Discharge"

model is unlikely since it predicts the wrong phase relation between the sonoluminescence pulse and the bubble motion. Moreover intracavity temperatures have been estimated by Sehgal et. al. [14] to be about 3,400 K and by Chendke and Fogler [20] to be about 4,900 K on the basis of sonoluminescence emissions from aqueous solutions. The thermal theory is also supported by the agreement between the predicted and experimental [7,8,46] dependence of sonochemical reaction rates on temperature and liquid vapor pressure.

1.3 ACOUSTIC STREAMING

The passage of intense ultrasound through a medium is accompanied by stationary (time - independent) flows known as acoustic streaming. Such flows occur either in a free non-uniform sound field, or (especially) in the vicinity of obstacles placed in a sound field or near an oscillating body. The velocity of these flows increases with the acoustic intensity, however even at the highest intensities, it remains smaller than the particle velocity in the acoustic wave [21].

Acoustic streaming was first observed by Faraday in 1831 when the noted stationary vortex flows over an oscillating membrane. The first theory of stationary acoustic streaming was developed by Rayleigh near the end of the last century.

Three types of acoustic streaming are presently known and all have been well studied. A review of this work is available in reference [29].

The first type of streaming occurs in a viscous boundary layer, near an obstacle placed in a sound field. Under the influence of sound, the stationary flows in the boundary layer have a vortex character. The scale of these boundary vortices is generally determined by the thickness of the boundary layer. The dimensions of the boundary layer are much smaller than the acoustic wavelength. Thus, this type of streaming occurs on a microscopic scale.

The second type of streaming occurs outside the boundary layer and also has a vortex nature. The scale of the vortices is much greater than that of the boundary layer vortices of the preceding discussion. One form of this type of streaming, studied by Rayleigh, is two dimensional flow between two planes (or in a cylinder) under the action of a standing wave. In this case the scale of the vortices is roughly the same as the acoustic wavelength.

Finally, the third type of streaming occurs in a free non - uniform sound field. The scale of the inhomogeneity in

this field is much greater than the acoustic wavelength. Eckart first solved the problem of flows generated in a confined volume by a well collimated sound beam. Consequently, this type of flow is known as Eckart streaming. The scale of the vortices in Eckart streaming, is generally determined by the medium volume and greatly exceeds the acoustic wavelength. Thus, unlike the first two types, Eckart streaming is a large scale phenomenon. Figure 1.6 shows a diagram of Eckart streaming in a tube with a totally sound absorbing end.

The classification of streaming on the basis of scale is, to some extent, arbitrary. Firstly, different types of streaming can occur simultaneously. Secondly, they can have the same dependence on viscosity and other parameters of the medium and sound field. For the purposes of this work, the nature of the streaming is not important since it only provides a mechanism for mixing.

1.4 CAVITATION AND POLYMERS

1.4.1 ULTRASONIC DEPOLYMERIZATION

It has long been known that solutions of macromolecules undergo an irreversible depolymerization when they are irradiated with intense ultrasound. Several studies were

Figure 1.6 Diagram Of Eckart Streaming In A Liquid.

carried out by Schmid and coworkers [47-52]. This was followed by several publications [53-67] on both the theoretical and experimental work done on ultrasonically induced depolymerization. Reviews of this work have been published by Jellinek [68], El'piner [41], and Basedow and Ebert [40].

The process of ultrasonic depolymerization is one in which chemical effects play a very small part. Consequently mechanisms developed to explain this process focus on its mechanical nature. It is now widely accepted that ultrasonic depolymerization results from mechanical forces associated with cavitation in a liquid. Collapsing cavitation bubbles generate shock waves and strong velocity gradients in their immediate vicinity. Goberman [66] proposed a mechanism in which it is assumed that solvent molecules are compressed within a stationary polymer molecule by a cavitation shock wave. The solvent molecules expand when the pressure falls, generating frictional forces between them and the polymer molecule. The forces so generated cause scission of the polymer bond. Theories proposed by Schmid [47] suggest scission to be the result of frictional forces between the

polymer molecule and solvent molecules flowing rapidly around it.

Kinetic studies have produced several common observations. The extent of depolymerization depends on: the chemical structure of the polymer [64], molecular weight and its distribution [54,67,69-71], polymer concentration [55], viscosity and surface tension [72], nature of the solvent [73,74], bulk temperature [62,74], acoustic intensity [59,74] and dissolved gases [56]. It has also been found that there is a limiting chain length below which depolymerization does not occur which is also dependent on the parameters listed above. A rigorous treatment of the rate of ultrasonic depolymerization requires a simultaneous solution of a large number of differential equations, one for each molecular weight species in the sample. For such a treatment the reader is referred to one of the reviews mentioned above.

In most polymers bond scission is a homolytic scission of the main chain C-C bonds. This has been verified by recent spin trapping studies [76,77] of the "macro radicals" which are produced. In the case of poly-(methyl methacrylate) the major radical species are identified as the species shown in Figure 1.7. Some inorganic polymers undergo heterolytic

Figure 1.7 Ultrasonic Degradation Of Poly-(Methyl Methacrylate).

scission while others disproportionate [78].

1.4.2 POLYMERIZATION REACTIONS

Most studies of the effects of ultrasound on polymer systems have concentrated on its depolymerizing effects. Numerous studies of the effects of ultrasound on polymerization processes have also been reported.

Polymerization due to ultrasound has been reported for monomers in aqueous media. In 1951 Lindstrom and Lam [79] reported polymerization of acrylonitrile in aqueous media. They concluded that the initiating radicals were formed both as a result of cavitation degradation of the monomer and depolymerization of the polymer formed during the reaction. Henglein and coworkers studied the ultrasonically induced polymerization of acrylamide in water [80,81]. They showed that the polymerization was inhibited by both oxygen and hydroquinone, thus demonstrating its free radical nature. They were also able to show the importance of cavitation by using pulsed ultrasound. The polymerization rate was reduced when the duration of the pulse was reduced. Cavitation is also reduced with a reduction in pulse duration.

Ultrasound has also been found to cause and/or accelerate emulsion polymerization of several monomers [83-

86]. This has been attributed to several factors including formation of hydroxyl radicals in the water and reduction in the size of emulsion droplets.

Polymerization has also been reported when vinyl monomers containing dissolved polymers are subjected to ultrasonic irradiation. Berlin and coworkers [86,87] attributed the polymerization in several monomers containing dissolved polymers to be the result of macro-radicals formed as a result of ultrasonic depolymerization. They also reported that no polymerization took place in monomers which were free of water or dissolved polymer [86]. The production of block copolymers by this method has been the subject of many investigations [86,88-94] since copolymers of both vinyl and non-vinyl polymers are possible. In spite of this, quantitative treatment of this type of polymerization has so far been limited to the work of Fujiwara et al. [89,91,93]. They have also reported a lack of polymerization for monomers which initially contain no polymer.

The effects of ultrasonic irradiation on a variety of conventional polymerization systems (ie. systems in which a chemical initiator is used) has also been the subject of several investigations [95-100]. The results are often

qualitative and inconclusive since the effects are small and depend on the experimental set up.

In conflict with previous studies, recent results from this laboratory have indicated-it is possible to consistently obtain polymerization in purified styrene, vinyl acetate and methyl methacrylate [101-103]. Since cavitation in many anhydrous organic liquids has been shown to produce free radicals that can cause further reactions in the liquid [5,8,49] it could provide a source for polymerization initiating free radicals.

1.5 METHYL-METHACRYLATE

Methyl-methacrylate (2-propenoic acid-methyl ester) is one of the most studied and commercially important vinyl monomers in existence today. It is produced by heating acetone cyanohydrin (from the addition of hydrocyanic acid to acetone) with sulfuric acid. The methacrylamide sulfate formed in this way; is then reacted with methanol and water to give methyl-methacrylate.

The free radical addition polymerization of methyl-

methacrylate initiated by benzoyl peroxide is shown in figure 1.8. This process can be repeated until very long chains have been built up. The polymer (poly-(methyl-methacrylate)) is valued for its optical clarity, physical strength and excellent weathering characteristics. Thus, it has found use in lenses, dial covers, windows, and skylights.

Figure 1.8 Polymerization Reaction Of Methyl-methacrylate.

CHAPTER 2 EXPERIMENTAL

2.1 ACOUSTIC APPARATUS

Ultrasound with a frequency of 20 kHz was produced with a Bransonic W-350 Sonifier ultrasonic generator (Branson Sonic Power Company Division of Branson Ultrasonics Corporation, Danbury, Connecticut 06810). A standard titanium horn was used to couple the piezoceramic transducer to the liquid of interest. The power output was measured calorimetrically and could be varied between 0 and 76 W. Determinations of the power output at all power settings throughout the study showed no change with time. The reproducibility of the power output at a given power setting was typically within 3% of the mean of at least 3 separate determinations.

The face of the coupling horn had an area of 2.84 cm^2 ; the acoustic intensity could thus be varied between 0 and 27 W cm^{-2} .

2.2 INSONATION CELL

Ultrasonic irradiation of the monomer was carried out with the tip of the coupling horn immersed directly in the

monomer.. Throughout the irradiation the monomer was contained in a glass insonation cell, which is shown in fig.2.1. The cell design incorporates separate ports and removable fittings for: monomer introduction, temperature measurement, sample withdrawal and introduction of the saturation gas (Ar in this case). A large central opening allowed the coupling horn to be inserted into the cell. The clearance between the widest section of the horn and the walls of this opening was about 0.5 mm with a polyethylene sleeve providing a seal between the cell and the horn. An indentation in the bottom of the cell was located directly below the horn tip when the horn was inserted into the cell. This geometry provided efficient stirring as a result of strong acoustic streaming.

2.3 REAGENTS AND PURIFICATION

2.3.1 GASES

Linde prepurified grade argon was further purified prior to its use by passing it through an oxygen scavenger (Ridox, Fisher R-30). Activation of the scavenger was effected by reduction with a mixture of 5% hydrogen/95% argon (by volume) at 350 °C for 2 hr.

Figure 2.1 Experimental Apparatus

Key: 1 Cell, 2 Acoustic Horn, 3 Thermocouple Well,
4 Sampling Inlet, 5 Monomer Inlet, 6 Argon Inlet,
7 Polyethylene Sleeve.

2.3.2 MONOMER

Reagent grade methyl methacrylate (MMA) (Fisher 0-3629) was purified according to the procedure detailed below.

2.3.2.1 INHIBITOR REMOVAL

Approximately 900 ml of MMA was washed twice with an equal volume of 10% by weight aqueous solution of sodium hydroxide in order to remove the hydroquinone inhibitor. The MMA was then washed twice with equal volumes of distilled water. A slight emulsion resulting from the water washing was eliminated with a single wash using an equal volume of a saturated, aqueous sodium chloride solution.

2.3.2.2 DRYING

The MMA contained a small amount of water after removal of the inhibitor. This was removed by a two step process. The MMA was initially dried for 40 min over about 300 g of anhydrous sodium sulfate. The MMA was then dried for 40 min over about 130 g of activated molecular sieves (type 4a, Fisher M-514).

2.3.2.3 DEGASSING

Reproducible results were obtained only if the MMA was degassed by boiling it under vacuum with vigorous stirring for

about 10 min immediately prior to distillation.

2.3.2.4 DISTILLATION

The MMA was distilled under argon from about 2 g of cuprous chloride. Approximately 400 ml of MMA was collected in a special receiving cell that allowed transfer of the MMA without atmospheric exposure. Analysis of the final fraction was accomplished, using a Hewlett-Packard FM-402 gas chromatograph equipped with a 6 ft. column (6 mm od.) packed with OV-101. The temperature was programmed to rise from 90 °C at injection to a final temperature of 250 °C, at a rate of 5 °C min⁻¹. The resulting chromatogram showed no appreciable impurities in the MMA. The refractive index of the purified MMA was in agreement with that reported for pure MMA (1.4147 at 298 K)[108].

2.3.3 OTHER REAGENTS

HPLC grade methanol (Fisher A-452) and reagent grade 2,2-diphenyl-1-picrylhydrazyl (DPPH) (Aldrich D21,140-0) were both used without further purification.

2.4 METHODS

2.4.1 POLYMERIZATION STUDIES

Freshly distilled MMA was introduced into the

preweighed, argon filled insonation cell directly from the distillation receiving cell without atmospheric exposure. Argon was vigorously bubbled through the monomer for 45 min to ensure saturation. The argon flow rate was reduced and an appropriate thermostat bath placed around the insonation cell. The cavitation was initiated by turning on the ultrasonic generator at a preset power level. The temperature, as measured by a single chromel-alumel thermocouple, rose roughly 5 °C within the first 5 min after the ultrasound was turned on. It could be maintained to ± 1 °C thereafter.

Samples of MMA (approximately 8 g) were periodically withdrawn with a syringe, weighed and shot into a 20 fold excess of methanol to precipitate the polymer. The empty syringe was then weighed so that the sample weight could be found. A sample withdrawn immediately before the ultrasonic irradiation was started was treated in an identical fashion. The precipitated polymer was then collected on preweighed, fine porosity sintered glass filters. The polymer was next dried on the filter for 18 hr before it was weighed. Longer drying times did not affect the results. In some cases samples were withdrawn after the ultrasound was stopped in order to determine the effect of any background reaction. After the final sample was withdrawn, the weight of the insonation cell

and any excess MMA was measured.

2.4.2 DPPH STUDIES

Approximately 30 mg of DPPH was transferred directly into the insonation cell prior to the introduction of the MMA. The procedure followed from this point was identical to that described in section 2.4.1 except that each sample was immediately analyzed for its absorbance at 525 nm (using pure MMA as a reference). Syringes used for sampling were cleaned with spectral grade acetone (Caledon) and dried between samples since the DPPH concentration became progressively lower with each sample. The conversion of absorbance at 525 nm to DPPH concentration was accomplished using an experimentally determined Beer's law calibration.

In several experiments samples were analyzed for their polymer content to determine the effect of the DPPH on the polymerization reaction. Samples taken during these experiments were not, however analyzed for their absorbance.

2.4.3 MONOMER ABSORBANCE

At lower temperatures (below 20 °C) the monomer exhibited a faint yellow colouration after the ultrasonic irradiation. Ultraviolet spectra taken (with pure MMA as a

reference) from 700 nm to 200 nm showed only one absorption band with its peak absorbance at 295 nm. A kinetic study of this colouration was carried out using the same procedure outlined in section 2.4.1 except that samples were immediately analyzed for their absorbance at 295 nm with pure MMA as a reference.

2.4.4 GEL PERMEATION CHROMATOGRAPHY

Gel permeation chromatography was performed on several polymer samples by Dr. S. Bywater at N.R.C., Ottawa. Samples were chosen to determine the effects of: time of irradiation, acoustic intensity and bulk monomer temperature on the molecular weight of the polymer.

Solutions of 2% by weight polymer in tetrahydrofuran were analyzed using a column packed with micro-Styrol gel. The instrument was calibrated using solutions of standard polystyrene in tetrahydrofuran.

2.4.5 ANALYSIS OF COLOURED IMPURITY

The excess reaction mixture from the study of the yellowing rate at the lowest temperature (-31 ± 1 °C) was transferred to a 10 fold excess of methanol. This mixture was

then filtered through a fine porosity sintered glass filter to remove the polymer. The volume was then reduced from about 3.5 l to about 300 ml using a rotary evaporator. The resulting material which had a bright yellow colour was stored under argon, in the dark at 0 °C. Attempts to identify this material by G.C. - mass spectrometry revealed only MMA and methanol.

CHAPTER 3
POLYMERIZATION KINETICS

3.1 MECHANISM

Equations [3.10-3.16], describe a simple mechanism for the polymerization reaction initiated by ultrasonic cavitation.

MECHANISM

Cavitation Degradation

Initiation

Propagation

Termination
(disproportionation)

Termination
(combination)

Depolymerization

Where: M is monomer, C is a cavitation bubble, $R_i^\cdot$ ($i = 0, 1, n, n+1, m, 2m, r, s$) are radical species, P_i ($i = 2m, r, s, r+s$) are dead polymer chains and k_i ($i = 1 \dots 6$) are rate constants.

In order to keep the kinetic analysis as simple as possible, several assumptions are made:

(1) Chain transfer reactions are excluded from the kinetic analysis. This implies that radicals formed by transfer are as reactive as the original propagating radicals. Thus such processes have no effect on the overall rate. This

is generally valid for the bulk polymerization of MMA [104].

(2) A source of initiating free radicals can be found in the direct degradation of MMA by cavitation. High temperature conditions would generate free radicals by a thermolytic process. Some of the free radicals so produced would have lifetimes sufficiently long to migrate into the bulk liquid, initiating polymerization. Several studies have shown that free radicals are produced in cavitating liquids [8,50,80,81,106]. Suslick and coworkers have recently demonstrated the similarity between products formed in cavitating alkanes and those formed during high temperature ($> 1200^{\circ}\text{C}$) pyrolysis [8]. They conclude the major reaction to be C-C bond scission similar to that which occurs during pyrolysis.

(3) An efficiency factor f can be introduced to represent the fraction of primary free radicals which actually initiate polymer chains. This factor should be less than unity since some free radicals may recombine or disproportionate before they can initiate polymerization.

(4) The reactivity of propagating radicals is independent of their length. Thus, all propagation steps have the same rate constant k_p . This assumption is commonly made in free radical polymerization kinetics. It should be valid since radical reactivity is mainly a function of the

environment in the vicinity of the unpaired electron which does not change with chain length [104].

(5) Although termination occurs both by combination and disproportionation [104], the termination reaction can be described by a single rate constant k_t which is the weighted mean of k_{tc} and k_{td} . This is common practice in the treatment of free radical polymerization processes since detailed information about the relative magnitudes of each type of termination is scarce. Separation of termination reactions however, is not necessary to adequately describe polymerization kinetics.

(6) The overall rate of polymerization is described by the rate of disappearance of monomer. The production of high molecular weight polymer requires a very large number of monomer units to be consumed by the propagation step. Normally the amount of monomer consumed in propagation is many orders of magnitude greater than the amount consumed in other steps [104]. Thus the rate of monomer consumption can be equated with the rate of the propagating step with little error.

(7) Cavitation bubbles can be treated as a reactant in the kinetic analysis.

(8) A steady state analysis can be applied to the radical species. Steady state concentrations are established

very early in free radical polymerizations [104] and in sonochemical reactions [106].

Application of assumptions (1)-(8) yields equation [3.17] for the overall rate of the polymerization (a complete derivation of [3.17] is given in Appendix A).

$$-\frac{d[M]}{dt} = \frac{k_p [M]}{(2k_t)^{1/2}} 2[C](fk_t[M] + k_s[P])^{1/2} \quad [3.17]$$

The concentration of cavitation bubbles [C], can be expressed as shown in equation [3.18].

$$[C] = \frac{N_c}{V} = \frac{FI}{V} \quad [3.18]$$

Where: N_c is the number of cavitation bubbles, V is the liquid volume, I is the acoustic intensity and F is a constant of proportionality.

The fractional conversion, x is frequently used to follow the course of a polymerization. It represents the fraction of monomer units which have been converted to

polymer. For low conversions x can be defined as:

$$x = \frac{[M]_0 - [M]_t}{[M]_0} \quad [3.19]$$

Where: $[M]_0$ is the initial monomer concentration and $[M]_t$ is its instantaneous concentration. In terms of the fractional conversion $[M]_t$ and $[P]$ are respectively given by equations [3.20] and [3.21].

$$[M]_t = (1 - x)[M]_0 \approx [M]_0 \quad [3.20]$$

for $x \ll 1$

(This is true for this study where conversions were below .03).

$$[P] = \frac{x[M]_0}{\bar{X}_n} \quad [3.21]$$

Where $\bar{X}_n$ is the number average degree of polymerization. Substitution for $[P]$ and $[M]$ into [3.17] and solution of the resulting differential equation yields:

$$x(t) = \frac{k_2 k_3}{8k_4} \left(\frac{2FI}{V} \right) \left(\frac{[M]_0}{x_n} \right) t^2 + \quad [3.22]$$

$$\frac{(fk_1)^{1/2} k_3}{(2k_4)^{1/2}} \left(\frac{2FI}{V} \right)^{1/2} [M]_0^{1/2} t$$

Appendix A contains a complete derivation of this equation.

3.2 INITIAL OBSERVATIONS

3.2.1 CONVERSION VERSUS TIME CURVES

Equation [3.22] predicts a quadratic time dependence for the conversion. Figure 3.1 shows a series of typical conversion versus time plots. In these and all cases a very strong linear time dependence for the conversion is evident. This indicates that the magnitude of the quadratic coefficient must be very small. (All attempts to fit the conversion data to a function of the form of equation [3.22] yielded negative values for the coefficient of t^2 which must be spurious).

The linear behavior of the observed conversion-time data indicates therefore, that the first term of equation [3.22] is negligible. Thus, the conversion x as a function of time can be described by:

Figure 3.1 Typical Plots Of Monomer Conversion As A Function Of Irradiation Time. Acoustic Intensity = $20.6 \pm 0.3 \text{ W cm}^{-2}$

$$x(t) = \frac{k_2}{(2k_4)^{1/2}} (fk_1)^{1/2} \left(\frac{2FI}{V}\right)^{1/2} [M]_0^{1/2} t \quad [3.23]$$

The curves in figure 3.1 also demonstrate that negligible polymerization occurs when the ultrasound is stopped.

3.2.2 EFFECT OF MONOMER VOLUME ON POLYMERIZATION RATE

The rate of polymerization in terms of fractional conversion is obtained by differentiation of equation [3.23]. Thus the rate is given by:

$$\frac{dx}{dt} = \frac{(fk_1)^{1/2} k_2}{(2k_4)^{1/2}} \left(\frac{2FI}{V}\right)^{1/2} [M]_0^{1/2} \quad [3.24]$$

This predicts that the rate of polymerization will be inversely proportional to the square root of the monomer volume; if all else is kept constant. This relationship can be verified by plotting the logarithm of the rate versus that of the monomer volume for a series of polymerizations carried out under identical conditions excepting the monomer volume. (A plot of this type should be linear with a slope of -0.5 if

the predicted relationship holds). Figure 3.2 shows such a plot for a series of polymerizations carried out at 32 °C with an acoustic intensity of 21 W cm⁻². (For the purposes of this plot the average monomer volume during the reaction was used since the act of sampling necessarily changed the monomer volume by up to 30%.) The slope of figure 3.2 is $-.50 \pm .04$ in agreement with that predicted on the basis of equation [3.24].

A knowledge of the volume dependence of the rate permits correction for both the differences in volumes between experiments and the effects of sampling. Accordingly, all polymerization data were corrected for volume effects assuming the inverse square root volume dependence to be valid. (Appendix B contains a complete derivation of the method for correction). On this basis the corrected rate is obtained from the slope of a plot of the left hand side of equation [3.25] versus time.

$$(xV^{1/2})_t = \sum_{i=1}^n x_i (V_i^{1/2} - V_{i-1}^{1/2}) = \frac{(fk_1)^{1/2} k_2}{(2k_s)^{1/2}} (2FI)^{1/2} [M]_0^{1/2} t \quad [3.25]$$

Table 3.1 shows values of polymerization rates before and after being corrected for the volume. This data clearly

Figure 3.2 Plot Of $\ln(\text{Rate})$ As A Function
Of $\ln(\text{Liquid Volume})$

Table 3.1 Corrected and Uncorrected Polymerization
Rates For Several Monomer Volumes.*

Average Monomer Vol. l	Polymerization Rate	
	Uncorrected 10^{-6} s^{-1}	Corrected $10^{-6} \text{ l}^{1/2} \text{ s}^{-1}$
0.214	9.07 ± 0.08	4.14 ± 0.07
0.275	7.58 ± 0.10	4.03 ± 0.07
0.385	6.45 ± 0.08	4.08 ± 0.09
0.387	6.52 ± 0.10	4.05 ± 0.09
0.395	6.45 ± 0.10	4.08 ± 0.08

*Polymerizations carried out at 32°C with an
intensity of $20.6 \pm 0.3 \text{ W cm}^{-2}$.

shows the validity of the correction method. Furthermore the data of table 3.1 also show the excellent reproducibility of the corrected rates.

3.2.3 EFFECT OF ACOUSTIC INTENSITY ON POLYMERIZATION RATE

According to equation [3.25], the volume corrected rate (simply referred to as the rate hereafter) should depend on the square root of the acoustic intensity. A series of polymerizations were carried out with the aim of examining the validity of this relationship. Figure 3.3 shows a plot of the rates of a series of polymerizations carried out at 32 °C versus the square root of the acoustic intensity. The existence of a threshold intensity (approximately 2.6 W cm^{-2}), below which no cavitation or reaction occurs is evident in the data in this figure. A good linear relationship is displayed for the data corresponding to the four lowest intensities. The rate obtained at the highest intensity is however, lower than would be expected from the trend of the other data. A large amount of foaming was observed during the course of this polymerization which was not observed for all of the others. This represents a limitation on the assumption of a simple linear relationship between acoustic intensity (above the cavitation threshold) and the number of cavitation bubbles

Figure 3.3 Polymerization Rate As A Function Of
The Square Root Of Acoustic Intensity.

(cf. equation [3.18]).

Sirotyuk [21] has reported that initially the number of cavitation bubbles increases with increasing acoustic intensity until a certain peak intensity is reached. Increasing the intensity further produces a decrease in the number of cavitation bubbles. He ascribes this to an increase in the collapse time for the cavitation bubbles. According to this hypothesis, the maximum radii attained by the bubbles increases with increasing acoustic intensity; as does their number. Moreover, increasing maximum radii results in increasing collapse times for the bubbles. This continues until the collapse time exceeds one half the period of the ultrasound. At this point, the bubbles can no longer collapse completely in every acoustic period. The increased time between collapse events can allow a partial coagulation of the cavitation bubbles to occur. These enlarged bubbles may then float to the surface of the liquid or produce foam in a viscous polymer solution. In summary, the overall effect is the production of fewer, larger and more stable cavitation bubbles. A further effect is the reduction in potential cavitation nuclei since fragments of cavitation bubbles which have undergone a violent collapse are also thought to act as cavitation nuclei [21].

3.2.4 EFFECT OF BULK MONOMER TEMPERATURE ON POLYMERIZATION RATE

There is at present no report of the temperature dependence of bulk polymerizations initiated solely by acoustic cavitation. Frequently such a study can provide additional insight into the reaction process. Several polymerizations were carried out at temperatures from -17°C to 40°C with an acoustic intensity of 21 W cm^{-2} . Figure 3.4 is an Arrhenius plot for these polymerizations. It exhibits a good linear form and the slope provides an activation energy of $19.3 \pm 0.8\text{ kJ mol}^{-1}$. This is in good agreement with the activation energy of $17\text{--}20\text{ kJ mol}^{-1}$ reported for the bulk polymerization of MMA excluding contributions from the initiation reaction [104,107] (ie. activation energy of propagation - $\frac{1}{2}$ activation energy of termination). This indicates that the initiation reaction is independent of temperature. In this respect it resembles photopolymerizations. The values in table 3.2 show the initiation rates (given by equation [3.26]) for these reactions calculated with

$$\text{Rate} = f k_i (2F I) [M]_0 \quad [3.26]$$

literature values [108] for the density and the rate constants for propagation and termination. The relative insensitivity

Figure 3.4 Arrhenius Plot For The Rate Of Polymerization

Table 3.2 Calculated* Rates of Initiation For
Polymerizations at Several Temperatures

Bulk Temp.	Initiation Rate
°C	$10^{-9} \text{ mol s}^{-1}$
-17	3.30
-5	3.46
9	6.89
19	5.07
22	4.56
32	4.97
40	4.52

* Calculated using data from reference [108].

Polymerizations were carried out with an acoustic
intensity of $20.6 \pm 0.3 \text{ W cm}^{-2}$.

of the initiation reaction to temperature is evident in these values.

3.2.5 POLYMER ANALYSIS

In polymerizations the nature of the resulting polymer can provide information about the reactions from which it derives. Gel permeation chromatography (G.P.C.) provides a facile method for the determination of both average molecular weights and their distribution.

Samples of polymer were analyzed by G.P.C. to determine the effects of:

- (1) acoustic intensity
- (2) bulk monomer temperature
- (3) duration of irradiation

Tables 3.3-3.5 show both weight and number average molecular weights calculate from the chromatograms. A correction was made to account for differences in the hydrodynamic volumes of poly-(methyl methacrylate) and the polystyrene used to calibrate the instrument [109]. The number average molecular weights range from 3.49 to $4.76 \times 10^5 \text{ g mol}^{-1}$, while the weight average molecular weights

Table 3.3 Effect of Irradiation Time On Molecular Weight of Product.*

Irradiation Time	Molecular Weight		Ratio M_w/M_n
	Weight avg.	Number avg.	
	M_w	M_n	
min.	10^5 g mol^{-1}	10^5 g mol^{-1}	—
45	6.39	3.73	1.71
65	6.28	4.01	1.56
85	5.92	3.49	1.69

* Polymerization carried out at 32 °C at an acoustic intensity of $20.6 \pm 0.3 \text{ W cm}^{-2}$.

Table 3.4 Effect of Acoustic Intensity on Molecular Weight of Product.†

Acoustic Intensity	Molecular Weight		Ratio M_w/M_n
	Weight avg.	Number avg.	
	M_w	M_n	
W cm^{-2}	10^5 g mol^{-1}	10^5 g mol^{-1}	—
13.7 ± 0.1	6.89	4.14	1.66
20.6 ± 0.3	5.92	3.49	1.69
26.9 ± 0.2	6.97	4.52	1.54

† Polymerization carried out at 32 °C with 85 min. of irradiation.

Table 3.5 Effect of Monomer Bulk Temperature on
Molecular Weight of Product.*

Bulk Temp.	Molecular Weight		Ratio M_w/M_n
	Weight avg. M_w	Number avg. M_n	
$^{\circ}\text{C}$	10^5 g mol^{-1}	10^5 g mol^{-1}	—
22	6.27	3.92	1.59
32	5.92	3.49	1.69
40	7.24	4.76	1.52

* Polymerization carried out at $20 \pm 0.5 \text{ W cm}^{-2}$ after
85 min of irradiation.

range from 5.92 to $7.24 \times 10^5 \text{ g mol}^{-1}$. There is no clear trend in any of the data shown in tables 3.3-3.5, however the sparsity of data precludes ruling one out.

In the absence of chain transfer the ratio of weight to number average molecular weight is 2.0 for termination purely by disproportionation and 1.5 for termination purely by combination. Free radical bulk polymerizations of MMA normally yield values of 1.5 - 1.6 for this ratio [104] but it is generally agreed that both termination mechanisms are operative with MMA [104]. The values obtained for this ratio are also listed in tables 3.3-3.5. They fall in the range 1.5 - 1.7 which is typical for other free radical bulk polymerizations of MMA.

The degree of polymerization X_n , can be found from the number average molecular weight simply through division with the molecular weight of the monomer. In terms of reaction rates X_n can be defined by equation [3.27].

$$X_n = \frac{[M]_0 \left(\frac{dx}{dt} \right)}{\left(\frac{d[P]}{dt} \right)} \quad [3.27]$$

to produce equation [3.28].

$$\left[\frac{\left(\frac{dx}{dt} \right)}{\left(\frac{1}{X_n} - C_m [M]_0 \right)} \right]^{1/2} = \frac{k_2}{(k_{tc} + 2k_{td})^{1/2}} \quad [3.28]$$

Where C_m is the chain transfer to monomer constant. The term on the right hand side of equation [3.28] is usually considered a characteristic for the polymerization of a given monomer at a given temperature. In the absence of detailed information on the termination reaction mechanism, it frequently denoted as $k_2/(2k_t)^{1/2}$. Table 3.6 contains values of $k_2/(2k_t)^{1/2}$ calculated from the data in tables 3.3-3.5 using transfer constants from the literature [104] along with literature values [108] for this parameter. In view of the relative imprecision associated with values of this constant evaluated using X_n ; the agreement between calculated and literature values is excellent. Accordingly, the use of literature values for other calculations is justified.

Table 3.6 Comparison of Calculated and Literature[†]
Values of $k_3/(2k_4)^{1/2}$.

Bulk Temp. °C	$\frac{k_3}{(2k_4)^{1/2}}$	
	Calc.	Lit.
	$10^{-2} \text{ (l mol}^{-1} \text{ s}^{-1})^{1/2}$	$10^{-2} \text{ (l mol}^{-1} \text{ s}^{-1})^{1/2}$
22	4.7	4.59
32	$6.0 \pm 0.3^*$	5.78
40	6.8	6.81

[†]From ref.[108]

*Average of 5 samples. A similar uncertainty is expected for the other two temperatures.

CHAPTER 4

DPPH REACTION KINETICS

4.1 INTRODUCTION

The stable free radical 2,2-diphenyl-1-picrylhydrazyl (DPPH) has the structure shown in figure 4.1. It reacts quickly and irreversibly with many other free radicals to form a non-radical species. DPPH has been used for many years to obtain a measure of the rate of initiating free radical production in a wide variety of free radical polymerizations [110-114]. Several investigators have used this highly coloured material to measure the rate of free radical production in sonochemical reactions [8,46,78,115-117]. Thus, DPPH can provide more details about the mechanism of free radical production resulting from acoustic cavitation in MMA.

4.2 MECHANISM

The overall reaction scheme is identical to that proposed for the polymerization reaction with two additional steps. These steps are given by equations [4.10] and [4.11].

Figure 4.1 2,2-diphenyl-1-picrylhydrazyl
(DPPH)

Where: $Z^{\cdot}$ is DPPH, ZR_0 and ZR_n are non radical reaction products. The assumption is made that each DPPH radical reacts with one and only one radical. This assumption has been questioned in some polymerization systems [104,115] but it is accepted as valid for MMA [114].

A steady state analysis (see appendix C) gives equation [4.12] for the rate of DPPH consumption.

$$-\frac{d[Z^{\cdot}]}{dt} = 2fk_1[M]_0 \left(\frac{F1}{V}\right) \quad [4.12]$$

This equation predicts the rate to be inversely proportional to the volume of monomer. A volume correction is therefore required. By analogy to the polymerization reaction, the corrected rate is obtained from the slope of the left hand side of equation [4.13] as a function of time.

$$(V[Z^{\cdot}])_t - (V[Z^{\cdot}])_0 - \sum_{i=1}^n [Z^{\cdot}]_i (V_i - V_{i-1}) = -2fk_1[M]_0 F1t \quad [4.13]$$

Figure 4.2 shows a typical plot of the left hand side of [4.13] versus the time. A very good linear relationship is displayed by this and the other data as predicted by [4.13]. Moreover, when the ultrasound was stopped no further reaction was observed. This demonstrates the necessity for cavitation if any reaction is to occur.

4.3 EFFECT OF ACOUSTIC INTENSITY ON DPPH REACTION RATE

Although DPPH has been used previously [8,46,105], to study the rate of production of free radicals generated by acoustic cavitation, no study of the effect of acoustic intensity on the DPPH reaction has been reported. Equation [4.13] predicts a linear dependence of the rate on acoustic intensity. A series of reactions were carried out at a bulk temperature of 6 °C and varying acoustic intensities in order to verify this relationship. Figure 4.3 shows the rate of these reactions as a function of the acoustic intensity. Qualitatively, a good linear correlation is displayed by this data in agreement with the predicted relationship.

4.4 EFFECT OF BULK TEMPERATURE ON DPPH REACTION RATE

Relatively few studies of the effects of bulk liquid temperature on the rate of cavitation free radical formation have been reported [15,105]. A study of several reactions

Figure 4.2 Typical Plots Of The Left-Hand Side Of Equation [4.13] As A Function Of Irradiation Time

Figure 4.3 Rate Of DPPH Consumption As A Function Of Acoustic Intensity

carried out at an acoustic intensity of 21 W cm^{-2} and bulk temperatures ranging from -17°C to 40°C yields the Arrhenius plot shown in figure 4.4. Clearly, the simple Arrhenius relationship is not obeyed if the bulk monomer temperature is used.

Although other physical parameters influence cavitation, it has been reported that liquid vapor pressure is dominant [7,8,15,46,105]. The nature of the relationship between the rate and liquid vapor pressure however, is disputed [7,8,46,105]. Kruus et al. [7] suggested that the maximum temperature reached within the collapsing cavity should be used in the Arrhenius relation and not the bulk liquid temperature. They assumed an irreversible adiabatic collapse against the final pressure inside the bubble in order to obtain some maximum temperature. The relation derived on this basis is given by:

$$\ln(\text{rate}) = \ln(A) - \frac{E_a}{RT_{\text{max}}} \quad [4.14]$$

$$= \ln(A) - \left(\frac{P_v C_p}{P_{\text{max}}} \right) \left(\frac{E_a}{R^2 T_0} \right)$$

Where: E_a is the Arrhenius activation energy, P_v is the liquid

Figure 4.4 Arrhenius Plot For The Rate Of DPPH Consumption

vapor pressure (assumed to be the pressure at the start of the bubble collapse), $P_{\max}$ the pressure at the end of the bubble collapse, T_0 is the bulk liquid temperature and $T_{\max}$ the maximum temperature achieved by the bubble contents on collapse and C_p is the heat capacity of the vapor in the bubble.

In 1980 Sehgal et al. [15] showed the total free energy of cavity formation (ΔA) is related to the vapor pressure (P_V) and the ambient pressure (P_0) by the relation:

$$\Delta A = RT_0 \ln \frac{P_V}{P_0} \quad [4.15]$$

They demonstrated a linear correlation between $\ln(\text{rate})$ and ΔA . According to their model the free energy released during cavitation collapse is related to the energy gained by the bubble during its growth.

Very recently Suslick et al. [8,106] derived a relation using the same approach used by Kruus et al., the only difference being the assumption of a reversible adiabatic collapse by Suslick et al. This allowed them to use equation [1.47] for the maximum temperature attained by the bubble

Figure 5.1 Sample Plot Of Volume Corrected Monomer Absorbance At 295 nm As A Function Of Irradiation Time.

Temperature = -17°C

Acoustic Intensity = $20.6 \pm 0.3 \text{ W cm}^{-2}$

contents (the assumption is also made that Q in [1.47] is equal to P_V for a vapor filled cavity). The relation obtained by Suslick et al. is given by equation [4.16].

$$\ln(\text{rate}) = \ln(A) - \frac{E_a P_V}{RT_0 P_0 (\gamma - 1)} \quad [4.16]$$

Where all terms are as previously defined.

The temperature-vapor pressure dependence predicted by equation [4.16] is identical to that predicted by Kruus et al. except for the meaning of the constants. Consequently the relations given in [4.15] and [4.16] will be referred to as the Kruus-Suslick relation. Figure 4.5 shows a plot of the logarithm of the DPPH reaction rate as a function of P_V/T_0 . (Values of P_V were taken from the literature [118]). In spite of the crudeness of the models on which this plot is based, the correlation is excellent.

The slope of the line in figure 4.5 is $-14.9 \pm 0.7 \text{ torr}^{-1} \text{ K}$. A value of E_a can be estimated for the primary dissociation process from equations [4.14] and [4.16]. Setting $P_{\text{max}} = 760 \text{ torr}$ and estimating C_p as $100 \text{ J K}^{-1} \text{ mol}^{-1}$

Figure 4.5 Plot Of $\ln(\text{OPPH Rate})$ As A Function
Of (Vapor Pressure)/Bulk Temperature

by analogy to similar compounds [118] results in a value of 8 kJ mol^{-1} for E_a , well below energies needed to break chemical bonds. This result is very similar to the results obtained by Kruus et al. [7] in experiments where the vapor pressure was altered by variation in composition rather than temperature. It has, however, been suggested [22] that the pressure P_{max} can be an order of magnitude or more higher. If P_{max} is set at 10 atm, then E_a increases to 80 kJ mol^{-1} .

The use of the Suslick equation ([4.16]) gives $E_a = 5 \text{ kJ mol}^{-1}$ if a value 1.05 is assumed for γ by analogy with similar compounds [118]. Again, the value of E_a is linearly dependent on the value assumed for P_0 . The temperature T_{max} achieved in a reversible compression will however always be less than that resulting from an irreversible collapse, and thus equation [4.16] will always predict a lower value of E_a than equation [4.14].

A test of the Sehgal relation ($\ln(\text{rate})$ versus $\ln(P_v)$) is shown in figure 4.6. The correlation displayed in figure 4.6 is qualitatively not as good as that exhibited for the Kruus-Suslick relation. It has been previously reported [8,105] that the relation of Sehgal et al. only holds over a limited range of vapor pressures. This is also demonstrated by the data shown in figure 4.6.

Figure 4.6 Plot Of $\ln(\text{DPPH Rate})$ As A Function Of $\ln(\text{Vapor Pressure})$.

4.5 EFFECT OF DPPH ON THE POLYMERIZATION REACTION

The inhibitory effect of DPPH on free radical polymerizations has been well documented [104,110-114]. No studies have yet reported the effect of DPPH on an ultrasonically induced polymerization. Such a study would demonstrate the free radical nature of the initiating species.

Thus, a series of experiments were carried out to determine the effect of DPPH on the polymerization reaction.

Figure 4.7 shows a plot of the corrected conversion as a function of irradiation time for a series of polymerization reactions. The only difference between the conditions under which these reactions took place was the initial concentration of DPPH. Figure 4.7 clearly shows inhibition periods, when the MMA originally contained DPPH. During the inhibition period no polymerization was detected. Moreover, the length of the inhibition period is roughly proportional to the initial concentration of DPPH. This demonstrates the free radical nature of the polymerization.

The post inhibition rate of polymerization was found to be within 2% of the uninhibited rate. This type of behavior has been observed in past studies of the inhibition of bulk

Figure 4.7 Corrected Conversion Versus Time Curves Showing Inhibition With DPPH. (Temperature = 32 °C, Acoustic Intensity = $20.6 \pm 0.3 \text{ W cm}^{-2}$).

Initial DPPH Conc.: Δ -0.0 mol l^{-1} , $\bullet$ - 2.1×10^{-6} mol l^{-1} , $\circ$ - 5.2×10^{-5} mol l^{-1}

free radical polymerizations of MMA [114]. This indicates that the DPPH reaction products are unreactive towards the initiating or propagating species. This is not the case for other monomers such as styrene [114].

CHAPTER 5

FORMATION OF COLOURED COMPOUND

Cavitation induced reactions have in many cases resulted in the formation of a coloured compound [7,102,103,119]. This has made it possible to easily monitor the rate of the reactions. Attempts to characterize the nature of these compounds completely have however not been very successful [7,102,103].

The appearance of a yellow colour in the liquid was also noted on cavitation of methyl methacrylate, especially at low bulk temperature. The yellowish colour was due to an absorption band which had a maximum absorbance in the ultraviolet at 295 nm. As shown in figure 5.1, it increases linearly with time.

The rate of formation of this coloured compound has a temperature dependence which is in agreement with the Kruus-Suslick equation i.e. $\ln(\text{rate})$ vs. P_v/T is linear, figure 5.2, as in the case of the DPPH experiments (figure 4.5). The slope of this line ($-29.2 \pm 2.5 \text{ torr}^{-1} \text{ K}$) can be analyzed in

Figure 5.1 Sample Plot Of Volume Corrected Monomer Absorbance At 295 nm As A Function Of Irradiation Time.

Temperature = -17 °C

Acoustic Intensity = $20.6 \pm 0.3 \text{ W cm}^{-2}$

Figure 5.2 $\ln(\text{Rate Of Monomer Colouration})$ As A Function Of $(\text{Vapor Pressure})/(\text{Bulk Temperature})$.

the same way as the corresponding DPPH line (figure 4.5), and would give E_a values about twice those found in the DPPH analysis. This suggests that the reaction mechanism in the disappearance of DPPH has a considerably lower activation energy than that for the formation of the coloured compound.

It is probable that the coloured compound is due to the recombination or disproportionation of the primary free radicals formed on collapse of transient cavitation bubbles (assumption (3) in the mechanism). At lower bulk temperatures, the effective local temperature on collapse of the bubbles is greater as there is less vapor pressure to cushion the collapse. Hence there is a greater local concentration of MMA fragments which can recombine. Such a mechanism for the formation of coloured compounds in cavitation induced reactions is supported by the decrease in the rate of formation of these compounds on introduction of small amounts of liquids with higher vapor pressures [7,102].

The exact nature of the coloured compounds formed and the mechanism for their formation cannot be well defined on the basis of the experimental data available at this time. The amounts of the compounds available for analysis are very

small [119] and their molecular structures are complex [7,102].

CHAPTER 6

DISCUSSION

6.1 POLYMERIZATION REACTION

Several investigators [86,89-93] have reported an absence of any polymerization when purified vinyl monomers undergo acoustic cavitation. The results of the present work do not support this observation. In fact, when polymerization conditions were identical, it was possible to consistently obtain reproducible rates of polymerization in purified MMA. Furthermore, it has been found that acoustic cavitation is a prerequisite for significant rates of polymerization in purified MMA exposed only to intense ultrasound. This is attested to by the lack of any detectable rate of polymerization in the absence of the ultrasound.

In contrast with past reports [79,86-94], there is no evidence to suggest that acoustic depolymerization plays any significant role in the initiation of polymerization. It is possible however, that this process may be significant at higher fractional conversions than those studied.

The effect of the liquid volume on the rate of reaction, has not been reported in past studies. This is rather

surprising in view of the large volume effect observed in this work. This may cast some doubt on the results of studies in which the reaction rate was determined by analyzing aliquots removed from a fixed reaction volume. This would be particularly true if sampling changed the reaction volume significantly. It may be preferable to use fixed reaction volumes or to state the acoustic intensity per unit volume in all sonochemical studies.

The existence of a threshold intensity below which no cavitation occurs, has been well established [21,39]. This behavior has also been observed in this work. At 32 °C, the cavitation threshold for MMA is about 2.6-W cm^{-2} . Unfortunately the value of the cavitation threshold depends on so many factors that its interpretation is not very meaningful.

Systematic studies of the effects of the acoustic intensity on the rates of ultrasonically induced reactions are quite rare in the literature [100,121,122]. One of these studies has reported the same form for both the dependence of the reaction rate on the acoustic intensity and the photo intensity dependence for the analogous photochemical reaction. This type of behavior was also observed in this study. Above the threshold intensity, the rate of the polymerization

reaction exhibited a square root dependence on the acoustic intensity. This is the same functional form as the dependence of the rate of a typical photopolymerization on the intensity of the initiating light [104,109].

The simple mechanism described by equations [3.10]-[3.16] is based on several crude assumptions. In view of this, it predicts the volume and acoustic intensity dependence of the reaction rate remarkably well. Unfortunately other methods frequently used to elucidate the mechanism of a polymerization cannot be used in the study of ultrasonically induced polymerizations. For example, the dependence of the reaction rate on the monomer concentration is often used to verify a rate law [109]. This is frequently accomplished by polymerizing a monomer which has been diluted by an inert solvent [109]. In the case of ultrasonically induced polymerizations, adding a diluant would have many more significant effects than just monomer dilution. Firstly, there is no solvent which could be considered inert when subjected to acoustic cavitation. A recent study by Suslick and coworkers [105] showed that free radicals are generated in each of a wide variety of solvents. Additional free radicals generated by the degradation of the solvent would cause effects which could not be separated from the effects caused

by monomer dilution. Secondly, the dynamics of the cavitation bubbles themselves are sensitive to many factors such as surface tension, vapor pressure etc. [39]. A solvent would certainly change these factors. - Thus, complicating effects would mask the true effects of dilution.

The dependence of the sonochemical reaction rates on the bulk temperature of a liquid has been the subject of some debate in the past [7,8,15,100,105,122]. Several studies [100,122] have reported that the temperature dependence follows the simple Arrhenius relation. The activation energies in these cases are essentially equal to those of the same reactions carried out in the absence of ultrasound. More complicated forms for the dependence of the rates of sonochemical reactions have also been reported [7,8,15,105,122].

The polymerization reactions carried out in this work displayed the simple Arrhenius temperature dependence. The activation energy for the overall polymerization reaction was $19.3 \pm 0.8 \text{ kJ mol}^{-1}$. This agrees well with values reported ($17 - 20 \text{ kJ mol}^{-1}$) [104,107] for the activation energy of bulk free radical polymerizations of MMA excluding any contribution from the initiation reaction. This indicates an effective

activation energy for the initiation step which is near 0 kJ mol^{-1} . One cannot draw any conclusions from this, since the temperature behavior of the efficiency factors f and F are unknown. The possibility exists that either f or F or both have temperature dependencies which exactly cancel any temperature dependence of k_i .

The polymer produced in this study showed no significant difference in either average molecular weight or molecular weight distribution from polymer produced by more conventional sources of initiation (provided that no chain transfer agents are involved and the rates of initiation are similar). Values of the parameter $k_t/(2k_p)^{1/2}$ calculated from the number average degree of polymerization were in very good agreement with literature values for this parameter at the same temperatures [108]. This suggests that the propagation and termination reactions in ultrasonically induced polymerization are very similar to those under conventional polymerization conditions. This may seem self evident, but it does indicate that these reactions occur in the bulk liquid under ambient pressure and bulk liquid temperature conditions. Very strong shock waves are generated in the liquid immediately surrounding the collapsing cavity (estimated to be as high as several hundred to a thousand atmospheres [39]). Past studies [104] have shown

that the value of $k_s/(2k_t)^{1/2}$ increases by a factor of 2 at about 250 atm and a factor of 4 at a pressure of 1000 atm (at 30 °C). If most of the polymerization were to occur in the immediate vicinity of the collapsing cavity, one might expect a significant difference in the value of this parameter from that obtained under ambient pressure conditions.

6.2 DPPH REACTIONS

The free radical nature of the ultrasonically induced polymerization of MMA is evident by its inhibition with DPPH. In the past, the lengths of inhibition periods have been used to obtain rates of initiation for free radical polymerizations [104,110-114]. In this work however, the inhibition periods were too short to be used for this purpose. Longer inhibition periods could have been produced using larger initial amounts of DPPH; but this would not have been practical.

DPPH has been suggested as a dosimeter for non-aqueous sonochemical reactions [105]. No study has yet determined the effects of acoustic intensity on the DPPH reaction rate. Such a study is of prime importance if DPPH is to be considered as a dosimeter. Above the cavitation threshold at 6 °C of about 9 W cm^{-2} , the rate of DPPH consumption shows a good linear

dependence on the acoustic intensity. This supports its potential use as dosimeter. Furthermore, it also agrees with the acoustic intensity dependence predicted by the simple mechanism [3.10]-[3.16] with the addition of steps [4.10] and [4.11].

The dependence of the rate of DPPH consumption on the bulk liquid temperature does not obey the simple Arrhenius relationship. Instead, it displays a form predicted by both Kruus [7] and Suslick and coworkers [105]. These relations suggest that the rate of the DPPH reaction depends more on the conditions (particularly the liquid vapor pressure) within the collapsing cavity than those which exist within the bulk liquid. It also suggests that the relation proposed by Sehgal and coworkers [15] is only obeyed over a very limited range of temperatures.

6.3 COMPARISON OF THE POLYMERIZATION AND DPPH RESULTS

According to the analysis in appendices A and C, the rate of DPPH consumption should be equal to the rate of initiation for the polymerization reaction. Thus, both the rate of initiation calculated from the overall polymerization reaction and the DPPH reaction rate should have the same

dependence on the bulk monomer temperature. Clearly, the results show that this is not the case. One might speculate that some radicals, which would react with the DPPH, recombine before they can initiate polymerization. In this case however, the rate of the DPPH reaction would always be greater than the rate of initiation (calculated from the overall rate of polymerization). Table 6.1 contains values of the DPPH reaction rate and the calculated rate of initiation for reactions carried out under the same conditions. This table also shows the value of the ratio of the calculated rate of initiation to the rate of the DPPH reaction. Clearly, this ratio is not always less than unity, as it should be if the discrepancy were to be explained by recombination.

It may be possible that the efficiency factor f is significantly different for radicals reacting with DPPH and those initiating polymerization. Thus, the temperature dependence of f could be quite different for the two reactions. In the case of the polymerization reaction, the increased number of radicals produced at lower temperatures would be effectively cancelled by mutual scavenging. Consequently, the value of f would be lower at lower temperatures.

Table 6.1 Comparison of Initiation Rates* Calculated From The
DPPH and Polymerization[†] Reaction Rates.

Bulk Temp.	Initiation Rate Polymerization I_p	Initiation Rate DPPH Reaction I_d	Ratio I_p/I_d
°C	$10^{-9} \text{ mol s}^{-1}$	$10^{-9} \text{ mol s}^{-1}$	—
-17	3.30	6.6	0.50
19	5.07	2.7	1.9
32	4.97	0.56	8.8
40	4.52	0.28	16

* Initiation Rate is given by :
Rate = $fk_i(2FI)[M]_0$

[†] Calculated using data from reference [108].

2

The lower value of E_a for the disappearance of DPPH as compared to the appearance of the colored material suggests that the DPPH may itself be dissociated in the primary cavitation bubble collapse action rather than through reaction with fragments of MMA. This would also predict the ratio I_p/I_d to be less than unity, in contradiction to the data in table 6.1.

The discrepancy between the two rates might be explained by the values of the parameter $k_i/(2k_t)^{1/2}$ used to calculate the initiation rate from the polymerization rate. If the actual values for the propagation and termination rate constants were different from those used in the calculation, a significant discrepancy could develop. However, the analysis of the number average degree of polymerization indicates that the values of $k_i/(2k_t)^{1/2}$ used for the calculation of the initiation rates are valid. Consequently the reason for the discrepancy between the two rates is not clear at this time. The formation of the compound(s) giving an absorption at 295 nm might also be involved in any explanation of the difference in initiation rates, and this phenomenon cannot be explained with any

confidence on the basis of the experimental evidence available.

CHAPTER 7

CONCLUSIONS

The experiments described here seem definitely to prove the possibility of initiating polymerization in a pure vinyl monomer through ultrasonic cavitation. A simple mechanism predicts correctly the time, volume and acoustic intensity relationships found experimentally. The temperature dependence of the polymerization reaction fits an Arrhenius relation and gives an activation energy in the range of those reported for the bulk polymerization of MMA. G.P.C. analysis of the products indicate a number average weight of $4 \times 10^5 \text{ g mol}^{-1}$ and a weight to number average molecular weight ratio of 1.6, typical for a free radical bulk polymerization of MMA carried out under similar initiation rates. Rate constants obtained in these experiments agree well with literature values.

Introduction of the radical scavenger DPPH inhibits the polymerization. The temperature dependence of the reaction of DPPH agrees over a wide temperature range (-17 to 40 °C) with the relations previously reported by Kruus et al. [7] and

Suslick et al. [105]. The analysis in terms of activation energy gives results very similar to those of Kruus et al. [7] where composition rather than temperature was altered to vary the vapor pressure.

The rate of initiation can be calculated from both the polymerization rate and the rate of the DPPH reaction. Although the two methods give rates of the same order of magnitude, the variation of their ratio with temperature is considerable. Further experiments are necessary to explain this variation.

The nature and mechanism of formation of a coloured material (peak absorbance at 295 nm) formed at lower temperatures can also not be properly explained on the basis of these experiments.

SUGGESTIONS FOR FUTURE WORK

There are a number of questions raised by the results of this work. These questions can only be answered with more research. In particular, a thorough investigation of the reaction mechanism would be of great interest. For instance, the initial degradation of the MMA might produce some gaseous reaction products. If these were produced, their analysis would provide additional insight into the nature of the degradation reaction.

Secondly, a detailed analysis of the DPPH reaction products might provide some explanation for the discrepancy between the calculated values of the initiation rates. Such an analysis might also provide some information as to the identity of the initiating species. Additional information about the nature of the initiating species might also be obtained from a thorough spin trapping study.

More information about the role of cavitation in the reaction could also be derived by a study of the effects of frequency, pulsing, and high conversion.

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APPENDIX A
DERIVATION OF THE POLYMERIZATION RATE LAW

Application of the steady state approximation to the mechanism shown in equations [1] to [7] gives:

$$\frac{d[R_n^{\cdot}]}{dt} = 2fk_1[M][C] - k_2[M][R_n^{\cdot}] = 0 \quad [a.1]$$

$$\frac{d[R_n^{\cdot}]}{dt} = k_1[M][R_n^{\cdot}] + 2k_3[C][P] + k_4[R_n^{\cdot}][C] - \quad [a.2]$$

$$2k_4[R_n^{\cdot}]^2 = 0$$

Solving for $[R_n^{\cdot}]$ yields:

$$[R_n^{\cdot}] = \frac{k_3[C]}{4k_4} + \quad [a.3]$$

$$\frac{1}{4k_4} \{ (k_3[C])^2 + 16k_4[C](fk_1[M] + k_3[P]) \}^{1/2}$$

Assuming $k_3 \approx k_4 \ll k_1$, $[R_n^{\cdot}]$ is given by:

$$[R_n^{\cdot}] = \frac{1}{(2k_4)^{1/2}} \{ 2[C](fk_1[M] + k_3[P]) \}^{1/2} \quad [a.4]$$

The overall rate of polymerization is given by the rate of the propagation step, thus:

$$-\frac{d[M]}{dt} = k_p[M][R_n^{\cdot}] \quad [a.5]$$

Substituting for $[R_n^{\cdot}]$ from [a.4] into [a.5] gives:

$$-\frac{d[M]}{dt} = \frac{k_p[M]}{(2k_t)^{1/2}} \{2[C](fk_1[M] + k_s[P])\}^{1/2} \quad [a.6]$$

Expressing [a.6] in terms of fractional conversion (x) and substituting for $[C] = (FI)/V$ gives:

$$\frac{dx}{dt} = \frac{k_p}{(2k_t)^{1/2}} \left(\frac{2FI}{V} \right)^{1/2} \left\{ fk_1 + \left(\frac{k_s x}{X_n} \right) \right\}^{1/2} [M]_0^{1/2} \quad [a.7]$$

Separating the variables x and t gives:

$$\frac{dx}{(fk_1 X_n + k_s x)^{1/2}} = \frac{k_p}{(2k_t)^{1/2}} \left(\frac{2FI}{V} \right)^{1/2} \left(\frac{[M]_0}{X_n} \right)^{1/2} dt \quad [a.8]$$

Solution of [a.8] with the boundary condition $x = 0$ at $t = 0$ gives:

$$\frac{2(fk_1 x_n + k_3 x)^{1/2}}{k_3} = \frac{k_3}{(2k_4)^{1/2}} \left(\frac{2FI}{V} \right)^{1/2} \left(\frac{[M]_0}{x_n} \right)^{1/2} t \quad [a.9]$$

$$+ \frac{2(fk_1 x_n)^{1/2}}{k_3}$$

Solution of [a.9] for x yields:

$$x(t) = \frac{k_3 k_4}{8k_4} \left(\frac{2FI}{V} \right) \left(\frac{[M]_0}{x_n} \right) t^2 + \quad [a.10]$$

$$\frac{(fk_1)^{1/2} k_3}{(2k_4)^{1/2}} \left(\frac{2FI}{V} \right)^{1/2} [M]_0^{1/2} t$$

APPENDIX B
DERIVATION OF VOLUME CORRECTION METHOD

The polymerization rate is given by:

$$\frac{dx}{dt} = \frac{(fk_1)^{1/2} k_2}{(2k_4)^{1/2}} \left(\frac{2FI}{V} \right)^{1/2} [M]_0^{1/2} \quad [b.1]$$

Now recognizing that:

$$V^{1/2} \left(\frac{dx}{dt} \right) = \frac{(fk_1)^{1/2} k_2}{(2k_4)^{1/2}} (2FI)^{1/2} [M]_0^{1/2} \quad [b.2]$$

and as $V = V(t)$

$$V^{1/2} \left(\frac{dx}{dt} \right) = \frac{d(xV)^{1/2}}{dt} - x \frac{dV^{1/2}}{dt} \quad [b.3]$$

Then the following differential equation can be written:

$$\frac{d(xV)^{1/2}}{dt} - \frac{dV^{1/2}}{dt} = \frac{(fk_1)^{1/2} k_2}{(2k_4)^{1/2}} (2FI)^{1/2} [M]_0^{1/2} \quad [b.4]$$

Separating the variables and integrating both sides gives:

$$(xV^{1/2})_t - \sum_{i=1}^n x_i (V_i^{1/2} - V_{i-1}^{1/2}) = \frac{(fk_p)^{1/2} k_t}{(2k_a)^{1/2}} (2FI)^{1/2} [M]_0^{1/2} t \quad [b.5]$$

Thus, a plot of the left hand side of equation [b.5] versus t should be linear and eliminate the volume dependence of the rate of polymerization.

APPENDIX C
DERIVATION OF RATE EXPRESSION FOR DPPH CONSUMPTION

The rate of DPPH consumption is given by:

$$-\frac{d[Z^{\cdot}]}{dt} = k_1[Z^{\cdot}][R_0^{\cdot}] + k_2[Z^{\cdot}][R_n^{\cdot}] \quad [c.1]$$

The steady state assumption for $R_0^{\cdot}$ yields:

$$\frac{d[R_0^{\cdot}]}{dt} = 2fk_1[M][C] - k_2[M][R_0^{\cdot}] - k_1[Z^{\cdot}][R_0^{\cdot}] = 0 \quad [c.2]$$

The efficiency factor f used here will be the same as for the case of the polymerization reaction according to theoretical studies (c1). Solution of [c.2] for $[R_0^{\cdot}]$ gives:

$$[R_0^{\cdot}] = \frac{2fk_1[M][C]}{k_2[M] + k_1[Z^{\cdot}]} \quad [c.3]$$

Similarly for $R_n^{\cdot}$, the steady state treatment gives:

$$-\frac{d[R_n^{\cdot}]}{dt} = k_2[M][R_0^{\cdot}] - 2k_4[R_n^{\cdot}]^2 - k_3[Z^{\cdot}][R_n^{\cdot}] = 0 \quad [c.4]$$

Substituting for $[R_0^\cdot]$ from equation [c.3] and solving for $[R_n^\cdot]$ gives:

$$[R_n^\cdot] = \frac{1}{(2k_4)^{1/2}} \left[\left(\frac{k_1^2 [Z^\cdot]^2}{k_4} + \frac{8fk_1 k_2 [M]^2 [C]}{k_1 [Z^\cdot] + k_2 [M]} \right)^{1/2} \right. \quad [c.5]$$

$$\left. - \frac{k_1 [Z^\cdot]}{k_4^{1/2}} \right]$$

For the sake of clarity, let the rate of initiation be represented by ζ such that:

$$\zeta = 2fk_1 [M][C] \quad [c.6]$$

Substitution for $[R_0^\cdot]$, $[R_n^\cdot]$ and ζ from [c.3], [c.6] and respectively into [c.1] gives:

$$-\frac{d[Z^\cdot]}{dt} = \frac{k_1 [Z^\cdot] \zeta}{k_1 [Z^\cdot] + k_2 [M]} + \quad [c.7]$$

$$\frac{k_1 [Z^\cdot]}{(2k_4)^{1/2}} \left[\left(\frac{k_1^2 [Z^\cdot]^2}{k_4} + \frac{4k_2 [M] \zeta}{k_1 [Z^\cdot] + k_2 [M]} \right)^{1/2} \right.$$

$$\left. - \frac{k_1 [Z^\cdot]}{k_4^{1/2}} \right]$$

Simplifying [c.7] gives:

$$-\frac{d[Z^*]}{dt} = \frac{k_7[M]\zeta}{k_7[Z^*] + k_2[M]} \quad [c.8]$$

$$\frac{k_8[Z^*]^2}{2k_4} \left[\left(1 + \left[\frac{4k_4}{k_8^2[Z^*]^2} \right] \left[\frac{k_2[M]\zeta}{k_7[Z^*] + k_2[M]} \right] \right)^{1/2} - 1 \right]$$

Now $2k_4 \approx 10^7 \text{ mol}^{-1} \text{ l s}^{-1}$ (c2), $\zeta \approx 10^{-8} \text{ mol l}^{-1} \text{ s}^{-1}$ (calculated from the polymerization data), $k_8 \approx k_7 \approx 10^5 \text{ mol l}^{-1} \text{ s}^{-1}$ assuming radical reactivity is independent of chain length and a value for k_7 from the literature (c2) and $[Z^*] \approx 10^{-4} \text{ mol l}^{-1}$. Thus:

$$\left(\frac{4k_4}{k_8^2[Z^*]^2} \right) \left(\frac{k_2[M]\zeta}{k_7[Z^*] + k_2[M]} \right) \approx \frac{10^7}{(10^5 \cdot 10^{-4})^2} \left(\frac{k_2[M] 10^{-8}}{k_7[Z^*] + k_2[M]} \right) \quad [c.9]$$

$$\approx 10^{-3} \frac{k_2[M]}{k_7[Z^*] + k_2[M]}$$

$$\leq 10^{-3}$$

By analogy with $(1+x)^{1/2} \approx 1+x/2$, (for $x \ll 1$) the following expression can be written:

$$\left[1 + \left(\frac{4k_4}{k_8^2[Z^*]^2} \right) \left(\frac{k_2[M]\xi}{k_7[Z^*] + k_2[M]} \right) \right]^{1/2} \quad [c.10]$$

$$\approx 1 + \left(\frac{2k_4}{k_8^2[Z^*]^2} \right) \left(\frac{k_2[M]\xi}{k_7[Z^*] + k_2[M]} \right)$$

With the approximation of equation [c.10], [c.8] becomes:

$$-\frac{d[Z^*]}{dt} = \frac{k_2[Z^*]}{k_7[Z^*] + k_2[M]} + \quad [c.11]$$

$$\frac{k_7[Z^*]}{2k_4} \left[1 + \left(\frac{2k_4}{k_8^2[Z^*]^2} \right) \left(\frac{k_2[M]\xi}{k_7[Z^*] + k_2[M]} \right) - 1 \right]$$

Simplifying [c.11] yields:

$$-\frac{d[Z^*]}{dt} = \frac{k_2[M]\xi}{k_7[Z^*] + k_2[M]} + \frac{k_2[M]\xi}{k_7[Z^*] + k_2[M]} \quad [c.12]$$

Equation [c.12] reduces further to:

$$-\frac{d[Z^*]}{dt} = \zeta \quad [c.13]$$

$$= 2fk_i[M][C]$$

$$= 2fk_i[M]_0 \left(\frac{F1}{V} \right)$$

Thus, the rate of DPPH consumption should give the rate at which initiating free radicals are formed by acoustic cavitation.

References

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