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# A study of vapor phase self-initiated thermal polymerization of styrene with an expansion chamber

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Studies of the self-initiated polymerization of styrene have been performed in the uniform environment of an expansion cloud chamber, using nucleation of liquid monomer drops for detection. These studies are the first of this kind in an expansion chamber and, although preliminary and designed to explore feasibility, have yielded many interesting results. The occurrence of the self-initiated nonterminated gas phase processes, previously observed in a diffusion cloud chamber, has now been confirmed in an expansion chamber. At 15 °C the initiation rate is measured to be 2 to 6 radicals  $\text{cm}^{-3} \text{s}^{-1}$  and the propagation constant is approximately  $6 \times 10^{-21} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ . Additional studies in the presence of oxygen indicate the (expected) formation of polystyrene peroxide as well as its cleavage into additional radicals at 25 °C.

## I. INTRODUCTION

It has been recognized for more than a century that a supersaturated vapor will condense on a particle, ion, or surface in preference to condensing with molecules of its own vapor (heterogeneous vs homogeneous nucleation).<sup>1,2</sup> This preference produces rain in the atmosphere (at a relative humidity of approximately 100% or a supersaturation ratio of 1.0) and also allows one to detect by condensation extremely low concentrations of particles in a cloud chamber. For example, one can detect by means of nucleation 1 ion  $\text{cm}^{-3}$  in a gas containing about  $10^{19}$  atoms  $\text{cm}^{-3}$ . In the present work one detects a single polymer molecule in a gaseous mixture containing  $5 \times 10^{17}$  monomers  $\text{cm}^{-3}$  and about  $10^{18}$   $\text{cm}^{-3}$  molecules of carrier gas (argon).

Beginning in 1983, Reiss and co-workers<sup>3-5</sup> initiated studies of true homogeneous gas phase free radical addition polymerization, using nucleation to detect individual polymers as they were produced. The polymers were grown in supersaturated monomer vapor and, depending on the degree of supersaturation, nucleated a drop of liquid monomer when they attained a certain "tunable" size (see Refs. 3-8). The rate of formation of drops measures the rate of polymerization. The polymers were grown at such low concentrations that they could not encounter one another to condense out of the vapor. For the same reason bimolecular recombinative termination was absent.

The studies of Reiss *et al.* were conducted in a diffusion cloud chamber which, although having certain advantages,<sup>9</sup> has the serious disadvantage that it provides a nonuniform environment, gradients in both temperature and monomer concentration. Therefore, measured kinetic parameters are averaged over these gradients. In the work reported here an expansion cloud chamber was used. Thus, it is possible to study the kinetics of polymerization in a uniform monomer vapor and, in principle, to obtain nonaveraged parameters. The polymers are grown under the uniform conditions that prevail in the saturated vapor within the chamber prior to expansion, and are counted by means of droplet formation in

the supersaturated vapor produced by the expansion. Since this is the first investigation of its kind, it is necessarily incomplete, and should be regarded as a feasibility study more than a detailed investigation. However, many useful and interesting results have been obtained on the polymerization of styrene to polystyrene in the vapor phase.

Styrene in the liquid state is known to undergo self-initiated thermal polymerization at room temperature. The process is slow, producing only about  $10^{10}$  initiating free radicals  $\text{cm}^{-3} \text{s}^{-1}$  in the liquid. El-Shall, Bahta, Rabeony, and Reiss<sup>10</sup> using a diffusion cloud chamber, showed that self-polymerization also occurs in the vapor and estimated the rate of free radical production to be less than  $200 \text{cm}^{-3} \text{s}^{-1}$ . This study finds a considerably smaller rate of radical production (in the vapor).

If oxygen is present in liquid styrene, the polymerization process is altered, leading to the formation of the copolymer, polystyrene peroxide.<sup>11</sup> At high enough temperature this copolymer can cleave at the peroxide group and result in a multiplication of free radicals. This process appears also to have been observed in styrene vapor where it can prevent the achievement of a steady state of polymerization in the closed system of the expansion chamber.

## II. DETECTION OF POLYMER (POLYSTYRENE) IN THE EXPANSION CLOUD CHAMBER

Our cloud chamber has been described in considerable detail in Ref. 11 with additional details of general cloud chamber techniques found in Ref. 12. Therefore we will limit discussion to the most relevant properties of the device. The fast-expansion chamber<sup>2</sup> is basically a device for momentarily creating a controlled (high) supersaturation. Figure 1 shows a schematic drawing of this chamber. It contains a pool of liquid over which the equilibrium vapor pressure is initially established in a carrier gas (for these experiments: argon). The gas is then rapidly expanded by lowering the piston at the bottom of the chamber so that the gas is adiabatically

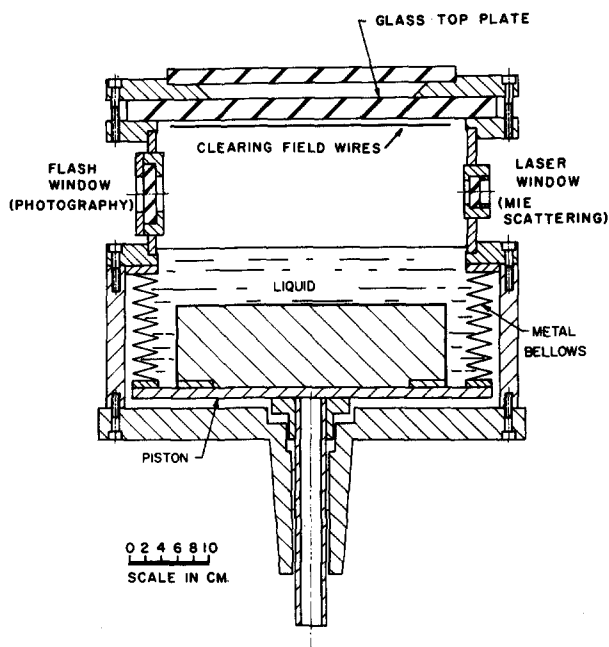


FIG. 1. A schematic cross section of the expansion chamber.

ically cooled to a state of supersaturation, determined by the extent of the expansion.

The chamber shown in Fig. 1 was designed, and has been used primarily for the study of homogeneous nucleation over ranges of temperature, supersaturation, and nucleation rate.<sup>14-16</sup> An analysis by means of which the accuracy of measurement required for variables such as pressure and temperature can be calculated is found in Ref. 13.

For the experiments on styrene the following design parameters are important. The chamber is constructed of stainless steel and glass with fluorocarbon plastic seals. Prior to expansion, conditions in the vapor are uniform, i.e., the polymers grow under the same conditions over the entire chamber (except possibly near the walls where polymers may be irreversibly adsorbed). The sensitive volume of the chamber is 38.4 cm in diameter and the height can be varied from 11 to about 19 cm (at 19 cm height the depth of expansion that can be achieved is very low). The large size is important because the growing polymers are eventually lost to the walls, so that if appreciable degrees of polymerization are to be achieved the lifetime of the polymer before loss to the walls cannot be too short. Furthermore, the interior "sensitive" volume of the chamber should not be affected by the walls, i.e., the time for the exchange of heat and vapor with the walls during an expansion should not exceed 1 s. It has been demonstrated that, in the sensitive volume, the expansion is adiabatic. A disadvantage of its large size is that, in its present configuration, about 23  $\ell$  of liquid are required for satisfactory operation.

Temperature control in the chamber is very accurate; the walls are controlled to about  $\pm 0.01^\circ\text{C}$ , and pressure is measured and controlled to  $\pm 0.5$  mmHg (initial pressure: 1200 mmHg). Excellent pressure and temperature control allows accurate and reproducible measurements.

A typical operating cycle is exhibited in Fig. 2. The

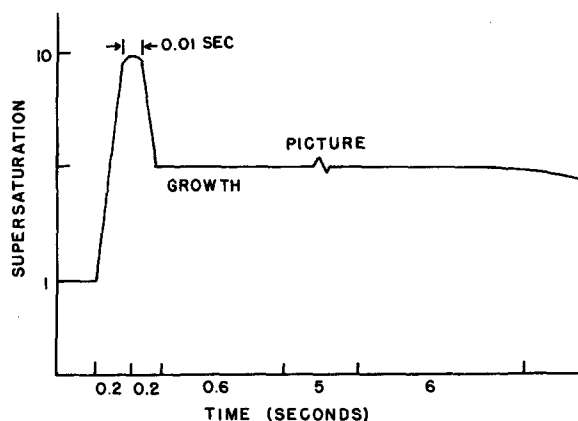


FIG. 2. A typical operating cycle for the expansion chamber.

chamber is allowed to come to thermodynamic equilibrium (ready), then the piston is lowered by lowering the air pressure beneath it. At a predetermined lowest pressure (peak), the piston is immediately driven up, held for some time at an intermediate location, and finally returned to its initial position. Typical times are indicated in Fig. 2. The motion of the piston is reversed at the peak of the expansion to limit the duration of the peak supersaturation to about 0.01 s, thus resulting in a well-defined nucleation event (especially important in the case of homogeneous nucleation), a well known value of the peak supersaturation and the length of the expansion. The rapid recompression also restricts nucleation to polymer sizes which have already contributed to nucleation and subsequent vapor depletion and latent heat release, during drop growth, do not influence the nucleation event.

Heteromolecular nucleation involving polymers with monomers has been discussed by Reiss *et al.*<sup>7,8</sup> In distinction from the homogeneous nucleation of liquid monomer drops within a supersaturated monomer vapor, the presence of the polymer reduces the free energy barrier opposing nucleation, so that nucleation occurs at a level of supersaturation (ratio of actual pressure of vapor to saturation pressure at a given temperature) below that required for the "homogeneous" process (absence of the polymer). Furthermore, there is a critical size of polymer such that polymers below this size will not nucleate drops, while those above it will surely nucleate drops. One adjusts to different critical sizes by changing the supersaturation. Thus as a function of supersaturation, or of the depth of expansion, one at first detects no nucleation events (producing no drops); a few nucleation events for a deeper expansion (producing enough supersaturation to nucleate the largest polymers); a large number of events at a supersaturation high enough to nucleate all but the smallest polymer; until finally with enough expansion, a supersaturation (the critical supersaturation for homogeneous nucleation) is reached capable of initiating monomer nucleation in the absence of polymer.

The nucleation of a macroscopic drop of liquid monomer forms the basis of detection of a polymer molecule, since at levels of supersaturation below that required of homogeneous nucleation of the monomer vapor, no drops form

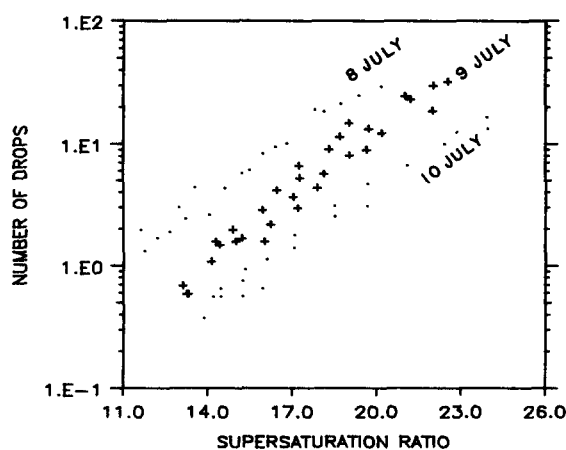


FIG. 3. Number of drops  $\text{cm}^{-3}$  as a function of supersaturation ratio at 15°C. Data taken in pure styrene four, five, and six days after its addition to the chamber. Chamber height is: 11.4 cm.

in the absence of polymers of the tunable size or larger. This presumes that the polymers are so few in number that they do not encounter one another so that a condensation nucleus does not include more than one polymer. El-Shall *et al.*<sup>10</sup> discuss this question. Indeed the method permits one to detect a single polymer molecule among  $5 \times 10^{17}$  monomers  $\text{cm}^{-3}$  at 15°C.

A typical experiment proceeds as follows. The chamber is allowed to attain thermodynamic equilibrium at 1200 mmHg pressure for a time set by current experience. The pressure and temperature are recorded and the chamber is cycled. The "peak" pressure (at greatest expansion) is recorded and the drop embryos are allowed to grow to visible size (approximately  $10 \mu$ ) at a maintained supersaturation between the peak and the initial values. The drops are then photographed and from the photographic film the number of drops  $\text{cm}^{-3}$  is determined. The peak temperature and supersaturation are calculated from the initial temperature, initial pressure and the peak pressure. References 12, 13, and 14 state the rationale for the selection of these variables and

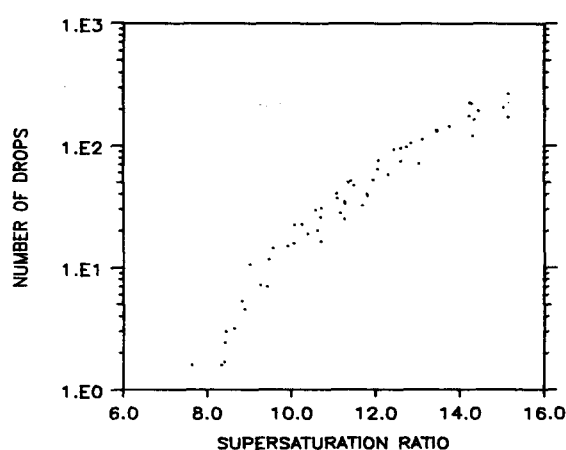


FIG. 5. Number of drops  $\text{cm}^{-3}$  as a function of supersaturation ratio at 20°C. Data taken on three days over a period of five days. Chamber height: 11.4 to 14.2 cm; oxygen content: 3.2% to 2.5%; and wait time: 15 min to 1 h.

the methods for calculation of the supersaturation. The technique used to obtain drops/ $\text{cm}^3$  from the photographs is also given in Ref. 12. Figures 3 through 9 exhibit data obtained in this way. Each point is the result of one expansion.

A careful calculation of supersaturation reveals that it is very sensitive to the thermodynamic parameters that are used. For this reason one should obtain parameters from the most reliable sources, and explicitly state which ones were used in the calculation. Other investigators can then use the raw data, if and when more precise values are available. The thermodynamic parameters used in this work are listed in Table I along with appropriate literature references. In particular it should be noted that a value of the second virial coefficient for styrene was not found in the literature and in its place the value for the second virial coefficient for the thermodynamically similar ethylbenzene was used. The error, though possibly nontrivial, should not be large.

Experiments were performed with styrene purchased from the Aldrich Chemical Company, Inc., and used as received, i.e., polymerization was inhibited with 10 to 15 ppm

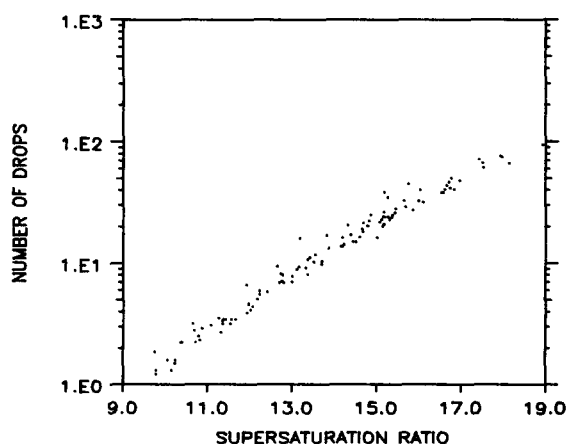


FIG. 4. Number of drops  $\text{cm}^{-3}$  as a function of supersaturation ratio at 15°C. Data taken on seven days over a period of one month. Chamber height: 11.2 to 14.3 cm; oxygen content: 6.1% to 3.2%; and wait time: 15 min to 2 h.

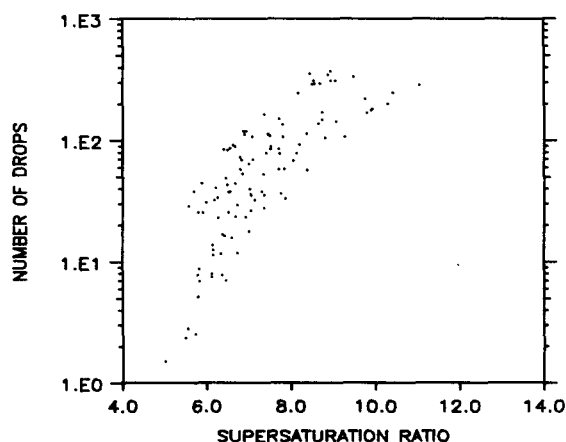


FIG. 6. Number of drops  $\text{cm}^{-3}$  as a function of supersaturation ratio at 25°C. Data taken on 4 days over a period of 20 days. Chamber height: 14.2 cm; oxygen content: 2.5% to 1.9%; and wait time: 15 min to 8 h.

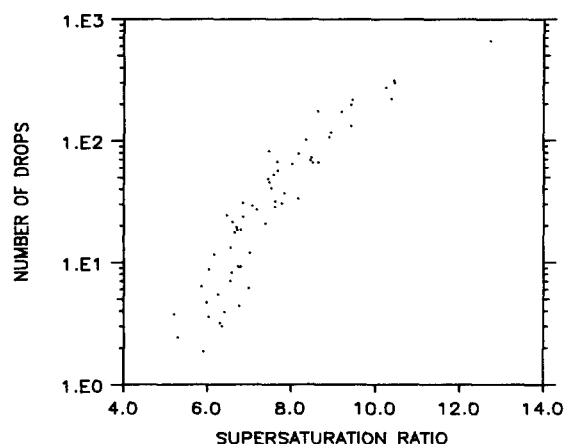


FIG. 7. Number of drops  $\text{cm}^{-3}$  as a function of supersaturation ratio at 25 °C. Data taken on 2 days separated by 23 days. Chamber height: 11.2 cm; oxygen content: 2.5% and 1.9% and wait time: 15 min to 8 h.

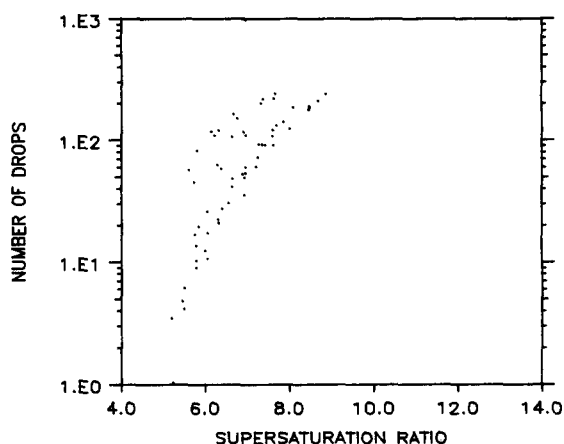


FIG. 9. Number of drops  $\text{cm}^{-3}$  as a function of supersaturation ratio at 25 °C. Data taken on three consecutive days. Chamber height: 11.6 cm; oxygen content: 4.0%; and wait time: 15 min to 1 h.

of 4-*t*-butylcatechol. Approximately 23  $\ell$  were required by the chamber. Later experiments were performed with styrene to which an additional 100 ppm of *t*-butylhydroquinone (also from Aldrich) was added as an inhibitor.

The chamber was cleaned with reagent grade chloroform and toluene. Cleaning was done both before the introduction of any styrene and before each time that the styrene was replaced. In each case the cleaning solvent was placed in a stainless steel tank pressurized with argon from the same tank as that containing the carrier gas. The solvent was then forced through fog nozzles in the center of the chamber so that the fog wetted all surfaces in the chamber and drained to the bottom where it was removed. This fogging was continued intermittently for about a week. Any remaining solvent was removed by vacuum evaporation.

Styrene was admitted by evacuating the chamber and drawing it through a Teflon tube from the supplier's container. This procedure also removed dissolved gas. The chamber was then alternately filled with argon and evacuated several times in order to dilute and remove gas that may have en-

tered with the styrene. A carrier gas of known composition was then added (argon and later argon and oxygen). The argon is supplied by Airco (grade 5) and is passed through activated charcoal and molecular sieve before entering the chamber.

TABLE I. Thermodynamic parameters.

Ideal gas heat capacities (ergs/mol K)<sup>a</sup>

$$C_{p1} = (4.186 \times 10^7) (29.9065 - 0.15643 T + 7.3068 \times 10^{-4} T^2 - 7.1821 \times 10^{-7} T^3)^b$$

$$C_{p2} = 2.0776 \times 10^8 {}^c$$

$$C_{p3} = 2.97482 \times 10^8 - 0.103040 T + 373.411 T^2 - 0.227862 T^3 {}^c$$

Saturation vapor pressure for styrene (dyn/cm<sup>2</sup>)

$$\ln(P_e) = 5443.828 - 121472.71/T + 2.9499094 T - 0.0014248823 T^2 - 1016.1135 \ln(T) {}^d$$

Second virial coefficients (cm<sup>3</sup>/mol)

$$B_1 = -6648218.2 + 123639.715 T - 970.93385 T^2 + 4.10702326 T^3 - 0.009848308 T^4 + 1.26746515 \times 10^{-5} T^5 - 0.68319274 \times 10^{-8} T^6 {}^e$$

$$B_2 = -1150.935 + 20.76920 T - 0.1678223 T^2 + 0.7125312 \times 10^{-3} T^3 - 0.1541841 \times 10^5 T^4 + 0.1341542 \times 10^{-8} T^5 {}^f$$

$$B_3 = -550.30742 + 6.02247394 T - 0.027282676 T^2 + 5.80387561 \times 10^{-5} T^4 - 0.47403886 \times 10^{-7} T^4 {}^g$$

<sup>a</sup>Subscript 1 refers to styrene, 2 to argon, and 3 to oxygen.

<sup>b</sup>Z. U. Rehman and L. L. Lee, *Fluid Phase Equil.* **22**, 21 (1985) (from Ref. 10).

<sup>c</sup>*Thermophysical Properties Research Center, Data Book* (Purdue University, Lafayette, IN, 1965), Vol. 6.

<sup>d</sup>B. D. Smith and R. Srivastava, *Thermodynamic Data for Pure Compounds, Part A: Hydrocarbons and Ketones* (Elsevier, New York, 1986).

<sup>e</sup>From a fit to data given for ethylbenzene in footnote d.

<sup>f</sup>From a fit to points in *The Thermodynamics Properties of Argon from the Triple Point to 300 K at Pressures to 1000 Atmospheres* (National Bureau of Standards, Washington, D. C., 1969).

<sup>g</sup>From fit to points in J. H. Dymond and E. B. Smith, *The Virial Coefficients of Pure Gases and Mixtures* (Clarendon, Oxford, 1980).

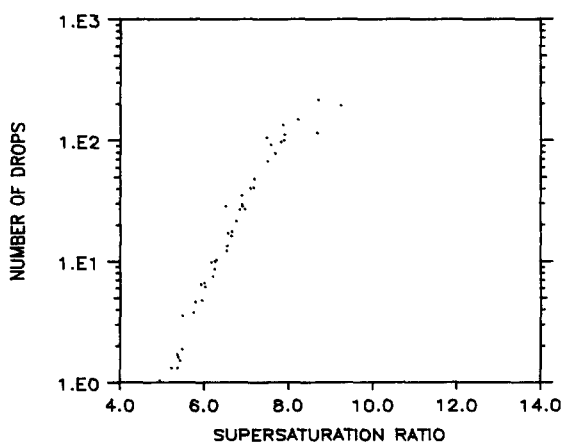


FIG. 8. Number of drops  $\text{cm}^{-3}$  as a function of supersaturation ratio at 25 °C. Data taken on two consecutive days. Chamber height: 11.6 cm; oxygen content: 4.9%; and wait time: all 15 min.

### III. EXPERIMENTAL RESULTS

Immediately after styrene was placed in the chamber, expansions were conducted which produced drops at supersaturations much too low for homogeneous nucleation indicating that polymers had formed in the vapor and were easily detected. However, since there was no previous experience with styrene in an expansion chamber, it was necessary to perform a series of preliminary experiments to determine how to operate the chamber properly.

The normal operating procedure when studying homogeneous nucleation requires an electric field (approximate 50 V/cm) to rid the chamber of ions, which could induce nucleation in some vapors, e.g., water, at supersaturations slightly less than homogeneous. It also includes several (usually three) "cleaning" expansions before each data expansion to rid the chamber of "reevaporation" nuclei (Ref. 17, p. 13). In addition one must ask the important question, concerning how long must the waiting time be between expansions so that thermodynamic equilibrium and/or a steady state polymer distribution is established.

Tests were conducted both initially and during the period of months in which these experiments took place, for the possible effects of the electric clearing field. In general, one compares data expansions with the field on and off while all other parameters remain the same. In no case in this work was a significant difference found in the nucleation count. Therefore, we dispensed with the clearing field and the data presented here were obtained without it.

Normally, when studying homogeneous nucleation, data expansions are preceded by cleaning expansions for the removal of nuclei, dust, reevaporation nuclei from a previous run, etc., which would induce heterogeneous nucleation. In a sense the polymers themselves are heterogeneous nuclei, but interference from extraneous nuclei must be avoided. Tests were conducted, involving expansion both shallower and deeper than those involved in the collection of data, in order to assess the effects of extraneous heterogeneous nuclei. No evidence was found, e.g., for the influence of reevaporation nuclei and therefore no cleaning expansions preceded the data expansions for the measurements on styrene. Each of the abovementioned tests were performed on data accumulated during a single day, and the comparisons were continued during the full period of the experiments.

The data were analyzed using a formula derived by Raabeony and Reiss<sup>18</sup> for the characterization of the propagation and transport of polymers in the chamber. These authors solved the boundary value problem in which polymers are initiated, grow, and diffuse to the walls, thus leading to a transient and finally steady distribution of polymers in size and space. However, as a boundary condition they assumed polymers to be irreversibly adsorbed at the walls. For the smallest polymers this might not be the case, so that the solution of the boundary value problem might not be precisely applicable.

We endeavored to make some test of this possibility in the following manner. The polymers reaching the walls are free radicals. If the walls are "wet" with liquid styrene these

radicals, even if small might propagate in the liquid and thus be retained. In contrast, at a dry wall, irreversible adsorption might be less complete. To exploit such a difference and therefore test this hypothesis we made runs with both wet and dry walls (wet walls can be produced by lowering the wall temperature for a period of time and thus inducing condensation on them). The tests exhibited no difference between wet and dry walls and therefore all of our measurements were performed with dry walls only. There remains, however, the caveat that there still could have been multi-layer adsorption of styrene on the walls so that some entrapment by propagation could have occurred on walls thought to be dry. In any event the issue of possible incomplete adsorption is by no means resolved, and future studies, both theoretical and experiments, are necessary for the improvement of the technique.

The boundary value problem also assumes the absence of convection in the chamber (stabilized by a small positive, vertical temperature gradient). In some earlier, unpublished, experiments employing vinyl acetate rather than styrene a "line" of poly vinyl acetate molecules was produced along a UV beam used to initiate polymerization. This line was developed into drops by an expansion after various intervals of time. The resulting photographs indicated the absence of convection or, at the most, acceptably slow convection.

In the course of these initial tests, it was noticed that the supersaturation required to achieve the same nucleation rate ( $\text{drops cm}^{-3} \text{ s}^{-1}$ ) increased with time. The cause (see below) proved to be polymerization of the liquid styrene in the chamber. This styrene, quite viscous, was removed. The chamber was cleaned and new styrene was added. On the assumption that the original inhibitor (10–15 ppm 4-*t*-butylcatechol) had been depleted, 100 ppm of another inhibitor, *t*-butylhydroquinone, was added. Both inhibitors have very low vapor pressure and should not influence the polymerization in the vapor.

Measurements of drop count as a function of supersaturation were performed on the fourth, fifth, and sixth days after the addition of the fresh styrene. Figure 3 exhibits the results of these measurements, and shows that the supersaturation required for the achievement of a given nucleation rate apparently increases with time. We interpreted this to mean that the inhibitor alone was inadequate to prevent polymerization in the chamber. Oxygen was therefore added to the carrier gas in an effort to increase the action of the inhibitor. The slow polymerization of liquid styrene in the bottom of the chamber does not change the polymerization in the vapor above the liquid pool. However, it does lower the vapor pressure of the styrene in the sensitive volume. The result is an apparent change in the supersaturation which is calculated on the assumption that all of the liquid is monomer. The actual supersaturation required to allow a polymer of given size to induce nucleation remains the same but the measured supersaturation becomes inaccurate if there is a reduction in the partial pressure of the monomer in the liquid. A lower vapor pressure requires a deeper expansion to achieve the same degree of supersaturation. Therefore, the calculated supersaturation is incorrect. Note the extreme

sensitivity of the nucleation process to small changes in the system.

The chamber was subsequently recharged with fresh degassed styrene and additional inhibitor. Oxygen was added via the carrier gas (argon). The initial oxygen content was established from the increase in pressure upon its addition. Subsequent oxygen content was calculated from the volume (the height of the experimental volume is measured with a linear voltage displacement transducer on the piston) and was decreased with time because carrier gas was removed and additional argon added to adjust the height of the chamber for various experiments.

The formula of Rabenoy and Reiss<sup>18</sup> indicates that experiments at different chamber heights and temperatures can yield information on initiation rates, critical polymer sizes, and propagation constants. Thus the experiments were designed to use their formula for the purpose of extracting this information.

Figure 4 exhibits data for 15 °C taken on seven separate days. In these experiments the chamber height was varied from 11.2 to 14.3 cm, while the oxygen content ranged from 6.10% to 3.17%. The wait time between successive data expansions (there were no cleaning expansions) was varied from 7.5 min to 2 h. Drop counts tended to be slightly lower than average for a wait time of 7.5 min but a 15 min vs a 2 h wait showed no differences. Typically the chamber requires 3 to 5 min to restore thermodynamic conditions (i.e., for the experimental volume to become uniform in vapor content and temperature) after an expansion. Thus tests were not made a times shorter than 7.5 min. A wait time of 15 min was adopted as standard, and data points with wait times of 7.5 min are not included in Fig. 4.

The fact that drop count increases with time is indicative of the formation of polymers. A deep enough expansion removes all polymers as drops (i.e., the minimum nucleated size is reduced to the monomer), and the development of the count as measured by a subsequent expansion occurs as the polymers are repropagated. In all other types of nucleation studies in cloud chambers this phenomenon (increase of count with waiting time) is absent. Thus using an expansion cloud chamber, we confirm the earlier observations of El-Shall *et al.*<sup>10</sup> made with a diffusion chamber, that self-initiated polymerization of styrene occurs in the vapor.

From these experiments it appears that at 15 °C polymerization in the vapor reaches the steady state in less than 15 min; a variation of a factor of 2 in the oxygen content causes no measured effect (at least in the range from 6% to 3%); and finally, the variation in the height of the chamber which we were able to achieve is not able to affect the number of polymers formed. Figure 4 is remarkable in that all the data cluster about a single curve.

Figure 5 shows the data taken at 20 °C. The graph is a composite of data taken on three separate days with chamber heights of 11.4 and 14.2 cm. The oxygen content was 3.17% and 2.54%. Data is presented for wait times from 15 to 60 min. Again, they are remarkable for their clustering about a single curve.

The situation is dramatically different at 25 °C. Figures 6–9 show the data taken at this temperature. All of these

graphs show the same basic features: A fairly well-defined edge at the right side (low counts) of the distribution of points, some breadth to the data, and a less well-defined left edge (high counts). The points that define the right edge are data from expansions with a wait time of 15 min (all points in Fig. 8 are 15 min wait points). As one increases the wait time (up to 8 h), the resulting data points fall farther to the left. The time now required for the polymer distribution to reach a steady state is no longer 15 min but on the order of hours.

Two additional comparisons can be made among Figs. 6–9. Figure 6 shows data at a chamber height of 14.2 cm. Figure 7 shows data at a height of about 11 cm (oxygen content is about the same for Figs. 6 and 7). Figure 9 is also at a chamber height of 14 cm and can be compared to Fig. 8 which was at a height of 11 cm (oxygen content is about the same for Figs. 8 and 9). In both comparisons we are not able to measure a difference, due to chamber height, in the drop count and thus in the number of polymers produced. Comparison of Fig. 7 with Fig. 8 and Fig. 6 with Fig. 9 indicates that the variation of the oxygen content (between 2% and 5%) also produces no change in the drop count (number of polymers). One should remember, when making these comparisons, that supersaturation is extremely sensitive to chamber conditions such as temperature and vapor pressure and the quality of the data is apparent because the graphs are coherent. However, the data was taken over a period of two months (while the building housing the Cloud Physics Center was under renovation) and small changes in the chamber could produce large differences. Only obvious differences in the data are considered valid at this time, and possible small differences should be reserved for further investigation.

The most remarkable feature of the 15, 20, and 25 °C data is the sharp increase in the time required to reach a steady state in the chamber upon proceeding from 20 to 25 °C.

#### IV. ANALYSIS

Although the measurements involving styrene in the absence of oxygen are unreliable due to the fact that polymerization may have occurred in the liquid (as shown by the apparent change with time of the supersaturation required for nucleation), it should still be possible to extract semi-quantitative information from them, especially from those of Fig. 3 where the data was taken before much polymerization had taken place (points labeled 8 July). A careful comparison of the data of Fig. 3 with those of Fig. 4 (both sets of data at 15 °C, but with oxygen present in Fig. 4) shows that both sets of data have the same slope, but that the set in Fig. 4, corresponding to the presence of oxygen indicates a drop count, at the same supersaturations, three times higher than for the case in which oxygen was absent. The observed difference cannot be attributed to error in the computed supersaturation due to the presence of oxygen.

Following the measurements summarized in Fig. 3, a quantity of oxygen (not carefully measured) was added to the chamber. An effect similar to that noted above was observed; oxygen increases the drop count by about a factor of



3 (similar to Fig. 3 vs Fig. 4). Because of this apparently reproducible behavior, it appears reasonable to use the data of Fig. 3 and to assume that they exhibit the proper slope while the actual drop count could be in error by as much as a factor of 3.

The steady state formula derived by Rabeony and Reiss<sup>18</sup> is the following:

$$P_j(z,r) = \sum_{\alpha} \sum_{m=0}^{\infty} \left[ \frac{(1)^m 4I}{D_i L \alpha J_1(\alpha) \omega_m} \right] \times \left\{ \frac{\prod_{i=1}^j (K_i/D_{i+1})}{\prod_{i=1}^j [(\alpha/a)^2 + (K_i/D_i) + \omega_m^2]} \right\} \times (\cos \omega_m z) J_0\left(\frac{\alpha}{a} r\right). \quad (1)$$

Here,  $P_j(z,r)$  denotes the steady state concentration of polymeric radicals of size  $j$  at the point in a cylindrical chamber whose coordinates are  $z$  and  $r$ ,  $z$  being the vertical and  $r$  the radial coordinate.  $2L$  is the height while  $a$  is the radius of the cylindrical chamber. The quantities  $\alpha$  and  $\omega_m$  are eigenvalues given by the roots of

$$J_0(\alpha) = 0 \quad (2)$$

for  $\alpha$  (where  $J_0$  is the Bessel function of order zero), while

$$\omega_m = \frac{(2m+1)\pi}{2L}, \quad m = 0, 1, 2, \dots, \quad (3)$$

$J_1$  is the Bessel function of order 1. Furthermore,  $K_i$  is given by

$$K_i = k_p^{(i)} [M], \quad (4)$$

where  $k_p^{(i)}$  is the rate constant for propagation of a polymer of size  $i$ ,  $[M]$  is the monomer concentration,  $D_i$  is the diffusion coefficient for a polymer of size  $i$ , and  $I$  is the rate of initiation ( $\text{cm}^{-3} \text{s}^{-1}$ ).

In the absence of an adequate theory for  $D_i$  we assume<sup>19</sup>

$$D_i = D_1/i^{1/2}. \quad (5)$$

We wish to emphasize that Eq. (1) assumes the absence of convection and also assumes irreversible adsorption of polymers of all sizes on the chamber walls.

As mentioned above, there is a smallest polymer capable of nucleating a drop for each value of supersaturation, i.e., a polymer of size  $x^*$ . When an expansion is performed to a given level of supersaturation, all polymers of sizes exceeding  $x^*$ , will nucleate and grow into countable drops. The drop count  $N$ , in  $\text{cm}^{-3}$ , will then be given by

$$N(I, \{K_i\}, \{D_i\}, x^*, L, a) = \sum_{j=x^*}^{\infty} P_j. \quad (6)$$

It is apparent from Eq. (1) that the right side of Eq. (6) is linear in  $I$  so that we may write

$$N = IF, \quad (7)$$

where  $F$  is the factor which remains when  $I$  is extracted from the sum in Eq. (6).

The size  $x^*$  can be estimated from the approximate theory presented in Refs. 6 and 10. From Fig. 3 and using this theory, one finds at 15 °C (corresponding to the figure) and for a supersaturation of 11, that  $x^*$  lies between 10 and 11, while for a supersaturation of 20, it lies between 5 and 6.

These supersaturations correspond to the left and right endpoints in Fig. 3 (points labeled 8 July). Note that the data show an approximately linear variation of drop count with supersaturation.

Indicating these endpoints by the subscripts 11 and 20, we find from Eq. (7),

$$\frac{F_{20}}{F_{11}} = \frac{N_{20}}{N_{11}} \approx 30, \quad (8)$$

where the 30 is estimated from Fig. 3,  $N_{20}$  refers to supersaturation 20 and  $N_{11}$  to supersaturation 11.

Since the diffusion coefficient for styrene (argon) was not available in the literature, we used that quoted for toluene, namely,  $D_1 = 0.08 \text{ cm}^2 \text{s}^{-1}$  (Ref. 20, p. 639). The data of Fig. 3 were measured with  $2L = 11.4$  or  $L = 5.7 \text{ cm}$ , while  $a$ , the fixed radius of the chamber is set equal to 19.2 cm. Although  $D$  is assumed to vary as indicated in Eq. (5), we assume that  $K_i = K$ , a constant. With these parameters and the assumption that Eq. (1) can be combined with Eq. (6) to numerically evaluate  $F$  as a function of  $x^*$  for various values of  $K$ . The results of course apply to Fig. 3.

Figure 10 illustrates the results (calculated for  $r = 0$ ,  $z = 0$ , where the drop counts were made) for a range of assumed values of  $K$ . In the figure,  $F$  is plotted vs  $x^*$ . Even though the plot is logarithmic, the slope of the curve is quite sensitive to  $K$ .

Furthermore, assuming the plot of  $F$  vs  $x^*$  to be approximately linear (as appears to be the case in Fig. 10), one can plot a "slope" appropriate to the measured  $F$  vs  $x^*$ , obtained for the conditions of Fig. 3. This plot, suitably identified, appears in Fig. 10. It most closely matches the curve with  $K = 0.003 \text{ s}^{-1}$ .

The known vapor pressure of styrene requires, at 15 °C, that  $[M] = 5 \times 10^{17} \text{ molecules cm}^{-3}$ . This value inserted in Eq. (4) gives

$$k_p = 6 \times 10^{-21} \text{ cm}^3 \text{ molecules}^{-1} \text{s}^{-1}. \quad (9)$$

Now, with  $K$ ,  $D$ ,  $L$ ,  $a$ , and  $x^*$  known, Eqs. (1) and (6) can be combined to calculate  $I$ , if the drop count  $N$  is known. Using the measured drop counts of Fig. 3 and the values of  $x^*$  corresponding to them (calculated from the theory of Refs.

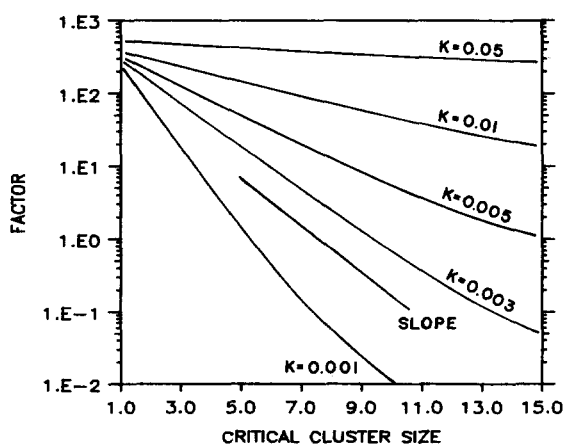


FIG. 10.  $F$  (factor) as a function of critical cluster size for values of  $K$  (propagation constant).

6 and 10), together with  $K = 0.003 \text{ s}^{-1}$ ,  $D = 0.08 \text{ cm}^2 \text{ s}^{-1}$ ,  $L = 5.7 \text{ cm}$ , and  $a = 19.2 \text{ cm}$ , we find

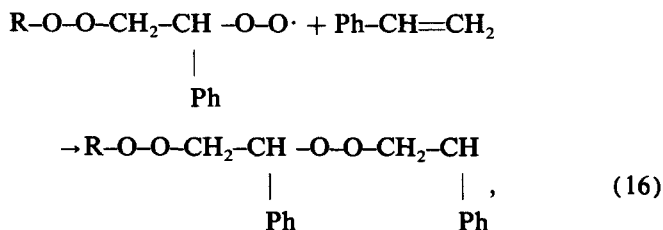
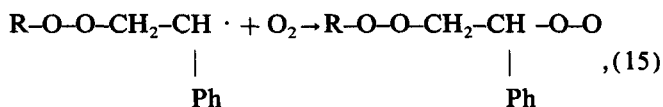
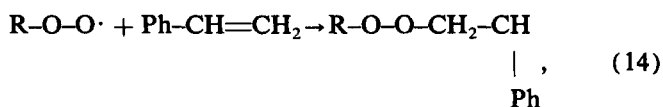
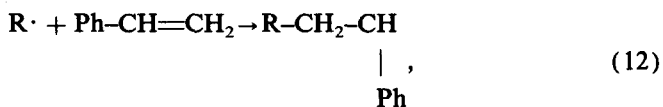
$$I \approx 2 \text{ radicals cm}^{-3} \text{ s}^{-1}. \quad (10)$$

If we allow an uncertainty in drop count of a factor of 3, as indicated above, we can say that  $I$  lies between 2 and  $6 \text{ cm}^{-3} \text{ s}^{-1}$ . The value of  $I$  measured here can be compared with the value quoted by El-Shall *et al.*,<sup>10</sup> namely  $200 \text{ cm}^{-3} \text{ s}^{-1}$ . However, these authors did not measure  $I$  but rather extrapolated its value from measurements which had been performed in the liquid. Our value of  $k_p$ , Eq. (9), is about 15 times lower than that listed by Odian<sup>21</sup> for the liquid.

It remains to offer some analysis of the data obtained in the presence of oxygen, and exhibited in Figs. 6 through 9, and, especially, to explain the sudden increase in wait time to achieve the steady state at  $25^\circ\text{C}$ .

The data in these figures presumably approximate the steady state, since they were obtained by waiting progressively longer times until the drop counts did not increase significantly. Again the striking feature of these results is that the steady state was achieved in about 15 min at 15 and  $20^\circ\text{C}$  but required hours to approach at  $25^\circ\text{C}$ . Also the count was insensitive to oxygen content. A simple explanation of this behavior due to El-Shall and Reiss<sup>22</sup> is the following.

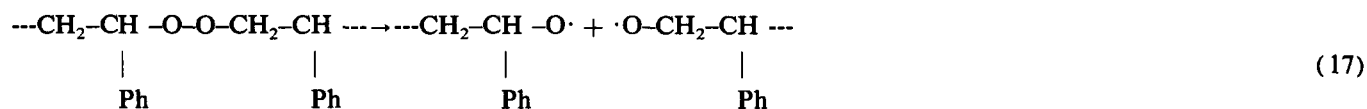
It is known from the work of Mayo and Miller<sup>11,23,24</sup> that the following reactions can take place in the presence of oxygen:



etc.,

where Ph represents a phenyl group, and  $\text{R}\cdot$  a free radical. Equation (11) is the usual self-initiation step and Eq. (12), the usual propagation process in the absence of oxygen. However Eqs. (13) through (16) illustrate the formation of the copolymer, styrene peroxide (which has actually been isolated<sup>23</sup>). Since the initiation step in Eq. (11) is much slower than the formation of the peroxide radical, Eqs. (13) and (15), the overall rate is insensitive to oxygen content, initiation being rate controlling. Nucleation is now induced by both polystyrene and polystyrene peroxide, and the insensitivity of the observed drop count to oxygen content is explained by the fact that the slow step (initiation) is independent of oxygen.

The difficulty in achieving the steady state at  $25^\circ\text{C}$  is also explained when the further known reaction



is considered. This cleavage at the peroxide group, producing two free radicals, begins to occur rapidly at the higher ( $25^\circ\text{C}$ ) temperature and results in a multiplication of radicals which resembles a chain reaction. Thus the steady state is difficult to achieve.

Based on Eqs. (11)–(17), El-Shall and Reiss<sup>22</sup> have carried out a simple mathematical analysis of the rate phenomena that allows a qualitative interpretation of the results. They assume that the reactions, Eqs. (13) and (15), are so fast that not only are they not rate controlling, but also the species  $\text{R}\cdot$  may be ignored since it is immediately converted to  $\text{R-O-O}\cdot$ . The reaction [Eq. (12)] may therefore also be neglected, and the polymers are then all polystyrene peroxide.

They proceed as follows. The concentration of polymers of size  $j$  is then denoted by  $P_j$ . The rate constant for propagation [Eqs. (14) and (16)] is, as usual, denoted by

$K = k_p [\text{M}]$ . The diffusional rate of loss to the walls is modeled by a simple linear term  $-\alpha P_j$  where  $\alpha$  is a constant ( $\alpha$  is related in an unknown fashion to  $D$ , the diffusion constant), and the cleavage [Eq. (17)] rate constant is denoted by  $k$ . Finally the initiation [Eq. (11)] rate is once again specified by  $I$ . Denoting time by  $t$ , it may be shown that the governing equations for this model are

$$\frac{dP_1}{dt} = I - KP_1 + 2k \sum_{j=2}^{\infty} P_j - \alpha P_1, \quad (18)$$

$$\frac{dP_2}{dt} = KP_1 - KP_2 + 2k \sum_{j=3}^{\infty} P_j - kP_2 - \alpha P_2, \quad (19)$$

$$\frac{dP_3}{dt} = KP_2 - KP_3 + 2k \sum_{j=4}^{\infty} P_j - 2kP_3 - \alpha P_3, \quad (20)$$

etc.

The solution for  $P_j$  is found in terms of a constant plus a

linear combination of exponentials of the form  $e^{\lambda_m t}$  where  $\lambda_m$  is an eigenvalue which depends on  $K$ ,  $k$ , and  $\alpha$ . For small values of  $\alpha$  (the cleavage constant) all  $\lambda_m$  are negative so that the system is stable and a steady state is achieved. However, at a large enough value of  $\alpha$  one of the  $\lambda_m$  becomes positive, resulting in the unlimited growth of  $P_j$  with time so that the system is unstable, and it is impossible to establish the steady state. Near but still below the critical value of  $\alpha$ , the time to the steady state becomes very long as is observed when the temperature is changed from 20 to 25 °C. It is significant the cloud chamber experiments detect this phenomenon in the vapor phase; its detection constitutes another demonstration that the self-initiated polymerization of styrene takes place (very slowly) in the vapor as well as the liquid.

## V. SUMMARY

First, we have demonstrated that the expansion cloud chamber may be used to study homogeneous gas phase polymerization of styrene. Results are of a preliminary nature, aimed at the demonstration of feasibility, and are semiquantitative. However, further work (theory and experiment) should produce more quantitative results. The expansion cloud chamber offers the advantage that it provides a uniform medium for the polymerization process.

Second, self-initiated polymerization of styrene in the vapor has been observed, thus confirming a similar demonstration of this process with a diffusion cloud chamber by El-Shall *et al.*<sup>10</sup> The self-initiation rate in the gas phase at 15 °C was measured to be

$$I = 2\text{--}6 \text{ radicals cm}^{-3} \text{ s}^{-1}$$

while the propagation rate at the same temperature was measured to be

$$k_p = 6 \times 10^{-21} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}.$$

Finally, strong evidence was obtained for the formation of polystyrene peroxide in the gas phase from the self-initiated styrene radicals in the presence of oxygen. Evidence was also obtained for its rapid cleavage, producing further initiating radicals at 25 °C. Rudimentary information on the transient process towards the establishment of the steady state (in the presence of oxygen) was also obtained. The

evidence for polystyrene peroxide further confirms the self-initiated polymerization of styrene in the gas phase, and it is consistent with what is known in the liquid.

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