

Homogeneous Gas Phase Polymerization

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True Homogeneous Gas Phase Polymerization

Despite the many papers dealing with so called "gas phase polymerization" almost none of them are *actually concerned with the gas phase process* since they are usually concerned with processes having the *monomer* in the gas phase while the *polymer* grows on the walls of the containing vessel or some other surface. True *homogeneous* gas phase polymerization is extremely difficult to study in situ because of the involatility of the polymer product. Led by Melville, there were early attempts^{1–7} to study such reactions by observing the associated reduction of monomer pressure. Although these investigations yielded useful information, they were eventually frustrated by the formation of a polymeric aerosol on whose extended surface further polymerization occurred *heterogeneously*.

In 1983, the present author and several collaborators^{8,9} initiated a series of new studies of the phenomenon based on the use of vapor phase nucleation for detection and amplification. The fundamental idea was to have few enough polymer molecules in the vapor to avoid condensation to an aerosol. Dramatically small reaction rates (smaller than $1.0 \text{ polymer cm}^{-3} \text{ s}^{-1}$) could be studied!

Why should one study homogeneous gas phase polymerization? A few examples, involving radical addition polymerization, provide an answer:

(1) In the gas phase, there is the possibility of observing the direct formation, in real time, of product polymeric radicals of a chosen size. In contrast, in the liquid phase,

one is usually forced to infer what has happened by the qualitative and quantitative analysis of products.

(2) In the gas phase, it is possible to suppress the processes of *recombinative* or *disproportionative termination*,^{10,11} as well as the process of *chain transfer*.^{10,11}

(3) As a corollary to the two preceding items, it is sometimes possible, in the gas phase, to study, in isolation, elementary steps (e.g., initiation, propagation, recombination, etc.^{10,11}) of a multistep reaction.

(4) A particular problem to which item 3 is relevant concerns the mechanism of the thermal self-initiated radical polymerization of styrene. This mechanism is still not fully elucidated although there is strong evidence that a Diels–Alder adduct plays an intermediate role.^{12–13}

(5) The thermal self-initiated polymerization of styrene (well documented in the liquid phase^{12–15}) has not been unequivocally demonstrated in the gas phase, so that there is incentive for the development of better methods for the study of the gas-phase process.

(6) It is of interest to study polymerization in a *poor* solvent since the polymer is likely to adopt a *globule* rather than a *coil* configuration¹⁶ and the rate, and possibly the mechanism of reaction, could be dramatically affected. However, in a poor enough solvent, the solubility of polymer is small enough to frustrate the quantitative measurement of rate. Perhaps the poorest "solvent" is the vapor so that the development of gas phase methods could contribute to measurements of this kind. The rate could also be affected by intrapolymer and polymer–solvent energy transfer processes, the competition between which may differ considerably in gas as compared to condensed media.

(7) Slow homogeneous radical polymerization (involving small numbers of molecules) in the gas phase will exhibit a stochastic *fluctuating* rate from which, in principle, the initial number of free radicals can be deduced.¹⁷ Thus for photochemical polymerization it is, in principle, possible to determine the quantum yield of initiating free radicals.

The author, co-workers, and a few other individuals have focused on the development of methods for the in

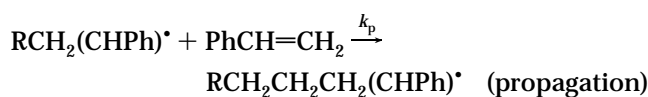
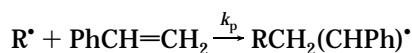
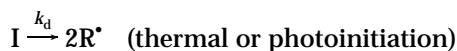
Born in New York City, Howard Reiss received B.A. and Ph.D. degrees from New York University and Columbia University, respectively. His studies were interrupted by the second world war, during which he served as a member of the U.S. Army Special Engineer Detachment associated with the Manhattan Project. He was trained in experimental physical chemistry but eventually learned to perform theoretical as well as experimental research. Half of his career was spent in industry (Bell Laboratories, 1951–1960, and North American Aviation (now Rockwell International), 1960–1968). The other half was spent in academia (Boston University, 1949–1951, and UCLA, 1968–present). At North American Aviation, he was the founding Director of the Company's Science Center at Thousand Oaks, CA, and a Corporate Vice President of the parent company. He has worked in a variety of fields including solid state, statistical mechanics, nucleation and colloid phenomena, polymers, electrochemistry, thermodynamics, and device physics. Honors include the American Chemical Society Tolman Medal, Kendall Award (Colloid and Surface chemistry), and Hildebrand Award (Physical Chemistry of Liquids). He is a member of the National Academy of Sciences and a fellow of both the American Physical Society and the American Association for the Advancement of Sciences. He has also been a Guggenheim Fellow. Recently, he held the (1994) Van Arkel Honorary Chair in Chemistry at Leiden University of the Netherlands. Professor Reiss was founding editor of both the series *Progress in Solid State Chemistry* and the *Journal of Statistical Physics*. He is the author of the monograph *Methods of Thermodynamics*. His current research involves statistical mechanics, nucleation, microemulsions, membrane separations, and electrochemistry.

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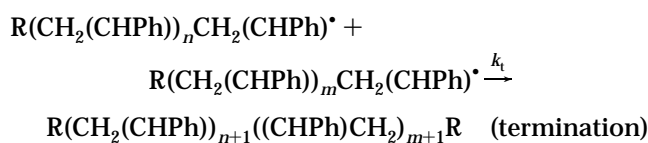
situ study of the gas phase process. Although progress has been slow, promising *semiquantitative* success has been achieved and further effort should result in *quantitative* accuracy. Such effort would require new instrumentation and a larger community of interested workers. It is hoped that this Account will stimulate others to enter the field.

Radical Addition Polymerization and Nucleation

The radical polymerization of styrene (PhCH=CH₂, where Ph represents a phenyl group) furnishes a good example of radical polymerization. Key steps in the process are listed below:



and so forth



In this scheme k_d , k_p , and k_t are rate constants for dissociation, propagation, and termination, respectively, I is an initiator that can decompose thermally or photolytically, and R^* is a free radical. Other elementary steps are possible (such as chain transfer^{10,11}), in which both “dead polymer and a monomeric radical that can still propagate are formed. A separate initiator may not be necessary with photochemical initiation.

The polymerization rate is usually defined as the average rate of disappearance of monomer or as the rate of increase of average molecular weight.¹⁸ The growing radicals are themselves present in low concentrations ($\approx 10^{-8}$ M), and little attempt is made to observe them directly.

As mentioned earlier, studies of the homogeneous process in the gas phase have employed nucleation for the detection of products.¹⁹ An extensive literature on the subject of nucleation is available.^{20–26} The associated theory is difficult, and only recently have rigorous approaches been attempted.^{27,28} Here, we limit discussion

to the condensation of supersaturated vapors. Consider a simple one-component vapor (water vapor for example) supersaturated so that its relative humidity (RH) exceeds 100%. Attainment of stable equilibrium in this system depends on a “reaction” in which individual vapor molecules aggregate to form physical clusters and, finally, larger fragments of liquid. In the so-called *classical* theory of nucleation the cluster is treated as a liquid drop. The free energy change ΔF involved in the clustering process consists of two parts, (i) $\Delta F_{\text{volume}} = -nkT \ln S$ (where $S = p/p_s$ is the *supersaturation*, p and p_s are the pressure of the vapor and the saturation pressure, respectively, n is the number of molecules in the cluster, k is the Boltzmann constant, and T is the temperature) associated with the formation of the *volume* of the cluster and representing a free energy *decrease* because the vapor is supersaturated and (ii) $\Delta F_{\text{surface}} = \sigma A$ (where σ is the surface tension and A is the surface area of the drop) accompanying the formation of the interface between cluster and vapor and corresponding to a free energy *increase* proportional to the cluster surface area.

For small enough n , the cluster is mostly surface so that $\Delta F_{\text{surface}}$ dominates and ΔF increases with n . However, with enough increase of n , volume becomes dominant so that the negative ΔF_{volume} takes over and forces ΔF to pass through a maximum at some n denoted by n^* . The result, for ΔF plotted versus n , is a free energy barrier over which growing clusters must pass on their way to becoming fragments of the bulk stable liquid. The height of the barrier is $W^* = 16\pi\sigma^3 v^2 / 3(kT \ln S)^2$, where v is the molecular volume in the liquid.

The cluster (drop) of size n^* is the condensation “nucleus”. Once formed it can grow spontaneously (with a decrease of free energy) into a macroscopic liquid drop. n^* is typically small (10–1000). For later reference it is useful to indicate that, from the thermodynamic point of view, the nucleus, regarded as a drop, is just that drop whose vapor pressure, according to the Kelvin relation,²⁹ equals the pressure of the supersaturated vapor.

The nucleation *rate* (rate of drop formation) is the rate at which clusters of nucleus size form. This process involves a sequence of reversible “reactions” in which the cluster adds molecules one at a time. For the rate of nucleation J , analysis yields the Arrhenius-like expression

$$J = B e^{-W^*/kT} \quad (1)$$

in which the preexponential factor B is only weakly dependent on supersaturation.

Using eq 1, a calculation of J as a function of S , for water vapor at 300 K and 120% RH or $S = 1.2$, *an average of 10⁹⁶ seconds will pass before the appearance of a single drop in a cubic centimeter of vapor!* This is a meaninglessly long time, yet water condensation occurs readily at much lower relative humidities because preexisting surfaces such as dust particles and walls catalyze condensation by means of *heterogeneous* nucleation. The uncatalyzed process to which W^* in eq 1 refers is termed *homogeneous* nucleation. At 280% RH or $S = 2.8$, the

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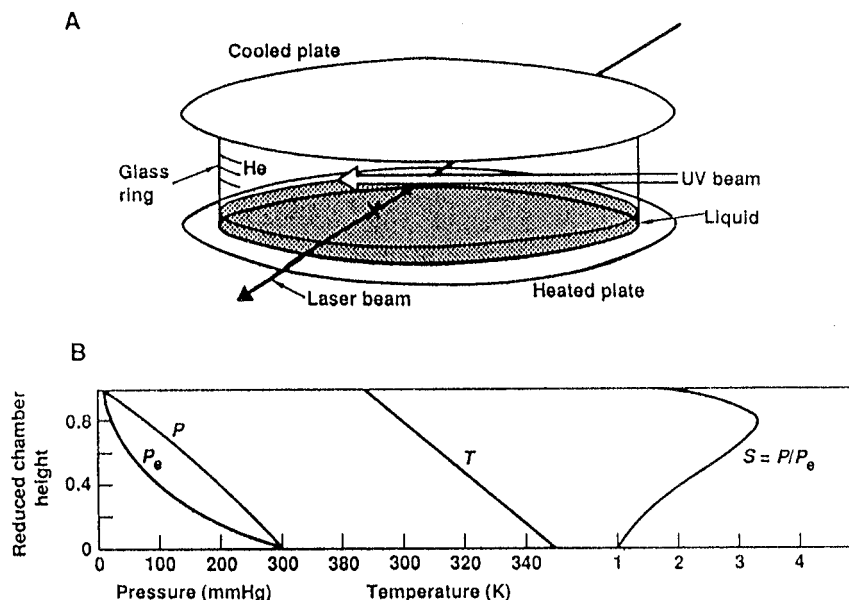


FIGURE 1. (A) Sketch of diffusion cloud chamber with relevant components indicated. The optically defined volume of observation in the laser beam through which the drops fall is marked by \times . (B) Typical courses of diffuser partial pressure P , saturation pressure P_e , temperature T , and supersaturation S in diffusion cloud chamber.

same calculation shows that 10^6 s will pass before a drop forms, while at $S = 3.11$, only 1 s is required, and for $S = 3.4$, 10^{-4} s is enough. Thus, at 300 K, for the homogeneous nucleation of water vapor to occur at a sensible rate, e.g. $1.0 \text{ drop cm}^{-3} \text{ s}^{-1}$, RH values in excess of 300% are required; J remains negligible until a *critical supersaturation* S_c is reached, at which point it increases explosively.

Measurements of S_c for homogeneous nucleation can be made in a "cloud chamber" of which two types are particularly important, (i) the upward diffusion cloud chamber and (ii) the expansion (Wilson) cloud chamber. The *diffusion* chamber (Figure 1A) was pioneered by Franck and Hertz³⁰ and developed to a high degree of perfection by Katz and co-workers.³¹⁻³⁴ It consists of two circular plates separated by a glass cylinder. The lower plate is heated and the upper one cooled. The liquid, within whose vapor S_c is to be determined, forms a shallow pool on the heated lower plate. The space above the liquid is filled with helium through which the vapor of the evaporating liquid diffuses to the cooler upper plate where it condenses to a smooth film and drains back to the pool so that a steady state of reflux is established. The various transport processes (mass, energy, and momentum) combine to produce the steady vertical distribution of supersaturation (Figure 1B).

The temperatures of the plates are adjusted until drops forming near the peak of the S curve are observed to fall through a laser beam at a rate of about 1 s^{-1} . The peak is then rotated 90° and mapped (as a function of T rather than reduced height) onto the space of Figure 2 (in this case for nonane³²) where many peaks that correspond to similar experiments with different pairs of plate temperatures are plotted. The "envelope" of these peaks (not

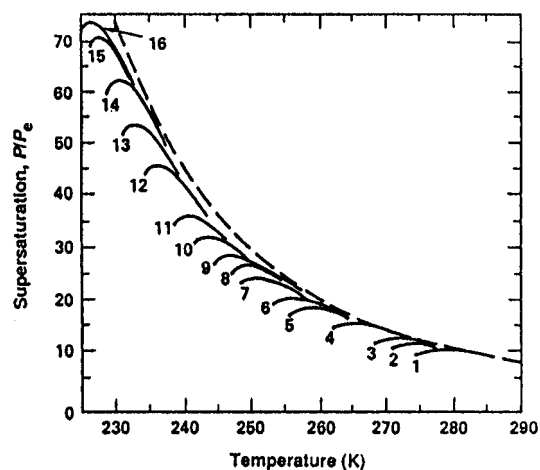


FIGURE 2. Critical supersaturation versus temperature;³¹ helium carrier gas. Dashed line represents theory. The envelope of the various peaks is the experimental curve.

shown) constitutes the *measured* curve of S_c versus T . The dashed curve predicted by theory (Figure 2) is calculated with eq 1 by setting $J = 1.0 \text{ cm}^{-3} \text{ s}^{-1}$ and solving for S_c . Agreement between theory and experiment is within a few percent. Such agreement is now typical for a very large variety of substances.³¹⁻⁴⁰

Turning to the *expansion* cloud chamber,⁴¹ the prototypical version contains a cylindrical vapor space and a pool of liquid as in Figure 1A, but the liquid rests on a piston that can be drawn downward to create an adiabatic expansion. The supporting gas in the vapor, *saturated* with respect to the liquid, is usually argon or nitrogen, and cooling during the expansion creates supersaturation and a condensate of drops. The chamber is "cleansed" of

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heterogeneous nuclei (e.g., dust particles) by repeated expansion and the settling out of the drops formed on such particles. From the degree of expansion of the clean vapor, necessary to create the first drops, one can calculate, from the adiabatic law, the level of supersaturation at the temperature of their appearance. This supersaturation is taken to be S_c at that temperature. Again the drops can be observed by light scattering from a beam that crosses the chamber.

Sophisticated means for improving this measurement are now available. For example "two-piston" chambers have been developed to produce a "pulse" of nucleation that makes it possible to measure the actual nucleation rate.⁴² It should also be remarked that the *diffusion* chamber must *also* be cleared of heterogeneous nuclei. This is accomplished by running it continuously until the vapor is clean. The salient differences between the two types of chambers are (i) the diffusion chamber operates continuously at a fixed supersaturation while the expansion chamber can only produce the requisite supersaturation by repetitive expansion and (ii) the vapor in the diffusion chamber is nonuniform with respect to temperature, pressure, etc. (see Figure 1B), while in the expansion chamber it is uniform.

For a polymerizable monomer, e.g. vinyl acetate, agreement between theory and experiment, as far as S_c is concerned, is no different than for a nonpolymerizable species.⁴⁰ Suppose, however, that a single polymer formed of the same monomer is inserted into a supersaturated monomer vapor. The polymer can then begin to aggregate (reversibly) with monomers so that a cluster of nucleus size is eventually created, followed by the appearance of a macroscopic liquid drop. To a first approximation the polymer acts like a dust particle serving as a heterogeneous nucleus in the vapor. An extremely crude theory,⁴³ unreliable except for its *qualitative* predictions, allows the estimation of the average time τ that elapses before the inserted polymer leads to a nucleus. For styrene vapor at 247.6 K and $S = 11.42$ (far below $S_c \approx 30$ for styrene at this temperature, so that *homogeneous* nucleation cannot occur), the theory predicts that, for a polymer with a DP (degree of polymerization) of 8, $\tau = 1.2 \times 10^7$ s. With DP = 9, $\tau = 6.2 \times 10^2$ s, while with DP = 10, $\tau = 3.1 \times 10^{-2}$ s, and with DP = 11, $\tau = 1.6 \times 10^{-6}$ s. τ decreases by 13 orders of magnitude with only a 37% increase in the size of the polymer!

Now suppose a polymer is grown *in the supersaturated monomer vapor* via a radical addition mechanism as in the scheme outlined at the beginning of this section. The polymer will in effect never nucleate a drop at DP = 8 but will do so almost instantaneously at DP = 11 so that the polymer can be detected by the arrival of the macroscopic drop that it produces. The size (DP) at which detection occurs depends on both S and T . One can therefore *tune* to this size, referred to as the "tunable" size, by controlling S and T .

A more accurate theory of polymer-induced nucleation would probably indicate that the process was not quite

so critical as the crude theory predicts, but it should be fairly critical since the phenomenon is simply another face of the same coin that accounts for the critical nature of ordinary homogeneous nucleation. That criticality is related to the fact that the phenomenon involves a quasiequilibrium between single molecules and the nucleus. Thus if the nucleus contains n^* molecules its "equilibrium" concentration should vary as $(p)^{n^*}$, where p is the pressure, so that if $n^* \approx 10^2$, that concentration will vary sharply with pressure. Although a polymer in a nucleus may be regarded as dissolved in a drop of its own monomer, it may be shown to be mostly bare during its growth. Growth therefore occurs truly in the vapor. This situation stems from the fact that the "equilibrium" concentration of a cluster formed on a polymer decreases very rapidly with its content of free monomer.⁴⁴

Cloud Chamber Studies of Radical Addition Polymerization

Figure 1 illustrates how the kinetics of polymerization may be investigated in a diffusion cloud chamber having monomer liquid on its bottom plate. In one approach,⁴³ a UV beam enters the monomer vapor at the level of maximum supersaturation. Radicals form in the beam and grow and diffuse until they are lost to the chamber walls. If the beam is steady, a steady distribution of polymer sizes is established up to, but not exceeding, DPs of the "tunable size", a quantity determined by the degree of supersaturation. Radicals of that size are removed from the distribution by the formation of drops. These fall through the laser beam and are counted. A low photon flux is used to ensure that few enough polymer radicals grow simultaneously. In this way recombination and condensation are avoided. The observed rate of nucleation then equals the rate of production of polymers of tuneable size. Some methods have been developed^{8,45} to ascertain that each nucleus contains *only one* polymer. The presence of more than one polymer would make it difficult to compare experiment and theory.

Both steady^{8,46} and nonsteady^{9,46} experiments have been performed. In a nonsteady experiment a brief pulse of UV photons creates radicals that grow into polymers. The number of polymers of tuneable size x that appear, at a time t after the pulse, can be predicted roughly^{9,47} to be

$$N_x = N_0 e^{-k_p M t} [(k_p M t)^{x-1} / (x-1)!] \quad (2)$$

where N_0 is the initial number of free radicals and M is the monomer concentration. Since x is fixed, the nucleation rate is given by $J = k_p M N_{x-1}$. Figure 3 exhibits measured values of J versus t for a pulse experiment on vinyl acetate.⁹ The curve is a least-squares fit of eq 2 to the measured points. In principle, this fit can be used to determine N_0 , k_p , and x , but eq 2 omits consideration of the loss of polymers to the walls so that it is only qualitatively correct. Nevertheless, the fit is very good.

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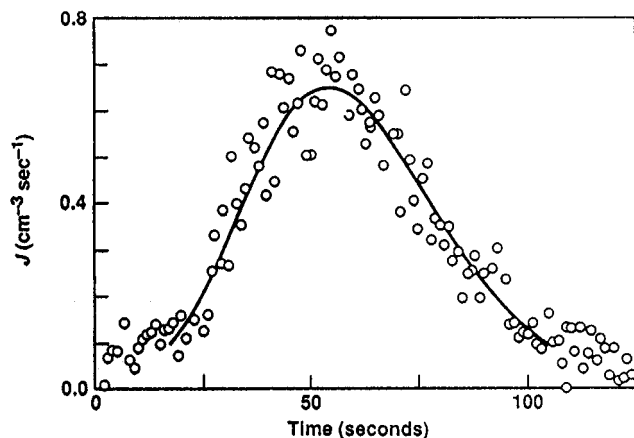


FIGURE 3. Non-steady-state nucleation in vinyl acetate vapor after a UV pulse.⁹ Open circles are experimental points averaged over 400 runs. The curve is a least-squares fit to eq 2.

Each point (circle) in Figure 3 is signal averaged over 400 runs, and the data are still "noisy". This is due to the ultraslow rate; the maximum rate of product molecule formation in Figure 3 is $0.6 \text{ cm}^{-3} \text{ s}^{-1}$. As indicated in the introductory section, N_0 and therefore the quantum yield of free radicals can be determined by the measurement of "noise";¹⁷ noise increases as N_0 decreases.

Not only does the fit of theory to experiment in Figure 3 confirm that the observed nucleation is due to polymers, but in a more general sense, the time lag after the pulse, before the maximum rate is achieved, indicates that the nucleating agent requires time for its development, i.e., time must be allowed for a polymer to form.

As indicated in the introductory section, attempts to demonstrate the thermally self-initiated radical addition process in styrene vapor, using conventional means, have been inconclusive.^{48,49} The pressure of styrene vapor does not seem to decrease with time for temperatures up to 400°C . Also, as indicated above, self-initiation is not fully understood.¹²⁻¹⁴ In the liquid phase, the average molecular weight of the polymer decreases with increasing temperature, an effect attributed to increased recombination at higher initiation rates.^{50,51}

Figure 4 refers to styrene⁴³ and is the counterpart of Figure 2 for nonane. The envelope of the many peaks is the experimental curve of S_c versus T . Unlike nucleation studies on other substances, it lies far below the curve predicted by theory (curve appearing in the figure) for homogeneous nucleation. This discrepancy is not a feature of nonpolymerizable styrene-like molecules as is demonstrated by a similar study⁴³ for ethylbenzene (PhCH_2CH_3 , Figure 5), in which theory and experiment are in agreement.

Figure 4 is explained as follows. The cloud chamber can be approximated as a cylindrical vessel of height $2L$ and radius, a , that contains styrene vapor in a uniform convectionless state. Radicals are initiated uniformly at rate I . Termination is absent, and the radicals grow into

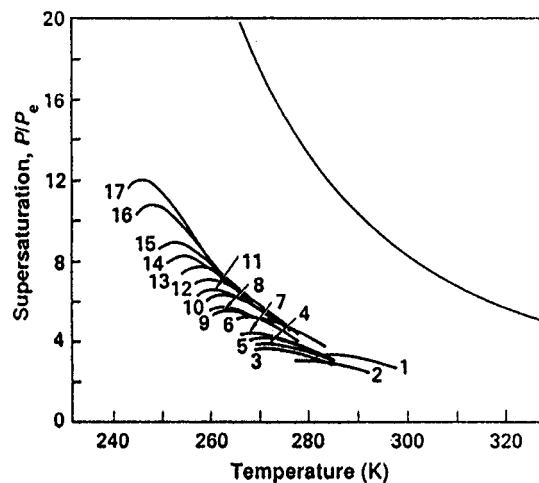


FIGURE 4. Critical supersaturation versus temperature for styrene.⁴³ Solid line represents theory; envelope represents experiment. Note the large discrepancy.

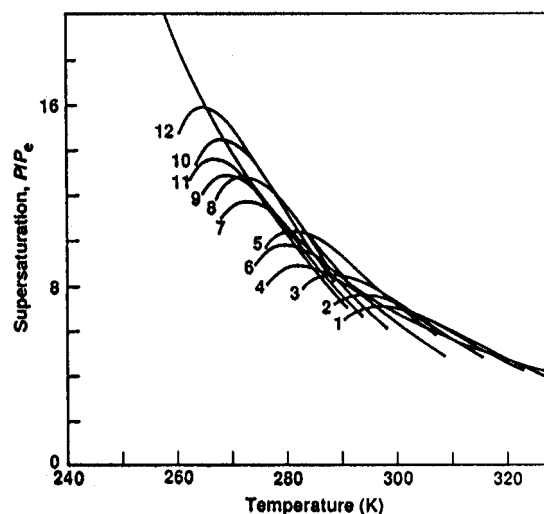


FIGURE 5. Critical supersaturation versus temperature for ethylbenzene.⁴³ Solid line represents theory; envelope represents experiment.

polymers which diffuse to be irreversibly lost to the walls. With r and z as cylindrical coordinates, the steady concentration of polymers^{52,53} with $\text{DP} = j$ is

$$N_j(z,r) = \sum_{\alpha} \sum_{m=0}^{\infty} \left[\frac{(-1)^m 4I}{D_1 \alpha J_1(\alpha) \omega_m} \right] \times \left\{ \frac{\prod_{i=1}^{j-1} (K_i/D_{i+1})}{\prod_{i=1}^j [(\alpha/a)^2 + (K_i/D_i) + \omega_m^2]} \right\} (\cos \omega_m z) J_0 \left(\frac{\alpha}{a} r \right) \quad (3)$$

in which i is the polymer size, $K_i = k_p^{(i)} M$, where M is the concentration of monomer in the vapor, D_i is the diffusivity, J_0 and J_1 are Bessel functions, and α and ω_m are specified eigenvalues. The appearance of i in $k_p^{(i)}$ and D_i indicates that propagation and diffusion can depend on DP.

The discrepancy between theory and experiment in Figure 4 can be explained⁴³ by the preestablishment of

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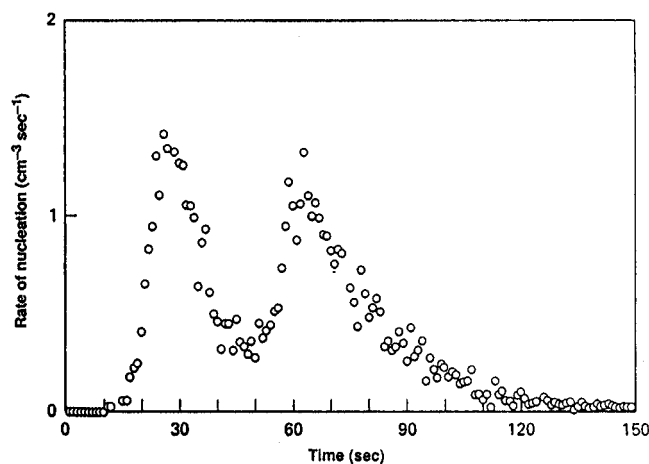


FIGURE 6. Non-steady-state nucleation in isoprene vapor after a UV pulse.⁴⁶ Open circles are points signal averaged over 200 runs. The existence of two maxima is probably the result of recombination as explained in the text.

the distribution described by eq 3. At given values of T and S , a polymer of tuneable size may not exist in this distribution. As S is increased, the tuneable size is reduced into the distribution and removed in a drop. Before another drop can form, another "tuneable" polymer must be propagated. Thus the rate of drop formation equals the rate of chemical propagation which can therefore be measured. This occurs below the value of S_c required for homogeneous nucleation, so that the envelope curve should lie below the theoretical one as the data of Figure 4 confirm.

Assuming that k_p is on the order of the value found in the liquid, the fit of eq 2 to the data of Figure 3 suggests that I , due to self-initiation in the vapor, is extremely small (e.g., less than $10 \text{ cm}^{-3} \text{ s}^{-1}$). Such a small value of I would require a waiting time on the order of millions of years in an experiment based on the reduction of pressure due to polymer formation in the vapor and explains why such experiments in the past have been inconclusive.

Studies of the photochemical gas phase polymerization of isoprene, a diene, have been conducted using the diffusion chamber.⁴⁶ The results are interesting and suggest a detailed mechanism that would be difficult to infer by another means. In the interest of brevity in the current exposition, the reader is referred to the original paper; however, Figure 6 (dealing with isoprene) merits comment because of the insight it provides. The data in this figure were obtained⁴⁶ in the same way as those in Figure 3, but the individual points were signal averaged over only 200 runs. The two "peaks" are almost certainly due to the high quantum yield of radicals in the case of isoprene which produces a high initial concentration of smaller polymeric radicals in the space originally occupied by the pulsed UV beam. This high concentration results in the early termination, via recombination, of these smaller radicals resulting in a quantum jump in the number of radicals that exceed the tuneable size and therefore nucleate drops. The first peak is due to this process. In the meantime the surviving radicals diffuse apart so that recombination is no longer viable, but they continue to grow to reach the tuneable size at a later time and account for the second peak.

Experiments in an Expansion Cloud Chamber

Although many interesting qualitative features of homogeneous gas phase polymerization can be demonstrated in the diffusion cloud chamber, experience has shown that it has many disadvantages when quantitative results are desired. Above all, it is a *nonuniform* device, e.g. temperature, composition, partial pressure, and supersaturation vary with elevation. As a result, a radical produced in a UV beam at one elevation can continuously diffuse to other elevations as it grows to polymeric size, and any interpretation of kinetic parameters can only represent some average taken over a diffusion path that has sampled different temperatures and compositions. For this reason alone, the expansion chamber, a *uniform* device, offers greater promise in the achievement of quantitative accuracy.

A study, using an expansion chamber, was recently completed.⁴⁵ The chamber was of the type developed at the University of Missouri⁴¹ and was quite large so that its walls could be, on the average, far from most of the growing radicals and ensure that polymers of reasonable size could be produced before they were adsorbed on the walls. The polymer was vinyl acetate (VA),^{8,9,54} a species which proved to be well behaved for the experiments in question, and which also has one of the largest propagation constants. Initiation was not photochemical; the initial radicals were produced by the thermal decomposition of *tert*-butylperoxide (TBP). The cloud chamber (the Missouri type) was the first to produce a "pulse" of supersaturation in order to "shut down" nucleation before the pressure of the superaturated vapor could be reduced by depletion due to droplet growth. Growth on the nuclei, generated during the pulse, could then be continued by maintaining a low supersaturation (not large enough for nucleation). This sequence of events was instituted by a rapid expansion followed by a rapid compression, not quite back to the original volume. The nucleation pulse had a duration of several hundredths of a second. Today, a similar series of events is produced in small "two-piston" chambers with much greater accuracy and efficiency; flat levels of supersaturation less than 1 ms in length are regularly achievable.⁴² This series of events can also be generated in shock tubes.^{55,56}

The idea of the polymer experiment is easily described. A pool of VA liquid rests on the upper surface of the cloud chamber piston. The space above the pool is filled with argon vapor mixed with saturated VA vapor at the uniform temperature of the chamber. A small amount of TBP is dissolved in the VA pool so that the gas space is saturated with TBP vapor as well. Temperatures in the neighborhood of room temperature are involved. At these temperatures, TBP dissociates *very* slowly into free radicals which initiate polymerization. Polymerization occurs in *both* the liquid and the vapor and undoubtedly more rapidly in the liquid. However, because of the slow rate of TBP decomposition, both processes are very slow. The effects of polymer formation are therefore not evident in

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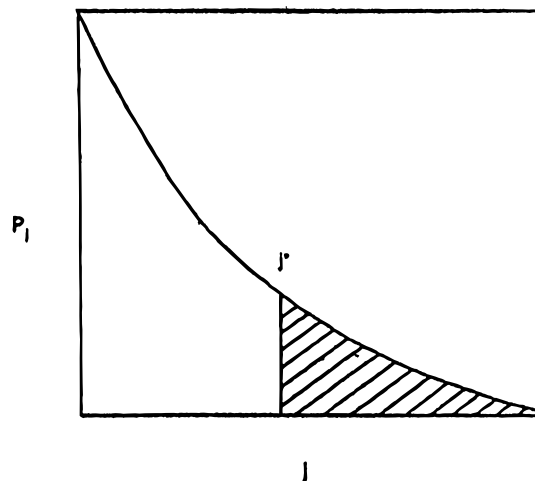


FIGURE 7. Plot of the steady-state distribution of P_j versus j . j^* indicates the polymer size at which nucleation is induced (i.e., the tuneable size) at a particular level of supersaturation. All polymers in the "shaded" area will form drops.

the liquid. On the other hand, even though the process is slower in the vapor, the formation of polymers is detectable because of the enormous amplifying ability of the nucleation process.

The ideal sequence of events in the experiment is as follows. Fixed concentrations of monomer and initiator are maintained in the argon vapor by replenishment from the liquid pool during a waiting period in which the VA vapor remains saturated and polymers grow under uniform conditions. The distribution of polymer sizes attains a steady state as a result of a balance between propagation and diffusion with loss to the walls. Termination via recombination or disproportionation is ruled out due to the small number of polymers, simultaneously in the vapor phase.

After the waiting period, during which the steady state is achieved, the expansion cycle of the chamber is performed in order to create, in the vapor, a "pulse" of supersaturation that is terminated by compression, after which drops of monomer nucleated during the pulse are allowed to grow to visible size so that they can be photographed and counted. If the idealized picture holds, then corresponding to each level of supersaturation during the expansion, all polymers beyond a certain critical (tuneable) size are capable of nucleating drops. Thus the number of drops formed during the pulse should be given by the shaded area in Figure 7. The curve in the figure is a schematic plot of N_j (P_j in the figure), the steady-state concentration of polymers of $DP = j$ versus j . The left boundary of the shaded area corresponds to the highest level of supersaturation achieved during the pulse, i.e., to the smallest polymer "activated" (smallest tuneable size) during the pulse. Thus the shaded area can be equated to the concentration C of drops in the photograph.

The theoretical approximation⁴⁵ for C is obtained from eq 3, simplified by assuming that (i) each drop is nucleated by a single polymer molecule, (ii) the cylindrical vapor space of the chamber has an infinite radius, (iii) C refers to $z = 0$, and (iv) K_i and D_i are constants independent of i . The resulting expression is

$$C = \frac{16(2k_d[\text{TBP}])L^2}{D\pi^3} \left[\frac{K}{d(\pi/2L)^2 + K} \right]^{j^*} \quad (4)$$

where $[\text{TBP}]$ is the concentration of TBP in the vapor, $2k_d[\text{TBP}]$ represents I , $K = k_pM = k_p[\text{VA}]$, and j^* is the tuneable size. In the experiment, the photograph is taken at the approximate level $z = 0$. Equation 4 incorporates many idealizations which the actual experiment⁴⁵ does not in fact meet, but it represents an acceptable first approximation.

There are seven parameters in eq 4. These are k_p , k_d , D , M or $[\text{VA}]$, $[\text{TBP}]$, j^* , and L . L poses no problem since it is an instrumental geometric quantity.

If k_d , D , M , $[\text{TBP}]$, and j^* are known, a measurement of C permits the evaluation of k_p through the use of eq 4. Unfortunately, both k_p and j^* are unknown so that, for example, k_p cannot be determined by this procedure. The quantities k_d and $[\text{TBP}]$ are not readily available. The former had to be extrapolated to room temperature from measurements of TBP decomposition limited to temperatures between 120 and 150 °C,⁵⁷⁻⁵⁹ while the latter was obtained from crude measurements⁴⁵ (using vapor phase spectroscopy) of the Henry's law constant, in liquid TBP-VA solutions, far more concentrated in TBP than those used in the chamber to control TBP in the vapor.

Some experimental results⁴⁵ are shown in Figure 8 and Table 1. Figure 8 shows the dependence of supersaturation on temperature for vinyl acetate in both the absence and presence of TBP initiator. The *critical* rate was chosen as 100 drops $\text{cm}^{-3} \text{s}^{-1}$. The preexpansion temperatures and TBP concentrations in the liquid solution in parts per million (ppm) are indicated. The differences in the results with and without TBP show that, in the presence of an initiator, nucleation occurs at levels of supersaturation below those required for the homogeneous case, thus providing strong evidence that polymers have formed in the vapor and have been detected.

More direct evidence for nucleation induced by polymers was obtained by measuring C as a function of TBP concentration in the chamber liquid at various levels of supersaturation (expansion depths). The results are presented in Table 1. Note the rough linear dependence of C on TBP concentration in each experiment. According to eq 4, C should be proportional to $[\text{TBP}]$, which in view of Henry's law is proportional to the concentration of TBP in the chamber liquid. Thus the linear dependence of C , or drop count, on TBP concentration supports the conclusion that nucleation is polymer induced by a nucleus containing only a *single* polymer molecule. Evidence, discussed below, indicates that encounters between polymers were negligible under the experimental conditions.

As intimated above, the measurements of ref 45 are unequal to the task of determining either k_p or j^* precisely. One crucial independent measurement is missing. If a reliable theory of polymer-induced nucleation were available, it would be helpful, but no such reliable theory exists. Thus the experiment must be designed to avoid any

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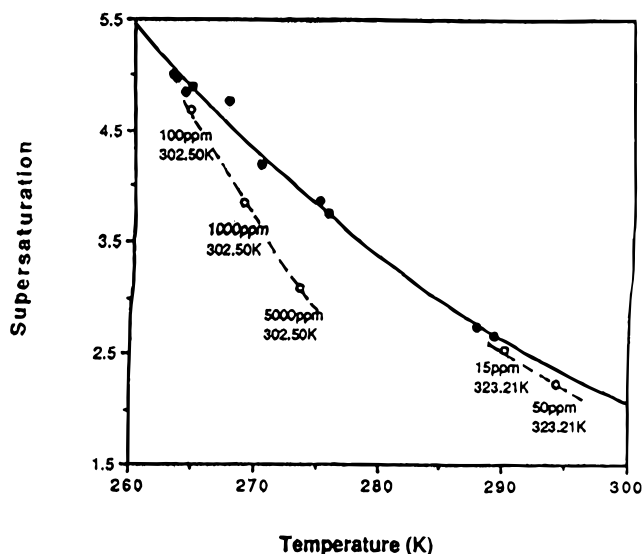


FIGURE 8. Measured dependence of supersaturation on temperature for vinyl acetate in the absence (filled circles) and presence (open circles) of initiator TBP.⁴⁵ Photographic observation was at about 1 drop cm^{-3} ($J = 100 \text{ drops cm}^{-3} \text{ s}^{-1}$). The preexpansion temperatures and concentrations of TBP in the liquid phase are indicated. The solid curve is the fit to the experimental data without TBP. Nucleation induced by polymers is clearly evident in the fact that lower critical supersaturations occur when TBP is present.

Table 1. Measurements of the Number of Drops Nucleated in Vinyl Acetate Vapor as a Function of the Concentration of TBP in the Liquid Phase at Different Supersaturations, Indicating the Approximate Linear Dependence of Drop Count on TBP Concentration

supersaturation	TBP (ppm)	drops (cm^{-3})
4.73	50	1.0
4.73	100	1.8
4.73	500	11.0
4.44	1000	1.6
4.44	5000	10.0
3.96	1000	1.3
3.96	5000	7.5
3.85	1000	0.7
3.85	5000	4.0
2.53	15	1.5
2.53	50	5.5
2.23	15	0.3
2.23	50	1.2

dependence on nucleation theory. Even though k_p and j^* are beyond precise determination, the method of ref 45 nevertheless allows the placement of acceptable upper bounds on these quantities, by using a strategy based on thermodynamic theory rather than nucleation theory. The general principle is that a polymer of size j , such that j exceeds the number of monomers (determinable from the Kelvin relation²⁹) in the *homogeneous* nucleus for VA vapor, will induce the nucleation of a drop. To complete the argument concerning the bound, it is also necessary to show that the above requirement cannot be met for j^* computed, using eq 5 below together with a measured value of C , unless k_p in the gas phase is substantially smaller than k_p in the liquid.

First eq 4 is rearranged to

$$j^* = \frac{\ln(D\pi^3 C/L^2 k_d [\text{TBP}])}{\ln\{K/[K + (D\pi^2/4L^2)]\}} \quad (5)$$

In all measurements $C \approx 1 \text{ drop cm}^{-3}$. In Figure 9, j^*

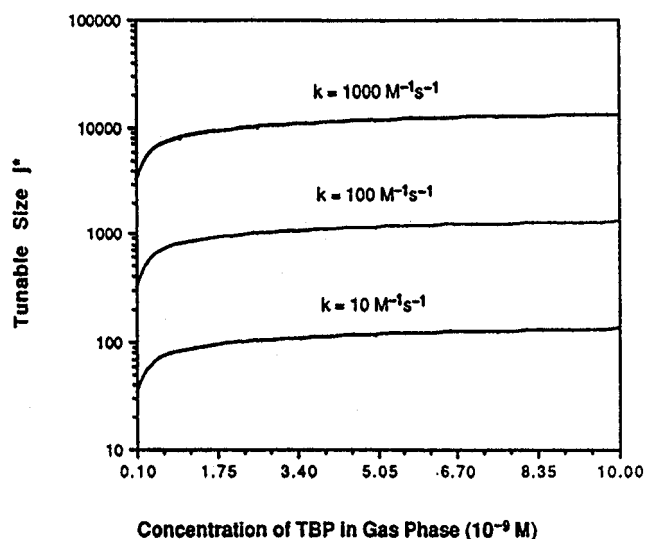


FIGURE 9. Plots of tunable size j^* versus the concentration of TBP in the vapor for three different rate constants of propagation.⁴⁵ Preexpansion temperature = 302.50 K, $2L = 17 \text{ cm}$, $D = 0.1 \text{ cm}^2 \text{ s}^{-1}$, concentration of vinyl acetate in gas phase $[M] = 7.21 \times 10^{-3} \text{ M}$, dissociation rate $k_d = 1 \times 10^{-13} \text{ s}^{-1}$, total concentration of polymeric radicals (of size larger than the tunable size) $C = 1.66 \times 10^{-21} \text{ M}$ (1 molecule cm^{-3}).

derived from eq 5 is plotted versus [TBP] for three values of k_p (denoted by k in the figure), namely $k_p = 10, 100$, and $1000 \text{ M}^{-1} \text{ s}^{-1}$. The temperature is assumed to be 302.50 K (one of the preexpansion temperatures at which the steady state was allowed to develop; see Table 1). At this temperature, $M = 7.21 \times 10^{-3}$ and $k_d = 10^{-13} \text{ s}^{-1}$. C is set equal to 1 drop cm^{-3} , the nominal drop concentration in the experiment. In terms of molecules (1 polymer per drop), this corresponds to $C = 1.66 \times 10^{-21} \text{ M}$. The known value of k_p in the liquid at 302.50 K is about $1000 \text{ M}^{-1} \text{ s}^{-1}$.⁵⁹ Finally, D is taken to be $0.1 \text{ cm}^2 \text{ s}^{-1}$. Several methods (either crude theoretical⁶⁰ or semiempirical^{61,62}) indicate this to be a nominal value at the temperature in question.

The salient features in Figure 9 are the following. First, the calculated j^* is insensitive to [TBP] except at very low concentrations of TBP. This allows an estimate of j^* even in the absence of very accurate data on the concentration of TBP in the vapor phase. The calculated j^* does however increase (slowly) with an increase in [TBP]. Second, we note that the calculated j^* increases with k_p (at fixed [TBP]) almost in proportion to k_p .

For the preexpansion temperature of 302.50 K, the peak (lowest) temperature during the expansion-compression cycle averaged about 264.6 K, which corresponded to a supersaturation on the order of 4.67. At this temperature and supersaturation, the classical nucleus for homogeneous nucleation contains, according to the Kelvin relation, about 90 molecules, i.e., $n^* = 90$. Application of the principle enunciated above would then require $j^* \leq 90$. It is clear from Figure 9 that this requirement can only be realized if $k_p \leq 10 \text{ M}^{-1} \text{ s}^{-1}$. Since, in the liquid, $k_p \approx 1000 \text{ M}^{-1} \text{ s}^{-1}$, its value in the gas phase must therefore be much

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Table 2. Estimated Values of j^* Corresponding to Various Experimental Conditions^a

TBP (ppm)	T_1 (K)	T_2 (K)	S	n^*	j^*
100	302.50	264.51	4.69	89	34
500	302.50	264.51	4.65	90	65
1000	302.50	268.69	3.85	122	83
15	323.21	290.14	2.53	220	204
50	323.21	294.26	2.23	309	246

^a TBP, the concentration of TBP in the liquid phase; T_1 , preexpansion temperature; T_2 , peak temperature after expansion; S , supersaturation; n^* , size of the homogeneous nucleus; j^* , the tunable size.

smaller than in the liquid, at least according to the analysis of Figure 9.

Reference 45 examined the possibility of maintaining k_p at its liquid value while forcing $j^* \leq 90$ by choosing D away from its nominal value of $0.1 \text{ cm}^2 \text{ s}^{-1}$, only to find that no reasonable value of D was able to accomplish this.

If it is assumed that k_p does indeed have the small value of $10 \text{ M}^{-1} \text{ s}^{-1}$, eq 5 can be used to calculate upper limits for j^* . Table 2 lists upper limits for j^* , calculated in this manner, together with the conditions to which each limit corresponds. It is seen that quite small *single* polymers are able to nucleate drops.

Using the same small estimate of k_p , together with the simplified version of eq 3 that led to eq 4, it was possible to estimate, under the experimental conditions, the total steady concentration of polymeric radicals in the chamber. This estimate proved to be 10^2 – 10^3 cm^{-3} , so that the number of encounters between radicals would be insignificant.

Why is k_p so much smaller in the vapor than in the liquid? Two possibilities suggest themselves: (i) the active radical on the polymer is shielded from attack from monomer by the body of the polymer that adopts the globule configuration in the poor solvent represented by the vapor or (ii) the very large exothermic heat involved in the addition of a monomer to the radical is transferred to the internal degrees of freedom of the polymer more

rapidly than it is transferred to the surrounding dilute vapor, with the result that the polymer decomposes. In regard to the second point, it is well-known that polymers have "ceiling temperatures".⁶³

Summary and Suggestions for Future Work

As it stands, the techniques described in this Account have been able, with some confidence, to demonstrate that in situ gas phase homogeneous radical addition polymerization can be studied and that single small polymers are capable of nucleating large drops of monomer liquid. Even highly fluctuating rates of less than $1 \text{ polymer cm}^{-3} \text{ s}^{-1}$ can be studied with the possibility that the stochastic nature of the reaction can be used to evaluate quantum yields of initiating radicals. In addition, the self-initiated polymerization of styrene in the vapor has been demonstrated. Furthermore it has been demonstrated with good reliability that the chain propagation rate constant in the vapor is much smaller than in the liquid. The reason for this disparity may lie either in the shielding properties of the globule configuration or in the poor heat sink represented by the dilute vapor.

Future work should be performed with specially designed cloud chambers in which all of the seven relevant parameters can be measured independently. One possibility involves a chamber in which an accurate variation of L , the chamber gas space height, could be effected, while all other parameters were maintained fixed, so as to provide additional deterministic equations. Another possibility would be to vary the monomer concentration M while not affecting the supersaturation of the condensable gas. This could only be accomplished if the monomer constituted only a small fraction of that gas. Finally, the development of a reliable theory for polymer-induced nucleation would be extremely helpful.

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