226. *The Photochemical Polymerisation of Vinyl Acetate Vapour.*

By H. W. Melville and R. F. Tuckett.

The kinetics of the polymerisation of vinyl acetate vapour under the influence of ultra-violet light of wave-lengths greater than 2500 A. have been investigated. Shorter wave-lengths cause decomposition of the molecule into products which inhibit the polymerisation. At high enough pressures the rate of polymerisation is proportional to the first power of the concentration of vinyl acetate and to the square root of intensity of the incident light. At pressures of about 20 mm. the rate falls off very rapidly and becomes immeasurably slow at lower pressures, *e.g.*, 15 mm. This phenomenon is apparently due to the fact that the photo-excited vinyl acetate molecule can lose its energy before another molecule of monomer can add on. This hypothesis is reinforced by the effect of other added gases. Quite small amounts of oxygen and of butadiene retard the reaction by terminating the growing chain. Amounts of inert gases like helium, argon, and hydrogen comparable with the amount of vinyl acetate also retard the polymerisation but these gases function, not by stopping growing chains, but by deactivating by collision the photo-excited vinyl acetate molecule.

This paper is a continuation of the work on the systematic examination of polymerisation reactions in the vapour phase. In practically every example of a vinyl derivative that readily polymerises in the vapour phase a number of unique observations have been made which have helped in elucidating the kinetics of such reactions. As will be seen below, the vinyl acetate reaction is no exception. As with methyl methacrylate and chloroprene, it happens that there are two distinct mechanisms whereby macromolecules are formed, and it turns out that it is easy to separate the two modes of polymerisation. Apart from these considerations, however, the polymerisation of vinyl acetate has been studied in the liquid phase, peroxide catalysts (Cuthbertson, Gee, and Rideal, *Proc. Roy. Soc.*, 1939, *A*, **170**, 300; Blaikie and Crozier, *Ind. Eng. Chem.*, 1936, **28**, 1155; Skirrow, *British Plastics*, 1939, **10**, 416, 507; Starkweather and Taylor, *J. Amer. Chem. Soc.*, 1930, **32**, 4708) and ultra-violet radiation (Taylor and Vernon, *ibid.*, 1931, **53**, 2527) being used. The results of these investigations are not sufficiently comprehensive to enable a decision to be made as to whether the mechanisms in the liquid phase are the same for photo- and peroxide-catalysed reactions : nor is it possible to say whether the mechanism in the gas phase is kinetically similar to that in the liquid phase.

It has been shown that in some dimerisations, *e.g.*, of *cyclo*pentadiene (Wassermann, *J.*, 1939, 362, 367, 371, 375), the bimolecular constants are the same in the liquid and in the vapour phase, and hence it seemed necessary to see whether in a suitable polymerisation process a similar identity of rates could be obtained. Vinyl acetate is one of the few monomers which polymerise equally well in both phases, and thus some information on this point might be obtained.

There is, however, another important reason for undertaking this work. In the liquid phase it is believed that polymerisation occurs by the free-radical mechanism, *i.e.*, the active polymer is a large free radical. Although it has been demonstrated that a free radical mechanism *can* occur in the liquid phase, it is by no means certain that every liquid-phase polymerisation proceeds by this mechanism. As will be shown, it is possible to characterise the free-radical polymerisation of vinyl acetate in the vapour phase. If therefore it can be shown that there is in fact a correlation in behaviour of vinyl acetate between the two phases, it may be possible to gain some more precise information about the behaviour in the liquid phase. The present paper is confined to the gas-phase polymerisation, and further communications will deal with the liquid-phase reaction. Polymerisation must be initiated by radiation, by excited mercury atoms, or by free radicals, since purely thermal polymerisation does not occur at all.

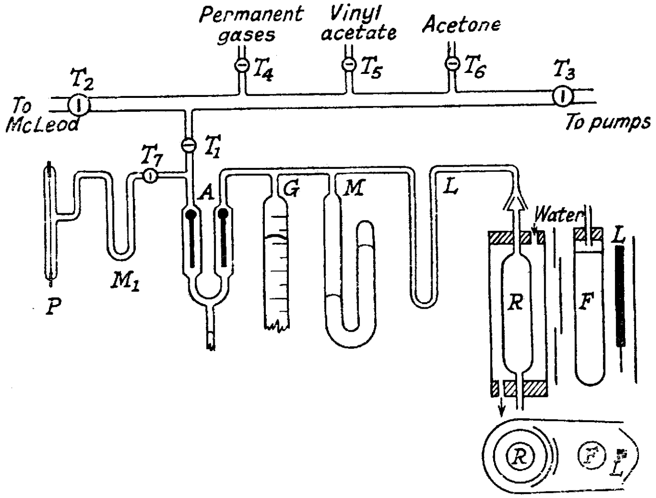
EXPERIMENTAL

Apparatus.—The apparatus used calls for no special comment, the general arrangement being shown in Fig. 1. The silica reaction vessel was placed in a thermostat, and the polymerisation could be carried out at various temperatures up to 100° either under constant pressure of vapour, using a gas burette, or at constant volume, using a mercury manometer. Mercury cut-offs were employed to isolate the reaction system to avoid trouble with greased joints. The apparatus was evacuated by a mercury diffusion pump. The sources of light were high- and low-pressure mercury lamps depending on the type of reaction being studied. Care was taken to ensure constancy of light output by controlling the voltage applied to the lamps. Experiment showed that, like other monomers, vinyl acetate is decomposed by the shortest wave-lengths emitted by the mercury lamp. Consequently it was necessary to screen off such radiation by acetic acid filters (30% aqueous solution). McLeod and Pirani gauges were used to measure the pressures of gases not condensable in liquid air.

Particular care was taken in the purification of vinyl acetate. This was originally obtained from Shawinigan Chemicals Ltd. and usually contained some acetaldehyde. The latter substance is a strong inhibitor of the liquid- and also the gas-phase polymerisation and hence its removal is essential. The monomer was first fractionally distilled twice at atmospheric pressure, only the 72—73° fraction being collected. The aldehyde is difficult to separate, and all fractions boiling below 72° were discarded. The nearly pure ester—which only gave a faint pink coloration with Schiff's reagent on standing for 5 minutes—was sealed into a tube on to the vacuum line of the apparatus. The ester was then frozen with liquid air and pumped out to 10^{-5} mm. It was melted and refrozen several times with evacuation between each cycle. Distillation was conducted in a vacuum, only the middle portion being used for experimental purposes.

" A.R." Acetone was used as a source of methyl radicals. It was freed from oxygen in a similar manner to the vinyl acetate. Oxygen came from potassium permanganate; hydrogen was purified by passing through palladium. Butadiene was taken from a cylinder and purified by vacuum distillation.

FIG. 1.

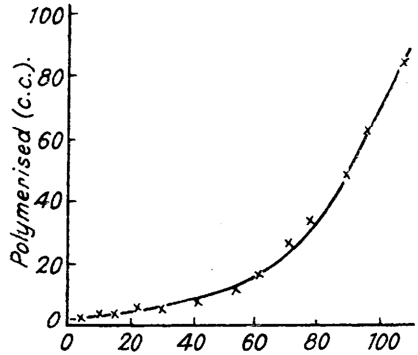


General arrangement of apparatus.

Direct Photo-reaction.—Several precautions have to be taken in measuring the velocity of polymerisation. Fig. 2 shows how the number of molecules polymerised increases with time of illumination, starting with a clean tube. There is a marked induction period, and gradually the rate attains a constant value. If illumination is prolonged, the rate begins to decrease again, but since this only occurs when very thick deposits of polymer are formed it is attributed to scattering and absorption of the effective radiation by the polymer. The long induction period is not due to the presence of gas-phase inhibitors, because a similar phenomenon is observed if successive separate portions of vinyl acetate are used. This points to an effect due to the reaction vessel itself. It is not due to the fact that the polymerisation really takes place in the deposited polymer. There are many reasons for supporting this contention. The customary mist of solid polymer is formed in the gas phase when the lamp is switched on, the polymerisation rate does not increase proportionally to the weight of polymer deposited, inert gases like helium, argon, and hydrogen inhibit the polymerisation, and the intensity exponent in the polymerisation does not tend to zero, as happens in the polymerisation of chloroprene where polymerisation does occur in the solid polymer. As will be shown later, there is little doubt that the induction period is due to the fact that the active polymer molecules are somehow destroyed when they collide with the clean silica walls, and that when these are covered by polymer there is more or less elastic reflection with a consequent lengthening of the chain until mutual destruction occurs in the gas phase. This suggestion is supported by covering the walls with a layer of Gelva 15—commercial polyvinyl acetate—whereby the induction period is diminished but curiously enough not completely eliminated. The other surprising fact is that walls need to be covered by a fairly thick layer of polymer. It might be expected that a monolayer of polymer would be sufficient. Assuming a degree of polymerisation of 100, a monolayer would correspond to a pressure decrease of 10^{-2} mm. whereas a very much greater decrease of pressure is required before the reaction rate is constant. Owing to the necessity for depositing polymer there is a measurable absorption of the monomer by the polymer, and as this amount of polymer increases so the amount of sorbed monomer increases. Corrections are made for the total observed consumption of monomer to give the true photo-rate. In order to cut down corrections of this kind to a minimum, the method of bracketing must be employed, and tubes are used for a relatively small number of runs just after conditions have become relatively steady. Experiments show there is no measurable induction period and that there is no long-continued reaction in the dark, as occurs with methyl methacrylate. This is in accord with the present experience with molecules of the type $CH_2{:}CHX$. If a heavily coated tube is being used there is sometimes an apparent induction period or even a pressure increase, due apparently to some desorption of monomer from the polymer when the light is switched on.

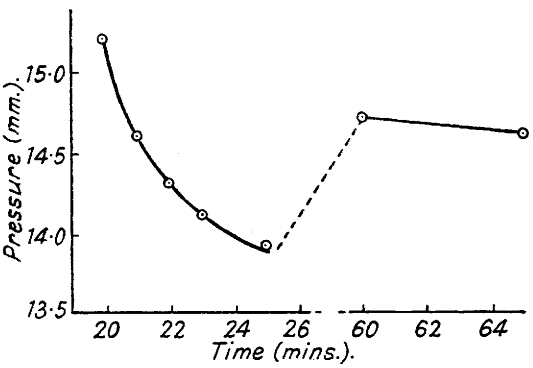
General Kinetics.—Decomposition. As has already been mentioned, unfiltered light from the mercury lamp leads to decomposition of the vinyl acetate, one of the products of decomposition being non-condensable in liquid air. This gas could only be hydrogen, carbon monoxide, or methane. A Pirani gauge was consequently calibrated by using carbon monoxide and hydrogen. The gas from vinyl acetate gave a calibration curve coinciding exactly with that for carbon monoxide. The calibration curve for methane lies very close to that for carbon monoxide and therefore it is difficult to say whether the gas is one or the other. The important point of this decomposition is that the products are strong inhibitors for the photo-polymerisation. This behaviour is shown most clearly by the following kind of experiment. Vinyl acetate is illuminated at constant volume for a given period and the rate measured. After this, the pressure is increased to the initial value and the run continued. As Fig. 3 shows, there is a very marked diminution in rate as a result of the accumulation of the products of decomposition. The acetic acid filter completely eliminates this decomposition, and hence it would appear that it has nothing to do with the polymerisation reaction. Another indication in support of this suggestion is that decomposition occurs just as readily below the critical pressure at which vinyl acetate ceases to polymerise. These observations are completely in accord with experience with methyl methacrylate and methyl acrylate. Short-wave radiation, instead of leading to activation and eventual starting of polymerisation, simply results in disruption of the molecule into products incapable of starting polymerisation.

FIG. 2.



Course of polymerisation at constant pressure starting with a clean tube.

FIG. 3.



Inhibition of polymerisation by the accumulated products of decomposition of vinyl acetate.

Effect of pressure. The constant-pressure technique being used, the variation of rate with pressure was investigated, due regard being paid to corrections owing to disappearance of monomer by absorption by the polymer. A typical run is shown in Table I, the bracketing pressure being 42·1 mm. Similar series of runs were made over other ranges of pressure, the maximum being fixed at about 60 mm., the saturation vapour pressure of vinyl acetate. Rates relative to that at 42·1 mm. are plotted as a function of pressure in Fig. 4. The most striking feature of this plot is the appearance of a limiting pressure below which the reaction rate is immeasurably slow. At high enough pressures the rate is approximately proportional to the first power of the pressure, whereas in the intermediate region 20—40 mm.

TABLE I.

Direct photo-polymerisation ; temp. 20° *; high-pressure* Hg *lamp.*

Pressure (mm.).	Observed rate (in c.c./min.) at 42·1 mm. pressure.	Dark " rate " (c.c./min.).	Net polymerisation rate (c.c./min.).
42·1	25·6	0·8	24·8
42·1	27·3	1·9	25·4
37·5	22·1	—	22·1
23·9	3·56	—	3·56
42·1	26·5	1·4	25·1
48·4	31·6	2·0	29·6
55·6	40·4	1·6	38·8
42·1	30·4	2·0	28·4

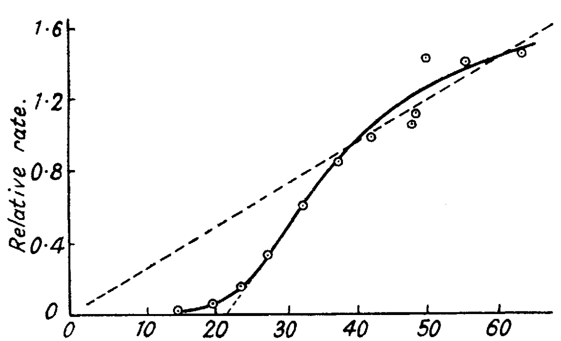
the rate = const. $(p - p_0)$, where p_0 may be defined as a critical pressure of about 21 mm. This limit has nothing to do with inhibition by decomposition products, for if the vapour is illuminated at, say, 20 mm. for a considerable period and the pressure is then raised to say 30 mm., polymerisation proceeds normally. Similarly, if polymerisation is occurring at 30 mm. and the pressure is reduced to 20 mm. polymerisation immediately ceases. To show this more clearly prolonged illumination with use of the acetic acid filter gave the following results :

Vinyl acetate pressure (mm.).	Time of illumination (mins.).	C.c. of vapour polymerised.	Pressure of products of decomposition (mm.) (non-condensable in liquid air).
12·9	120	—	$4·0 \times 10^{-2}$
15·0	100	8·0	$3·5 \times 10^{-2}$

It will be seen that a reduction in pressure of only 2 mm. reduces the very small rate of polymerisation at 0·08 c.c./min. to an immeasurable value, yet the decomposition is hardly affected. Likewise there is no photo-decomposition of the polymer and hence this could not be the cause of the appearance of the limit.

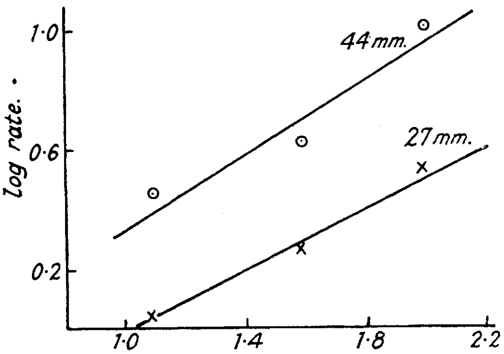
That the phenomenon has something to do with the initiation process is shown by the fact that if a low-pressure mercury lamp is used, and presumably therefore excited mercury atoms are responsible for starting polymerisation, the limit is displaced to a lower pressure at 12 mm.

FIG. 4.



Rate of polymerisation as a function of pressure.

FIG. 5.



Variation of rate with intensity of incident illumination.

Intensity exponent. The variation of polymerisation rate with intensity of light gives useful information in regard to the order of the process in which the active polymer molecule is destroyed. It is particularly important to measure this exponent in view of the gradual increase of rate with the amount of polymer deposited and the existence of the critical limit. The intensity was decreased by using perforated screens which had been previously calibrated by a photoelectric cell. Runs were made at high pressure where the rate is proportional to pressure and at as low pressure as possible to see whether in the vicinity of the limit there was any change in the mechanism of the termination process. A logarithmic plot of the results is given in Fig. 5. The slope of these curves is 0·60 and 0·55 for 44 and 27 mm., respectively, which is a sure indication that polymerisation stops when two active polymers mutually destroy each other. This again furnishes additional proof that the appearance of the limit has nothing to do with the termination process.

The same set-up being used, the value of the critical limit was measured for an intensity only one-eighth of that used in the measurements given on p. 1203. The following results give a limit on extrapolation of 21 mm. Thus, in spite of a diminution in rate of starting of polymerisation by a factor of 8 and an increase in chain length by a factor of 3, the limit is unaffected.

Vinyl acetate press. (mm.)	19·1	25·3	38·2	46·0
Rate (c.c./min.)	0·25	1·05	4·76	5·85

Effect of temperature. Rather a complicated procedure had to be adopted in these experiments, for at each temperature a series of runs at different pressure had to be made in virtue of the existence of the critical limit, since it was essential to find whether the limit itself was dependent on temperature. To ensure that the condition of the tube was as nearly similar as possible during these experiments, before and after each series of runs at elevated temperature standard runs were made at 20° and at 42 mm. pressure. It was not possible to go to temperatures greater than 100° since decomposition of the polymer led to complications and the rate fell off very quickly above this temperature. The results are summarised in Fig. 6, where the relative rates are plotted against pressure for a series of temperatures. At pressures above 30 mm. it will be seen that the rate decreases with increasing temperature. This phenomenon, although observed with methyl acrylate and methyl vinyl ketone, might be due to the intervention of some inhibitor or to a change in the nature of the termination reaction. Using a pressure of 60 mm. at 66°, a measurement of the variation of rate with intensity gave the following results :

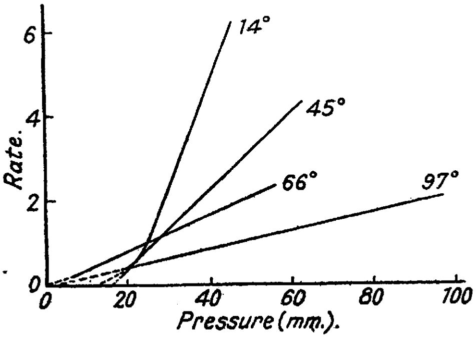
Intensity	1·00	0·384	0·125
Rate (mm./min.)	0·63	0·38	0·185

This corresponds to an exponent of 0·60, in agreement with the results at 20°. Hence, mutual termination of chains still operates at elevated temperatures. At each temperature the variation of rate with pressure is represented by the equation Rate $= k(p - p_0)$, except in the neighbourhood of the limit, defined for the sake of convenience by p_0 in this equation. The following results show how the value of p_0 varies with temperature :

Temp.	14·0°	46°	66°	97·0°
p_0 (mm.)	21·0	16·0	6·0	5·0

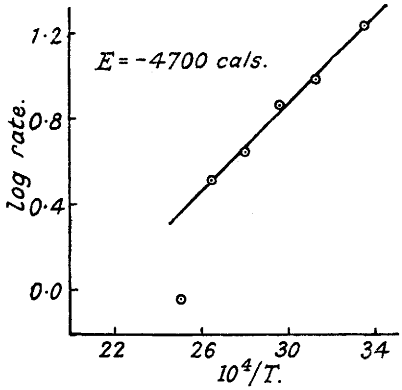
Hence, at above 100° the polymerisation pursues a normal course in which $R =$ const. $(I_{\text{abs.}})^{\frac{1}{2}}$ (M), which are kinetics compatible with the idea that all the light is absorbed and that mutual termination of the polymer chain occurs almost exclusively (Gee and Melville, *Trans. Faraday Soc.*, 1944, **40**, 240). Below 30° an inversion of the temperature coefficient occurs and the rate increases with increase in temperature. This kind of anomalous behaviour is, however, primarily due to the intervention of some reaction responsible for the appearance of the limit—a reaction which itself possesses a temperature coefficient. In absence of this complicating phenomenon, namely, at as high pressure as can be obtained, there is no doubt that the polymerisation rate decreases with increasing temperature. The temperature coefficient was therefore measured for a pressure of 50 mm. and the log Rate–$1/T$ plot is shown in Fig. 7. The slope corresponds to an apparent energy of activation of −4700 cals. The point at 128° is obviously so far off the straight line as to indicate a complete change in mechanism which has not been further investigated. It being assumed that the energy of activation for the initiation process is negligible, this means that there is an energy of activation for the termination process and that it exceeds that of the propagation reactions for with mutual termination $E_{\text{app.}} = E_{\text{prop.}} - \frac{1}{2}E_{\text{term.}}$, where $E_{\text{prop.}}$ and $E_{\text{term.}}$ are the energies for propagation and termination, respectively. Only in the case of methyl acrylate has there been made a *minimum* value for $E_{\text{prop.}}$ and this amounts to 4000 cals. (Melville, *Proc. Roy. Soc.*, 1938, *A*, **167**, 99). Even if it is supposed that $E_{\text{prop.}}$ in the vinyl acetate reaction is 5000 cals., $E_{\text{term.}}$ amounts to about 20,000—a very high value indeed. In fact, considering the small concentration of active polymers, it would appear that the termination reaction would hardly ever occur in the gas phase at room temperature. There is here a peculiarity in a number of photo-gas-phase polymerisations which is kinetically not easily understandable. Yet with methyl acrylate if a strong inhibitor, *e.g.*, oxygen or butadiene, is added to change completely the nature of the termination process the apparent temperature coefficient becomes positive, since a termination process normally requiring activation energy is replaced by one in which the energy of activation is practically zero. The phenomenon is not confined to gas-phase polymerisation, for in some liquid-phase polymerisations the chain length of the polymers decreases with increasing temperature, possibly owing to the energy of activation for termination exceeding that for propagation.

FIG. 6.



Rates of polymerisation as a function of pressure at a series of temperatures.

FIG. 7.



Temperature coefficient of the rate of polymerisation at 50 *mm. pressure of vinyl acetate* (T = ° K.).

The critical limit. Before attempting to discuss the abnormal pressure dependence of this polymerisation the main kinetic features may be summarised as follows : (*a*) The rapid falling off in rate at low pressures and temperatures—the reaction being apparently normal at high temperatures and pressures. (*b*) Dependence of the " limit " on temperature. (*c*) Independence of limit on intensity and state of the tube, *i.e.*, whether covered or not. (*d*) Termination mechanism of polymerisation not altered in the low-pressure, low-temperature region. (*e*) Limit apparently affected by *mode* of initiation.

The limit appears to have no connection with the explosion limit in other chain reactions, for the rate above the limit is in no sense indefinitely fast, the reaction being under complete control. The best proof of this suggestion is that the intensity exponent never falls below 0·5 whereas in an incipient explosion, *e.g.*, in the H_2–N_2O–O_2 system sensitised by hydrogen atoms, the exponent may fall below the normal value of 0·5 when the reaction gets out of hand (Melville, *Proc. Roy. Soc.*, 1934, *A*, **146**, 737).

It would appear to be necessary to introduce some mechanism at low pressures which leads to a diminution in velocity rather than introduce some phenomenon which leads to an abnormal increase in rate at high pressures as in gaseous explosions or in the polymerisation of methyl vinyl ketone (Jones and Melville, *ibid.*, 1946, *A*, **187**, 19). All the above evidence indicates that neither termination nor propagation factors are affected and that therefore the phenomenon has something to do with the initiation process. The shift of the limit by changing from direct to sensitised initiation and the non-existence of the limit in the radical-sensitised reaction are additional certain pointers to this conclusion. It is probable that the primary photochemical efficiency is not high, *i.e.*, some of the energy absorbed by the vinyl acetate molecule is lost before another molecule of monomer can react with it. Thus we may have two competing processes :

$$\begin{array}{lll} \mathrm{M} + h\nu = \mathrm{M}^* & \dots\dots\dots\dots\dots\dots\dots\dots & \mathrm{f}(I) \\ \mathrm{M}^* + \mathrm{M} = \mathrm{P}_2 & \dots\dots\dots\dots\dots\dots\dots\dots & k_{p_1} \\ \mathrm{M}^* \quad = \mathrm{M} & \dots\dots\dots\dots\dots\dots\dots\dots & k_s \end{array}$$

As the pressure is reduced, a greater proportion of the M* molecules lose their energy by some kind of a process not involving a collision with a monomer molecule. Mutual termination being assumed, then

$$\mathrm{d}[\mathrm{M}^*]/\mathrm{d}t = \mathrm{f}(I) - k_s[\mathrm{M}^*] - k_{p_1}[\mathrm{M}^*][\mathrm{M}] = 0$$

and in general

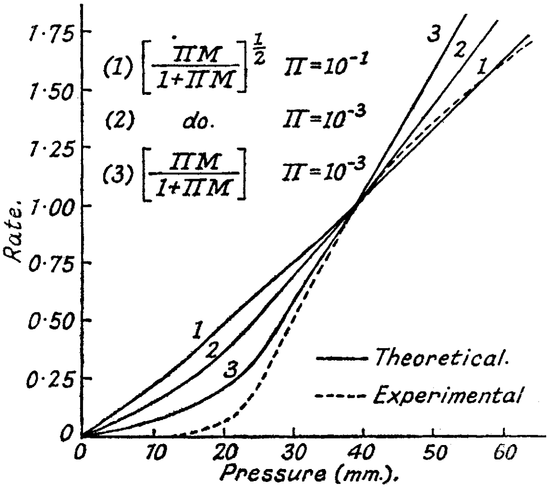
$$\mathrm{d}[\mathrm{P}_n]/\mathrm{d}t = k_{p_{n-1}}[\mathrm{P}_{n-1}][\mathrm{M}] - k_{p_n}[\mathrm{P}_n][\mathrm{M}] - k_{t_n}[\mathrm{P}_n]\Sigma k_{t_n}[\mathrm{P}_n] = 0$$

Solving these equations in the usual way, we have

$$\begin{aligned} -\mathrm{d}[\mathrm{M}]/\mathrm{d}t &= [\mathrm{M}]\{\mathrm{f}(I)\}^{\frac{1}{2}}\,\delta^{-1}\{k_{p_1}[\mathrm{M}]/[k_s + k_{p_1}(\mathrm{M})]\}^{\frac{1}{2}} \\ &= [\mathrm{M}]\mathrm{f}(I)^{\frac{1}{2}}\,\delta^{-1}\{\pi[\mathrm{M}]/[1 + \pi(\mathrm{M})]\}^{\frac{1}{2}} \end{aligned}$$

where $\pi = k_{p_1}/k_s$. At high values of [M], this gives linear dependence of rate on [M], but at low pressure the rate only varies as $[\mathrm{M}]^{3/2}$ and would obviously not fall off quickly enough to be in accordance with experimental results. This is best shown by computing a value of π from experimental results. Assuming that the reaction is normal at 50 mm. and taking the rate at 24 mm., we have in the region of abnormality $R = 0{\cdot}16$, $\pi = 3{\cdot}0 \times 10^{-3}$ with [M] in mm. At 20 mm. $\pi = 0{\cdot}6 \times 10^{-3}$. Hence, taking a mean value of 10^{-3} and plotting the rate–pressure curve in Fig. 8 such that at one point, namely, 40 mm., it is adjusted to coincide with the broken experimental curve, it will be seen that although the shape is approximately right the agreement both at low and at high pressures is such that the theory is not good enough to account for the observations. A better approximation may be obtained if it is assumed that not only the activated monomer but also the dimer may spontaneously lose its energy. Thus the scheme would be :

FIG. 8.



Relationship between theoretical and experimental curves, for the variation of rate with pressure.

$$\begin{array}{lll} \mathrm{M} + h\nu = \mathrm{M}^* & \dots\dots\dots\dots\dots\dots\dots\dots & \mathrm{f}(I) \\ \mathrm{M}^* \quad = \mathrm{M} & \dots\dots\dots\dots\dots\dots\dots\dots & k_{s_1} \\ \mathrm{M}^* + \mathrm{M} = \mathrm{M}_2^* & \dots\dots\dots\dots\dots\dots\dots\dots & k_{p_1} \\ \mathrm{M}_2^* \quad = \mathrm{M}_2 & \dots\dots\dots\dots\dots\dots\dots\dots & k_{s_2} \\ \mathrm{M}_2^* + \mathrm{M} = \mathrm{P}_3 & \dots\dots\dots\dots\dots\dots\dots\dots & k_{p_2} \end{array}$$

This leads to an expression

$$-\frac{\mathrm{d}[\mathrm{M}]}{\mathrm{d}t} = [\mathrm{M}]\delta^{-1}\mathrm{f}(I)^{\frac{1}{2}}\left[\frac{k_{p_1}[\mathrm{M}]}{k_{s_1} + k_{p_1}[\mathrm{M}]}\right]^{\frac{1}{2}}\left[\frac{k_{p_2}[\mathrm{M}]}{k_{s_2} + k_{p_2}[\mathrm{M}]}\right]^{\frac{1}{2}}$$

If $k_{p_1}/k_{s_1} = k_{p_2}/k_{s_2} = \pi$, which is a reasonable assumption, this simplifies to

$$-\frac{d[M]}{dt} = [M]\delta^{-1}f(I)^{\frac{1}{2}}\left(\frac{\pi[M]}{1+\pi[M]}\right)$$

and as will be seen from Fig. 8 gives a plot agreeing more closely with the results below 40 mm., although the high-pressure agreement is inferior. The intervention of this kind of deactivation process might be extended to higher active polymers, but it is evident that the process cannot extend indefinitely for it would constitute another way in which the active polymers are destroyed, whereas the intensity exponent clearly indicates mutual destruction of the active polymers. Although the above theory does not quantitatively account for the shape of the R–p curve, it is in accordance with the observations made in connection with the position of the so-called limit, namely, independence of intensity and of the state of the vessel. Since the limit depends on temperature, this means that π increases with increasing temperature. This is entirely in accordance with expectation; k_{s_1}, k_{s_2} are unlikely to be affected by temperature, since spontaneous loss of large amounts of energy is unlikely to be influenced by relatively small changes in energy; k_{p_1}, on the other hand, is a propagation coefficient and will certainly increase with increasing temperature. The theory is not good enough to enable π or some similar parameter to be accurately computed, but an approximate estimate may be made in the following manner. Suppose there is no appreciable spontaneous deactivation at 40 mm. and the pressure $p_{\frac{1}{2}}$ is found from Fig. 8 at which the rate is half what it would have been in absence of this effect; then at this pressure the probabilities of propagation and deactivation are equal, and if $p_{\frac{1}{2}}'$ and $p_{\frac{1}{2}}''$ are the pressures at two temperatures, the energy of activation of the propagation reaction will be given by

$$E_p = 4{\cdot}57 \log_{10}\frac{p_{\frac{1}{2}}'}{p_{\frac{1}{2}}''}\frac{T_1T_2}{(T_1 - T_2)}$$

where T_1 and T_2 are the corresponding temperatures. For 14°, $p_{\frac{1}{2}}' = 28$ mm. and at 45° $p_{\frac{1}{2}}'' = 22$ mm.; hence $E_p = 1400$ cals.

Nature of the Photopolymer.—The polymer deposited as a result of the photochemical reaction is insoluble—a drawback which prevents a direct measurement of the chain length of the reaction. In view of the small number of cross-links needed to render a polymer insoluble, it is not unreasonable to suppose that the reaction responsible for branching and the type of links involved in the process may be entirely different from those constituting the main bulk of the polymer. The polymer was therefore formed under carefully controlled conditions by running the experiment at a constant pressure of 30 mm. and 15° until about 0·6 g. of polymer was deposited. The polymer was then washed out of the reaction vessel with acetone, in which it swelled but did not dissolve. The resulting material was suspended in dry methyl alcohol and treated with methyl-alcoholic potassium hydroxide. The white suspension so obtained was poured into water, in which it was completely soluble. Hence, conversion of the polyvinyl acetate into polyvinyl alcohol resulted in a breakdown of the three-dimensional polymer, which points to the fact that a hydrolysable link is responsible for joining the primary chains of the polymer together.

Inhibition.—A study of the effect of inhibitors on a chain reaction throws much light on the mechanism of the reaction. As will be shown, this is particularly true with vinyl acetate where a variety of inhibitory mechanisms may operate. Oxygen and butadiene are both effective inhibitors but, surprisingly enough, chemically inert gases like argon, helium, and hydrogen also function as inhibitors.

Oxygen. According to the theory of polymerisation (Gee and Melville, *Trans. Faraday Soc.*, 1944, **40**, 240) the expression for the rate of a completely inhibited reaction is

$$-\,d[M]/dt = [M]f(I)/\beta[O_2]$$

where $\beta = k_d/k_p$, k_d being the velocity coefficient for the interaction of inhibitor with active polymer. In order to get reliable results, the bracketing technique was employed for these experiments, *i.e.*, every run with the inhibitor present was preceded and followed by a run with pure vinyl acetate. With a pressure of 30 mm., the results of a series of runs are shown in Fig. 9, where reciprocal rate is plotted against oxygen pressure. In accordance with the theory, a straight line may be drawn through the points. Another result of inhibition of a reaction which is normally terminated by mutual destruction of the active polymers is that the intensity exponent should simultaneously increase from 0·5 to a value approaching 1·0 depending on the extent of the inhibition. A typical set of runs is given in Table II, the bracketing technique being employed and decrease of pressure being used for the measurement of rate.

TABLE II.

Vinyl acetate pressure, 31 *mm. Temp.* 20°.

Oxygen (mm.)	0	1·2	1·2	1·2	0
Intensity	1·00	1·00	0·125	1·00	1·00
Time (mins.) for pressure to fall 1 mm.	1·8	5·0	23·0	5·0	2·1

Intensity exponent = 0·74.

This increase of exponent to 0·74 clearly shows that inhibition is termination of growth of the polymer by the interaction of oxygen with it.

As will be shown in the following paper, it is possible to study the kinetics of the free-radical polymerisation below the critical limit, and thus in absence of the direct photopolymerisation. Table III shows that oxygen has no effect on the reaction initiated by methyl radicals and only a comparatively small effect on that initiated by hydrogen atoms, and this in spite of the fact that the rates of polymerisation are approximately the same as those in Table II. The fact that oxygen slightly inhibits the

TABLE III.

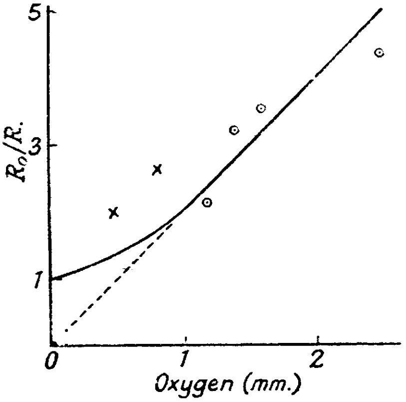
Effect of oxygen on free-radical-sensitised reaction at 20°.

Vinyl acetate press. (mm.).	Acetone (mm.).	Oxygen (mm.).	Rate (mm./min.).	Vinyl acetate.	Hydrogen.	Oxygen.	Rate.
Methyl radical reaction.				Hydrogen atom reaction.			
17·3	45	0·1	0·217	14·3	43	—	0·45
17·8	48	—	0·207	15·5	46	2·3	0·30
16·7	53	3·2	0·240	14·7	48	—	0·42
17·1	57	—	0·241				

hydrogen-atom reaction is quite possibly due to direct interaction of hydrogen atoms and oxygen molecules. The important point is that oxygen clearly discriminates between the two kinds of reaction.

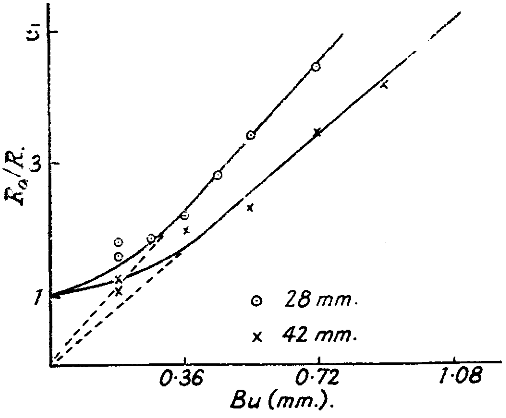
Butadiene. Butadiene is a more powerful inhibitor than oxygen and hence smaller pressures of the gas are needed. A gas pipette method was therefore adopted for introducing butadiene into the reaction system. The results at two vinyl acetate pressures are plotted in Fig. 10, in which the relative reciprocal rate is graphed against butadiene pressure. In these experiments bracketing methods were employed at all stages. Since in this case there is always the possibility of butadiene actually inter-polymerising with the vinyl acetate, with a resultant diminution in velocity, instead of acting as does oxygen, the variation of rate with intensity was measured. In the former case the square-root dependence would still hold, while in the latter a linear dependence should be observed. The detailed results need not be given here except the following summary :

FIG. 9.



Effect of oxygen in retarding polymerisation.

FIG. 10.



Effect of butadiene in retarding polymerisation, at 28 *and* 42 *mm. of vinyl acetate.*

R_0/R.	$R_{1\cdot00}/R_{0\cdot125}$.	Exponent.	R_0/R.	$R_{1\cdot00}/R_{0\cdot125}$.	Exponent.	R_0/R.	$R_{1\cdot00}/R_{0\cdot125}$.	Exponent.
1·0	3·4	0·60	2·8	5·3	0·80	4·2	7·9	0·99

As the degree of inhibition (R_0/R) increases, the ratio of rates ($R_{1\cdot00}/R_{0\cdot125}$) at a fixed ratio of intensities likewise increases, corresponding to a general increase in intensity exponent. Additional confirmation is obtained in the following typical experiment with a vinyl acetate pressure of 33 mm. and butadiene 0·1 mm. : R_0/R at maximum intensity was 2·8, increasing to 3·9 at 0·125 of the maximum intensity. Thus, by reducing intensity and increasing thereby the chain length, the degree of inhibition is correspondingly increased. All these experiments conclusively show that when butadiene reacts with vinyl acetate active polymer it adds on and then the reaction stops. Normal molecules of vinyl acetate cannot react with a butadiene end of the polyvinyl acetate.

There is, however, one discrepancy. For the normal and the inhibited reaction we have respectively for the two rate equations :

$$-\mathrm{d}[M]/\mathrm{d}t = R_0 = [M]f(I)^{\frac{1}{2}}/\delta \text{ and } R = [M]f(I)/\beta(X)$$

Hence

$$R_0/R = \beta[X]/\delta f(I)^{\frac{1}{2}}$$

As seen above, this relationship is followed in regard to butadiene concentration and light intensity. It will be noted that the value of R_0/R is independent of R_0 and, more important, independent of [M], yet in Fig. 10 the plots for two values of [M] are not coincident. One possibility is that $f(I)^{\frac{1}{2}}$ depends on [M] because of incomplete absorption of radiation. The slope of the R_0/R or [X] curve would be less for higher values of [M], which is in qualitative agreement with observation. The maximum change of slope in this case would be 1·2 : 1 whereas the observed value is 1·25 : 1. The linear dependence of R on [M] at high enough temperatures would preclude this explanation. At lower pressures such as

28 mm., however, the vinyl acetate reaction begins to deviate quite markedly from normal behaviour. In order to get an expression for the reaction rate as a function of inhibitor concentration, an additional term, *viz.*, $k_{d_n}[P_n][X]$, is introduced into the differential equations defining $[\cdot P_n]$. This gives by the usual method

$$-\,d[M]/dt = [M]\{f(I) - k_{s_1}[P_1^*]\}/\beta[X]$$

But

$$[P_1^*] = f(I)/\{k_{s_1} + k_p[M] + k_{d_1}[X]\}$$

Therefore

$$-\,d[M]/dt = \frac{[M]f(I)}{[X]\beta}\left\{\frac{k_{p_1}[M] + k_{x_1}[X]}{k_{s_1} + k_x[X] + k_{p_1}[M]}\right\}$$

Using the expression already obtained for the rate of reaction in absence of inhibitor, we have

$$R_0/R = \frac{\beta[X]}{\delta f(I)^{\frac{1}{2}}}\left\{\frac{k_{p_1}'[M]}{k_{p_1}[M] + k_{s_1}}\right\}^{\frac{1}{2}}\left\{\frac{k_{s_1} + k_{p_1}[M] + k_{d_1}[X]}{k_{d_1}[X] + k_{p_1}[M]}\right\}$$

It has already been shown that $k_p/k_s \approx 10^{-3}$, hence $k_s \gg k_p[M]$ or $k_x[X]$ and

$$R_0/R = \frac{\beta k_s^{\frac{1}{2}}}{\delta f(I)^{\frac{1}{2}}} \cdot \frac{[M]^{\frac{1}{2}}[X]}{[M] + \beta^{-1}[X]}$$

Thus if $[M] \approx \beta^{-1}[X]$, decreasing values of [M] will increase the slope of the R_0/R–[X] curve.

Effect of Inert Gases.—Experiments with polymer-coated tubes seemed to indicate the existence of wall deactivation of the active polymer with clean or partly coated tubes. Thus it might be expected that the decrease in diffusion coefficient effected by the addition of inert gas might accelerate the polymerisation rate. When the experiment was done, precisely the opposite effect was obtained, a marked inhibition being observed. At first sight, this phenonenon is difficult to explain, since it is inconceivable that gases like argon, helium, and hydrogen could effect any chemical change in the active polymer that would lead to deactivation. As will be shown, inhibition does not occur by the termination of growth of the chains but is due to deactivation of excited molecules in the very early stages of polymerisation. This effect, indeed, is not then so unexpected in view of the abnormal pressure dependence of reaction and, in fact, provides further support for the hypothesis advanced to explain the occurrence of an apparent critical limiting pressure. Thus we have the curious phenomenon that inhibition by inert gases leads to an *increase* in chain length of the polymer and not a decrease as is usually the case.

The argon was obtained from a cylinder of the gas and was oxygen free. The helium was purified from more condensable gases by repeated treatment with active charcoal.

The results with argon for a series of vinyl acetate pressures are shown in Fig. 11. R_0/R and also $(R_0/R)^2$ are plotted against argon pressure. It is difficult to say which relationship is the better approximation, but one observation is important. Unlike those for oxygen and butadiene, these lines do not go through the origin but make an intercept of unity in the R_0/R axis. This at once shows that a different kind of inhibition comes into operation apart altogether from the fact that very much higher pressures are needed for inhibition to be observed. This is completely confirmed by measuring the intensity exponent. With a vinyl acetate pressure of 40 mm. and an argon pressure of 67 mm., $R_0/R = 2$, the intensity exponent is 0·60, the same value being obtained in the uninhibited reaction. This evidence certainly points to inhibition occurring in the initial stages of the reaction. Since the theory of the critical limit postulates the existence of an excited monomer which does not necessarily add on another molecule of monomer but may spontaneously lose its energy, probably by some internal rearrangement (it is hardly likely that chemical decomposition occurs, since it was earlier shown that decomposition seems to be an independent process brought about by short wave-lengths), it is natural to suppose that deactivation can also be brought about by collision with another molecule which facilitates this rearrangement or removes some of the energy from the excited molecule. In the expression for the value of $[P_1]$ another term has therefore to be added and the appropriate equation becomes

$$d[P_1]/dt = f(I) - k_{p_1}[P_1^*][M] - k_{s_1}[P_1^*] - k_{A_1}[P_1^*][A] = 0$$

Hence

$$R_0 = [M]\delta^{-1}f(I)^{\frac{1}{2}}\{k_{p_1}[M]/k_{s_1} + k_{p_1}[M])\}^{\frac{1}{2}}$$

and

$$R = [M]\delta^{-1}f(I)^{\frac{1}{2}}\{k_{p_1}[M]/(k_{p_1}[M] + k_{\ 1} + k_{A_1}[A]\}^{\frac{1}{2}}$$

Therefore

$$R_0/R = \left\{1 + \frac{k_A[A]}{k_{s_1} + k_{p_1}[M]}\right\}^{\frac{1}{2}}$$

If argon deactivation is extended to P_2^* and we assume that $k_{p_1} : k_{s_1} : k_{A_1} = k_{p_2} : k_{s_2} : k_{A_2}$, then

$$R_0/R = 1 + k_A[A]/(k_{s_1} + k_{p_1}[M]$$

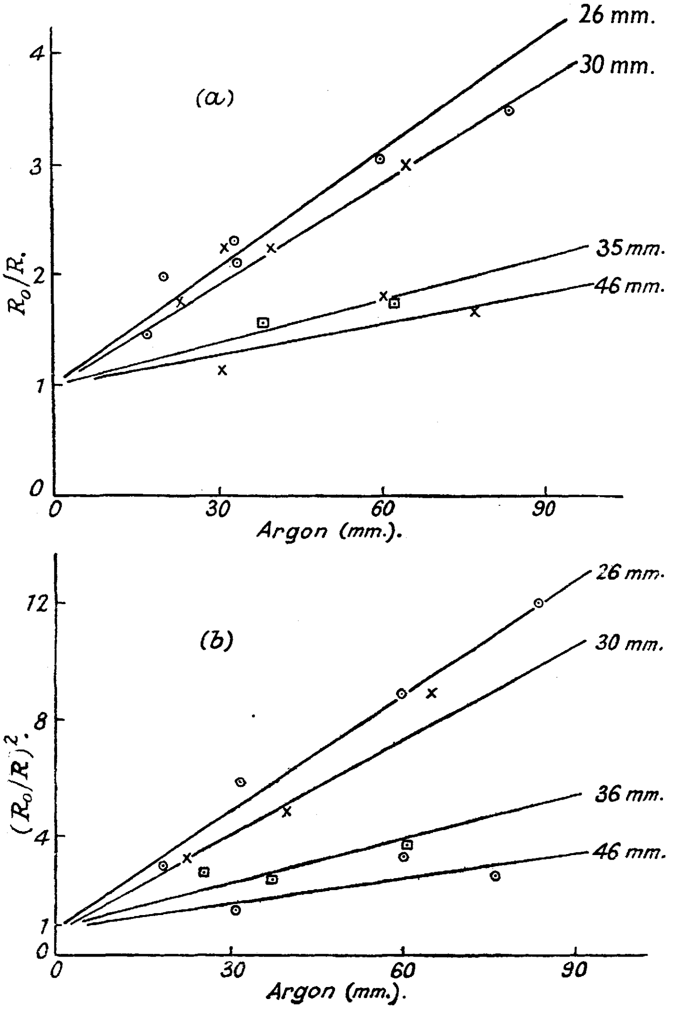
Rearranging these expressions, we have

$$\{(R_0/R)^2 - 1\}^{-1} = \frac{k_s}{k_A[A]} + \frac{k_p}{k_A[A]}[M]$$

$$(R_0/R)^2 - 1 = k_A[A]/k_s + k_{p_1}[M] \text{ and } R_0/R - 1 = k_A[A]/\{k_{s_1} + k_{p_1}[M]\}$$

Fig. 11 shows that a linear plot or R_0/R against argon pressure is obtained, and that the slopes of the lines are inversely proportional to the pressure of vinyl acetate. The intercept on the ordinate does not vary with argon pressure. This is not unexpected in view of the close approach to the critical limit when such relationships will break down. Experimentally it is difficult to decide between these two mechanisms.

FIG. 11.



Effect of argon in retarding the rate of polymerisation at various vinyl acetate pressures indicated. Figs. 11a *and* 11b *show alternative ways of plotting the results.*

Helium and hydrogen function in a similar manner, the intensity exponent not being affected when inhibition takes place. According to the above theory, the relative efficiencies of these gases can be obtained by plotting $(R_0/R)^2$ against the pressure of inert gas for a given vinyl acetate pressure. The relative slopes of these lines give the ratio of collision efficiencies A : He : H_2 = 1 : 0·6 : 0·5. If allowance is made for the different speeds, the collision efficiencies have the following values relative to argon : He 0·085, H_2 0·036. In passing it is worth noting that inert gases have absolutely no effect on the free-radical polymerisation.

THE UNIVERSITY, ABERDEEN.

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