8. *Thermal Polymerisation of Styrene and its Inhibition.*

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The effect of a considerable number of organic compounds on the rate of polymerisation of pure styrene has been investigated. They are classified as " inhibitors " or " retarders " according to whether they introduce a period of induction or retard the subsequent polymerisation, and a generalisation is given for the effect of certain substituent groupings. A class of strong inhibitors of which benzoquinone is a representative member has been examined in detail, and quantitative measurements made on the extended induction periods produced have been applied in support of a theory of the kinetics of stabilisation by inhibitors, whereby the inhibitor is assumed to react with the primarily activated styrene molecules which normally give rise to polymeric chains. Further work is suggested.

A NUMBER of investigations on the polymerisation of styrene has been made within the last few years. These are of two types, *viz.*, polymerisation of monomer and polymerisation in solution, and each of these methods has its own particular advantages and applications. In the electrical industry, styrene polymerised *in situ* is used extensively in cables for the construction of plugs and barrier joints of superior electrical properties, and for this reason and in view of certain theoretical advantages of the method, the polymerisation of pure styrene has been specially studied.

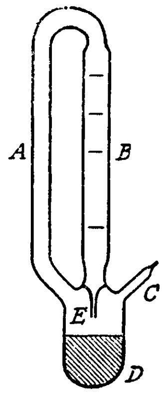
The results of previous workers have led to widely accepted ideas as to the mechanism of polymerisation, but conflicting evidence has been obtained concerning the nature of the initial stages of the reaction. The existence has been noted of an induction period during which the rate of polymerisation increases and reaches a maximum only after a finite period of time. The length of this induction period was somewhat ill-defined, and recent work (Schulz and Husemann, *Z. physikal. Chem.*, 1936, *B*, **34**, 187; 1937, *B*, **36**, 184; *Angew. Chem.*, 1937, **50**, 767), has suggested that it is produced by impurities in the styrene. It is now shown that by the addition of certain substances polymerisation of styrene can be almost completely inhibited for long but well-defined periods, after which the reaction rate increases to a maximum and then follows the normal course with time. Observations, both qualitative and quantitative, on this artificially introduced induction period provide a powerful means of investigating the separate primary and growth reactions which has apparently not been utilised by other workers, and forms one of the main parts of the present work.

The results of this work have an important practical application in that, by introduction of small amounts of such inhibitors, styrene may be stabilised against polymerisation when stored at comparatively low temperatures (*e.g.*, below 70°) or during distillation at higher temperatures, the period of stabilisation being accurately controlled by the amount of stabiliser added. The results now recorded form the basis of patents (Standard Telephones and Cables, Ltd., and Foord, B.Pp. 504765, 504780).

EXPERIMENTAL.

Two principal methods were used for following the course of polymerisation. The first was the known method of dissolving a weighed amount of the partly polymerised styrene in benzene, precipitating the polystyrene with ethyl alcohol, and weighing the precipitate. This method has been criticised on the grounds that complete precipitation is not obtained, but tests have shown that if a 0·5—1·0% solution in benzene is treated with twice its volume of industrial methylated spirit, reproducible and fairly complete precipitation of the polystyrene occurs. The method could be used to determine the degree of polymerisation at any point during the complete reaction. (Since the completion of this work an improved precipitation method for determination of polystyrene has been developed in this laboratory by Mr. A. J. Warner, and will be described in a forthcoming publication.)

FIG. 1.



The second method, an indirect one, involved measurement of the viscosity of the partly polymerised styrene as a function of the time of polymerisation. For this purpose a special type of viscometer was used (Fig. 1). The monomeric styrene is introduced through the side limb *C*, the vessel evacuated, and the side limb sealed off. If desired, the monomeric styrene can be purified and distilled into the viscometer in a vacuum. With the liquid in *D*, polymerisation is allowed to proceed for successive periods of time, and the relative viscosity (pure styrene = 1) is determined by transferring the liquid through *A* into *B* by tilting, and taking the time of flow through the capillary *E* between two marks on *B*, the whole measurement being conducted at a standard temperature of 25°. This method is applicable only to the initial stages of the polymerisation (*i.e.*, until the relative viscosity is about 50—100), the range being determined by the molecular weight of the polymer formed. As, however, most of the investigation dealt with measurements of the induction period and the maximum rate of polymerisation, the limitation of range was of little consequence. For reaction rate measurements with a viscometer it is necessary to know the relation between the viscosity and concentration of a solution of polystyrene, and this is a matter of dispute. The equation

$$\eta_{\text{sp.}} = KC \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where $\eta_{\text{sp.}}$ is the specific viscosity for a concentration C, was originally proposed by Staudinger, but it is recognised to be applicable only to very dilute solutions. The principal alternative which has been proposed is

$$\log \eta_r = kC \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where η_r is the relative viscosity for a concentration C, and k is a constant for a given polymer which is usually considered as proportional to the molecular weight. Both equations have been criticised (Danes, *Kolloid-Z.*, 1934, **68**, **110**), but as a result of a series of measurements on polymers of different molecular weights the author has found that the logarithmic relation is in approximate agreement with experimental values over a considerable range. Curves of log η_r against time are therefore of the same form as concentration–time curves, and are convertible by a single measurement of degree of polymerisation by the alcohol precipitation method, preferably carried out at a standard value of relative viscosity. As a matter of convenience such measurements were made at a value of $\log_{10} \eta_r = 1{\cdot}8$, at the end of a series of determinations of viscosity against time.

Measurement of the course of polymerisation by the change in viscosity offers several advantages over the more absolute precipitation method. In the first place the whole series of readings (and a large number can be taken) is made on the same sample without its being exposed to air, a procedure which is impossible or very laborious by the precipitation method, in which separate specimens are generally used. The importance of excluding air throughout a series of measurements will be realised in view of the known erratic catalytic effect of oxygen on styrene polymerisation (Schulz and Husemann, *Z. physikal. Chem.*, 1937, *B*, **36**, 184). For work on the measurement of induction periods, traces of impurity during the polymerisation must be rigidly excluded, and precise determination of the end of the induction period demands an accuracy of measurement which is more easily attained by the viscometric than by the precipitation method. Rapidity of measurement is also another deciding factor. For these reasons, the precipitation method has only been used for the conversion of log η_r–time curves into concentration–time curves, or for the construction of complete reaction curves.

Polymerisation of styrene was carried out either in 20 ml. portions in the vacuum viscometers described, or in sealed evacuated glass tubes 1 cm. in diameter, immersed in a thermostatically controlled oil-bath. The styrene was either a commercial product or made by dehydration of β-phenylethyl alcohol with molten potassium hydroxide. Immediately before use it was fractionally distilled under reduced pressure (15—20 mm.), and in one series of measurements it was distilled directly into viscometers. In general, the viscometers were filled at atmospheric pressure, pumped out, and sealed under vacuum.

Results.—(a) *Complete polymerisation.* Measurements of degree of polymerisation against time were made at 60°, 90°, and 120°, mostly within the range of 80—100% polymer. The results agree with those of previous workers, and are of little theoretical value in the principal region covered, but it is noteworthy that the polymers assume a rigid solid form while still containing up to 20% of monomeric styrene. It is therefore necessary to regard with caution any statements as to time of polymerisation unless its degree is also given. Further observations have shown that after reaching the solid state polymers become progressively harder as the degree of polymerisation approaches 100%, the hardness being independent of the temperature of polymerisation, at least within the range 60—120°. This phenomenon may be made the basis of a method of detecting free monomer in polystyrene.

(b) *Inhibition of polymerisation.* Most of the literature on the stabilisation of styrene against polymerisation is concerned with prevention of polymerisation during purification by distillation or during preparation of styrene during cracking processes. In this connection the following compounds are mentioned in the patent literature : sulphur, aromatic nitro-compounds, quinones, and substances containing a benzene nucleus in which oxygen replaces hydrogen atoms, quinol and other polyhydric phenols, anthracene, pyridine, etc. In some instances the use of these compounds is extended to the stabilisation of styrene during storage, but in none of the cases cited are any data given as to the nature or limitations of the stabilisation process. In all cases of stabilisation during storage it has been considered necessary to remove the stabiliser by, *e.g.*, distillation or washing before polymerising the styrene. To obtain more detailed information on these points a comprehensive search has been made for materials capable of acting as stabilisers when added in small amounts to monomeric styrene, particularly for use at low temperatures, and the more effective of these have been subjected to a quantitative examination.

In choosing the materials, advantage was taken of the close parallelism which appears to exist between the processes of autoxidation and polymerisation of unsaturated substances, the literature on inhibition of autoxidation being very extensive. Inorganic materials were excluded on the general grounds of insolubility in styrene and lack of a guiding principle in their choice. About 130 organic compounds were finally selected for test, so chosen as to obtain information on the general effects of different nuclei and substituent and other groupings, and further limited by the proviso that all were to be commercially obtainable. Preliminary tests were carried out on 2-ml. samples of styrene containing 0·5—1·0% of the added substance, sealed in evacuated glass tubes and heated for successive periods of time at 60°. After each period of heating the tubes were cooled, and the viscosity of the contents estimated from the rate of flow on tilting the tubes side by side with standards of known viscosity. By comparison with the polymerisation of pure styrene, the added substances could be divided into a number of groups, according to their effect in (*a*) introducing a more or less extended induction period, and (*b*) modifying the subsequent rate of polymerisation. These groups were as follows: (1) Accelerators, *i.e.*, rate of polymerisation appreciably greater than for pure styrene. (2) No appreciable effect on induction period or rate of polymerisation. (3) Polymerisation retarders, with or without the property of increasing the induction period. (4*a*) Substances which gave an induction period of not more than 240 hours at 60° in the stated concentration, and thereafter allowed polymerisation to proceed at the normal rate. (4*b*) Substances which completely inhibited polymerisation for at least 600 hours at 60° in the stated concentration (600 hours was the maximum period of test).

The substances of group (1) are of little interest in the present case, but those of groups (3) and (4), constituting about 50% of the compounds tried, are all more or less effective retarders or inhibitors. It is necessary to distinguish between the two methods by which these stabilising compounds may act. For present purposes the term " inhibitor " will be restricted to those substances which introduce a more or less protracted induction period during which very little polymerisation occurs, whereas those substances which cause the subsequent reaction to proceed at a reduced rate will be designated " retarders ". Some substances are both inhibitors and retarders, and the members of groups (3) and (4*a*) may be classified according to whether they belong to either or both of these classes. On the evidence provided by the 60° experiments, group (4*b*) cannot be classified in this manner owing to the extreme effectiveness of the added compounds. For this reason the members of group (4*b*) were subjected to a polymerisation test at 120°, quantitative measurements being made by the vacuum viscometer method and 0·2% solutions of the added substances in styrene being used. To economise space, full details of all of the compounds used cannot be given, but the effects of a number of molecular or atomic groupings are summarised as follows:

Effective groups for the stabilisation of styrene are quinonoid, nitro-, phenolic hydroxy-, amino-, and nitroso-. The general effects of several of these groups in a compound are additive.

One nitro-group in an aromatic compound gives a strong retardation without a period of complete inhibition. The retarding effect is much stronger with two nitro-groups and even stronger with three.

Quinonoid compounds generally are very strong inhibitors without any material retarding action in small concentrations. Notable exceptions are anthraquinone, which although mentioned in the patent literature as a stabiliser has been found to be ineffective, and acenaphthenequinone which has only a weak inhibiting effect.

Phenolic hydroxy-groups give rise to comparatively weak stabilisers. Phenol is ineffective, and cresol is a very feeble stabiliser. The effectiveness increases with the number of hydroxy-groups, but depends on their relative positions; *e.g.*, quinol and pyrocatechol lengthen the induction period, and the latter (probably owing to its higher solubility) retards polymerisation, whereas resorcinol gives only a short induction period and no retardation. Pyrogallol gives a very strong retardation with little increase in induction period. In general, phenolic compounds may be classified as retarding agents with a weak inhibiting action.

Amino-groups in a compound tend to increase the induction period without materially reducing the rate of polymerisation, and are most effective when attached to a benzene nucleus, particularly in presence of another active group. Substitution of the hydrogen atoms of the amino-group produces anomalous effects; *e.g.*, aniline and dimethylaniline give only a short induction period, but methylaniline gives a relatively long one. β-Naphthylamine is a more effective inhibitor than α-naphthylamine, and substitution of one hydrogen atom of the amino-group by phenyl gives a further increased effectiveness. Hydrazobenzene strongly retards polymerisation. Amides have no stabilising effect.

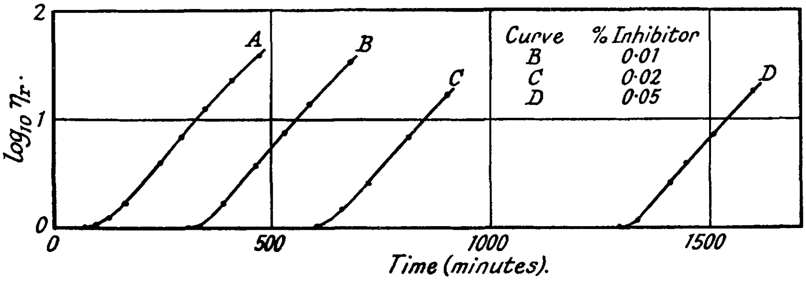
The data upon the nitroso-group do not suffice for generalisation, but those compounds investigated have shown a very strong inhibiting action without greatly reducing the subsequent rate of polymerisation.

Evidence with regard to oximes is conflicting, some having no effect (*e.g.*, acetophenone-oxime), others retarding (acetaldoxime, benzildioxime, piperonaldoxime), and one inhibiting (salicylaldoxime), although such effects are feeble and may be due to other groups in the molecules concerned. Halogen compounds do not in general differ in their effects from the parent substances. Ketones, ethers, and alcohols have no stabilising action, and pyridine has no effect on polymerisation at 60°, in spite of patents covering its use as a stabiliser.

For the practical utilisation of these materials as stabilisers for styrene, a clear-cut division may be made according to the particular use to which they are to be put. For the purpose of storage, the ideal stabiliser is one which will give an extended induction period followed by polymerisation at the same rate as would have been obtained in its absence. This induction period should be controllable as to length, and removable when required by simple means. For stabilisation during distillation or preparation of styrene, any materials may be used which give a long induction period or strong retardation of the polymerisation reaction or both, and therefore constitute a larger class. The first of these classes is designated the quinone class, since benzoquinone and its derivatives are representative members. The most important of these which have been tested are : benzoquinone, toluquinone, phenanthraquinone, chloranil, and *p*-nitrosodimethylaniline. Less effective but suitable compounds are 1-aminoanthraquinone, acenaphthenequinone, benzidine, 2 : 4-diaminoazobenzene, methylaniline, *p*-phenylenediamine, phenyl-α- and phenyl-β-naphthylamine. The second or distillation class, in addition to the above compounds, includes the following which act as strong retarders : hydrazobenzene, nitroso-β-naphthol, *o*-nitrophenol, 2 : 4-dinitroaniline, *m*-dinitrobenzene, dinitro-*o*-cresol, 2 : 4-dinitrodiphenylamine, 2 : 4-dinitrophenol, 2 : 4-dinitrophenylhydrazine, 2 : 4-dinitrotoluene, picric acid, naphthalene picrate, 1 : 3 : 8-trinitronaphthalene, and other highly nitrated compounds.

FIG. 2.

Polymerisation of styrene in presence of benzoquinone; 90°.



The most effective members of the quinone class show properties of particular interest from the theoretical point of view, and have been examined in greater detail. Since all have similar effects on the polymerisation of styrene, with only quantitative differences, detailed description of the experimental results will be confined mainly to the cases of benzoquinone and phenanthraquinone.

The course of polymerisation at 90° and 120° of styrene with and without addition of benzoquinone is shown in Figs. 2 and 3, which give the value of $\log_{10} \eta_r$ after various times of polymerisation in the vacuum viscometers. In view of the approximate validity of equation (2), these curves may be taken as representative of the change of degree of polymerisation with time if due allowance is made for any variation of molecular weight of the polymer formed in the various cases. Curve *A* in each case refers to the polymerisation of pure styrene, and shows that after a very short induction period, possibly due to traces of impurity, the rate of polymerisation rapidly increases to a maximum and thereafter gradually falls. The remaining curves refer to styrene with small amounts of benzoquinone added, and follow a similar course to curve *A* from the end of a definite period of induction during which no change of viscosity and therefore presumably very little polymerisation occurs. An important observation was that the yellow colour due to the benzoquinone gradually fades during the induction period, and almost disappears at the same moment that the period of induction ends. Some slight falling off of the maximum slope is to be observed in curves for the highest concentrations of benzoquinone, but measurements of the degree of polymerisation at the standard value of $\log_{10} \eta_r$ (1·8) have shown that this is due largely to a slight fall in the mean molecular weight of the polymer rather than to a retardation of the polymerisation. These results are of particular interest in view of the publication, since the completion of these experiments, of a somewhat similar series of measurements (Breitenbach, Springer, and Horeischy, *Ber.*, 1938, **71**, 1438), in which no evidence of a sharp induction period, but a considerable reduction in the rate of polymerisation was obtained.

FIG. 3.

Polymerisation of styrene in presence of benzoquinone; 120°.

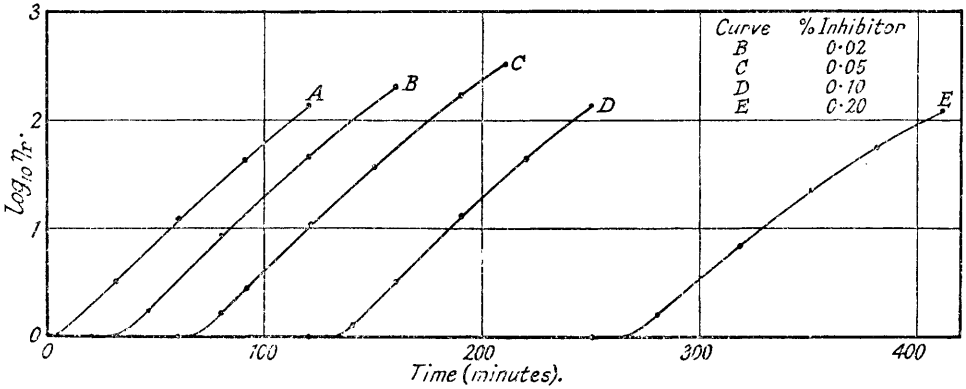


FIG. 4.

Polymerisation of styrene in presence of phenanthraquinone; 120°.

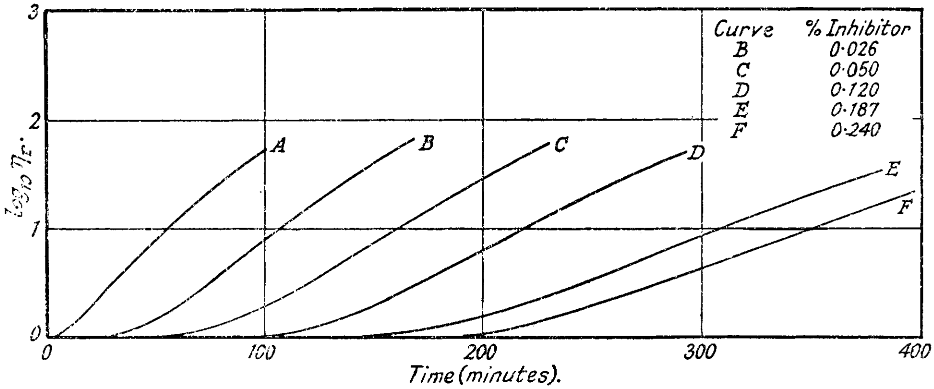
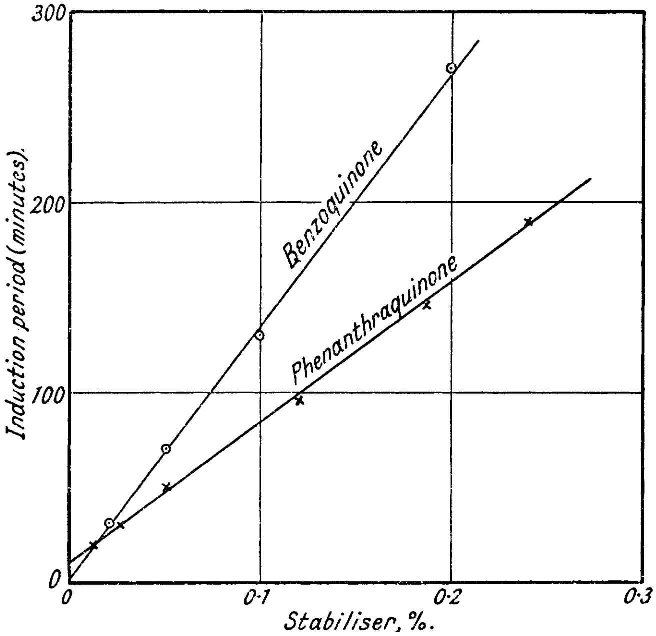


Fig. 4 shows a representative series of curves for the polymerisation of styrene at 120° in presence of phenanthraquinone, which are similar in form to those obtained with benzoquinone, but the transition at the end of the induction period to the point of maximum slope is more protracted, and the decrease in slope with high concentrations of phenanthraquinone is more pronounced. It was in connection with these measurements that the effect of special purification of the materials (see p. 50) was tested. The styrene was subjected to three successive fractional distillations in a vacuum, and distilled directly into the viscometers which contained the required quantity of phenanthraquinone. It has recently been pointed out that such a procedure does not completely remove any peroxidic substances that may be present in the original styrene, so some such impurity may still have been present. The phenanthraquinone was purified by formation of its bisulphite compound, reprecipitation with acid, and crystallisation from alcohol. The polymerisation curves obtained included those of Fig. 4, and do not differ from the curves measured by the usual methods using styrene after a single vacuum distillation, and A.R. quality phenanthraquinone, showing that the simple purification process used in other experiments was adequate.

Fig. 5 shows the dependence of the induction period at 120° on the amount of inhibitor added, curves being given for both benzoquinone and phenanthraquinone. The increase in induction period is a linear function of the concentration of inhibitor in both cases, and a similar result is obtained in the polymerisation in presence of benzoquinone at 90°, as shown in the following tables. Figures are also given for the maximum slope of the $\log_{10} \eta_r$–time curves (col. *A*) and the degree of polymerisation at the standard value of $\log_{10} \eta_r$ (col. *B*). The product of these two quantities gives an approximate measure of the true rate of polymerisation, and col. *C* of the tables gives the calculated figure for the maximum rate.

FIG. 5.



A = maximum value of $d \log_{10} \eta_r/dt$ (mins.$^{-1}$).
B = % polymer present when $\log_{10} \eta_r = 1{\cdot}8$.
C = calculated maximum polymerisation rate (g.-mols./c.c./hour).

The figures in the last two columns of Table II show that there is an appreciable retardation of the polymerisation reaction in presence of phenanthraquinone or its reaction product with styrene, and that the chain length of the molecules of polymer formed is considerably reduced.

TABLE I.

Polymerisation in presence of benzoquinone.

At 120°.					At 90°.				
Quinone, %.	Induction period (mins.).	*A*.	*B*.	$C \times 10^4$.	Quinone, %.	Induction period (mins.).	*A*.	*B*.	$C \times 10^4$.
0·000	5	0·023	12·6	8·4	0·00	80	0·0050	8·1	1·17
0·02	30	0·022	12·9	8·2	0·01	330	—	—	—
0·05	70	0·022	13·0	8·3	0·02	600	—	—	—
0·10	130	0·020	13·8	8·0	0·05	1300	—	—	—
0·20	270	0·016	—	—					

TABLE II.

Polymerisation at 120° *in presence of phenanthraquinone.*

Quinone, %.	Induction period (mins.).	*A*.	*B*.	$C \times 10^4$.
0·000	5	0·0230	12·56	8·4
0·012	20	0·0162	18·00	8·5
0·026	30	0·0148	19·34	8·3
0·050	50	0·0134	20·16	7·8
0·120	95	0·0114	21·17	6·7
0·187	145	0·0086	24·47	6·1
0·240	190	0·0077	25·95	5·8

DISCUSSION.

Interpreted in terms of the kinetics of polymerisation, inhibitors as defined on p. 51 have the effect of destroying the active centres produced in the primary process, whereas retarders deactivate the active entities in the chain growth processes and reduce the overall polymerisation rate and also the molecular weight of the polymer formed. In most cases, the effect of the added substances, although considerable, is insufficient completely to dominate the reaction, but in the case of the group referred to as the quinone class, the effect is so marked as almost completely to inhibit reaction so long as an appreciable amount of the added substance remains in solution.

Benzoquinone may be considered as an example; during the induction period it gradually disappears, and the linear relation which has been shown to exist between length of induction period and initial concentration of benzoquinone shows that the reaction reducing the latter is unimolecular with respect to the quinone. Similar behaviour is observed with other members of the quinone class. It is apparent that almost every active centre formed which would normally give rise to a polystyrene molecule is deactivated by collision with a quinone molecule, until the concentration of the latter reaches a very small value. Whether the reaction which removes the quinone is a direct result of the deactivating collision or whether the two processes are entirely independent is not yet certain. In this connection, the consumption of benzoquinone has been observed by Breitenbach, Springer, and Horeischy (*loc. cit.*), who suggested that it was either incorporated in the polystyrene or reduced to quinol. Neither of these appears to be the case, since the reaction product is yellow in very concentrated solution, no appreciable amount of polymer is produced during its formation, and it is retained in solution when the polystyrene formed in later stages is precipitated with alcohol. Unfortunately the slight solubility of polystyrene in benzene–alcohol made it a matter of some difficulty to obtain the reaction product of styrene and benzoquinone in a sufficiently pure state for analysis. A further suggestion (Springer, *Kautschuk*, 1938, **14**, 212) that polystyrene is first formed and then decomposed by the benzoquinone is disposed of by the fact that, if a solution of polystyrene in benzene is heated in presence of benzoquinone, the viscosity of the resulting solution is the same as that of a solution similarly treated in the absence of the quinone.

We must therefore conclude that benzoquinone is consumed by a simple non-polymeric reaction which may be a combination with the primarily activated styrene molecules. If the latter assumption is taken for the moment to be correct, several interesting calculations may be made concerning the kinetics of polymerisation. First, in view of the fact that activated styrene molecules are practically quantitatively removed during the induction period, the length of the induction period or alternatively the rate of consumption of benzoquinone at any temperature is a measure of the rate of the primary activation process, and by taking measurements at two temperatures an absolute value of the energy of activation may be obtained without having recourse to combined molecular-weight and rate of polymerisation measurements as has previously been necessary. From data of the type given in Table I the results given in the following table may be derived :

Consumption of styrene and benzoquinone during polymerisation.

	Rate of consumption (in g.-mols./c.c./hour).	
Temp.	Styrene.	Benzoquinone.
90°	$1{\cdot}17 \times 10^{-4}$	$2{\cdot}2 \times 10^{-7}$
120	$8{\cdot}4 \times 10^{-4}$	$4{\cdot}2 \times 10^{-6}$

From the last column, the energy of activation is calculated to be 28,000 cals., the calculation being independent of the actual mechanism by which the quinone combines with the active molecules. This value is somewhat higher than that given by other investigators (Schulz and Husemann, *loc. cit.*, 1936; Springer, *loc. cit.*; Schulz, *Kautschuk*, 1938, **14**, 128; Luschinsky, *Z. physikal. Chem.*, 1938, *A*, **182**, 384), although in many cases the activation energy has been calculated from the overall rate of polymerisation. The second column gives the rate of consumption of styrene which would have resulted if benzoquinone had been absent, so that if the number (n) be known of primarily activated molecules which react with one molecule of quinone before the latter loses its activity, it is possible to calculate the mean molecular weight of polystyrene formed at a given temperature. It is important to realise that calculation of such mean molecular-weight values from data obtained with different inhibitors provides a means of distinguishing between the two possible modes of action of an inhibitor. If the reaction removing the inhibitor is identical with that removing the primarily activated molecules, as provisionally assumed above, the same value of mean molecular weight should be obtained independently of the inhibitor used. If, on the other hand, the process of removal of the inhibitor by reaction with styrene is independent of the deactivating effect, widely different values are to be expected, since it is extremely unlikely that all such reactions would have the same velocity constant. The mean molecular weight (M) calculated from measurements of induction period at 120° is given below for a number of strong inhibitors, in terms of n as defined above.

Calculated molecular weights for 120° *polymer.*

Stabiliser.	Mn.	Stabiliser.	Mn.
Benzoquinone	20,800	*p*-Nitrosodimethylaniline	24,000
Toluquinone	23,600	Chloranil	41,200
Phenanthraquinone	24,800		

Approximate agreement for M is obtained for the same value of n, except with chloranil, for which a value of n twice as great is required. The existence of two such values of n is not impossible, since the steric effect of the four chlorine atoms in chloranil may enable both the quinonoid groups to be effective for inhibition, whereas only one such group may normally be effective; n cannot be less than unity, and the molecular weight found cannot exceed the above values. Comparison with the accepted value of about 100,000 for the molecular weight of the 120° polymer—the accepted value has risen some 5—10 fold in the last 10 years—might be supposed to discredit the basis of the above calculation, but it must be remembered that the presence of a comparatively small mass of short chains can reduce the true average molecular weight by a considerable amount, while the effect on the standard methods of molecular-weight measurement is less pronounced.

The complete explanation of the anomalous result with chloranil, and further discussion of the validity of the above molecular-weight determinations and their bearing on the mechanism of inhibition must be deferred until the separate reaction products of styrene with the above stabilisers have been prepared and identified, enabling substitution of the appropriate value of n. In the event of complete agreement being obtained in this manner, and in view of the wide variation in molecular weight of the stabilisers, a good case could then be made for the assumed mechanism whereby strong inhibitors affect the process of polymerisation of styrene.

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