111. *The Kinetics of Catalytic Polymerizations. Part I. The Polymerization of Styrene catalyzed by Aluminium Chloride in Carbon Tetrachloride Solution.*

By D. O. Jordan and A. R. Mathieson.

The aluminium-chloride-catalyzed polymerization of styrene in carbon tetrachloride solution has been found to proceed according to a second-order law, the initial rate being proportional to the first power of the concentration of both styrene and aluminium chloride. This law is also obeyed up to high degrees of polymerization, although the values of the velocity constant thus obtained are found to vary with the conditions of the polymerization. The energy of activation calculated from the velocity constants for the initial rate at 0° and 25° is low, being 1200 cal./mole.

From experiments in which the polymerization did not go to completion, it is inferred that one molecule of aluminium chloride initiates, on an average, only one polymer chain. On the addition of further catalyst to an uncompleted reaction, further polymerization occurs. Reactions under very dry conditions proceed at a rate approximately twice that occurring when the drying procedure was less severe; the addition of water and methyl alcohol was found to have little effect on the reaction rate under the latter conditions. It is concluded that the reaction does not require the presence of a co-catalyst.

The polymers obtained are of low molecular weight, being in the range 700—1800. One in every four polymers on an average was found to possess an olefinic double bond. An empirical relation between intrinsic viscosity and molecular weight has been obtained for these polymers of low molecular weight.

The kinetics of the polymerization of certain unsaturated compounds by catalysts of the Friedel–Crafts type have been shown, in the systems so far investigated, to be more complicated than those of the corresponding thermal, photochemical, or peroxide-catalyzed reactions, which can be explained completely by the theory of radical chains. The Friedel–Crafts-catalyzed reactions show a wide divergence of behaviour : the order and mechanism, and the influence of inhibitors and of water and other so-called co-catalysts vary with the nature of the monomer, the catalyst, and the solvent.

The rate of the stannic chloride-catalyzed polymerization of styrene in carbon tetrachloride at ordinary temperatures has been shown by Williams (*J.*, 1940, 775) to be of the first order with respect to the catalyst and of the third order with respect to the monomer. For the same reaction in ethylene dichloride solution, however, Pepper (*Trans. Faraday Soc.*, 1949, **45**, 404) has concluded that the reaction rate is more closely proportional to the second power of the monomer concentration. This result is in agreement with the kinetics of the polymerization of octyl vinyl ether catalyzed by stannic chloride, silver perchlorate, and triphenylmethyl chloride in light petroleum, ethyl ether, and *m*-cresol solutions respectively (Eley and Richards, *ibid.*, p. 436). On the other hand, the titanium tetrachloride-catalyzed polymerization of *iso*butene between −20° and −120° is independent of the catalyst concentration, provided that it is above a certain limit, but is dependent on the concentrations of the co-catalyst and the monomer (Evans, Holden, Plesch, Polanyi, Skinner, and Weinberger, *Nature*, 1946, **157**, 102; Evans, Meadows, and Polanyi, *ibid.*, 1946, **158**, 94; Plesch, Polanyi, and Skinner, *J.*, 1947, 257; Plesch, *Research*, 1949, **2**, 267), the exact kinetic relationships not being known. A similar result has been reported by Norrish and Russell (*Nature*, 1947, **160**, 543) for the polymerization of *iso*butene in ethyl chloride solution catalyzed by stannic chloride.

The widest divergence between the various reactions appears to exist in the necessity, or otherwise, for the presence of traces of water. The presence of water has been shown to be essential for the polymerization of *iso*butene at low temperatures catalyzed by stannic chloride (Norrish and Russell, *loc. cit.*), and by titanium tetrachloride (Plesch, Polanyi, and Skinner, *loc. cit.*), which are both relatively weak Friedel–Crafts catalysts. The more active boron trifluoride catalyzes the polymerization of *iso*butene in the absence of water in the liquid phase at low temperatures, but not in the gas phase (Evans, Meadows, and Polanyi, *Nature*, 1947, **160**, 867). The early work of Williams (*J.*, 1938, 246, 1046; 1940, 775) and of Eley and Pepper (*Trans. Faraday Soc.*, 1947, **43**, 112) cannot be discussed in this connection since at that time the possibility that water might be a co-catalyst was not realised. However, the results of Williams (*loc. cit.*) have been re-examined by Plesch (*loc. cit.*), who has argued that it would appear that water accelerates the catalysis of styrene by stannic chloride and does not retard it as originally suggested by Williams. Eley and Richards (*loc. cit.*) also find that the silver perchlorate-catalyzed polymerization of octyl vinyl ether is accelerated by the addition of water, but it must be clearly pointed out that there is a marked difference between the action of water in these reactions, where the presence of water accelerates the reaction but is not an essential co-catalyst, and the low-temperature polymerization of *iso*butene described above, where the reaction does not take place at a measurable rate except in the presence of water in addition to the Friedel–Crafts catalyst. In marked contrast to both these types of behaviour, Eley and Richards (*loc. cit.*) have found that the stannic chloride-catalyzed polymerization of octyl vinyl ether was unaffected by the addition of water, and Pepper (*Trans. Faraday Soc.*, 1949, **45**, 397) has observed that the effect of careful drying of the reactants and solvent is to *increase* the rate of polymerization of styrene catalyzed by stannic chloride in ethylene dichloride and nitrobenzene solutions. For the same reaction in a mixture of carbon tetrachloride and nitrobenzene as solvent, George and Wechsler (*J. Polymer Sci.*, 1951, **6**, 725) found that addition of small amounts of water had no effect and that the presence of large amounts of water markedly decreased the reaction rate.

In view of these differences in behaviour it is evident that before a detailed interpretation of the data in terms of general reaction mechanisms can be made, other catalyzed polymerizations must be studied. In the present work, which has been briefly reported elsewhere (Jordan and Mathieson, *Nature*, 1951, **161**, 523), aluminium chloride has been employed as the catalyst for the polymerization of styrene, partly in order that comparison could be made with the results of Williams and of Pepper (*locc. cit.*), but also because the reaction proceeds at a rate convenient for kinetic study.

RESULTS

Quantitative Character of the Polymerization.—Any analysis of the kinetic data must necessarily involve the assumption that consumption of monomer in side reactions is negligible. The results given in Table I show that this is so in the reaction under consideration, the weight of polystyrene recovered being the same, within the limits of experimental error, as the weight of monostyrene consumed.

TABLE 1. *The quantitative character of the polymerization.*

Initial concn. of monomer (mole/l.)	Temp.	Monomer consumed (%)	Monomer consumed in arbitrary volume of solution (g.)	Polymer recovered from same volume (g.)
0·523	0°	80·9	0·950	0·946
0·657	0	83·7	1·372	1·368
0·272	25	89·9	0·482	0·412
0·141	25	86·0	0·120	0·129
0·219	25	73·5	0·129	0·131
0·277	25	43·7	0·264	0·260
0·380	25	56·0	0·440	0·464
0·320	35	54·2	0·400	0·399

The Time Course of the Polymerization.—Typical curves showing the course of the reaction at 25° and 0° are given in Figs. 1 and 2. The results show that the method of analysis of the reaction mixture adopted leads to an excellent definition of the shape of the curves such as is essential for kinetic analysis. In Fig. 1 one reaction shows a short induction period. Only three such reactions have been observed in the twenty-seven experiments performed in which the initial concentrations of monomer and catalyst have been varied. It is evident that a period

FIG. 1. *The course of polymerization at 25° (typical curves).*

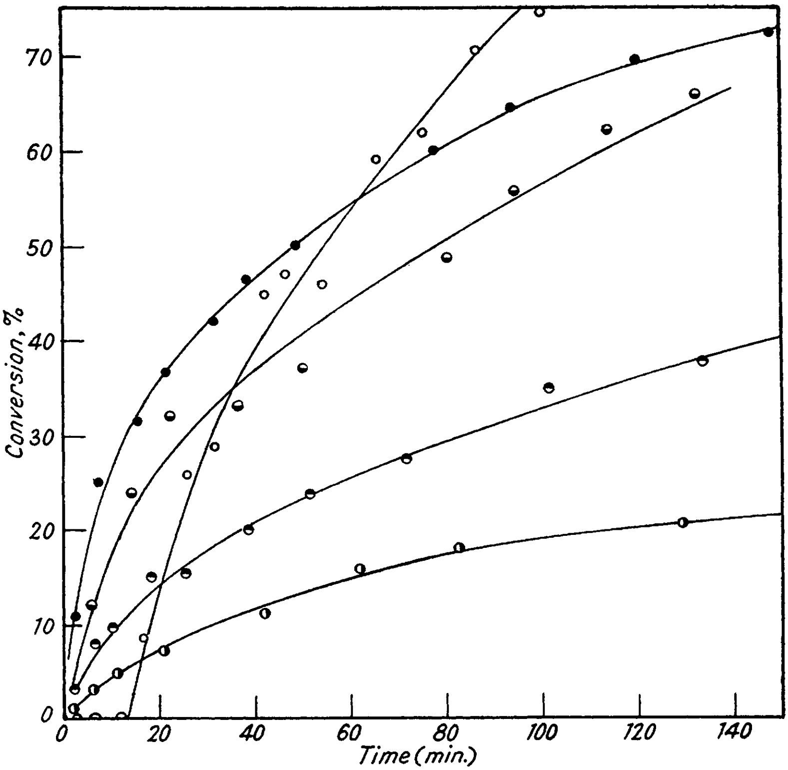
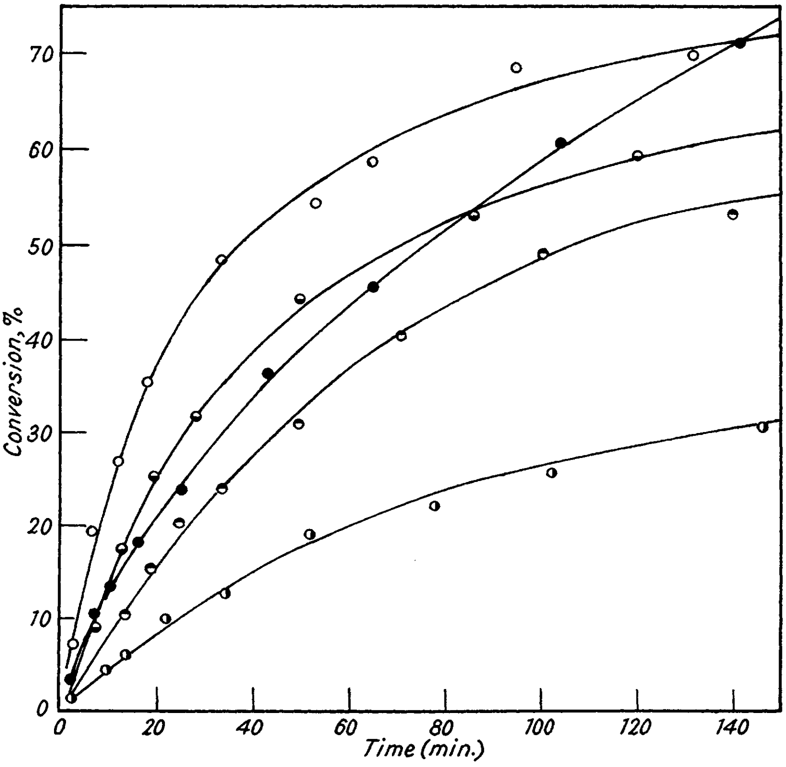


FIG. 2. *The course of polymerization at 0° (typical curves).*

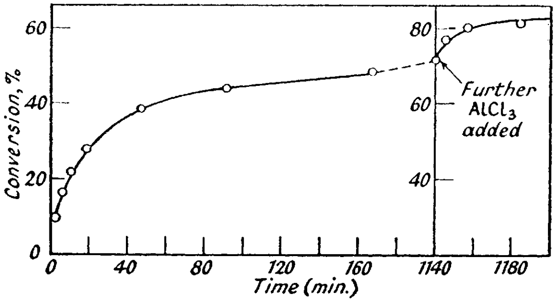


of induction is not a general feature of this reaction, and the reason for an occasional reaction possessing such a period is not yet known. The reactions showing induction periods have therefore not been further considered.

The Function of the Aluminium Chloride in the Reaction.—That the catalyst is consumed during the course of the reaction may be inferred from the results shown in Table 2. First, the reaction does not always go to completion when the aluminium chloride is present in relatively low concentration, and, secondly, the values given in column 6 of Table 2 of the ratio of styrene polymerized to aluminium chloride present is a constant for those reactions which do not proceed to completion. The value of this ratio approximates to the value of the chain length of the polymer, which indicates that, on average, one aluminium chloride molecule initiates only one polymerization chain. Furthermore, if fresh catalyst is added to a reaction in which polymerization has ceased before all the monomer has polymerized, it is found that further polymerization takes place (Fig. 3).

Another instance of the consumption of catalyst is afforded by the results of Hersberger, Reid, and Heiligmann (*Ind. Eng. Chem.*, 1945, **37**, 1073) for the polymerization of α-methylstryene catalyzed by aluminium chloride in ethyl chloride solution at —50°.

FIG. 3.



The Influence of Water on the Reaction.—In view of the marked influence of water that has been observed in some other systems (Norrish and Russell, *loc. cit.*; Plesch, Polanyi, and Skinner, *loc. cit.*) the effect of careful drying and of traces of water has been studied. The solvent was normally dried over calcium chloride; more vigorous drying over phosphoric oxide, and the complete exclusion of atmospheric moisture led to an increased rate of reaction (Table 3). This result is similar to that obtained by Pepper (*loc. cit.*) for the stannic chloride-catalyzed polymerization of styrene in ethylene dichloride. It is evident that water does not behave as

TABLE 2. *The consumption of aluminium Chloride during the polymerization of styrene.*

Initial concn. of monomer (mole/l.)	Temp.	Extent of polymerization (%)	Monomer consumed (x) (mole/l.)	Concn. of AlCl$_3$ (B) (mole/l.)	x/B	Chain length in monomer units
0·505	0°	46	0·234	0·0326	7·2	7·3
0·559	0	67	0·374	0·0250	15·0	—
0·277	25	44	0·121	0·0176	6·9	10·5
0·380	25	56	0·213	0·0300	7·1	7·1
0·279	25	36	0·101	0·0182	5·5	5·3
0·498	25	34	0·170	0·0233	7·3	—
0·320	35	54	0·174	0·0240	7·1	8·7

TABLE 3. *Influence of water and methyl alcohol on the rate of polymerization.*

Conditions of experiments	Specific reaction rate at 25°, l. mole^{-1} sec.$^{-1}$
Rigorous drying	3·3 × 10^{-2}
Dried with CaCl$_2$ (normal exptl. conditions)	1·68 × 10^{-2} *
0·0035 mole/l. of water	1·5 × 10^{-2}
0·0075 mole/l. of water (saturated solution)	1·8 × 10^{-2}
0·0388 mole/l. of CH$_3$·OH	1·8 × 10^{-2}

* Average of ten determinations.

a co-catalyst, but very small concentrations of water and perhaps methyl alcohol are clearly capable of producing a small decrease in the rate, the rate becoming constant at a very low and as yet undetermined concentration of water.

It is conceivable that traces of other substances present in the carbon tetrachloride or the styrene might act as co-catalysts. Co-catalysts have been shown to be consumed during the course of reaction (see Plesch, *loc. cit.*), and hence the further addition of catalyst only to an incomplete reaction should not promote further polymerization. That this does not obtain in the present system is clear from Fig. 3; it may also be concluded that co-catalysts do not exist either in the carbon tetrachloride or in the styrene, although the possibility of their existence in the aluminium chloride is not excluded.

FIG. 4.—*The relation between* $[\eta]$ *and molecular weight.*

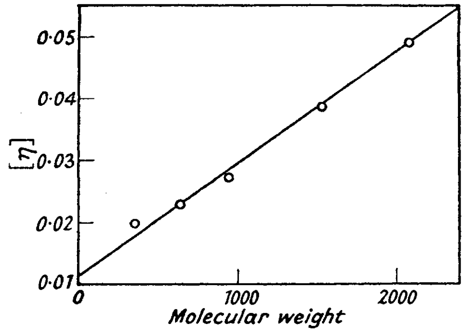


FIG. 5. *Variation of freezing-point depression with concentration of polystyrene (molecular weights :* ● 630; ○ 930).

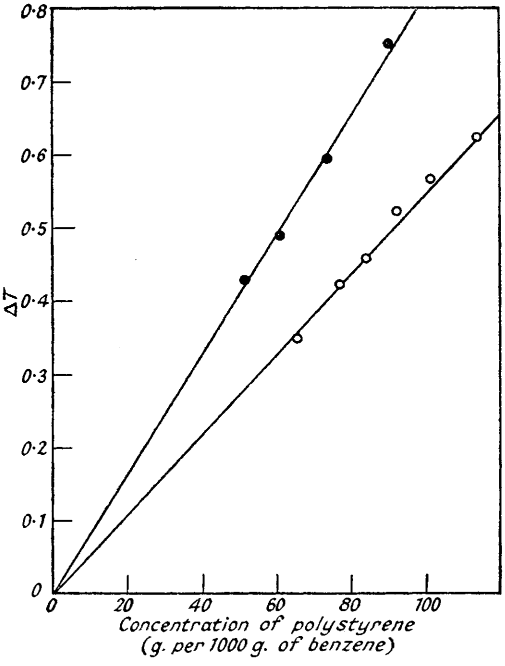
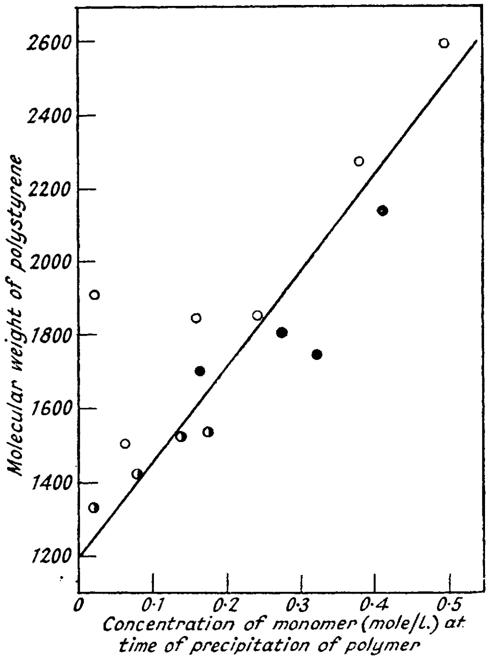


FIG. 6.



The Molecular Weight of the Polystyrene.—Various empirical formulæ of the type $[\eta] = A + BM$ or $[\eta] = BM^{\alpha}$ have been proposed relating the polymer molecular weight to the intrinsic viscosity (see Kemp and Peters, *Ind. Eng. Chem.*, 1942, **34**, 1097; Bamford and Dewar, *Proc. Roy. Soc.*, *A*, 1948, **192**, 329) and the formula of Bamford and Dewar (*loc. cit.*), $[\eta] = 4{\cdot}40 \times 10^{-4}M^{0{\cdot}65}$ where $[\eta] = \eta_{sp}/c$ and c is the concentration in g. per 100 c.c. of solution, in particular has been frequently used.* However, the molecular weights of the polystyrenes isolated in the present study are low and fall outside the range of molecular weights on which the Bamford and Dewar formula was based; furthermore, owing to the low values of the molecular weights of our polystyrenes direct comparison with the molecular weight determined cryoscopically is possible. We have therefore obtained the empirical formula

$$[\eta] = 0{\cdot}0115 + 1{\cdot}81 \times 10^{-5}M \qquad (1)$$

(where $[\eta]$ is defined as above) by determining the intrinsic viscosity and the cryoscopic molecular weights in benzene solution (Fig. 4). That the cryoscopic method gives a true value for the number average molecular weight is shown in Fig. 5, which shows clearly that Raoult's law holds for these low-molecular-weight polymers in benzene solution. The empirical relation (1) may be compared with the original formula proposed by Staudinger (" Die Hochmolecularen organischen Verbindungen," 1932, Berlin, Julius Springer), $[\eta] = 1{\cdot}8 \times 10^{-5}M$. The results of Kemp and Peters (*loc. cit.*) yield a similar relation, but, without a knowledge of the temperature of their viscosity measurements, direct comparison is of little value.

The molecular weight of the polystyrene formed decreases during polymerization as shown in Fig. 6 for three typical experiments. The results for the three polymerizations having different initial concentrations of monomer and catalyst are seen to lie on the same straight line.

The molecular weight of the polymers formed generally lay between 700 and 1800, the variation showing some dependence on the initial monomer concentration as found by Pepper (*loc. cit.*) but not on the catalyst concentration. This is to be expected from the results shown in Fig. 6 and is in agreement with the results of Williams (*loc. cit.*) and Pepper (*loc. cit.*). Over the small temperature range studied little variation of molecular weight with temperature was observed.

The Constitution of the Polymer.—Estimations of olefinic double bonds have been made on some of the polymer samples prepared, and the results are summarized in Table 4. On average there was only one double bond in every four polymer molecules, so that any mechanism postulated for chain termination must account for only an occasional double bond in the polymer molecules.

TABLE 4. *Double bond content of the polymers.*

Mol. wt. of polymer sample	No. of polymer mols. per olefinic double bond	Mol. wt. of polymer sample	No. of polymer mols. per olefinic double bond
350	8·7	900	1·0
580	1·0	930	7·3, 5·8
630	4·3	1100	1·1
740	9·6	1520	3·9, 4·1
760	2·6		

It has not been possible to determine whether or not the polymer molecules contain a catalyst fragment, since no method has as yet been devised whereby precipitation of the polymer can be made without the use of hydroxylic solvents which would remove any catalyst fragment. The presence of catalyst fragments in the polymer molecules has been demonstrated by Staudinger (*loc. cit.*) for a similar system, and since it has been shown that the catalyst is consumed during the course of the reaction it seems probable that it is combined in the polymer.

DISCUSSION

Kinetic Analysis of the Rate Curves.—The initial reaction rate is found to be a linear function of the product of the first powers of the initial styrene (M_0) and initial catalyst concentrations (B_0) at both the temperatures studied (Fig. 7), *viz.* :

$$-\,\mathrm{d}M/\mathrm{d}t = kM_0B_0 \qquad (2)$$

The agreement between this relation and the experimental results is such as to exclude completely the law

$$-\,\mathrm{d}M/\mathrm{d}t = kM_0{}^2B_0 \qquad (3)$$

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* In Table III (p. 334) in the paper of Bamford and Dewar (*loc. cit.*), it has been erroneously assumed that the values of $(\log \eta)/c$ given by Kemp and Peters (*loc. cit.*, table III, p. 1099) were equivalent to $[\eta]$; this is not so since the logarithms used by Kemp and Peters are to the base 10. The values of the molecular weight calculated by Bamford and Dewar from Kemp and Peters's viscosity data are therefore too low by a factor of $2{\cdot}303^{1/0{\cdot}65} = 3{\cdot}63$ and therefore do not agree with the cryoscopic molecular weights given by Kemp and Peters. It would thus appear that Bamford and Dewar's formula is not generally applicable to polystyrenes of low molecular weight.

FIG. 7. *The concentration dependence of the initial rate of polymerization* (○ *at* 25°; ● *at* 0°).

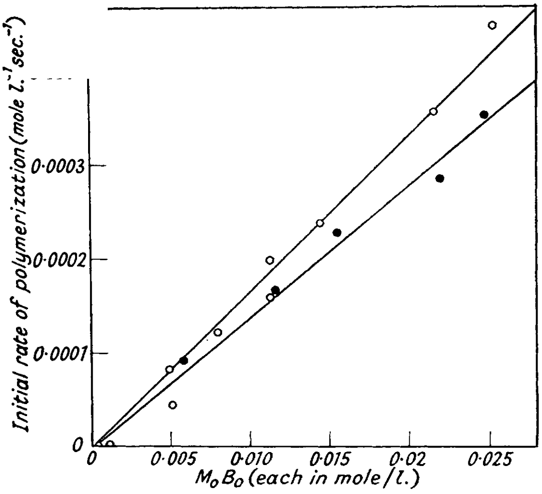
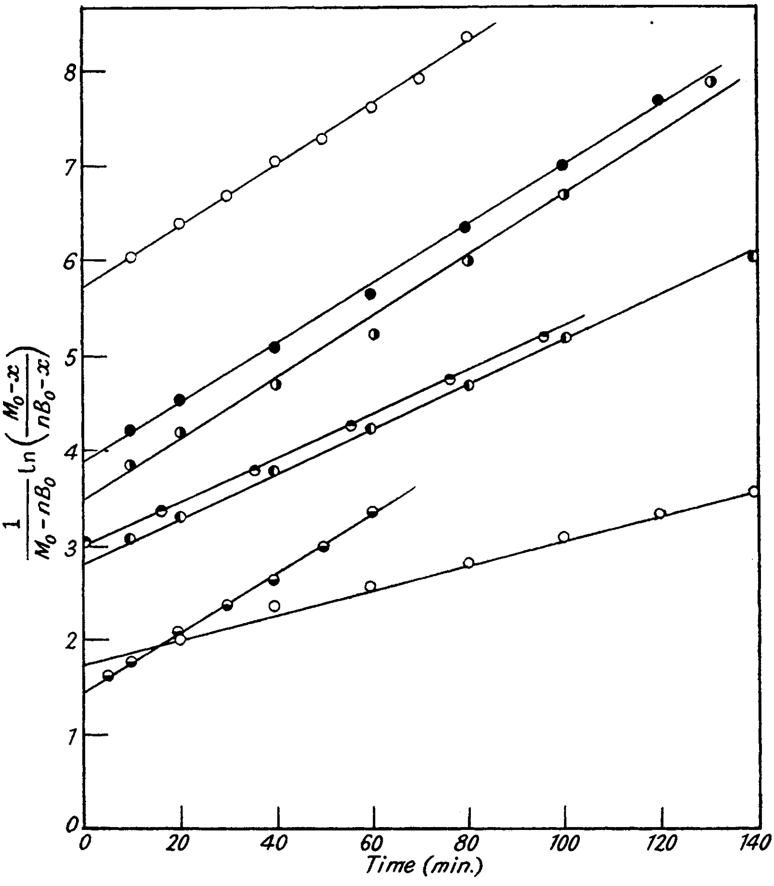


FIG. 8.



observed by Eley and Richards (*loc. cit.*) for the polymerization of octyl vinyl ether catalyzed by stannic chloride, silver perchlorate, and triphenylmethyl chloride, and by Pepper (*loc. cit.*) for the stannic chloride-catalyzed polymerization of styrene. From Fig. 7 the following values of the overall velocity constant are obtained :

$$\text{at } 0^\circ,\ k = 1{\cdot}40 \times 10^{-2} \text{ l. mole}^{-1} \text{ sec.}^{-1}$$
$$\text{at } 25^\circ,\ k = 1{\cdot}68 \times 10^{-2} \text{ l. mole}^{-1} \text{ sec.}^{-1}$$

The validity of the kinetic equation (2) is confirmed by an analysis of the rate curves up to high degrees of polymerization. The equation,

$$-\,\mathrm{d}M/\mathrm{d}t = k'(M_0 - x)^p(B_0 - x/n) \quad . \ . \ . \ . \ . \ . \ . \quad (4)$$

where x is the amount of monomer consumed in time t, and n is the chain length in monomer units, was found to fit the rate curves always when $p = 1$. This is illustrated in Fig. 8, where $\frac{1}{M_0 - nB_0} \cdot \ln \frac{(M_0 - x)}{(nB_0 - x)}$ is plotted against time, for some typical experiments. When $p = 2$ or 3 the equation did not generally fit, although in a few instances owing to the form of the integrated expressions all the equations gave equally good agreement. The values of k' in the integrated form of (4), *viz.*,

$$k' = \frac{1}{t} \cdot \frac{n}{M_0 - nB_0} \cdot \ln \frac{nB_0(M_0 - x)}{M_0(nB_0 - x)} \quad . \ . \ . \ . \ . \ . \ . \quad (5)$$

were obtained by plotting $[1/(M_0 - nB_0)] \ln [(M_0 - x)/(nB_0 - x)$ against t, the slope of the straight lines then giving k'/n (see Fig. 8). The values of k' so obtained varied from one experiment to another within the range $0{\cdot}15 \times 10^{-2}$ to $0{\cdot}94 \times 10^{-2}$ l. mole^{-1} sec.$^{-1}$. These values are lower than that obtained from the initial slope. This variation in k' is to be expected since the method is not to be regarded as accurate for the evaluation of velocity constants in polymer kinetics (see Pepper, *loc. cit.*) in view of the complexity of the reaction, and also because of the sensitivity of the value of k' (but not of k) to the factor $(M_0 - nB_0)$ occurring in the denominator of equation (5), since nB_0 frequently approaches M_0 in the later stages of a polymerization.

Temperature Dependence of the Reactions.—The value of the energy of activation calculated from the values of the velocity constant obtained from the initial rates at 0° and 25° is 1200 cal./mole. This very low value is less than that obtained by Eley and Richards (*loc. cit.*) for the polymerization of octyl vinyl ether catalyzed by stannic chloride (10,000 cal./mole) but in reasonable agreement with the statement of Williams (*loc. cit.*) that the energy of activation for the stannic chloride-catalyzed polymerization of styrene is less than 3000 cal./mole. As pointed out by Eley and Richards (*Research*, 1949, **2**, 147 ; *loc. cit.*) the overall energy of activation is the sum of the energies of activation of several intermediate stages (*e.g.*, initiation, propagation, and termination), the energies of activation for which are not necessarily so low. The overall energy of activation is then given by $E = E_i + E_p - E_t$.

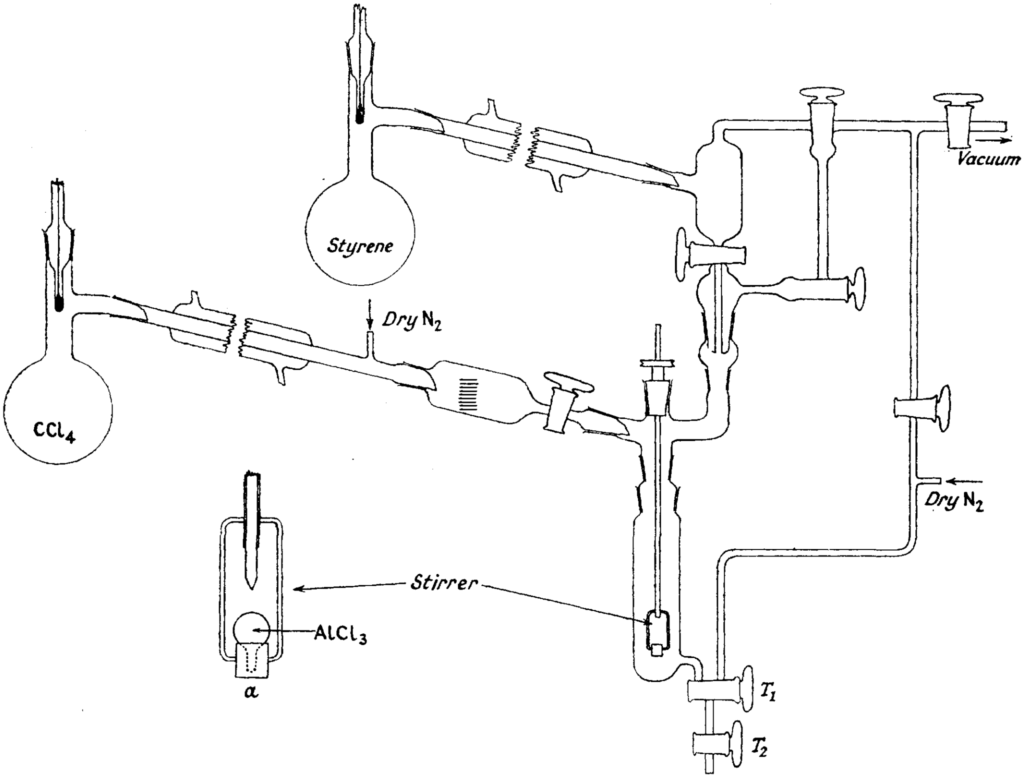
EXPERIMENTAL

Reaction Apparatus.—The apparatus, which was constructed of Pyrex glass, is shown in Fig. 9. It consists essentially of three isolatable parts, the reaction vessel, and the styrene and the carbon tetrachloride stills. Each section was evacuated and filled twice with dry nitrogen. The stirrer in the reaction vessel was not high-vacuum tight, although it could hold low vacua. It was made high-vacuum tight by being sealed on the outside with " Apiezon " ' Q ' compound, which was subsequently removed when stirring was begun. During the reaction the vessel was filled with dry nitrogen at a pressure slightly above atmospheric further to ensure that no air could leak in. The catalyst was originally contained in evacuated glass bulbs which were placed in the saddle of the specially constructed stirrer (Fig. 9*a*). The bulb could be shattered at a specified time by means of the copper ramrod which was then lifted clear of the solution. The ramrod, which slid in the stirrer tube, was lubricated with silicone grease and was vacuum tight. All ground joints and taps were lubricated with silicone grease. The withdrawal of samples of known volume of the reaction mixture was made without influencing the dry character of the reaction by manipulation of taps T_1 and T_2. Solvent and monomer were distilled directly into the reaction vessel.

Normally, reactions were carried out in a simplified apparatus which resembled the reaction vessel in Fig. 9 but the solvent and monomer, although dry and redistilled, were not distilled straight into the vessel. The weight of aluminium chloride employed in the reactions was determined by weighing the bulb containing it before the experiment, and isolating and weighing the glass residue at the end of the experiment.

Determination of Styrene.—Samples of the reaction mixture were withdrawn and added to excess of a standard solution of bromine in glacial acetic acid. The excess of bromine was immediately destroyed by the addition of potassium iodide, and the liberated iodine titrated with standard sodium thiosulphate. It has been shown by Williams (*loc. cit.*) that this method accurately determines only the monostyrene present so long as the excess of bromine is quickly removed.

FIG. 9.



Temperature Control.—Reactions at 25° and 35° were carried out in a water-thermostat, with an accuracy of ± 0·05°. Reactions at 0° were carried out in melting ice in a vacuum-flask.

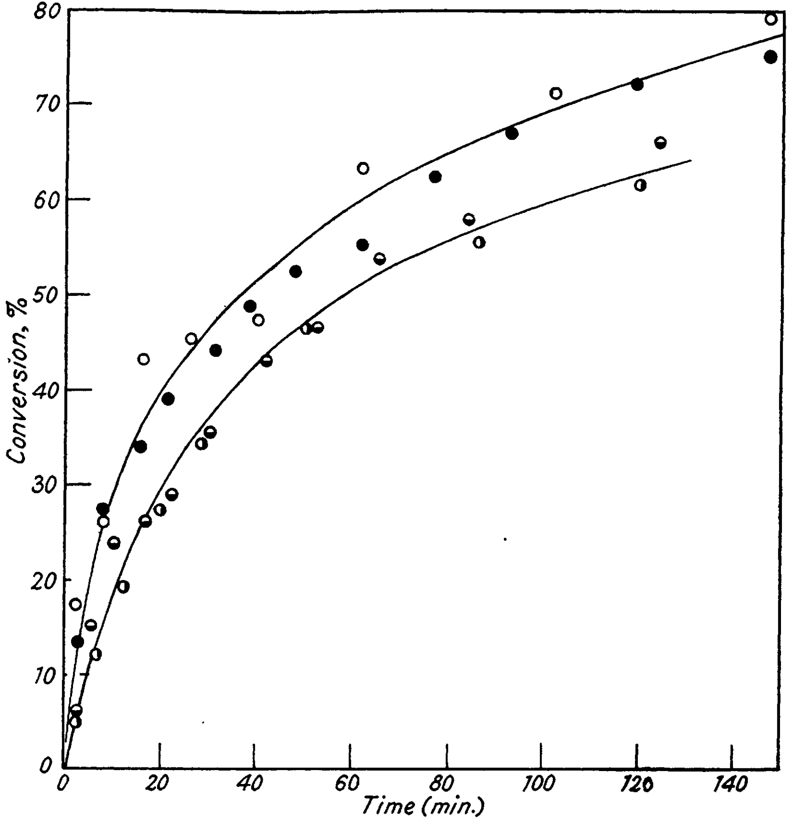
Reproducibility of Reaction Rate.—The satisfactory nature of the procedure outlined is demonstrated in Fig. 10 where the degree of polymerization is plotted against time for two sets of two experiments having the same initial value of M_0B_0. Excellent agreement is obtained up to 40% polymerization, and even beyond this value the scatter of points is quite small.

Precipitation of the Polymer.—Two methods have been used for the isolation of the polymer from the reaction mixture, and both yielded identical polymers, as shown by cryoscopic and viscosity determinations from the same reaction mixture. The methods adopted were (1) precipitation with methyl alcohol followed by evaporation of the whole mixture to dryness at room temperature, washing of the solid residue with methyl alcohol to remove styrene and aluminium chloride, and finally drying with slight warming, and (2) as in (1) but with the first step omitted. The necessity of evaporating the whole of the reaction mixture instead of collecting the precipitated polymer is due to the non-precipitation of the fraction of low molecular weight by the methyl alcohol. Once obtained in the semi-solid state, however, these fractions of low molecular weight did not redissolve in the methyl alcohol washings. Method (1) was always employed when it was necessary to stop the reaction at a particular time. Table 1 indicates that these procedures were effective in recovering all the polymer.

Viscosity.—This was measured in an Ostwald viscometer in a thermostat at 25° ± 0·05°. The polymer was dissolved in benzene, and the solution freed from dust by passage through a sintered-glass filter. Below a polymer concentration of 6 g./100 c.c., η_{sp}/c was constant, but this was always verified by determining η_{sp} at least at two concentrations.

Cryoscopic Measurements.—Molecular weights of the polymers were determined in benzene solution by the Beckmann freezing-point method. Solid solutions were not formed since the solid separating was shown to be pure benzene.

FIG. 10. *Reproducibility of polymerization.* ○, ●, M_0B_0 = 0·0250 *mole*^{2} *l.*$^{-2}$; ◒, ◑, M_0B_0 = 0·0114 *mole*^{2} *l.*$^{-2}$.



Determination of Olefinic Double Bonds in the Polymers.—This was made by treating the polymer in carbon tetrachloride in a greased-stoppered bottle with a solution of bromine in glacial acetic acid for several hours; the unchanged bromine was determined as previously described. Blank determinations were always made.

Materials.—Styrene, obtained from Messrs. Lights Ltd., was kept in amber-coloured bottles in the presence of a quinone inhibitor. It was given at least three vacuum-distillations immediately before use. In experiments carried out under rigorously dry conditions eight such distillations were given. Aluminium chloride, obtained from the British Drug Houses Ltd., was sublimed once in air, and then eight successive times in a vacuum in an enclosed system. The specimens were kept in evacuated glass bulbs. Carbon tetrachloride was redistilled from calcium chloride immediately before use; where careful drying was necessary, phosphoric oxide was used. Benzene, of AnalaR quality, was redistilled and kept over sodium.

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