145. *Kinetics of the Catalysed Polymerisation of Styrene. Part III. On the Mechanism of Metal Chloride Catalysis.*

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In the presence of stannic chloride, the rate of polymerisation of styrene, in carbon tetrachloride, to form products of molecular weight 1200—3000, is best represented by the equation $-\,\mathrm{d}(a-x)/\mathrm{d}t = kca(a-x)^3$, where a and c are the concentrations of styrene and catalyst respectively at zero time and x is that of polystyrene at time t. The energy of activation over the range 0—38° is small and probably not more than 3000 cals. The mean chain-length of the polymers is independent of c and approximately proportional to $\sqrt{a}$.

The kinetics have not been fully explained, but the function of the stannic chloride catalyst is thought to lie in facilitating triple collisions between styrene molecules, whereby a polymerisation chain can be initiated at an activated trimer stage. The catalyst probably participates in the chain-growth and chain-termination reactions. With different metal chlorides as catalyts, the total rate of polymerisation with antimony pentachloride is about 10^4 times greater than with boron trichloride; but the polymers formed with the latter have only three times the molecular weight of those formed with the former. The catalytic position of stannic chloride is intermediate, and the molecular weights of polystyrenes formed by its means do not vary greatly in different solvents. With antimony pentachloride as catalyst, polymerisation is not quantitative and the catalyst is rapidly destroyed, with formation of chlorinated by-products.

POLYMERISATIONS of vinyl compounds are regarded as chain reactions, in which formally distinct phases of chain initiation, chain growth, and chain termination may be differentiated in the formation of each long-chain polymer molecule. Chain initiation has been generally supposed to be the step which usually determines the *rate* of polymerisation (Staudinger and Frost, *Ber.*, 1935, **68**, 2351), whilst the average polymer *chain length* is determined by the relative speeds of chain growth and chain termination. Both polymerisation rate and chain length are affected by a polymerisation catalyst, which may influence one or more of the three steps in the polymerisation process.

Among catalysts which increase the rate of polymerisation of styrene, peroxides and metallic halides have received attention (*e.g.*, Milas, *Proc. Nat. Acad. Sci.*, 1928, **14**, 844; Houtz and Adkins, *J. Amer. Chem. Soc.*, 1931, **53**, 1058; 1933, **55**, 1609; Staudinger and Lautenschläger, *Annalen*, 1931, **488**, 1; Staudinger, " Die Hochmolekularen Organischen Verbindungen," Berlin, 1932). Schulz and Husemann (*Z. physikal. Chem.*, 1938, *B*, **39**, 246) conclude, from a kinetic study of benzoyl peroxide catalysis of styrene polymerisation in toluene solution; (*a*) that the catalyst accelerates chain initiation through formation of a benzoyl peroxide–styrene complex, which breaks down to give a reaction centre; (*b*) that chain growth then proceeds without further intervention of the catalyst; and (*c*) that chain termination occurs by mutual deactivation and stabilisation of growing polymer chains, meeting in binary collisions. The same mechanism has been postulated for benzoyl peroxide catalysis of vinyl acetate polymerisation (Cuthbertson, Gee, and Rideal, *Proc. Roy. Soc.*, 1939, *A*, **170**, 300).

In the " spontaneous " (*i.e.*, non-catalytic) polymerisation of styrene, a solvent, when present, may enter into the mechanism of chain initiation (Suess, Pilch, and Rudorfer, *Z.*

physikal. Chem., 1937, *A*, **179**, 361; Suess and Springer, *ibid.*, **181**, 81); but there is evidence that chain growth and chain termination proceed in spontaneous polymerisation in the same way as with the peroxide catalyst present (Schulz, Dinglinger, and Husemann, *ibid.*, 1939, *B*, **43**, 385). If this is correct, it follows that the peroxide catalyst accelerates polymerisation simply by increasing the concentration of reactive centres present in the system, the average chain length of the polymers being simultaneously reduced, owing to the increased opportunities existing for mutual deactivation of the growing chains. The presence of benzoyl peroxide does not alter the activation energy appreciably; in toluene solution, according to Schulz and his collaborators, the activation energies for chain initiation, in the absence and the presence of benzoyl peroxide, are 24,700 and 23,700 cals. respectively.

On the other hand, metal halide catalysts appear to alter the kinetics of styrene polymerisation more drastically. Starting with undiluted monomer, molecular weights of polystyrenes formed, at room temperature, with and without a stannic chloride catalyst are of the order 7,000 and 500,000 respectively (Staudinger, *op. cit.*, pp. 159, 186), whereas polystyrenes of molecular weight 280,000—61,000 are formed with increasing proportions of benzoyl peroxide catalyst at 27° (Schulz and Husemann, *loc. cit.*). In carbon tetrachloride solution at 25° (Williams, Part I, J., 1938, 246), catalysis by stannic chloride reduces the molecular weights of the polystyrenes to 1,200—3,000, enhances enormously the degree of variation of polymerisation rate with initial styrene concentration, and greatly diminishes the activation energy. These effects, which are not confined to carbon tetrachloride as solvent, are examined in the experiments to be described. The method employed for analysing the reaction was that described in Part I (*loc. cit.*), *viz.*, quantitative bromination of the residual monomer present in the polymerising mixture at different times.

Range of Polystyrenes formed with Metal Chloride Catalysts.—Styrene was polymerised, boron trichloride, stannic chloride, and antimony pentachloride being used as catalysts in carbon tetrachloride solution at 25°. Average molecular weights were derived from viscosity measurements on solutions of the polystyrenes formed, the following equation (Part I, *loc. cit.*) being used:

$$\eta_{sp.}/c = 2{\cdot}5 \times 10^{-2}n + 0{\cdot}2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

This gives approximate values for unfractionated polystyrene mixtures of average molecular weight less than 5,000 ($\eta_{sp.}$ = specific viscosity; c = polystyrene concentration, as mols. of C_8H_8 per l.; n = degree of polymerisation = $M/104$).

The results are shown in Table I. Both catalyst and solvent might be considered to participate in reducing the molecular weights of the polystyrenes to the relatively small values observed. Evidence exists (Suess and Springer, *loc. cit.*; Stanley, *Chem. and Ind.*, 1939, **58**, 1080) that carbon tetrachloride has itself a marked effect, not shared by toluene or benzene, in accelerating spontaneous polymerisation at 80—120° and in reducing polymer

TABLE I.

Polystyrenes made with Metal Chloride Catalysts at 25°.

Expt. No.	Solvent.	Catalyst.	Catalyst concn., M.	Initial C_8H_8, M.	$\eta_{sp.}/c$.	Mol. wt.	t_r, mins.
84	CCl_4	BCl_3	0·061	1·89	1·152	4000	2·62 × 10⁴
80	CCl_4	BCl_3	0·139	1·70	1·06	3600	1·24 × 10⁴
74	CCl_4	BCl_3	0·230	3·46	0·932	3000	0·168 × 10⁴
104	CCl_4	$SnCl_4$	0·050	1·732	0·769	2400	25
3	$CHCl_3$	$SnCl_4$	0·102	1·74	0·76	2300	1
15	$CHCl_3$	$SnCl_4$	0·1	1·74	0·56	1500	1
22	$CHCl_3$ *	$SnCl_4$	0·090	1·73	—	—	23
111	C_6H_6	$SnCl_4$	0·034	1·720	0·924	3000	4
112	C_7H_8	$SnCl_4$	0·047	1·72	0·521	1300	—
113	C_7H_8	$SnCl_4$	0·068	1·72	0·626	1800	—
82	CCl_4	$SbCl_5$	0·073	0·773	0·564	1500	Polymerisation apparently instantaneous
77	CCl_4	$SbCl_5$	0·063	1·71	0·778	2400	
83	CCl_4	$SbCl_5$	0·186	1·73	0·518	1300	
81	CCl_4	$SbCl_5$	0·213	1·75	0·704	2100	
79	CCl_4	$SbCl_5$	0·25	1·68	0·586	1600	

* Specially purified chloroform.

size. At 140°, chlorine from this solvent may even be incorporated in the polymer to the extent of 20% (Breitenbach, Springer, and Abrahamczik, *Österr. Chem.-Ztg.*, 1938, **41**, 182). Polystyrenes made by catalysis with stannic or boron chloride are not contaminated in this way (see analyses in Table VI), and experiments with different solvents, included in Table I, show that carbon tetrachloride does not reduce polymer size more powerfully than hydrocarbons, when used as a solvent for polymerisation catalysed by stannic chloride. It seems therefore that the low molecular weights in Table I are due to the action of the catalysts.

In Table I, the greatest variations in molecular weight, for comparable conditions, occur between the boron chloride and the antimony chloride polystyrenes. They are, at most, in the ratio 3 : 1, and are small in comparison with the corresponding differences in the *speeds* of polymerisation. A rough measure of the rate of polymerisation is given for each catalyst in Table I, where t_r represents the time required for the reaction range 5—20% styrene consumption. (This reaction range is taken in order to eliminate the effect of initial inhibition periods.) With boron and tin chlorides, styrene is consumed almost quantitatively to form polystyrene (see Table VI), but the catalytic action of antimony pentachloride is very violent. Polymerisation is almost instantaneous, and stops before the styrene has been completely used up, owing to destruction of the catalyst with formation of by-products in addition to polystrene. Polymerisation is at least 10^4—10^5 times faster with antimony pentachloride than with boron trichloride and, in carbon tetrachloride, about 10^3 times faster with stannic chloride than with boron trichloride. The significance of these results is considered later.

Polystyrenes from Stannic Chloride Catalysis.—Table II shows that, for stannic chloride as catalyst and carbon tetrachloride as solvent, the chain length of the polymer is independent of the catalyst concentration. The same result (already advanced provisionally in Part I) has been obtained with other initial concentrations of styrene. Values of n for 3·5M initial styrene are shown in Fig. 1 (line II, upper scale). Average values for n at different initial styrene concentrations are collected in Table III, in which results from Part I are included for comparison.

TABLE II.

Stannic Chloride Concentration and Polymer Size.

Styrene¯ = 1·73M approx. Temp. 25°.

$SnCl_4$ *	13·7	11·6	11·6 †	9·23	8·94	8·08	7·73	3·38
$\eta_{sp.}/c$	0·855	0·807	0·825	0·771	0·848	0·796	0·764	0·812
n	26	24	25	23	26	24	23	23
$SnCl_4$ *	3·17	2·91	2·72	2·72 †	1·91	1·65	1·30	
$\eta_{sp.}/c$	0·746	0·769	0·836	0·851	0·764	0·835	0·769	
n	22	23	25	26	23	25	23	

* Expressed as mols. $SnCl_4$ per 100 mols. styrene.
† Reaction vessel packed with glass wool.

As shown in Fig. 1 (line I, lower scale), the average polymer chain length n is found to be approximately proportional to the square root of the initial styrene concentration, over the range 0·4—3·6M-styrene, although there are signs that, at the higher concentrations, the dependence of n upon [styrene]$^{\frac{1}{2}}$ may become less than linear. The measurements recorded in Fig. 1 and Table III were made on polymer accumulated over a considerable range of reaction. It is nevertheless justifiable to plot the mean chain length against *initial* styrene

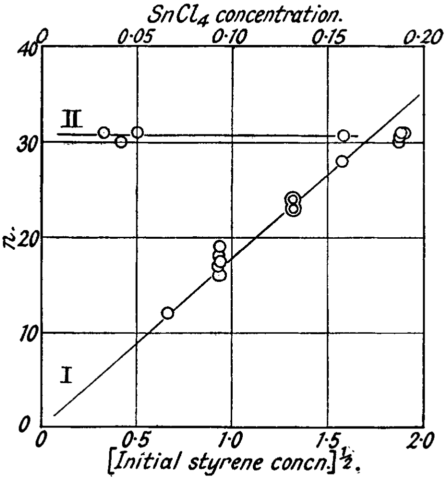
TABLE III.

Average Degree of Polymerisation.

	Initial styrene, M	0·43	0·86	1·73	2·46	3·5
n	New results	—	19	24	28	31
	From Part I	12	17	23	—	—

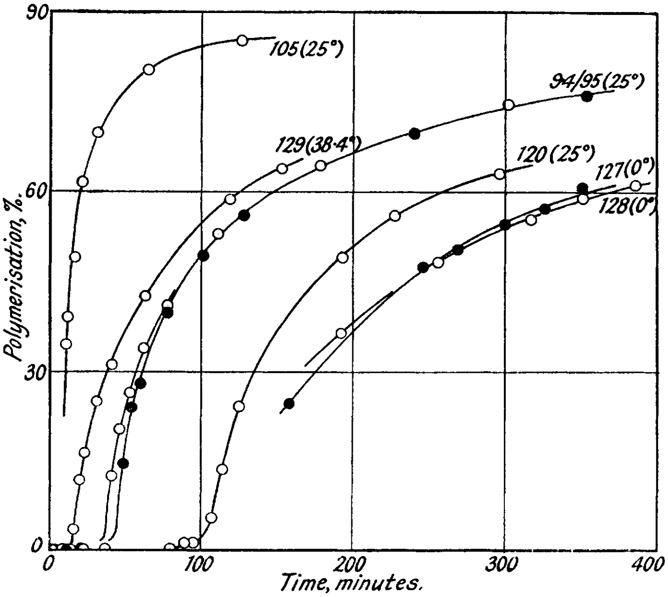
concentration, because it has been shown in Part I that n remains approximately constant throughout the range of any individual polymerisation experiment.

Fig. 1.



Rate of Polymerisation.—It has been found (Part II, J., 1938, 1046) that the reaction whereby stannic chloride catalyses the formation of polystyrene is inhibited in the presence of hydrogen chloride and replaced by a dimerisation associated with the addition of hydrogen chloride to the styrene double bond. In certain experiments, inhibition periods were found to precede polymerisation by stannic chloride, and these were thought to be due to the presence of hydrogen chloride in the catalyst, since they were eliminated by distillation of stannic chloride in a vacuum. In the present series of experiments, repeated distillation

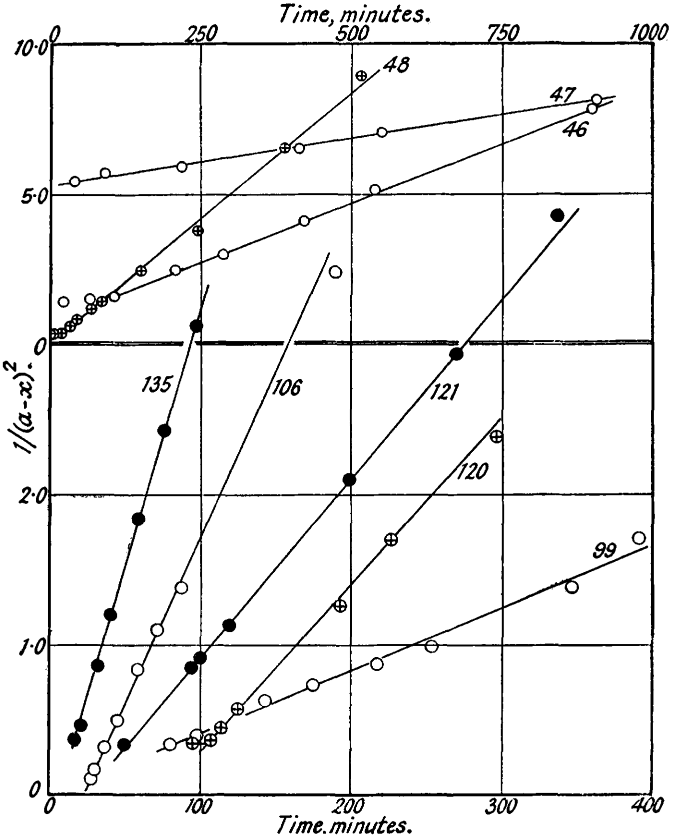
Fig. 2.



Styrene = 3·49M *for* 105 *;* 1·7M *for other curves.*

in a vacuum has failed to remove the last traces of hydrates from commercial stannic chloride of British origin; and in all the new experiments, periods of inhibition (of 10—50 mins.) intervened between the mixing of the reactants and the commencement of polymerisation. The results may, nevertheless, be used as a basis for conclusions concerning the mechanism of polymerisation; for, on comparing the new results with those given in Part I, in which the preliminary inhibition had been eliminated, we find for the two series of experiments: (*a*) practically quantitative polymerisation (see experimental section), therefore the amount of styrene consumed in removing the inhibitor is very small; (*b*) the same mean chain lengths for the polymers (Table III); (*c*) the same order of reaction (Table IV); (*d*) identical mathematical form of individual polymerisation curves (Fig. 3).*

FIG. 3.



Full black circles—packed reaction vessels.
Lines on lower scales—styrene ca. 1·7M.
Expts. 46, 47, 48 (*upper scales*)—*see Table IV.*

The shapes of individual reaction curves (Fig. 2) suggest that the rate of polymerisation depends on a high power of the styrene concentration; and this is confirmed (Fig. 3) by the observation that, in a given experiment, $1/(a - x)^2$ is a linear function of the time. For each line in Fig. 3, the slope gives a third-order velocity coefficient k_3, values of which are given in Table IV. The velocity coefficients k_3 are used as a measure of the rate of polymerisation.

The reaction is essentially homogeneous. Packing the reaction vessel with glass wool

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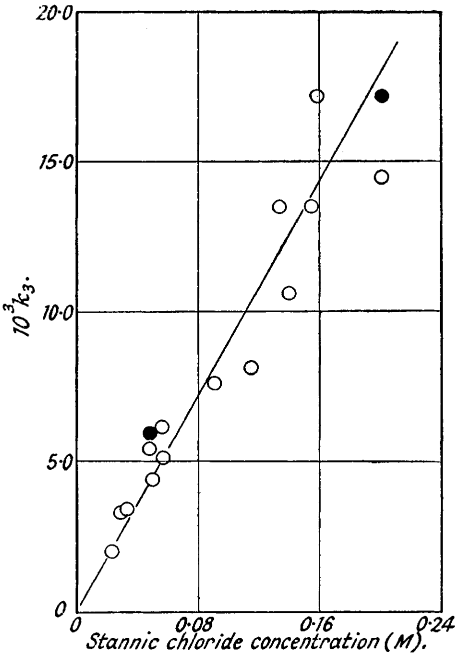
* In both series, the actual commencement of polymerisation is attended by an *induction period.* It is not known whether this represents removal of the last portions of inhibitor, or whether it is a property of the reaction.

does not appreciably alter chain length (Table II), form of the polymerisation curve (Fig. 3), or rate of polymerisation (Fig. 4).

FIG. 4.



Full black circles—packed reation vessels.

Fig. 4 shows the dependence of polymerisation rate upon catalyst concentration. Despite random variation of k_3 values at the higher catalyst concentrations, k_3 is seen to be approximately proportional to the concentration of stannic chloride. A linear relation between catalyst concentration and the maximum rate of styrene consumption has been observed previously (Part I) over a limited range.

Order of Reaction.—Fig. 4 shows that reproducibility of absolute rate is not perfect for experiments started with independent specimens of catalyst. This may be due to the traces of impurity in the catalyst, referred to above. The influence of initial styrene concentration upon polymerisation rate was determined by using several series of experiments, the reaction mixtures in each series being made up from a common specimen of stannic chloride. Curves 94/95 of Fig. 2 illustrate the reproducibility attainable within each series, and Table V shows the extent of reproducibility between the different series.

Results are shown in Table IV and the following relations are established :

$$t_r = \text{const.}/a^3;\ {}^*r_m = \text{const.} \times a^4;\ k_3 = \text{const.} \times a \quad . \quad . \quad . \quad . \quad (2)$$

where t_r is now the time required for the reaction to cover the range 25—50% styrene consumption; r_m is the maximum rate of consumption of styrene (mols. l.$^{-1}$ min.$^{-1}$), calculated from the reaction curves; a is the initial concentration of styrene.

TABLE IV.

Order of Reaction in Carbon Tetrachloride. (Temp. 25°.)

No.	Initial C_8H_8, M.	$\eta_{sp.}/c$.	n.	$10^3 . k_3$, min.^{1}.	t_r, mins.	$10^4 . r_m$.	$10^3 . k_3/a$.	$10^3 . r_m/a^4$.	$t_r . a^3$.
Series A.	$SnCl_4$ = 0·0507M.								
48	1·730	0·757	22	7·45	46	315	4·30	3·5	238
46	0·866	0·602	16	3·93	369	19	4·53	3·4	239
47	0·433	0·507	12	1·57	—	1	3·63	2·8	—
Series B.	$SnCl_4$ = 0·0504M.								
103	3·60	0·975	31	8·67	9·0	—	2·41	—	420
104	1·732	0·769	23	4·41	84	245	2·55	2·7	435
102	0·874	0·639	17·5	2·45	595	14·5	2·80	2·5	400
Series C.	$SnCl_4$ = 0·0416M.								
106	3·49	0·939	30	11·4	8·0	3140	3·27	2·1	340
107	2·456	0·907	28	8·10	22	850	3·30	2·3	326
Series D.	$SnCl_4$ = 0·0332M.								
116	3·53	0·976	31	7·30	12·3	2460	2·07	1·6	541
115	1·741	0·764	23	3·4	82·5	185	1·95	2·0	435
118	0·885	—	—	4·53	322	16·5	(2·56) *	(1·4) *	(446) *

* In expt. 118, $SnCl_4$ = 0·0664M. The figures in brackets are calculated for 0·0332M-catalyst.

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* r_m should, strictly, be correlated, not with a, but with s_m, the residual concentration of styrene which actually corresponds to the maximum rate in each experiment. On substituting s_m for a the general relationship remains the same, but the numerical values of r_m/s_m^4 are less concordant. s_m is difficult to determine accurately. Since s_m is slightly less than a, the constants in col. 4 of Table V tend to be too low.

Concordant values for the constants in equations (2) can be derived from the three sets of data given in Table IV. Average values are collected in Table V for each set of experiments. The figures in cols. 3—5 of this table represent velocity coefficients corresponding to the relations (2) above, and should be concordant (along the rows) for each series.

TABLE V.

Series.	$\frac{152}{81} \cdot \frac{10^3}{t_r . a^3}$.*	$\frac{10}{9} \cdot \frac{10^3}{t_r . a^3}$.†	$10^3 . r_m/a^4$.‡	$10^3 . k_3/a$.	$SnCl_4$, M.	$10^2 . k_3/ac$.
A	7·9	4·6	3·2	4·15	0·0507	8·18
B	4·5	2·7	2·6	2·59	0·0504	5·14
C	5·6	3·3	2·2	3·29	0·0416	7·90
D	4·0	2·3	1·7	2·19	0·0332	6·63

* Expression for *k* in equation $dx/dt = k(a - x)^4$.

† Expression for *k* in equation $dx/dt = ka(a - x)^3$ (cf. equation 3, below).

‡ See footnote, p. 780.

Those in the last column represent velocity coefficients corresponding to equation (3) below, and should be identical for all series if the experimental results were accurately reproducible.

The over-all reaction is evidently of the fourth order, a result which conflicts with the third-order progress of individual polymerisations, indicated by Fig. 3. Plotting $1/(a - x)^3$ against time, however, justifies Fig. 3, without question, as the better representation of the course of polymerisation over an extended range of reaction. Even velocity coefficients for the first 20% of the reaction, calculated from t–$(a - x)^{-3}$ curves, are not very consistent and agree better numerically with col. 3 of Table V than with col. 2. It seems that the maximum rate of polymerisation varies with the fourth power of the initial styrene concentration, whilst the diminution of rate during polymerisation is governed by the third power of the residual styrene concentration.

From the foregoing results, equation (3) is deduced as an empirical representation of the course of polymerisation :

$$-\,d(a - x)/dt = kca(a - x)^3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

whilst

$$n = \text{const.} \times a^{\frac{1}{2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where x is the concentration of styrene used up at time t and other symbols are as before. In carbon tetrachloride at 25°, k is of the order $7{\cdot}0 \times 10^{-2}$ (Table V, last column).

Temperature Coefficient.—Experiments have been made over the range 0—38·4°. As shown by curves 129, 120, 128, and 127 of Fig. 2, the increase in polymerisation rate over this range is slight. Consequently, it is difficult, in view of the imperfect reproducibility of different experiments, to determine the activation energy accurately. The extreme variation of k (equation 3), in comparable experiments, was from $4{\cdot}48 \times 10^{-2}$ at 0° to $9{\cdot}06 \times 10^{-2}$ at 38·4°, giving an activation energy of 3,200 cals. The maximum variation of n over the same range of temperature was from 29 to 24.

DISCUSSION.

A satisfactory detailed reaction mechanism has not yet been formulated, but certain conclusions from equation (3) may be discussed briefly. In the following, M_n and P_n denote, respectively, stable and activated polymer molecules, each composed of n styrene molecules; C denotes a catalyst molecule.

Chain Initiation.—If chain initiation is normally the slowest phase in the polymerisation process, then stannic chloride must accelerate this phase; because its presence increases the total rate of polymerisation. At the same time, stannic chloride induces a high-order reaction of small activation energy. One possible initiation mechanism is represented by equations (5) and (6).

$$\text{Chain initiation}\begin{cases} M_1 + C \rightleftharpoons M_1C \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . & (5) \\ M_1C + 2M_1 = P_3C \text{ (or } P_3 + C) \quad . \quad . \quad . \quad . \quad . \quad . & (6) \end{cases}$$

A styrene–stannic chloride complex is first formed. A molecule of complex collides with a second styrene (M_1) molecule and holds it for a time long enough to provide a fair chance of collision with a third styrene molecule, thus starting a polymerisation chain at an activated trimer stage (P_3C or P_3), with an activation energy which must be assumed to be so small that all possible uni- or bi-molecular initiation processes are overshadowed. According to this view, the function of the stannic chloride is to side-track the difficult formation of initiation centres of type P_1 or P_2, by introducing complexes which can survive long enough to facilitate three-body collisions between styrene molecules.

Chain Growth.—In the presence of stannic chloride, the distinction between a slow initiation reaction and rapid chain growth loses much of its significance, but chain initiation, involving triple collisions, may still be considered the slowest phase in the polymerisation process. Since the polymer chain length is independent of the catalyst concentration (Table II), the catalyst must influence chain initiation alone, or, alternatively, it must participate both in chain growth and in chain termination.

Chain Termination.—If *either* of these alternatives is correct, the mutual stabilisation of growing polymers cannot be the chain-termination reaction in the polymerisations catalysed by stannic chloride; for, at a given styrene concentration, this mechanism would require the chain length to diminish proportionately as the total rate of polymerisation increases with rising catalyst concentration (Schulz and Husemann, *loc. cit.*), which is contrary to the combined results of Table II and Fig. 4. On the other hand, the rising rate of polymerisation implies increasing concentration of active polymer centres in the system; and, of all chain-termination mechanisms which do not involve the catalyst, mutual stabilisation is the one most favoured by increase in the concentration of growing polymers. If mutual stabilisation actually occurs in the relatively slow spontaneous and peroxide-catalysed polymerisations of styrene, then, since n is independent of c, this chain-termination reaction must always be overshadowed, for stannic chloride catalysis, by another termination reaction involving participation of the catalyst. This being so, chain growth must also involve the catalyst. These considerations are supported by the following results with different catalysts : (*a*) on comparing stannic chloride with benzoyl peroxide catalysis, we find that a 200-fold increase in the total rate of polymerisation corresponds to only a 10-fold decrease in chain length; (*b*) with different metal chloride catalysts (Table I), the total rate of polymerisation may be multiplied by 10^4, with a 3-fold decrease in chain length.

It seems possible that the catalyst remains attached to the growing polymer, and that chain termination occurs through internal stabilisation of each growing polymer, perhaps by isomerisation at the active end of the chain (cf. Risi and Gauvin, *Canadian J. Res.*, 1936, *B*, **14**, 255). The simplest formulation of these ideas, with a growth reaction $P_nC + M_1 = P_{n+1}C$ and a termination $P_nC = M_nC$ (or $M_n + C$) leads, in combination with equations (5) and (6), to kinetic expressions which do not accurately represent the experimental facts, as summarised in equations (3) and (4). The resulting expressions (cf., *e.g.*, Breitenbach, *Monatsh.*, 1938, **71**, 275) for the total rate of polymerisation and chain length are $-\, d[M_1]/dt = k\,[C][M_1]^4$ and $n = \text{const.}\ [M_1]$. Other mechanisms have been considered, but their discussion may be withheld until further experiments on this and on allied reactions have been completed.

EXPERIMENTAL.

Materials.—Styrene was made from β-phenylethyl alcohol by the method of Sabetay (*Bull. Soc. chim.*, 1929, **45**, 69). Traces of the undecomposed alcohol were removed either (*a*) by repeated washing with sodium benzoate solution, in which the alcohol is noticeably soluble (Neuberg, *Biochem. Z.*, 1916, **76**, 107), or (*b*) by distillation from sodium under reduced pressure. Specimens purified by these two methods gave (microanalyses by Weiler and Strauss, Oxford) C, 92·6, 92·5; H, 7·7, 7·6 (Calc. : C, 92·3; H, 7·7%). Dry styrene was preserved with quinol as polymerisation inhibitor and freshly distilled (at 13 mm.) before use. It gave no positive response to a peroxide test.

" AnalaR " grade solvents were employed. Carbon tetrachloride was further washed, dried, and distilled before use.

Catalysts.—Commercial stannic chloride was purified by repeated distillation in a vacuum (see Part I). The starting material contained appreciable quantities of hydrate, traces of which came over even after six distillations. Antimony pentachloride was similarly distilled. Boron trichloride was shaken, in a vacuum, with mercury to remove chlorine, and then distilled into receivers cooled with liquid air, first fractions being taken off separately to eliminate hydrogen chloride. All three catalysts were finally collected in glass bulbs, sealed off in a vacuum.

Reaction Products.—It has been shown in Part I that stannic chloride brings about quantitative polymerisation of styrene to long-chain polystyrene. Polymerisation is almost quantitative with boron trichloride as catalyst (see Table VI), but not with antimony pentachloride.

Antimony Pentachloride as Catalyst.—When antimony pentachloride is added to a styrene solution, much heat is evolved and charring occurs unless the catalyst is previously diluted with solvent. Polymerisation is immediate but incomplete. The reaction stops at once and proceeds no further on standing. The following is a typical experiment (cf. also Table VI) :

Expt. 77. Styrene 1·71M. $SbCl_5$ 0·063M. Solvent CCl_4. Temp. 25°.

Time (mins.)	0	5·4	11·1	153	1280
Concn. of styrene (M)	1·71	1·46	1·46	1·46	1·45

As shown in Table VI, even the actual proportion of styrene consumed (which varies with catalyst concentration) is not completely converted into polystyrene. Furthermore, the polymer (precipitated in methyl alcohol) is impure even after repeated reprecipitation. As pointed out by Staudinger *et al.* (*Ber.*, **1929**, **62**, 260), polystyrene made with stannic chloride catalyst is not easily freed from inorganic impurities, but can be obtained pure by repeated precipitation. It appears that halogen may be incorporated in the polymer molecules formed with the aid of antimony pentachloride.

TABLE VI.

Reaction Products with Metal Chloride Catalysts.

No.	Catalyst and concn., M.	Initial styrene, M.	Styrene consumed, %.	Polystyrene * recovered, % of initial.	Analysis of polymer (Calc. : C, 92·3; H, 7·7%). C, %.	H, %.
111	$SnCl_4$ 0·0338	1·72	(93)	98·8	92·6	7·6
74	BCl_3 0·230	3·46	64·4	62·6	—	—
84	BCl_3 0·0611	1·89	23·6	19·6	89·7	7·5
80	BCl_3 0·139	1·70	14·4	6·5	—	—
77	$SbCl_5$ 0·063	1·71	14·6 †	4·3	§ 89·5 89·7	7·2 7·2
83	$SbCl_5$ 0·186	1·75	79·4 †	(56)	—	—
81	$SbCl_5$ 0·213	1·75	60·5 †	16·2	—	—
82	$SbCl_5$ 0·0725	0·77	64·6 †	‡ 35·0 35·2	—	—

* Polymers precipitated in methyl alcohol, dried and weighed.
† Reaction ceased at per cent. consumption shown.
‡ Duplicate precipitations.
§ Analyses after one and after three precipitations in MeOH.

Antimony pentachloride can act as a chlorinating agent (Rosenheim and Stellmann, *Ber.*, **1901**, **34**, 3377; Meyer, *ibid.*, **1910**, **43**, 157; Hilpert and Wolf, *ibid.*, **1913**, **46**, 2215; Hutton and Webb., J., **1931**, **1518**) and is probably destroyed rapidly when mixed with styrene. In one experiment (79), styrene (0·17 mol.) in carbon tetrachloride (80 c.c.) was completely consumed by gradual addition of antimony pentachloride (0·026 mol. in 11 c.c. of solvent). Of the original styrene, 86% was recovered as impure polystyrene of molecular weight about 1600 (Found : C, 89·4; H, 7·1%; traces of halogen detected) and 7% as styrene dichloride (b. p. 95—97°/11 mm. Found : Cl, 40·4. Calc. for $C_8H_8Cl_2$; Cl, 40·5%), corresponding to about half the amount of catalyst added. Some inorganic solid recovered from polymerisation catalysed by antimony pentachloride was thought to be antimony oxychloride.

Molecular-weight Measurements.—These were made by viscosity determinations, with a No. 0 British Standard Viscometer, on portions of the polymerising mixtures, suitably diluted and filtered. For reaction mixtures in which polymerisation was not quantitative, solutions for viscosity measurements were made up from polymers precipitated in methyl alcohol. The consistency of specific viscosity determinations may be illustrated by the measurements made with each of the duplicate polymer precipitates from Expt. 82, Table VI. Solution A (0·108M, calc. as mols. C_8H_8/l.) gave $\eta_{sp.}/c = 0·566$; solution B (0·0545M) gave $\eta_{sp.}/c = 0·561$.

Velocity Measurements.—These were made as in Part I. Reaction was started by crushing a sealed bulb containing catalyst under the surface of a styrene solution, and followed by periodical estimation of residual styrene by quantitative bromination. The method of analysis has been justified in Part I. One experiment, at the highest styrene concentration, is given below.

Expt. 116. Styrene = 3·53M. $SnCl_4$ = 0·0332M. Temp. 25°.

Time, mins.	0	4·30	14·00	19·40	22·80	29·25	33·60	37·75
Styrene concn., M	3·53	3·52	3·53	3·55	3·53	3·53	3·49	3·18
Polymerisation, %	0	0	0	0	0	0	1·1	10·1
Time, mins.	39·40	44·15	51·15	62·25	75·75	102·4	138·5	1309
Styrene concn., M	2·87	2·33	1·917	1·483	1·280	0·979	0·685	0·181
Polymerisation, %	18·7	34·0	45·6	58·0	63·7	72·2	77·7	94·9

The experiments were done at the University College of North Wales, Bangor. My thanks are due to the Chemical Society for a research grant and to Prof. J. L. Simonsen, F.R.S., for the hospitality of his laboratory.

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[*Received, April 2nd*, 1940.]