48. *Kinetics of the Catalysed Polymerisation of Styrene. Part I. Experimental Methods and Some General Features of Stannic Chloride Catalysis.*

By Gwyn Williams.

The polymerisation of styrene, catalysed by pure stannic chloride, has been examined in carbon tetrachloride solution at 25—45°. The process can be followed by quantitative bromination of the residual monomer present in a polymerising mixture. The styrene disappearing during polymerisation is shown, by quantitative precipitation of the polymer, to be equivalent to the polystyrene formed (mean molecular weight 1200—2700). Both polymer size, which usually remains constant through the course of a given reaction, and polymerisation rate are more sensitive to change in concentration of styrene than of catalyst. The reactions have induction periods and, over a three-fold concentration range, the maximum rate is approximately proportional to the concentration of catalyst. The rate of polymerisation is reproducible with freshly distilled styrene and is not affected by the addition of benzoyl peroxide. The polymerisation of styrene, which has been kept for some time and contains peroxides, is retarded in its early stages.

The thermal polymerisation of styrene is influenced by oxygen (Staudinger and Lautenschläger, *Annalen*, 1931, **488**, 1), and significant kinetic results for uncatalysed polymerisation are obtainable only with rigid exclusion of oxygen (Breitenbach and

Rudorfer, *Monatsh.*, 1937, **70**, 37; Dostal and Jorde, *Z. physikal. Chem.*, 1937, *A*, **179**, 23; Suess, Pilch, and Rudorfer, *ibid.*, p. 361; Schulz and Husemann, *ibid.*, 1937, *B*, **36**, 184). In the presence of a powerful polymerisation catalyst, such as stannic chloride, the influence of oxygen should have less importance, particularly since it is possible to study the catalysed polymerisation at temperatures at which the spontaneous polymerisation of styrene is very slow, with or without a solvent.

With anhydrous stannic chloride as catalyst, styrene polymerises in carbon tetrachloride or chloroform solution at a rate measurable at room temperature, giving hemi-colloidal products with an average molecular weight of the order 3,000 (Staudinger, "Die Hochmolekularen Organischen Verbindungen," Berlin, 1932, p. 159). Polymerisation may be preceded by periods of initial inhibition (Williams, *Nature*, 1937, **140**, 363), but, with pure materials, these are absent. The purpose of this paper is to define conditions affecting the consistency of kinetic results, and to describe certain characteristics of the stannic chloride polymerisation of styrene. Inhibition phenomena and detailed kinetics will be considered in later papers.

Styrene may be estimated by quantitative bromination of the double bond. Since it can be established that the styrene disappearing during polymerisation is equivalent to the polymer formed, bromination analysis for residual monomeric styrene provides a convenient method for following the progress of polymerisation. It is of particular advantage for catalysed polymerisation, because the presence of stannic chloride in the system would require the modification of methods depending on isolating and weighing the polymers, either by distilling off solvent and residual monomer (Mark and Raff, *Z. physikal. Chem.*, 1936, *B*, **31**, 275) or by precipitating the polymer in methyl alcohol (Schulz and Husemann, *ibid.*, **34**, 187). The objection in the latter case is that, with stannic chloride, under certain conditions, part of the polystyrene produced is of low enough molecular weight to be soluble in methyl alcohol.

We find that the method of bromination analysis can also be used to follow the polymerisation of vinyl acetate; and Hammick and Langrish (J., 1937, 797) have applied a similar procedure to the polymerisation of indene and *cyclo*pentadiene.

EXPERIMENTAL.

Materials.—Styrene, made from cinnamic acid, and containing originally a quinol inhibitor, was repeatedly distilled (through a column) under nitrogen at 5—10 mm. pressure. Comparison experiments were made with commercial styrene, specially purified by low-pressure fractionation through the kindness of Dr. K. C. D. Hickman.

Carbon tetrachloride, "Eastman, free from sulphur," was washed, dried, and distilled through a fractionating column before use as solvent.

Stannic chloride was purified essentially as described by Briscoe (J., 1915, **107**, 63) and by Baxter and Starkweather (*J. Amer. Chem. Soc.*, 1920, **42**, 905). The anhydrous substance ("c.p. analysed") was distilled in a sealed, evacuated, Pyrex-glass apparatus, which had been previously heated in a flame at a pressure of 10^{-5} mm. After two distillations at room temperature, the substance was distilled twice by evaporation at − 20° into receivers cooled with liquid air. A first fraction was each time collected separately in liquid air, to remove hydrogen chloride, and a residuum was left in the distilling vessel. Finally, the stannic chloride was collected in a U-tube, from which known volumes were evaporated into small bulbs of thin glass, cooled with liquid air. These were sealed off one by one, and weighed. The final specimens were free from any trace of the solid fragments, present in commercial stannic chloride, which survived the earlier distillation stages.

Estimation of Styrene.—The styrene solution in carbon tetrachloride is run into a standard solution of bromine in glacial acetic acid. Addition to the double bond takes place at once, and the excess of bromine is destroyed with potassium iodide, the liberated iodine being titrated with sodium thiosulphate. Table I illustrates the accuracy of the analysis and shows that the method is still valid when polystyrene and stannic chloride are present in the solution. Stannic chloride appears to catalyse a slow bromine attack on the polymer, but this does not spoil the analysis, provided that the bromine excess be destroyed without delay.

Rate Measurements.—Polymerisation was started by crushing a weighed glass bulb, containing stannic chloride, under the surface of a standard solution of styrene in carbon

TABLE I.

Styrene concn., mols./l.		Ratio Br_2/C_8H_8.	$SnCl_4$, mols./l.	$(C_8H_8)_n$ concn., as mols. of C_8H_8/l.
Calc.	Found.*			
1·733	1·735 (3; 0·15%)	1·4	—	—
1·733	1·738	1·4	0·04	0·1
1·724	1·721	1·3	—	—
0·866	0·867 (5; 0·14%)	1·4	—	—
0·866	0·866	1·5	—	1·0
0·866	0·860	1·5	0·05	0·5
0·432	0·431 (4; 0·3%)	1·1	—	—
0·432	0·430	1·1	—	0·1
0·432	0·432	1·1	0·03	0·1
0·174 †	0·175 (2)	1·8	—	—
0·0867	0·0866 (3; 0·2%)	1·6	—	—

* The figures in parentheses represent the number of individual measurements and the mean deviation from the mean.

† In chloroform solution.

tetrachloride. The reaction vessels were 100 c.c. or 50 c.c. standard flasks or stoppered bottles of brown glass. 2-C.c. portions of the reaction mixture (kept in a thermostat) were extracted at intervals and analysed for monomeric styrene by the bromination method. At the end of the experiment, the crushed glass in the reaction vessel was filtered off and weighed, in order to determine the amount of stannic chloride introduced.

Molecular-weight Measurements.—Portions of the polymerising mixture were also removed at intervals and diluted to a known volume in carbon tetrachloride. The polystyrene content at the moment of extraction was found from the reaction curve, and the mean molecular weight of the polymer was determined by viscosity measurements on the diluted solutions, an Ostwald viscometer being used at 25°. The polystyrene content of the diluted extracts did not alter during the viscosity measurements; the dilution applied (at least ten-fold) reduced the polymerisation rate to negligible proportions. The dissolved stannic chloride did not affect the viscosity of carbon tetrachloride (*e.g.*, viscometer flow-times for pure solvent and for 0·065M-$SnCl_4$ in the solvent were 353·8 and 353·9 secs., respectively). The polystyrene dilution was chosen so as to give an increment of 15—40 secs. in the flow-time over that for pure carbon tetrachloride, but the concentrations were always well below the upper limits recommended by Schulz (*Z. Elektrochem.*, **1937**, **43**, 479). The solutions were filtered when necessary.

The results thus obtained from solutions made up directly from the reaction mixture were checked occasionally by measurements made with solutions of dry polystyrene, isolated from the reaction mixture by precipitation in methyl alcohol (*e.g.*, $\eta_{sp.}/c$ values for solution made from isolated polystyrene and for diluted reaction mixture were 0·876 and 0·887 respectively).

Results.—*Course of the reaction.* In order to determine whether the loss of monomeric styrene during polymerisation was fully accounted for by the formation of polystyrene of high molecular weight, 10-c.c. portions of reaction mixture were run into pure methyl alcohol. The precipitated polystyrene was filtered off through porous porcelain, washed with dilute hydrochloric acid and methyl alcohol, and dried to constant weight at 100°. Table II contains results for several reaction mixtures, made up from different lots of styrene and catalyst, with various rates of polymerisation.

The fall in concentration of monomeric styrene is evidently equivalent to the increase in concentration of high molecular weight polystyrene. With lower initial styrene concentrations, part of the polystyrene formed is soluble in methyl alcohol (cf. Staudinger *et al.*, *Ber.*, **1929**, **62**, 260), and a further yield of polystyrene can be obtained by adding water to the methyl alcohol filtrate. It is thus possible to state that, with low initial styrene concentrations, polymers with molecular weights below 1000 (Staudinger, *op. cit.*, p. 161) are formed in appreciable amount. These are absent at higher styrene concentrations, as indicated in Table II.

Chain-length of polymeric product. The results of viscosity measurements are given in Tables III and IV. The immediate application of Staudinger's law to these viscosity results presents certain difficulties. They arise from three causes, now discussed. Staudinger's viscosity law is generally used in the form

$$\eta_{sp.}/c = K_m \,.\, M \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

TABLE II.

Quantitative precipitation of polymerised product.

Expt. No.	Temp.	Initial C_8H_8, mols./l.	$SnCl_4$, M.	Time, hrs.	Polymer found, g.	Mol. wt.	% Polymerisation. By Br_2 titrn.	% Polymerisation. By wt. of polymer.
67	25°	1·730	0·0571	0·59	0·258	—	16·9	14·3
66	25	2·110	0·0139	1·26	0·407	—	18·6	18·6
37	25	1·710	0·0644	1·68	0·423	2470	26·3	23·8
23	25	1·734	0·1258	23·3	0·738	—	39·1	40·8
35	25	1·686	0·0950	1·70	0·691	2740	40·6	39·5
54	35	1·743	0·0641	1·43	0·980 0·082*	2240	59·1	58·6
36	25	1·72	0·0644	2·75	1·072	1790	62·8	60·1
38	25	1·710	0·0870	19·2	1·493	2890	80·5	83·6
43	25	0·866	0·1090	8·63	0·363	2730	46·4	(40·2) *

* Some polymer, soluble in methyl alcohol, precipitated in water. Water precipitate not recovered in No. 43.

where $\eta_{\text{sp.}}$ = specific viscosity = $[\eta(\text{soln.}) - \eta(\text{solvent})]/\eta(\text{solvent})$, c = polymer concentration (as mols. of C_8H_8/l.), and K_m = a constant for a given polymer-homologous series. K_m will not have the value appropriate to a set of individually uniform homologous polymers, because (*a*) branching of the polystyrene chain, which occurs in high-temperature polymerisation (Staudinger and Schulz, *Ber.*, 1935, **68**, 2320; Signer, *Helv. Chim. Acta*, 1936, **19**, 897), is not known to be excluded in catalytic polymerisation; (*b*) K_m for polystyrenes increases steadily as the molecular weight falls below 5,000 (Staudinger, *op. cit.*, p. 179); (*c*) we are dealing with unfractionated polymer mixtures (cf. Schulz, *Z. physikal. Chem.*, 1935, *B*, **30**, 393; 1936, *B*, **32**, 27).

It seems best, therefore, to lay emphasis on the values for $\eta_{\text{sp.}}/c$ in the tables, rather than on any molecular weights calculated from them. An estimate of the average degree of polymerisation (n in tables) has been calculated from the following equation (Staudinger, *op. cit.*, p. 181; *Z. Elektrochem.*, 1934, **40**, 434) :

$$\eta_{\text{sp.}}/c = an + b \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where a and b represent, respectively, the contributions of the chain carbon atoms and of the end-groups to the viscosity; b is taken as 0·2 (Staudinger, *op. cit.*) and a as $2{\cdot}5 \times 10^{-2}$, being the mean of six values determined by Staudinger for unfractionated polymers, having cryoscopic molecular weights between 2,500 and 4,900. Equation (2) then gives values of n for our polymers which are in reasonable accord with Staudinger's cryoscopic values for unfractionated mixtures with corresponding $\eta_{\text{sp.}}/c$. No reliance can be placed on the absolute values of n given in the tables, but their variation may have significance.

It appears from Table III that, within experimental error, the average molecular weight of the polymer formed is the same at all stages of the reaction. Constancy of polymer size during polymerisation has been observed in the non-catalytic polymerisation of styrene without a solvent (Staudinger and Frost, *Ber.*, 1935, **68**, 2351; Schulz and Husemann, *loc. cit.*), and a similar result is referred to by Flory (*J. Amer. Chem. Soc.*, 1937, **59**, 241) for the (probably catalytic) polymerisation of methyl methacrylate. On the other hand, Schulz and Husemann consider that, when a solvent is present, polymer size should fall during the reaction. A tendency in this direction is visible in Expt. 54/55 in Table III.

Table IV(*a*) emphasises that the initial styrene concentration is a dominant factor in determining polymer size, a four-fold change of styrene concentration being sufficient to produce a far more noticeable effect on polymer size than changes in the other possible variables shown in Table IV(*b*) and IV(*c*). In fact, although it is an established feature of polymerisation processes that rise of temperature and increase in the concentration of a catalyst both tend to lower the molecular weight of the polymer product (cf., *e.g.*, Staudinger, *op. cit.*, pp. 159, 339), the range of experimental conditions shown in Table IV(*b*) and IV(*c*) is not wide enough to bring out any systematic change of polymer size with either of these variables. The results in Table IV(*c*) are for experiments in which polymerisation was preceded by periods of total inhibition (*Nature*, 1937, **140**, 363), probably caused by the presence of hydrogen chloride in the stannic chloride catalyst.

TABLE III.

Variation of polymer size with extent of polymerisation.

Expt. No.	Temp.	Initial C_8H_8, M.	$SnCl_4$, M.	Polymerisation, %.	$\eta_{sp.}/c$.	n.
48	25°	1·73	0·0507	29·5	0·769	23
				43·9	0·767	23
				54·3	0·826	25
				65·9	0·765	23
				76·9	0·728	21
				96·6	0·689	20
49	35	1·743	0·0763	29·7	0·753	22
				62·8	0·825	25
				81·8	0·702	20
54/55	35	1·743	0·0641	24·3	0·914	29
				45·4	0·836	25
				67·1	0·818	25
				81·6	0·761	22
51	45	1·753	0·0450	14·1	0·706	20
				37·7	0·900	28
				68·6	0·813	25
46	25	0·866	0·0507	29·8	0·620	17
				40·8	0·565	15
				91·3	0·622	17
50	35	0·880	0·0560	11·8	0·514	13
				17·0	0·525	13
				36·3	0·500	12
				48·0	0·554	14
				58·2	0·539	14

TABLE IV.

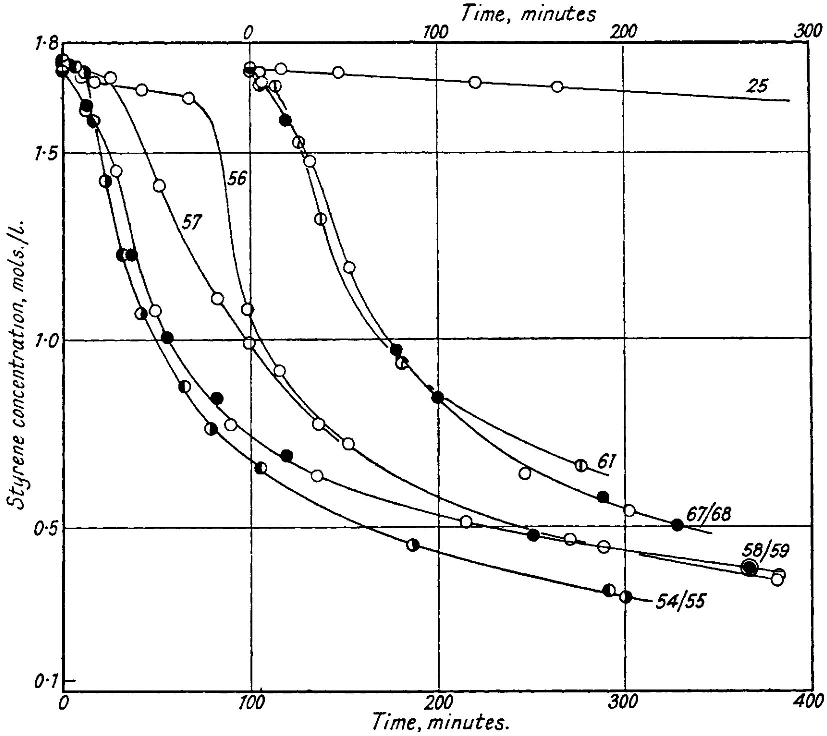
Expt. No.	Temp.	Initial C_8H_8, mols./l.	$SnCl_4$, s, mols./l.	$\eta_{sp.}/c$.	n.	Maximum rate,* r_m, min.$^{-1}$.	r_m/s.
(*a*) Dependence of polymer-size on initial styrene concentration.							
50	35°	0·880	0·0560	0·526	13	—	—
49	35	1·743	0·0763	0·760	22	—	—
54/55	35	1·743	0·0641	(0·827)	(25)	—	—
47	25	0·433	0·0507	0·507	12†	0·00010	0·002
46	25	0·866	0·0507	0·602	16	0·0019	0·037
48	25	1·730	0·0507	0·757	22	0·0315	0·62
(*b*) Variation of catalyst concentration.							
66	25	2·110	0·0139	—	—	0·012	0·86
39	25	1·724	0·0791	0·691	20	—	—
42	25	1·697	0·0715	0·755	22	—	—
36	25	1·736	0·0644	0·860	26	0·042	0·65
37	25	1·714	0·0644	0·817	25	—	—
58	25	1·732	0·0422	0·758	22	0·027	0·64
59	25	1·732	0·0422	0·831	25		
56	25	1·732	0·0422	0·744	22	—	—
57	25	1·732	0·0422	0·738	22	—	—
44	25	0·870	0·0560	(0·690)	(20)	0·0016	0·029
43	25	0·866	0·109	(0·64)	(18)	0·0026	0·024
45	25	0·860	0·150	0·603	16	0·0048	0·032
30	25	0·850	0·0939	0·631	17		
29	25	0·855	0·114	0·645	18		
51	45	1·753	0·0450	0·806	24		
52	45	1·753	0·0816	0·755	22		
53	45	1·753	0·0816	0·769	23		
(*c*) Experiments with initial inhibition.							
7	25	1·724	0·0133	0·792 0·819	24 at 29·3% polymn. 25 at 92·0% polymn.		
10	25	1·74	0·0894	0·834	25		
9	25	1·75	0·157	0·887	27		
11	25	1·734	0·193	0·772	23		

* The maximum rate of polymerisation is expressed as mols. per litre of styrene disappearing per minute.

† In Expts. 47, 46, 48, n is approximately proportional to the square root of the styrene concentration (cf. Schulz and Husemann, *Z. physikal. Chem.*, 1937, *B*, **36**, 193).

DISCUSSION.

The Rate of Polymerisation.—Effect of peroxides. The rate of polymerisation is measured at temperatures (25—45°) at which the spontaneous polymerisation of styrene is negligibly slow even in the presence of oxygen (cf. Staudinger and Lautenschläger, *loc. cit.*). It follows that oxygen can only influence the reaction by acting on polymerisation chains which have already been started by the stannic chloride catalyst. The styrene used for polymerisation experiments was tested for the presence of peroxides by shaking with sodium thiocyanate solution and ferrous ammonium sulphate (Kharasch and Mayo, *J. Amer. Chem. Soc.*, 1933, **55**, 2468). Freshly distilled styrene gave no response, but a detectable peroxide content developed in styrene after a few days' keeping at room temperature. In order to test the influence of peroxide content on the rate of polymerisation, benzoyl peroxide was added to certain reaction mixtures. Results are shown in the diagram, which illustrates ten experiments. On curves 58/59 and 67/68, the black circles represent reaction mixtures containing 0·01M- and 0·02M-benzoyl peroxide respectively. The white circles on the same curves are for identical reaction mixtures without peroxide. Added peroxide has thus no detectable effect with freshly distilled styrene at 25°. On the other hand, styrene which had been kept in a stoppered bottle for 18 days after distillation gave a positive reaction to the peroxide test; its polymerisation was slow in the initial stages (compare curve 57 with curve 58/59). Slow initial polymerisation rates were often observed with "aged" styrene (*e.g.*, curve 56). An extreme example is illustrated by curve 25, which shows the initial stages of polymerisation for some styrene which had been kept for 3½ months; polymerisation proceeded in approximately zero-order reaction to 60% completion in 73½ hours.



Polymerisation of styrene in carbon tetrachloride with stannic chloride catalyst. Curves 25, 61, *and* 67/68 *are on the upper time scale. Data for the curves are given in Table IV.*

Polymerisation of styrene without an added catalyst is said to be faster in "aged" styrene than in fresh styrene (Stobbe and Posnjak, *Annalen*, 1909, **371**, 259; Stobbe, *ibid.*, 1915, **409**, 1). This acceleration is almost certainly due to the catalytic effect of peroxides formed by the autoxidation of styrene (cf. Cuthbertson, Gee, and Rideal, *Nature*, 1937, **140**, 889), since an anti-oxidant, such as quinol, stabilises styrene against spontaneous polymerisation at room temperature, and does not influence polymerisation in the absence of oxygen at 100° (Suess, Pilch, and Rudorfer, *loc. cit.*). The retardation of polymerisation in "aged" styrene may be due to the inhibiting action of an autoxidation product, which is allowed full play owing to the catalytic inactivity of peroxides towards the polymerisation of styrene at 25° in the presence of stannic chloride. The mechanism of this "ageing" effect is, however, a matter for further experiment. "Ageing" does not seem seriously to alter the molecular weight of the polymerisation product. Thus, the polystyrene from reaction 25 gave $\eta_{sp.}/c = 0{\cdot}87$ ($n = 27$), which may be compared with the data in Table IV for other reaction mixtures with 1·73M. initial styrene concentration. In general, polymer size seems to be less influenced by adventitious circumstances than is the rate of polymerisation.

Reproducibility of rate measurements. The reaction is not sensitive to casual surface influences, as are some polymerisations (Breitenbach and Raff, *Ber.*, 1936, **69**, 1107); curve 54/55 is for a reaction mixture which was divided into two parts immediately after mixing. Polymerisation was followed in the two parts separately, one being in a standard flask and one in a bottle of amber glass. To secure comparable conditions for a series of experiments at varying styrene concentrations, appropriate quantities of a freshly made stannic chloride solution were added as quickly as possible to solutions of freshly distilled styrene. The reproducibility obtainable under these conditions is illustrated by curve 58/59, which represents two reaction mixtures made up in this way. Curve 61 and curve 67/68 represent entirely independent reaction mixtures made up to approximately the same concentrations with different styrene solutions and two separate stannic chloride bulbs (see p. 247). Curve 67/68, like curve 54/55, represents two mixtures, examined separately, but obtained by division of an original mixture into two parts.

Maximum rate. As may be seen from the diagram, the reaction shows an induction period.* A typical experiment is given in full below.

Expt. 48. Styrene = 1·730M. $SnCl_4$ = 0·0507M. Temp. 25° ± 0·02°.

Time (mins.)	0	6·20	19·60	33·10	45·0	67·7	86·2
Styrene concn. (M)	1·730	1·689	1·651	1·298	1·106	0·926	0·836
Polymerisation, %	—	2·37	4·57	25·0	36·1	46·5	51·6
Time (mins.)	153·0	245	388	516	900	(6 days)	
Styrene concn. (M)	0·640	0·513	0·391	0·334	0·221	0·062	
Polymerisation, %	63·0	70·4	77·4	80·6	87·2	96·5	

In this particular experiment, the maximum rate of disappearance of styrene (0·0315 mol./l./min.) is reached at the stage of 9·3% polymerisation. In a series of comparable experiments with fresh styrene (see Table IV), the maximum rate r_m is found (within rather narrow concentration limits) to be approximately proportional to the concentration of stannic chloride for a given initial concentration of styrene. It increases enormously as the initial styrene concentration is raised. A wider variation of the reactant concentrations is required before definitive conclusions can be reached.

A curious feature in certain experiments is the appearance of a short preliminary stage of *decreasing* velocity, succeeded by the induction period leading to the main reaction (*e.g.*, curve 56). The significance of this preliminary stage has not yet been determined. It may, perhaps, be due to an independent reaction forming a distyrene, which plays no part in the growth of long polymer chains (cf. Risi and Gauvin, *Canadian J. Res.*, 1936, *B*, **14**, 255), and which is detectable only at the very beginning of the reaction, before the long-chain polymerisation has got fairly under way.

Conclusion.—The reaction kinetics and the form of the polymerisation curves will be discussed in a later paper. If we adopt the chain theory of polymerisation processes, which has been considered recently by a number of authors, the stannic chloride catalyst may play a part (*a*) in the initiation of polymerisation chains (probably by forming a

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* To be distinguished from the *inhibition* periods referred to previously (*Nature*, 1937, **140**, 363).

complex with monomeric styrene), (*b*) in the growth of chains, (*c*) in breaking the chains. The results given in this paper indicate that the following features may be characteristic of the stannic chloride catalysis of styrene polymerisation in solution: (1) greater sensitiveness of polymer size and polymerisation rate to changes of styrene concentration than to changes of catalyst concentration, (2) approximate proportionality between maximum polymerisation rate and catalyst concentration, (3) relative constancy of polymer size through the whole course of a given reaction. If these results can be substantiated over a wider range of conditions, the simplest interpretation may prove to be that the principal function of the catalyst lies in the chain-initiation stage. If the catalyst influences stage (*b*), it must also participate in stage (*c*).

The results given in Table IV for different temperatures are not for comparable specimens of styrene and are therefore unsuitable for calculations of activation energy.

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